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МАКЕДОНСКА АКАДЕМИЈА НА НАУКИТЕ И УМЕТНОСТИТЕ
ОДДЕЛЕНИЕ ЗА ПРИРОДНО-МАТЕМАТИЧКИ И БИОТЕХНИЧКИ НАУКИ
MACEDONIAN ACADEMY OF SCIENCES AND ARTS
SECTION OF NATURAL, MATHEMATICAL AND BIOTECHNICAL SCIENCES

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ON THE EVE OF THE GREAT JUBILEE – 50 YEARS OF THE MACEDONIAN ACADEMY OF SCIENCES AND ARTS
1967 – 2017

Taki Fiti

President of the Macedonian Academy of Sciences and Arts

This year the Macedonian Academy of Sciences and Arts (MASA) marks and celebrates a great jubilee – 50 years of existence and work of our highest institution in the field of sciences and arts. Although on 22 February 2017 the 50th anniversary of the enactment of MASA in the Assembly of the Socialistic Republic of Macedonia was marked, and on October 10 it will be 50 years since the solemn establishment of MASA, we proudly emphasize that our roots, the roots of the Macedonian and Slavic cultural and spiritual continuity, are far back, in a time dimension which is measured in centuries. Because the mission of the Ss. Cyril and Methodius, the historical events that made Ohrid, with the famous Ohrid Literary School, already in the IX century to become the center of the Slavic educational and enlightening activity, which then spread throughout all Slavic countries, have fundamentally changed our contribution to the treasury of the European culture and civilization. And furthermore, centuries later, in the middle of the XIX century the Macedonian revival began, with a pleiad of our cultural and national activists. These processes at the beginning of the XX century resulted in the establishment of the Macedonian Scientific and Literary Fellowship in Saint Petersburg, led by Dimitrija Chupovski and Krste Petkov Misirkov, whose rich scientific, literary and cultural activities were a significant reflection of our spiritual continuity and identity, and an event that has marked the dawn of the Macedonian Academy of Sciences and Arts. This continuity will remain in the period between the two world wars, with a pleiad of artists in literature, art, music, philological, economic, legal and technical sciences. A few years after World War II, in 1949, in free Republic of Macedonia, the first state University of "Ss. Cyril and Methodius" was established, within which, in less than two decades, solid personnel resources were created which allowed rapid development of the higher education and scientific activity in our country. It was an event of great importance for the establishment of MASA as the highest institution in the field of sciences and arts.

This millennium pace and continuity in the development of art and scientific thought in our region is an indication and evidence that we are not a nation without its own roots, without its own history, without its own culture, and that the attempts to deny our identity, language, name, no matter where they come from, are residual of the Balkan anachronisms, and essentially speaking, they are absurd and retrograde.

Immediately after the establishment of MASA followed a period of rapid development, diversification and enrichment of its scientific and research activities and artistic work. Almost two decades after the establishment MASA entered the phase of its maturity and has grown and has affirmed as the fundament of the Macedonian science, language, culture and history and as one of the pillars and symbols of the statehood of the Republic of Macedonia.

Today, MASA, according to its integral concept, structure and function, has all the necessary attributes of a modern national academy of European type, and of course, performs the three basic functions typical of the European national academies: creating communication space for confrontation of different views and opinions on important issues in the field of sciences and arts, scientific and research work and advisory role.

The scientific and research activities and artistic work, in fact, constitute the core of the activity of MASA. The number of completed scientific and research projects and projects in the field of arts within MASA is impressive – more than 1,000 projects in the past 50 years. Some of these projects are long-term and are mainly related to the strategic issues of specific national interest, and significant is the number of fundamental and applied research in all fields of science and art represented in the Academy. MASA members in their scientific research increasingly incorporate the international dimension in the work – in the recent years more than 60% of the scientific papers have been published in international journals, most of which have been published in journals with impact factor; 50% of the papers that have been published in proceedings of scientific and professional meetings are related to meetings held abroad, etc. In addition, the works of our renowned writers and poets, members of MASA, are translated into foreign languages, and their work has found its place in world anthologies. Our prominent painters and sculptors of the older and the younger generation have created and create masterworks that are regularly exhibited at home and abroad. It should be particularly noted that our two research centers – Research Center for Energy and Sustainable Development and the Research Centre for Genetic Engineering and Biotechnology "Georgi D. Efremov", that have gained high reputation in the region and beyond, continue to successfully maintain the attained position. The work of the other research centers also enhances, including the newly established ones, which have begun to work on significant international scientific and research projects.

In its half-century of existence and work MASA developed a rich publishing activity. Since its establishment until today around 700 titles have been published – monographs, results of scientific projects, proceedings from scientific meetings, music releases, facsimile and jubilee publications, joint publications with other academies and scientific institutions, publications of solemn meetings, special issues of the departments of MASA etc. A special contribution to the publishing activities of MASA provides the "Trifun Kostovski" Foundation that has been existing and working for 18 years.

MASA proactively follows the changes and the new trends in the scope of the advisory function of the modern European national economies, and in that context the obligations arising from the project SAPEA - Science Advice for Policy by European Academies, initiated by the European Commission in order to intensify the cooperation of the European academies within their advisory role. Through the publication of the results of our scientific and research work, their presentation to the wider scientific and professional public in the country, to the government officials, etc., MASA participates in the policy-making in the field of sciences and arts and in the overall development of the country. The maintenance of the independence of MASA in carrying out the advisory role is our highest priority and principle.

In the recent years MASA has developed extensive international cooperation that contributes to the affirmation of the Macedonian scientific and artistic work and to the increasing of the reputation of MASA and of the Republic of Macedonia in international scale. Today, our Academy cooperates with more than 30 foreign academies and scientific societies and is a member of 7 international associations of academies. In the recent years the cooperation with the academies from the neighboring countries has been intensified, as well as with the Leibniz Society of Sciences from Berlin, and also, within the so-called Berlin process (Joint Science Conference of Western Balkans Process / Berlin Process) the cooperation with the German National Academy of Sciences – Leopoldina, with the French Academy of Sciences, the academies of Southeast Europe and others.

Due to the results achieved in its work, MASA and its members have won a number of high national and international awards. In the past 50 years, MASA has won around 90 awards and recognitions – charters, plaques, certificates of appreciation, medals and decorations from national and international scientific, educational, artistic and other institutions. Particularly, it should be noted that MASA has been awarded with the high decoration Order of the Republic of Macedonia for the contribution to the development of the scientific and research activity and artistic creativity of importance to the development and affirmation of the Macedonian science and state, which is awarded by the President of the Republic of Macedonia, as well as the prestigious Samuel Mitja Rapoport award of the Leibniz Society of Sciences from Berlin, which, for the first time, has been awarded to MASA. Today, 22 members of MASA have the status of foreign, corresponding and honorary members, as well as holders of honorary PhDs at around 60 foreign academies, scientific societies and universities.

***

The developmental trajectory of MASA unambiguously confirms that the Academy, in its 50 years of existence and work, faced with periods of heights, but also periods of descents and turbulences that are most directly linked to the situation in the Macedonian society, i.e. with crisis periods of different nature – the dissolution of the former common state (SFR Yugoslavia), problems with the recognition of the international status of the country after its independence, the embargoes and the blockades of the country in the early transition years, the internal conflict in 2001 and the political crisis in the last two-three years. In such crises and tense periods the criticism for the Academy grew – that MASA is an institution closed in itself, that MASA stays away from the current issues and developments in the country, and so on. On the one hand, it is a result of the insufficient understanding of the social role of the Academy – MASA is the highest scientific institution, where hasty reactions of columnist 'type', with daily political features are not characteristic. On the contrary, MASA uses facts and arguments. The basic activity of MASA, the results achieved in the scientific research and the artistic work is our identification within the national and international professional and scientific community, and beyond, within our society. On the other hand, this criticism and perception of MASA has a real basis in the fact that MASA, as opposed to the huge opus of implemented scientific and research and artistic projects still insufficiently affirms the results of its scientific and artistic production to the public. It is our weakness that we must overcome in the future. Of course, we cannot and must not “turn a blind eye” to the other weaknesses and omissions which, at least from time to time, we have faced with over the past 50 years and which we will face with in the future – insufficient scientific criticism of the events in the field of sciences and arts, insufficient resistance to political influence etc. On the contrary, in the future, we will have to clearly identify the weaknesses and the oversights in our work and to find out the right approaches to overcome them.

Today we live in a world of great science. The strong development of sciences, the new technological model based on information and communication technologies, the new wave of entrepreneurial restructuring of economies and societies, the globalization of the world economic activity, opened new perspectives to the economic growth and the development of individual countries and of the world economy as a whole. However, these processes, by their nature, are contradictory. The latest global financial and economic crisis of 2007-2009 revealed the contradictions of the globalization and the discontent of the people from it – the uneven distribution of wealth and power among individual countries, destruction of the resources and the environment worldwide, exhaustion of power of the existing technology and development models. These processes resulted in other problems – refugee and migration crises, strengthening of the regional and national protectionism despite the efforts to liberalize the international trade, fencing of the countries with walls at the beginning of the new millennium, changes in the economic and technological power and of the geo-strategic position and importance of entire regions and continents, etc. Nevertheless, one thing is a fact – societies that aspire to grow into societies and knowledge-based economies more easily deal with all the above mentioned problems, challenges and risks of the modern world. Of course, moving towards a development knowledge-based model assumes large investments of resources in education, science, research and development and in culture, simultaneously accompanied by well-conceived and devised strategies on development of these crucial areas of the human spirit and civilizational endurance. Hence, this fact, undoubtedly, emphasizes the special significance of the national academies of sciences and arts in achieving this objective.

In the recent years the Republic of Macedonia has been facing with the most difficult political and social crisis in the period after its independence. We are facing a crisis of the institutions, breach of the principles of the rule of law, the phenomenon of “captured state”, a decline in the process of democratization of the society and falling behind on the road to the Euro-Atlantic integration processes. The problems that are now in the focus of our reality will require major reforms, much knowledge, energy and political will to overcome them. In this sense, and in this context, the role of MASA and of the overall scientific potential of the country in overcoming the crisis is also particularly important.

The above summarized evaluations and considerations about the development of MASA in the past 50 years, about the achievements in the realization of its basic activity, about the problems it faced and faces with, about the major challenges arising from the new age and which are determined with the changes in the international and national environment, they alone define the main priorities of our Academy in the forthcoming period:

- Our long-term goals are contained in the mission and vision of MASA as the highest institution in the field of sciences and arts. The mission of MASA is through the development of the basic functions that are characteristic for all modern national academies of European type, to give its full contribution to the inclusion of the Macedonian science and art in the modern European and world trends, and our vision is the Republic of Macedonia to become an advanced society based on science and knowledge;
- In the forthcoming years the focus of the scientific and research activity and artistic work of MASA, in cooperation with the other scientific and research institutions in the country and with government experts, will be particularly focused on the elaboration of issues and topics that are most directly related to the sources of the current political and social crisis in the country in order to offer possible solutions, approaches and policies to overcome it;
- The issues related to the Euro-Atlantic integration processes of the Republic of Macedonia, their continuous and persistent scientific monitoring and elaboration and active participation of MASA members in the preparation for the accession negotiations with the EU will remain a high priority on the agenda of

MASA. Our ultimate goal is the Republic of Macedonia to become a democratic, economically prosperous and multicultural European country.

- The increasing incorporation of the international dimension in the scientific and artistic work of MASA, through the cooperation with foreign academies, scientific societies and other scientific institutions, through application and work on scientific projects financed by the European funds and the funds of other international financial institutions, also remains our important priority.

Let us congratulate ourselves on the great jubilee – 50 years of the Macedonian Academy of Sciences and Arts.

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IN HONOUR OF ACADEMICIAN BOJAN ŠOPTRAJANOV'S 80th BIRTHDAY

Bojan Šoptrajanov was born on 26 January 1937 in Čačak, Serbia. His parents were then high-school teachers, Nevena a teacher in geography and Todor a teacher in history. He was given a name which, that time, was rather rare.

He grew up in Čačak and Prokuplje (then Kingdom of Yugoslavia) and in 1941 moved to Skopje (then under Bulgarian occupation). Later on he lived in Belgrade and Veles, returning to Skopje in 1950 and stayed there ever since, except for a year and a half while working for a master degree in USA.

In 1965 he married Lidija, presently a retired full professor of chemistry.

He has two daughters, Jasna and Lada, a granddaughter, Viktorija and three grandsons: Ivan, Bojan and Marko. Lada is married to Velimir (Veljo) and Viktorija and Marko are their children.

EDUCATION

His first grade (which, during the war times, lasted for only three weeks) was in Skopje (in Bulgarian) and the rest of the primary schooling took place in Skopje (in Macedonian), Belgrade (in Serbian) and Veles (again in Macedonian). He then attended a high school ("Cvetan Dimov") in Skopje up to 1955 when he enrolled in the studies of chemistry at the Ss. Cyril and Methodius University in Skopje. He graduated in 1960 as the best student of the Ss. Cyril and Methodius University on graduation and was the best student of the Faculty of Natural Sciences and Mathematics in the first 25 years of its existence (1946–1971).

His graduate studies were at Indiana University in Bloomingon, IND (1964–1965) completed with the master`s thesis entitled "*Vibrational Assignment of the Infrared Spectrum of 1,2,5-Thiadiazole*".

The doctoral thesis (1973) of Bojan Šoptrajanov is enitled "*Spectroscopic Investigation of Crystallohydrates with Particular Attention to the Spectrum of Water – Systems with Very Low δ(HOH) Frequencies*" (The original title in Macedonian is "*Спектроскопско изучување на кристалохидрати со посебен осврт на спектарот на водата – Системи со мошне ниски δ(HOH) фреквенции*".).

TEACHING POSITIONS

The first teaching position of Bojan Šoptrajanov was as an assistant-lecturer at the then Techical Faculty – Technological division (1960–1961).

After a year in the army, in 1962 he was elected to the position of assistant-lecturer in the Faculty of Natural Sciences and Mathematics – Division of Chemistry and held that position until 1969.

In 1969 he was elected to the position of docent (assistant professor) at the Faculty of Natural Sciences and Mathematics, University of Skopje, remaining at that position until 1974.

He became an associate professor in 1974 and held that position until 1974, at first at the Faculty of Natural Sciences and Mathematics – Division of Chemistry and then at the Faculty of Chemistry (1978).

Bojan Šoptrajanov was elected to the position of full professor in 1978 and held that position until 2002 when he retired.

Nominally he was a professor of physical chemistry but taught (for undergraduate or graduate students in Skopje, Štip and Leskovac) other subjects such as Radiochemistry, History of chemistry, Spectroscopic applications of group theory, Spectroscopic methods for determination of molecular structures, Methodology of chemistry teaching and Methodology of research. Most of these courses were taught for the first time by him except for his two physical chemistry courses that he reshaped and modernized.

PROFESSIONAL AND OTHER POSITIONS

Bojan Šoptrajanov held a number of professional positions, among them:

Vice dean (prodekan) of the Faculty of Chemistry (1983–1985); vice president (prorector) for education and research of the Ss. Cyril and Methodius University in Skopje (1988–1990); member of the Macedonian Academy of Sciences and Arts (MASA) from 1994; vice president of MASA (2008–2011); head of the Division of Mathematical and Technical Sciences in MASA (2003–2007). Presently he is the head of the Research Center for Environment and Materials in MASA.

He is a member of the European Academy of Sciences and Arts (since 2008).

Also: The last president of the Union of the Chemical Societies of Yugoslavia; president and vice president of the Union of Chemists and Technologists of Macedonia (Sojuz na hemičarite i tehnolozite na Makedonija); president of the Commission for Spectroscopy of the Union of the Chemical Societies of Yugoslavia) and others.

RESEARCH ACTIVITIES, PUBLICATIONS AND COMMUNICATIONS

- Main area of research: **structural chemistry** (particularly vibrational spectroscopy);
- Other areas of research interest: education in general; use of computers in education; systems of scientific information;
- Principal investigator: A number of projects within Macedonia and former Yugoslavia, and projects for cooperation in science with colleagues from Uppsala, (Sweden), London (UK), Moscow (Russia), Sofia (Bulgaria), Halle (Germany) and Siegen (Germany);
- Papers: Over 200 scientific and professional papers of which more than 100 are included in the data base of the Institute for Scientific Information (ISI);
- Scientific communications: Approximately 350 communications at scientific meetings (around 150 at international conferences and approximately 90 at meetings outside Macedonia);
- Invited speaker: Plenary lecturer at scientific meetings in Macedonia, in former Yugoslavia, in Ukraine, in Turkey and key-note speaker at Colloquium Spectroscopicum Internationale;
- Lectures abroad: In Uppsala, London, Halle, Siegen, Belgrade, Sofia;
- Scientific journals: Founder and editor-in-chief of the *Macedonian Journal of Chemistry and Chemical Engineering* (formerly *Bulletin of the Chemists and Technologists of Macedonia*), presently member of the Editorial Council of the Journal, previously member of the editorial boards of two Yugoslav journals (*Hemijska industrija*, *Yugoslav Chemical Papers*).

TEACHING EXPERIENCE

- Subjects taught (for undergraduate or graduate students in Skopje, Štip and Leskovac): Physical chemistry, Spectroscopic applications of group theory, Spectroscopic methods for determination of molecular structures, Methodology of chemistry teaching, Methodology of research;
- Mentor of eight doctoral candidates of which seven are already university teachers (active or retired) and eighteen candidates for the master degree;
- Author of a number of high-school text-books in chemistry and texts for university students.

ORGANIZATION OF SCIENTIFIC MEETINGS

- President of the scientific committee at four all-Yugoslav congresses;
- Other organizational activities: Member of the organizing and scientific committees of a number of meetings (one international), mainly in chemistry.

AWARDS

- Best student of the Ss. Cyril and Methodius University on graduation;
- Best student of the Faculty of Natural Sciences and Mathematics in the first 25 years of its existence;

- Medal: Merits for the people with a silver star;
- Two plaques (1999 and 19840 of the Ss. Cyril and Methodius University;
- The national award "11. Oktomvri" in 2005;
- The Throne Medal "Macedonian Cross" of the Macedonian Orthodox Cherch;
- The Tomasius Medal of the University of Halle;
- President of the Board for awarding the "Sv. Kliment Ohridski" award (two terms), member of the Board;
- Member of the Board for awarding the "Sv. Kliment Ohridski" award;
- Member of the Board for awarding the "Goce Delcev" award;
- Others such memberships.

OTHER INTERESTS

- He was an active "izvidnik" (boy scout);
- He has a keen interest in the language in general and, especially, in the language of chemistry (holding a degree of *honorary linguist* bestowed by the members of the Research Center for Areal Linguistics at MASA);
- Bojan Šoptrajanov has been, for quite a long time, abstractor in the best known referral publication Chemical Abstracts;
- His work has been appreciated by colleagues from abroad and within his research group.

Editorial Board

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Overview

Thinking about a suitable topic to be put at the opening pages of this special issue dedicated to the 80th anniversary of academician Bojan Soptrajanov, we deemed more than appropriate to place the thought provoking overview of a big friend of Macedonia and the Ss. Cyril and Methodius University in Skopje, our honorary professor James Trefil, a Clarence Robinson Professor of Physics, from the George Mason University in Fairfax, Virginia. Prof. Trefil is a great scientist and even greater educator (the latter is known to anyone that has read at least one of the 50+ books written by him). The overview is on the (always relevant) topics like science, science education, science teaching and scientific literacy, as a need in a truly democratic society.

SCIENCE EDUCATION AND THE TWO CULTURES[•]

James Trefil

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In 1959 the British scientist, novelist, and government official C.P. Snow (1905–1980) gave the prestigious Rede Lecture at Cambridge University. His argument, which has come to be known as the 'Two Cultures' view, was that the academic world was divided into two non-overlapping camps which he characterized as the scientific and the literary cultures. He argued that while scientists generally have some background in the humanities – how many scientists do you know, for example, that have never seen or read a play by Shakespeare?–literary types generally know little about science. In what is perhaps the most famous passage in his book, he recounts the experience of listening to literary types going on about the illiteracy of scientists and then asking "How many of you can tell me what the Second Law of thermodynamics is?" He was, as you might expect, met by a thundering silence.

Approaching the Two Cultures divide from the science side, there is a question that comes naturally to the mind of someone involved in science education: given that we want to provide those in the literary culture with some knowledge of science what, exactly, is the kind of science we need to teach? What, in other words, do scientists need to do to help our colleagues learn enough about what we do to help erase the chasm that Snow spoke about almost 60 years ago? In what follows, I will address this question from the point of view of the American educational system.

There is, in fact, a long tradition of thought on the issue of science education in America. Like almost everything else in American educational philosophy, it can be traced back to John Dewey (1859–1952). At the opening of the twentieth century, he wrote:

> *Contemporary civilization rests so largely upon applied science that no one can really understand it who does not grasp something of the scientific method… on the other hand, a consideration of scientific resources and achievements from the standpoint of their application to the control of industry, transportation (and) communication, not only increases the future social efficiency of those instructed, but augments the immediate vital appeal and interest of the subject….*

Dewey summarized his philosophy this way:

[•] Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

The formation of scientific habits of mind should be the primary aim of the science teacher in the high school

A word of explanation: in 1910, when Dewey wrote these words, fewer than 10% of Americans actually finished high school (i.e. remained in school to age 18). To translate this directive to modern times, then, you would probably want to substitute "high end university" for "high school" in the above.

But regardless of the level of students we’re talking about, Dewey’s notion of imparting a ‘scientific habit of mind’ has carried through ever since it was first uttered. It would, I think, be the consensus view of scientists today, as it was back in 1910. In the words of Nobel Laureate Carl Weiman,

We want them to think like us

Another way of characterizing this approach to science education is to say that the goal of providing science education should be to produce miniature scientists–people who can do, in a limited way, what scientists do. Leaving aside the question of whether this goal is actually attainable – and I have grave reservations on that score – we can ask whether it is desirable. Is this really the best use of the limited time available for us to teach non scientists?

I suggest that it is not. In the spirit of this festschrift, in fact, I would propose another goal:

Students should know as much about science as they do about Shakespeare

Or, in a sentence I often use when I want to annoy my colleagues,

Students should be able to read the newspaper on the day they graduate

The traditional goal enunciated by Dewey is basically a requirement that students be able to *do* science at some level. This is the goal that I am arguing is inappropriate. To make this point, let me take an example from my own education. At the university I took a number of courses with names like "music appreciation" and "introduction to renaissance art". These courses enriched my life immeasurably, which is easy enough to understand. What they did *not* do, however, was demand that I be able to play a musical instrument or create a painting. Instead, they gave me the background I needed to make judgments about music and works of art without asking that I actually to what musicians and artists do.

To make this point crystal clear, let me point out that as a lifelong opera buff, I feel perfectly qualified to decide whether the tenor did or did not do a good job on his marvelous first act aria in *La Boheme*, even though I would never dream of trying to perform that aria myself. I would suggest that a similar approach to science education for non-scientists is more appropriate that wanting them to acquire a 'scientific habit of mind'.

Having said this let me make a brief diversion to talk about a subject that often arises at this point. Given that we want students to 'appreciate' science the way they appreciate music, should we teach them about what we know of the way the world operates or should be instead emphasize the way that knowledge is gained? Should we, in other words, emphasize content or method?

Unfortunately, the debate on this issue often involves setting up straw men ("You just want them to memorize facts" or "You can’t think critically about a subject you know nothing about."). My own view is that everyone can be placed somewhere on a method-content continuum, with few people at either extreme. As will be clear from what follows, I locate myself rather more toward the content end of the spectrum, because I believe that that better serves the achievement of scientific literacy. Having said this, I hasten to add that I believe that the correct answer to the question of content vs. method is 'yes'. Some mix of the two is necessary for scientific literacy but, as I shall argue below, I think the weight of the educational system should be on the content side. We want our students to have a wide acquaintance with the scientific worldview, and this is not something that can be acquired by learning about something called the 'scientific method'. I would, in fact, suggest yet another general rule we can adopt:

If you expect a student to know something, you should tell him or her what it is

Teaching students about mechanics by having them roll balls down inclined planes may indeed impart something about the scientific method, but it won’t help them grapple with an issue like stem cell research, any more than learning French will help them understand Chinese. To argue otherwise is to advocate what I call the "teach them relativity and they’ll derive molecular biology on the way home" school of thought.

One way to approach the issue of the proper goal of science education is to ask ourselves how students will encounter science in later life. A cursory glance at a newspaper or a magazine shows that science will always come up in a way that is (1) multidisciplinary, and (2) part of a much larger issue. The global warming discussion, for example, involves many branches of science, but quickly moves into areas of economics, law, international relations, and ethics. The science, then, serves as an entry pass into the wider debate and is not an end in itself.

I often find is useful to think about scientific literacy in terms of a broader concept called cultural literacy. Cultural literacy is defined as the knowledge that people, in a given place and at a given time, assume other people possess. Americans, for example, will use a term like "World Series" or "Wall Street" without explaining what they mean because they assume the person to whom they are speaking already knows what they are. The sum of all these unspoken assumptions comprises cultural literacy. In passing, I should note that the acquisition of cultural literacy would be an admirable goal for the entire educational system.

Scientific literacy is that part of cultural literacy that deals with science and technology. It is important to understand that, while the rationale for needing to know the content of other parts of cultural literacy revolves around the fact that other people make assumptions about your knowledge, the rationale for scientific literacy is slightly different. I will define scientific literacy as what you need to know to enter the kind of science-tinged public debates discussed above.

When it comes to scientific literacy, we are in a classic good news-bad news situation. The good news is that scientists are pretty much in agreement about what the important parts of science are–you’d have to look a long time, for example, to find someone who wanted to exclude Newton’s Laws of Motion from the list of essential scientific principles. The bad news is that we’ve done a pretty poor job of producing a scientifically literate population. Considering the data on American scientific literacy that has been collected over the years, we see that over two thirds of Americans don’t possess even the minimal amount of knowledge needed to deal with everyday issues.

Fortunately, the inherent structure of science suggests a scheme for imparting exactly this sort of knowledge. I often use the analogy of a spider web, where all the world’s phenomena, from stars to microbes, are located on the outer rim. Start anywhere and begin asking questions, and you begin to move in toward the center, finding unexpected connections along the way (think of Maxwell’s discovery of electromagnetic radiation as an example). At the very core of the web are a relatively small number of governing principles–I call them Great Ideas–that form the superstructure, the skeleton, on which the scientific view of the world is based. *Everything* in the universe, from the smallest subatomic particle to the largest galactic cluster, operates according to these laws. This means that the matrix of knowledge represented by the Great Ideas is an ideal framework that out students can use to deal with public issues, since anything they are likely to encounter will involve some subset of these laws.

For reference, here are the Great ideas as given in one reference:

The Universe is Regular and Predictable

The energy of a closed system is conserved

Heat will not flow spontaneously from a cold to a hot body

Maxwell’s Equations

Matter is made from atoms

The properties of materials depend on the identity, arrangement, and binding of the atoms of which it is made

In the quantum world, you cannot measure an object without changing it

The laws of nature are the same in all frames of reference

There is a great deal of energy in the atomic nucleus

The nucleus is made of particles, which are made of quarks……

Stars live and die like everything else

The universe began in a hot, dense state about 14 billion years ago and has been expanding ever since

The surface of the Earth is constantly changing

The Earth works in cycles

Life is based on chemistry

The behavior of molecules in living systems depends on their shape

Life’s chemistry is coded for in DNA

All living thing share the same genetic code

Life evolved through the process of natural selection

In addition to their universality, there is another aspect of modern science, seldom discussed, that argues in favor of a Great Ideas approach to science education and scientific literacy. The fact of the matter is that science has changed in a fundamental way over the last 50 years, a way that has yet to be incorporated into educational thinking. The cause of the change is simple: the advent of the digital computer.

Look at it this way: from Isaac Newton on, the progress of science was governed by the ability to do pencil-and-paper mathematics. A seemingly simple question like "Will the planets in the solar system ever occupy the same positions they do now?" involves so many variables (the positions and speeds of the planets, their moons, the larger asteroids, etc.) that the question couldn’t be answered with the mathematical techniques available at the time, and, indeed, regular prizes were awarded to scientists who developed techniques for approximating the answer. Later on, when major astronomical observatories in Europe and North America began accumulating mounds of data, they hired teams of human beings (usually women) to analyze it. Interestingly enough, these people were called 'computers'.

Up until the middle of the twentieth century, in other words, scientists concentrated on describing relatively simple systems – systems that could be analyzed by hand. The advent of the digital computer changed all that. For the first time in history, the growing power of the computer could be used to analyze every more complex systems, from trans-sonic flow over an airfoil (the 747 was the first airplane to be designed by computer) to, today, gene networks and global climate. And this development, in turn, has changed the way that science presents itself to the average citizen.

Take global warming as an example. The primary tool in climate prediction is the so-called global circulation model (GCM). These giant computer programs, monuments to human ingenuity, try to incorporate all the different phenomena that can influence the climate. For example, they have to account for the effects of sea ice, since ice reflects sunlight while water absorbs it. They have to deal with vegetation, aerosols, clouds, and everything else that might be important. As a result, there probably isn’t an individual on the planet who really understands everything that these models do. Furthermore, most PhD scientists have no more ability to judge the output of these models than does the average citizen–being an expert in string theory or molecular genetics just isn’t going to get you very far in analyzing claims based on GCM calculations.

So what does it mean to talk about a 'scientific habit of mind' in this kind of situation? Measuring the melting of an ice cube or keeping weather record for a few months–the sorts of activities often associated with teaching the scientific method–isn’t going to help much in understanding climate change. I would suggest, instead, that the best way to equip our students to deal with the world they will be living in is to give them the intellectual superstructure embodied in the Great Ideas, instill in them an appreciation of the world’s complexity, and let them work things out for themselves.

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Original scientific paper

MULTI-SCALE MODELLING OF WATER AND HYDROXIDE IN SOLIDS AND SOLUTIONS•

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This report discusses some of the most pressing challenges that need to be overcome for computational condensed-matter chemistry to become fully accepted, at par with experiments. The prospects are rather bright. By means of a few examples, all connected to the bound *water molecule* and *hydroxide ion*, and their mysteries, the unique capabilities of theoretical calculations will be demonstrated. They provide new insights and details, and can even surpass experiments in accuracy.

Key words: Multi-scale modelling; condensed-matter chemistry; water molecule; hydroxide ion; solids; solutions

INTRODUCTION

Chemical industries worldwide make use of catalytic surfaces to produce enormous amounts of thousands of different chemicals. The very same factories use catalytic surfaces to mitigate the consequences of this production through pollution control processes. Many of the key processes in environmental and atmospheric chemistry, electrochemistry and materials chemistry are even governed by ion-water interactions and water/solid interfaces. As water is omnipresent, it affects a range of important chemical processes at functional surfaces and interfaces, with beneficial or damaging consequences. To improve and develop the materials themselves and the accompanying molecular processes, new knowledge and insights will be needed. These developments are unfortunately hampered by the fact that the atomic-level mechanisms that govern the key functionalities of materials and their interfaces are usually unknown.

Here Computational Materials Chemistry can be of immense help as it provides results of unmatched detail, as well as the needed atomic-level understanding – *if* the computational models and methods are accurate and realistic enough. Also, on the experimental side, new powerful characterization techniques for surface and interface systems have emerged in the last decades and new infrastructures are under development in Europe and in particular in Sweden (Max-IV and ESS). The role of modelling will now become even more important as the dimensions of experimental and computational targets approach each other.

A main scientific challenge in focus of my own research concerns the exploration of the links between microscopic structural features and the properties and (re)activity of solid surfaces and nanoparticles. We also devote much effort to the design of modelling strategies that can make "calculations meet reality", or reach the slightly less ambitious goal of making "calculations meet experiments". *Water* has a prominent position in this effort of ours and this molecule insists on much attention because of its importance, intricacies and ubiquity, and because it is such a delicate and difficult molecule to model.

In these endeavors we are grateful for the many important contributions made by Professor Bojan Šoptrajanov and his research team regarding

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•Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

molecular vibrations and structure-property relationships in crystalline hydrates and other hydrogen-bonded and aqueous systems. These findings are of great scientific value not only to myself and my colleagues in the former Hydrogen-bond project led by professor Ivar Olovsson at Uppsala University, but also to the international scientific community at large. Below I will give a brief overview of the research I and my group are involved in, the challenges that we are up against, and some promising results. I will focus on our studies involving water and vibrational calculations.

COMPUTATIONAL CHALLENGES

Computational materials chemistry is a challenging topic because:

- Chemistry deals with interactions, reactions, and bonding *between* species, and not just with their individual properties. Complicated electronic structures and their changes often need to be described.
- The thermodynamic conditions, in particular temperature effects, as well as dynamical processes, also often need to be taken into account.
- The structures of real materials systems are generally very complex, containing imperfections and defects, interfaces or multiple phases, and attached molecules. Large-scale computational models are needed to accommodate such diversity.

Given this complexity, the development of methods and strategies to build relevant models is clearly central. There exists no single model or work-flow capable of treating simultaneously the full length-, time- and energy-ranges, from the electronic level to macroscopic devices. Instead a set of models and work-flows along a multi-scale ladder, illustrated in Figure 1a, need to be interconnected in clever ways. At the core of this daunting task lies the issue of obtaining “sufficient accuracy” for the problem at hand. Together with my co-workers, my own piece in this puzzle is the development of multi-scale methods and models to bring modelling closer to the complexity of realistic applications. With combinations of high- and low-level electronic structure and force-field models, we explore structure-activity relations for inorganic crystals, surfaces and nano-particles, and in aqueous media.

RESULTS – METHOD AND MODEL DEVELOPMENT

Some methodological areas in need of close attention and developments that we contributed to are:

- Multiscale modelling techniques: on the one hand protocols to move "sequentially" and seamlessly along the multiscale ladder (see Figure 1a) and on the other "concurrent" approaches such as the embedding, or QM/MM, models (see Figure 1b).
- High-quality alternatives to standard quantum-mechanical methods, e.g. advanced force-fields or approximate quantum-mechanical (QM) methods.
- Improved models to describe the short- and long-range interactions with a system’s surroundings, such as solvent effects of molecules in solution or at solid-liquid interfaces (see Figure 1c).
- Strategies and software that allow us to link simulated data to experimental results (spectra, images, etc.); see Figure 1c.

Our multi-scale modelling efforts focus on the "chemical scales" within the multi-scale ladder in Figure 1a. In the lower left-hand corner (QM), we use various flavors of density functional theory (DFT) and wavefunction-based methods. One step up the ladder, we currently use the self-consistent charge density functional based tight-binding approximation (SCC-DFTB), which is an approximate DFT method, about two orders of magnitude faster than standard DFT calculations. The accuracy and transferability of SCC-DFTB models crucially depend on a set of parameters, which have to be carefully optimized, an area to which we devote considerable effort.

At the next step up on the ladder, we dispose of the explicit electronic information and use/develop parametrized force-fields (FFs), often of a sophisticated form that allows for bond breaking and formation (e.g. of the ReaxFF type). Force-fields allow to reach experimentally relevant system sizes and time scales. As indicated in Figure 1, we use data obtained at the QM-level to parametrize models higher up in the ladder. A great deal of research and insight is required to determine which degrees of freedom are safe to sacrifice when approximations need to be made. Some recent publications here are our SCC-DFTB work on H_2O/ZnO (10–10) [1] and CeO_2 [2], and our ReaxFF work on CeO_2 [3].

Data generation is one side of the coin, data analysis for property calculations and materials characterization is the other. Both aspects require adequate models and workflows, and both present theoretical and computational challenges. Our simulated IRRAS spectra of the CO/TiO_2(110) system compared to experiment is a good example [4]. Another one is our generation of simulated STM images of a defective CeO_2(111) surface, where we mimicked experimental images for three cases of surface defects – oxygen vacancies, F substituents and H substituents – and challenged the interpretation of experimental STM images prevailing in the literature [5].

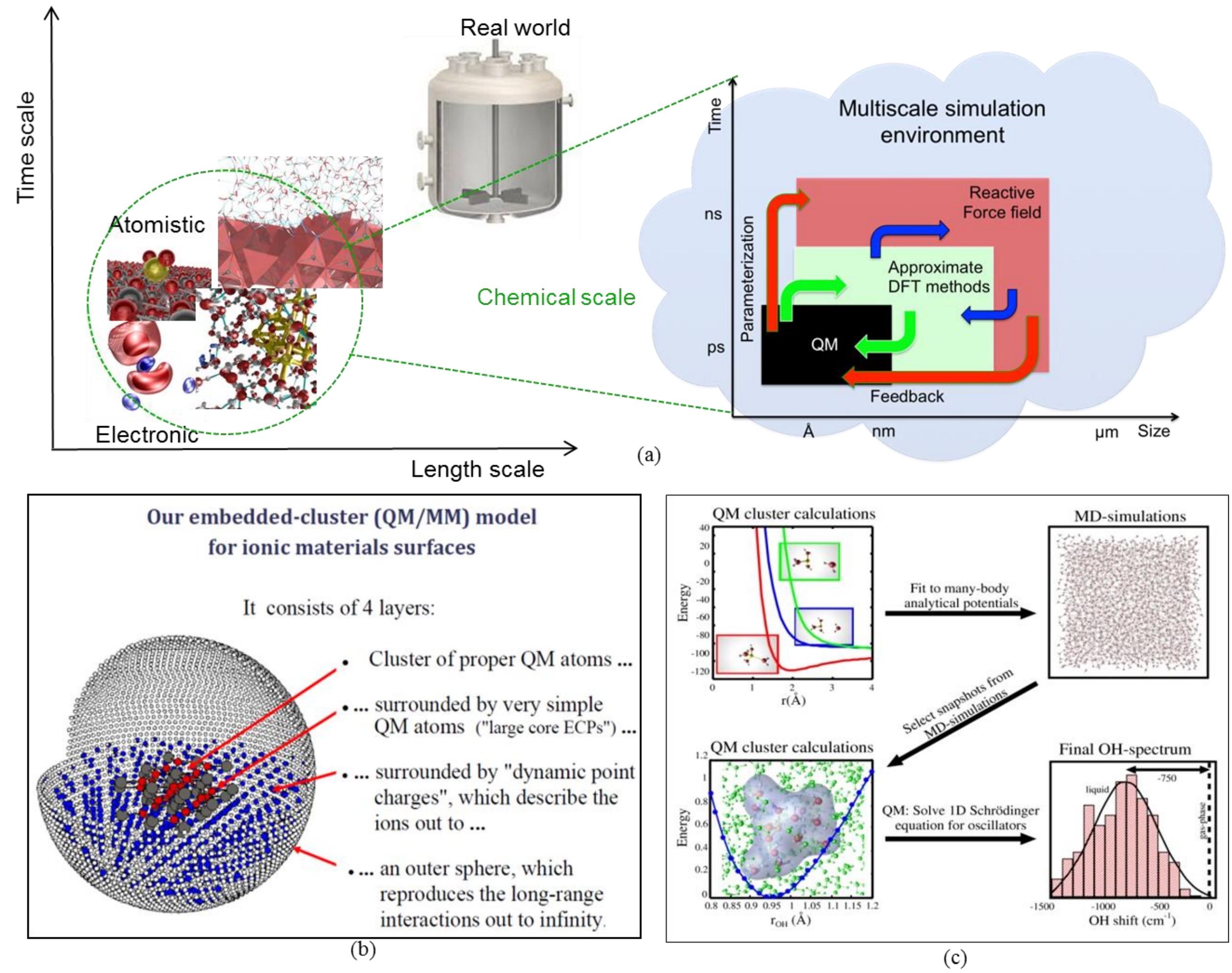


Figure 1. Overview of the multi-scale modelling efforts in our group. **(a)** The multi-scale ladder to the left indicates systems with electronic and atomistic resolution, while more coarse-grained (mesoscopic) models and continuum models, which lie in the gap between atomistic models and the Real World, are not included in the figure. The figure to the right lists the methods most frequently used in our group. The arrows pointing upwards along the ladder indicate that fine-grained model are used to parametrize more coarse-grained models. **(b)** Our QM/MM approach for solid ionic surfaces. **(c)** An illustration of our multi-stage strategy to calculate vibrational spectra in liquid solutions: QM_{elec} => FF-based MD => QM_{elec}/MM potential energy curve => $QM_{nuclear}$ calculations of the vibrational energies. The sample system in this figure is $Al^{3+}(aq)$ with 10000 water molecules interacting through an ab initio-generated force-field with effective three-body terms [12].

RESULTS – SCIENTIFIC APPLICATIONS

Three examples from our current research are presented below. They are connected to experimental investigations, either as collaborations, or using data from the literature.

Water in crystalline hydrates

As already commented on above, water is an important and treacherous molecule: seemingly so simple, but in practice so difficult to model satisfactorily. We have found that theoretical calculations for ionic hydrate crystals present a unique opportunity to gather novel information about the water molecule and its structure-property relations [6]. Ample high-quality structural data are available from diffraction experiments for a large number of crystalline hydrates where water coexists with metal ions, sulphates, nitrates, halides etc., and we, the modelers, can then focus on modelling *the properties* themselves. Our ongoing study of structure-property relations for crystalline hydrates can be seen as a "Materials informatics" project for the water molecule.

We recently proposed that *highly hydrated* crystals, represent an "economical" advantage, allowing us to collect information about many water molecules "in one go"; for example the nine structurally different water molecules in the $Al(NO_3)_3 \cdot 9H_2O$ crystal. Figure 2 displays a property which is difficult to extract from experiment, namely the *in* *situ* polarisation of water inside a crystal. The contour diagrams display two of the nine unique water molecules and reveal that the nature of each of them is strongly altered by the surroundings; the reference in the figure is the gas-phase molecule, which would thus have no contours at all. The crystal-induced polarisation in Figure 2 is especially dramatic for the molecule labeled W5, which is bound to an Al^{3+} ion.

This result ties back to the multi-scale picture in Figure 1c, which displayed the computational scheme that we used to generate the infrared vibrational spectrum for the first-shell water molecules around the Al^{3+} ion in an aqueous solution. Figure 2c demonstrates that water molecules binding to Al^{3+} in the solid state become highly polarized and we may infer that this should happen in aqueous solution as well, thereby offering a likely explanation for the large frequency downshift observed in the vibrational spectrum in Figure 1c.

Diffraction-determined *r*(OH) and *R*(O···O) distances taken from the literature for four highly hydrated crystals, $Na_2CO_3{\cdot}10H_2O$, $MgSO_4{\cdot}7H_2O$, $MgSO_4{\cdot}11H_2O$, and $Al(NO_3)_3{\cdot}9H_2O$ are shown in Figure 3a**.** The result is not impressive. In Figure 3b the results from the X-ray diffraction data-set have been removed, leaving only the three neutron diffraction studies.

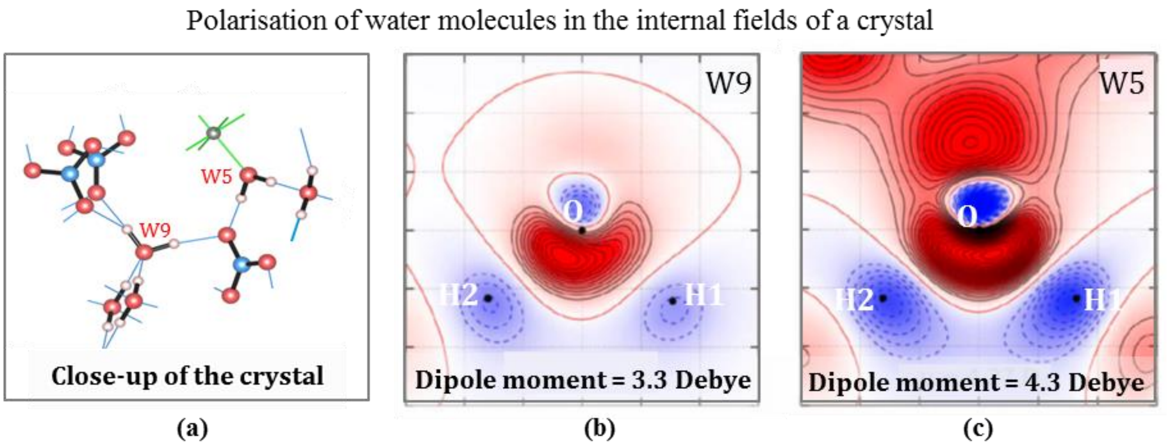


Figure 2. Polarization of water molecules inside a crystal of the water-rich $Al(NO_3)_3 \cdot 9H_2O$ crystal, from quantum-mechanical calculations [6]. The figures display both the difference electron density (total electron density of the crystal *minus* the sum of the electron densities of the isolated building blocks) and the total dipole moment of the water molecules. Red areas in the difference electron density maps indicate "more electrons" than in an isolated molecule, blue means "fewer electrons".

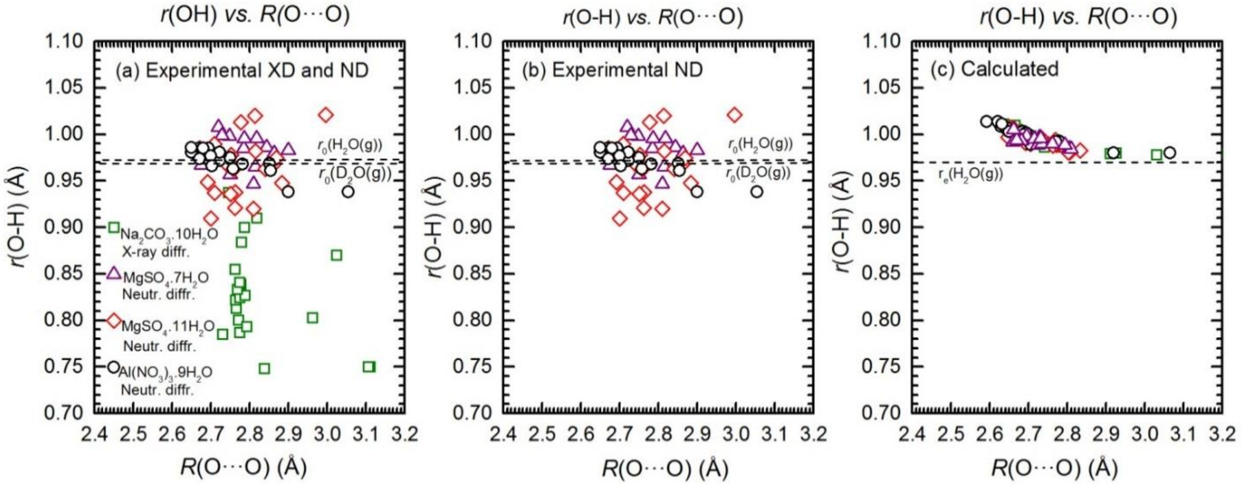


Figure 3. *r*(OH) and *R*(O···O) correlations from experiments and from our calculations for four highly hydrated crystals, $Na_2CO_3{\cdot}10H_2O$, $MgSO_4{\cdot}7H_2O$, $MgSO_4{\cdot}11H_2O$, and $Al(NO_3)_3{\cdot}9H_2O$. **(a)** Correlations based on X-ray and neutron diffraction experiments (references are given in Ref. [6]). **(b)** The same figure as in (a) except that the X-ray diffraction data have been excluded. **(c)** Correlations based on the optimized structures from our DFT calculations described in Ref. [6].

The result is somehow improved, although no correlation is discernible. We also note that the intra-molecular water OH distances in the crystals are sometimes shorter than the gas-phase value, a result which is obviously unphysical. The reason behind these systematic experimental distance "errors" is known and was elaborated on in Ref. 6. The resulting '*r*(OH) vs. *R*(O···O)' correlation curve from the quantum-mechanical crystal calculations is shown in Figure 3c. As should be, the scatter of the points is reasonable and all points lie above the free-water value. Clearly, the calculations perform better than experiment in locating the H atom.

We are of course concerned with the accuracy of the methods and models we use. In a current (unpublished [7]) study we investigate the performance of a range of dispersion-corrected DFT methods concerning the structure of the four crystalline hydrates mentioned above. Without going into details here, we note from the dart board in Figure 4 that, while the traditional LDA method is not competitive, many of the methods reproduce the experimentally determined hydrogen-bond distances very well.

Next we will turn to the OH vibrational frequencies. We routinely calculate anharmonic intra-molecular OH vibrational frequencies as the OH vibrational anharmonicity is large and very frequency-dependent. Moreover, we routinely calculate uncoupled OH vibrational frequencies to make use of the fact that an uncoupled OH frequency (i.e. corresponding to a one-legged OH vibration) only pertains to one OH oscillator; its gas-to-crystal frequency shift is a descriptor of only that oscillator's environment. The uncoupled OH vibration is thus more informative than the coupled ones, as far as intermolecular interactions go. For the very same reason experimentalists often try, whenever possible, to perform isotope-isolated experiments. Figure 5 shows our calculated OH frequencies for the four crystalline hydrates mentioned above against the electric field strength component along the vibrating OH bond, probed at the equilibrium H position. The figure displays quite a good correlation and a rather narrow distribution around the least-squares-fitted line. A comparison of our curve with that of Auer and Skinner [8] for instantaneous structures in liquid water reveals that our correlation is tighter, in spite of the fact that it it covers larger frequency and field ranges.

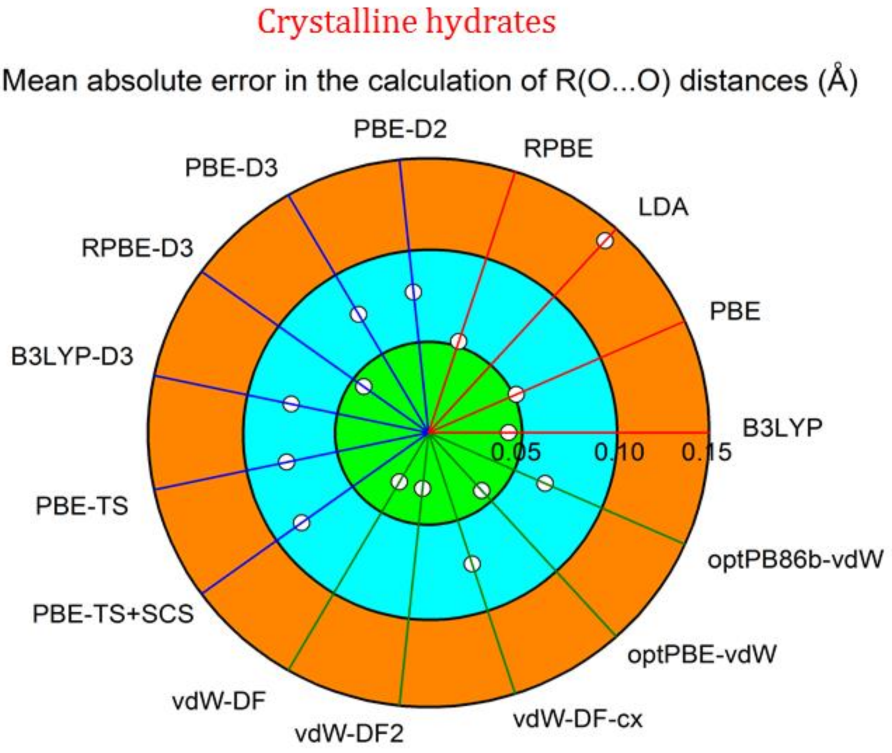


Figure 4. Assessment of the performance of various DFT functionals with respect to reproducing the experimental *R*(O···O) hydrogen-bond distances for four crystalline hydrates. A point at the center of the dart-board would mean that the functional produces all distances in total agreement with experiments.

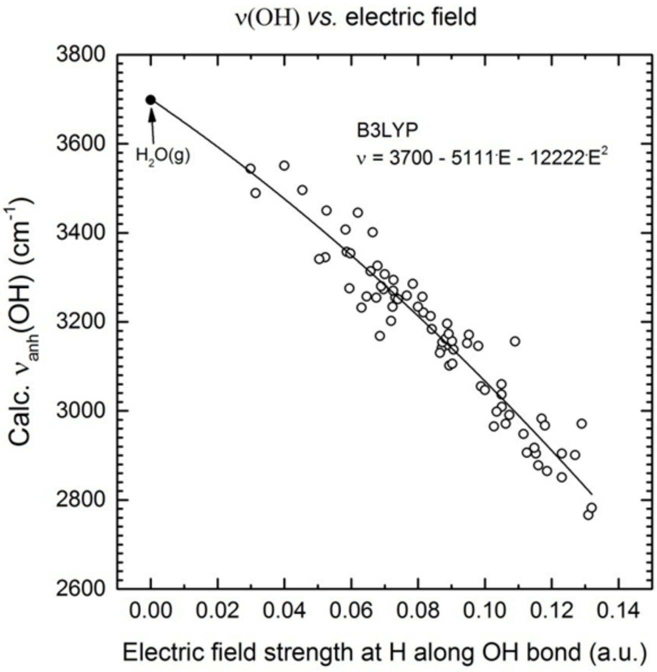


Figure 5. *ν*(OH) vs. "external" electric field. Each electric field value in the plot is the electric field calculated at one of the 74 water water H atoms in our sample of 37 water molecules in crystalline hydrates listed in the caption of Figure 3. For each water OH bond, the electric field generated by the whole crystalline surroundings outside the probed molecule itself was calculated at the equilibrium H position, and the component of this electric field along the OH bond was used in the plot. The frequency plotted is the corresponding anharmonic, uncoupled OH frequency.

Water on surfaces

We are also interested in water molecules on surfaces: we have studied intact and dissociated water molecules and the transfer between them on metal oxide surfaces. Figure 6 is a snapshot from a Molecular dynamics simulation of a thick water film on wurtzite ZnO (10–10) [9]; it illustrates the dynamic nature of the system and shows that many of the water molecules are dissociated also on the common ZnO (10–10) surface (without extra steps; stepped surfaces were also investigated in Ref. 9). The Molecular Dynamics simulations in Figure 6 were based on a ReaxFF force-field that was derived from electronic QM calculations in a consistent manner, as indicated by the red arrows in the right-hand part of the multi-scale scheme in Figure 1a (in a collaborative project between A. van Duin (Penn State U) and the Uppsala group). We have also studied the ZnO and water-ZnO systems in the approximate (tight-binding) DFT approach in the SCC-DFTB formulation and developed a parameter set for these systems, again based on QM calculations in a consistent set-up.[1] Such an endeavor can be illustrated by the light-green arrows in the right-hand part of Figure 1a. This work was developed as a collaboration with the group of Th. Frauenheim (Bremen Center for Computational Materials Science).

Using a range of dispersion-corrected DFT functionals and water coverages, we recently studied water on the archetypical NaCl(001) and MgO(001) surfaces [10], and found that, for both NaCl(001) and MgO(001), the dispersion-flavored functionals stabilize the water-surface interface by 20%-40% compared to the PBE-results. A monolayer water coverage on MgO(001) leads to a mixed overlayer with both intact and dissociated water molecules in an intricate hydrogen-bonded scheme. For NaCl(001), the water molecules remain intact for all water coverages, which allows a more elaborate analysis of "the nature of a surface water molecule" compared to the gas-phase. Thus to probe the strength of the perturbations from the surface and the rest of the water layer on an adsorbed water molecule, we calculated water dipole moments and found an increase of up to 85% for water at the MgO(001) surface and 70% at the NaCl(001) surface, compared to the gas-phase dipole moment. Likewise, for intact water molecules, it was meaningful to divide the total adsorption energy into water-surface and surface-surface contributions: they were found to be approximately of the same magnitude but the dispersion correction affected the water-surface interactions more than the water-water interactions.

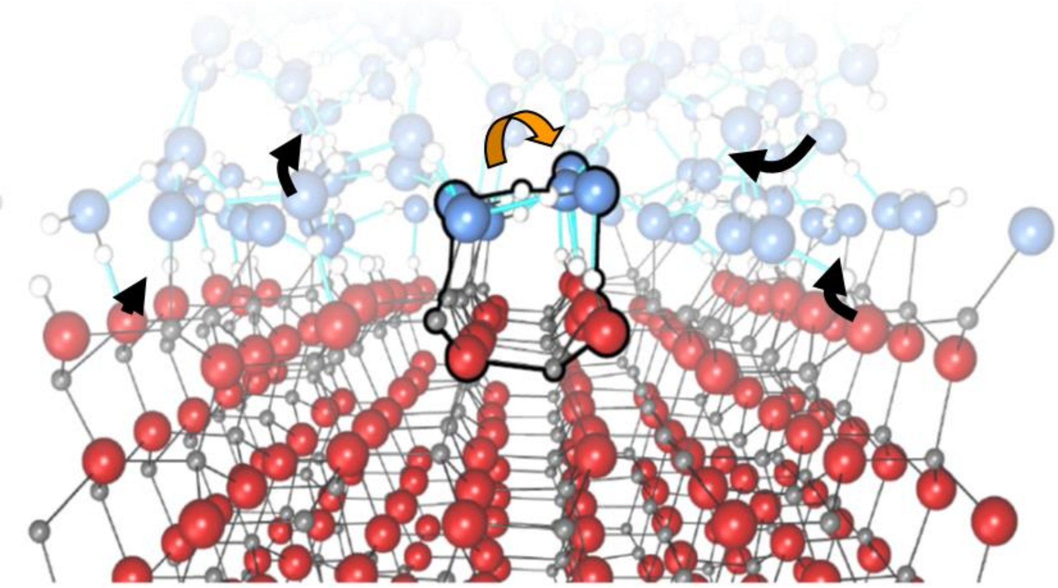


Figure 6. Snapshot from the ReaxFF-based MD simulation of a water-covered wurtzite ZnO(1 0 -1 0) surface, reported in Ref. [9]. The picture was drawn from the trajectory of the simulation.

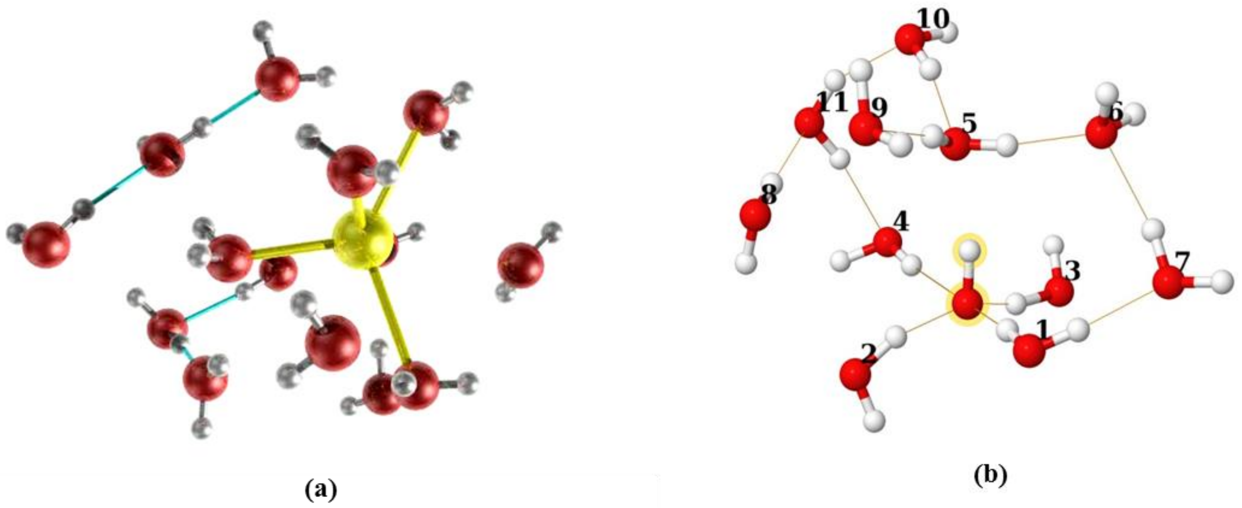
Water in aqueous solution

It is particularly challenging to calculate vibrational OH spectra in a liquid because the liquid configurations have to be properly sampled or the spectrum will be scewed and misleading. We have continued to develop this approach ever since our first computational study of the (anharmonic) infrared OH spectrum for liquid water in 1991 [11]. Our approach contains several stages. A Molecular Dynamics or a Monte Carlo simulation is performed, a suitable number of snapshots are collected for analysis, and for each of these a large number of *electronic* QM calculations are performed to generate potential energy curves for the OH stretching modes for each of the first-shell water molecules around the ion in solution. In our approach, this step is in fact in itself a QM/MM calculation, where our preferred QM method for water is B3LYP. This step is followed by a quantum-mechanical calculation for each potential energy curve, but here it is a *nuclear* QM calculation, which generates the vibrational energy levels. The energy difference between the ground and first excited vibrational energy levels is collected into a frequency spectrum. The scheme is illustrated in Figure 1c. In practice we sometimes do not include the first step (a QM-based force-field generation) but instead go straight to the MD stage using an available force-field or an *ab initio-MD* approach.

Figure 7 shows results from two collaborative projects with Lj. Pejov (Sts. Cyril and Methodius University). Figure 7a displays a snapshot from the force-field-based MD simulation of Li^+ (*aq*) [12]; all water molecules except those closest to the cation have been removed for visual clarity. There resulting gas-to-solution frequency shift is given in Table 1, together with similar results for a divalent and a trivalent ion. The agreement with experiment is overall good, and this is actually also true for the absolute frequencies (not shown here). The water OH-frequency of bound water molecules are always downshifted with respect to the gas-phase and this effect is very large in the cases of Mg^{2+}(*aq*) and Al^{3+} (*aq*); in both cases the OH band origin even lies much below that of liquid water.

The last line in Table 1 does not refer to water but to the OH vibrations of the hydroxide ion itself, when immersed in water. A snapshot from the ab initio MD simulation is given in Figure 7b and illustrates the strong hydrogen-bonds donated to the hydroxide's O atom, and the much loser and cage-like water structure around the hydroxide's H atom, as discussed in Ref. [13]. The eperimentally measured gas-to-solution frequency shift is seen to be well reproduced by our calculations. The shift is quite modest, much smaller even than that of the water molecules around the monovalent Li^+ ion, in spite the strong hydrogen bonds donated to the hydroxide ion. *How can this be*? The explanation was given in Ref. [13] and confirms that the hydroxide ion in water conforms with the behavior that we had earlier found in the gas-phase [14]: when the ion is exposed to a small electric field (from an external source, e.g. its surrounding molecules) the frequency is up-shifted (opposite to what happens for the water molecule), reaches a maximum as the field is increased and then decreases and, for very large electric fields, gives a large downshift compared to the gas-phase OH$^-$ frequency. The effect is illustrated in Figure 8 for the ideal cases of a water molecule and a hydroxide ion (separately) exposed to a uniform electric field [14]. We conclude that the study in [13] *both* demonstrated that the calculations were able to reproduce the experimentelly determined gas-to-liquid frequency shift (and actually here also the absolute values), *and* provided an explanation for the observed – positive and modest – frequency shift observed for the hydroxide ion, which is contrary to our experience from the behavior of water molecules.

In summary, water molecules in aqueous solutions, in crystals, and on surfaces are always found to be downshifted (red-shifted) in OH frequency by their surroundings. Examples given in this mini-review, demonstrate, however, that while the hydroxide ion can be red-shifted when bound in a strongly polarizing environment, it is in fact often found to be up-shifted (blue-shifted). We found this parabola-like behavior for the hydroxide ion in crystalline hydroxides as well [15]. The explanation underlying this qualitatively different behavior of the water molecule and the hydroxide ion is related to the relative signs and magnitudes of the permanent and induced dipole moment derivatives along the OH-stretching coordinate: the sign relations are different for water and OH$^-$ [14].



(a) (b)

Figure 7. (a) Snapshot from an MD simulation for Li$^+$(aq) based on an ab initio-generated many-body force-field. The simulation is described in Ref. [12], where references to the force-field generation is given. **(b)** Snapshot from an ab initio-MD simulation for OH$^-$(aq). The simulation is described in Ref. [13].

Table 1. Calculated and experimental gas-to-solution OH-frequency shifts for water molecules in the first hydration shell of a series of metal cations (lines 1–3) and for the hydroxide ion surrounded by water molecules in an aqueous solution (line 4)

System	Calc. Δν(OH) (cm^{-1})	Expt. Δν(OH) [a] (cm^{-1})	Refs for calc. Δν(OH)
Water OH vibrations @ Li$^+$ (*aq*)	–305	–290[b]	[12]
Water OH vibrations @ Mg^{2+}(*aq*)	–440	–420	[12]
Water OH vibrations @ Al^{3+} (*aq*)	–750	–850	[12]
OH$^-$ vibrations in OH$^-$ (*aq*)	+90	+75	[13]

[a] References to the experimental work: see references within [12] and [13], respectively.
[b] One of the two experimental values that have been presented in the literature; see [12].

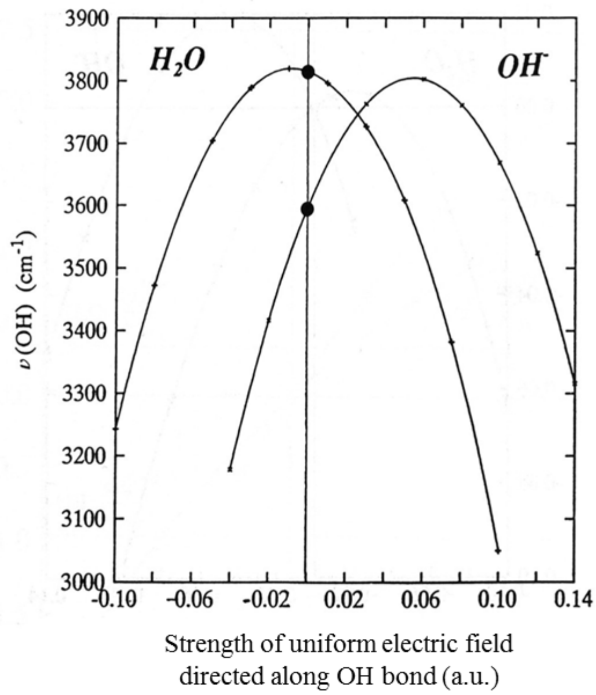


Figure 8. Ab initio-calculated anharmonic OH frequency vs. electric field strength for the uncoupled OH stretching vibration of an isolated HDO molecule exposed to a uniform electric field directed along the vibrating OH bond, and the corresponding result for an isolated OH^- ion in a uniform electric field. The calculations are described in Ref. [14]. The positive field direction is from O, towards H, i.e. the field is directed as if there is a positive charge far away on the O side and a negative charge far away on the H side. This is the energetically favored direction.

CONCLUSION, IMPACT AND OUTLOOK

The examples above demonstrate that Computational Materials Chemistry delivers unique quantitative and qualitative information, and knowledge that is unattainable from experiments. In my opinion, the most valuable and long-lasting results from modelling are likely to be the scientific insights that can be formulated in terms of rules-of-thumb and structure-property relations: they will save time and money for many categories of end-users of modelling results, from high-school science students to industrial stakeholders.

Considerable methodological challenges remain, however. In fact, one of the narrowest bottlenecks, and one which currently limits the wider use of modelling in e.g. industry, is the lack of appropriate models to treat large-scale systems of realistic complexity, and their time evolution. This was recently demonstrated in a survey [16] conducted by the European Materials Modelling Council (EMMC, https://emmc.info) where interaction models of high accuracy and computational efficiency were requested as well as techniques to perform multi-scale modeling of materials. In fact, the Royal Swedish Academy of Sciences awarded the Nobel Prize in Chemistry for 2013 to Martin Karplus, Michael Levitt and Arieh Warshel "for the development of multiscale models for complex chemical systems" but it was the development of QM/MM models for biological molecules that was in focus in this prize. In the field of *materials modelling,* however, the use of QM/MM models and other multiscale approaches (cf. Figure 1) is much less mature. Significant development efforts are needed.

In this brief review we have discussed diffraction experiments, vibrational spectroscopy data and, of course, theoretical calculations. The importance of combining different techniques was early on realized by Professor Bojan Šotrajanov and his research team at the Sts. Cyril and Methodius University. Many of my colleagues and I at the Structural chemistry program at Uppsala University are grateful for many years of inspiring collaboration and friendship. Some of the first contacts were shaped at the fourth Horizons in Hydrogen Bond Research meeting at Sånga-Säby in Sweden in 1980. This has been followed by research visits in both directions, including those of Professors Gligor (Glišo) Jovanovski and Ljupčo Pejov, who both spent a research year in Uppsala. The scientific discussions between Uppsala and Skopje are still very much alive.

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МОДЕЛИРАЊЕ НА РАЗЛИЧНИ СКАЛИ НА МОЛЕКУЛАТА НА ВОДА И НА ХИДРОКСИДНИОТ ЈОН ВО ЦВРСТА СОСТОЈБА И ВО РАСТВОР

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Во трудов се дискутирани некои од најголемите предизвици коишто треба да се разрешат за резултатите од пресметувањата во областа на хемијата на кондензирана материја да станат рамноправно прифатливи со оние добиени по експериментален пат. Проспекциите се прилично јасни (надежни). Со помош на неколку примери (сите поврзани со *молекулата на водата* и со *хидроксидниот јон* и нивните мистерии), демонстрирани се уникатни можности на теоретските пресметувања кои даваат нови видувања и понекогаш, според степенот на точноста, дури и ги надминуваат експерименталните сознанија.

Клучни зборови: моделирање на различни скали; хемија на кондензирана материја; молекула на вода; хидроксиден јон; цврста состојба; раствори

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Short overview

INFRARED EMISSION SPECTROSCOPY OF CARBON VAPORS AND PLASMAS[•] – A SHORT OVERVIEW –

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A short review is given about infrared emission spectroscopy of hot carbon vapors and plasmas obtained using Fourier transform infrared emission and laser induced breakdown LIB spectroscopies in the mid-infrared range. Laboratory FTIR emission spectra contain vibrational bands from fullerenes C_{60}, C_{70}, whereas laboratory mid-infrared LIB spectra show bands that belong to mostly unidentified carbon molecules and clusters. Both kinds of spectra are compared to spectral results from infrared astronomy. The spectra are discussed with a view for possible applications in carbon nanostructure research and in infrared astronomy. Possible extensions for laser induced breakdown (plasma) spectroscopy are suggested.

Key words: carbon plasma; carbon vapor; cluster; infrared emission spectra; FTIR; LIBS; laser-induced breakdown; astronomy

EXPERIMENTAL METHODS

There were several spectroscopic methods used in these studies. Laboratory methods were Fourier-transform infrared emission spectroscopy and laser-induced breakdown spectroscopy in the mid-infrared range. FTIR spectra were taken on the National Solar Observatory Fourier-transform spectrometer at Kitt Peak, Arizona, USA, while mid-infrared LIB spectra at Hampton University, Department of Physics, Hampton, Virginia, USA. Infrared astronomical spectra referred to in the text were taken by the Infrared Spectrograph on the NASA Spitzer Space Telescope.

INTRODUCTION

Even before the discovery of fullerenes [1], and their macroscopic production [2], interest arose in finding carbon molecules in interstellar medium, in carbon rich stars and in other cosmic sources. Identification of large and small carbon molecules are easiest in infrared spectra as they contain molecular 'fingerprints' generally used in physical organic and analytical chemistry in molecular structure research. With the developments of infrared facilities on boards of space telescopes and available on ground based infrared observatories detection and identification of carbon molecules became possible.

It is obviously important to study carbon molecules in the laboratory in order to obtain sample spectra to compare to observations, e.g. by astronomical means. Such infrared spectra may be obtained by several techniques. One method is to use low temperature rare gas matrix isolation that provides absorption spectra of solid phase molecules, another method is to generate carbon vapors and study their infrared emission from gas-phase molecules. Yet another approach is the application of laser-induced plasma breakdown emission spectroscopy (LIBS) to study carbon plasmas. Plasma spectra are related to the spectra of molecules isolated in the gaseous phase and differ in several aspects from solid phase spectra, for example in relative intensities of the bands.

[•] Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

The technique of LIBS is widespread in atomic and diatomic spectroscopy as such spectral transitions are mostly observed in the visible and ultraviolet spectral ranges. However conventional LIB spectra of carbon plasmas in these spectral domains do not yield molecular information for C_3 and larger carbon molecules. The electronic transitions for such carbon molecules are extremely difficult to observe under the usual LIBS conditions.

In recent times a new method has been elaborated for the observation of mid-infrared emission from laser generated plasmas [3–6] that was extended to carbon plasmas [7]. Although application to carbon is still in developmental stage it has already provided preliminary results that will be discussed in this paper with a view of their applicability for materials science research as well as for infrared astronomy.

Infrared emission from hot carbon vapors

Gas-phase infrared emission spectra of fullerenes were reported [8, 9] and the temperature-dependence of the vibrational bands of C_{60} and C_{70} were determined [9]. Solid fullerenes were evaporated in a high temperature furnace and the infrared emission was recorded by a Fourier-transform spectrometer. Together with previous studies of temperature-dependence in solid state spectra of fullerenes [10] and theoretical calculations for infrared and Raman modes [11] enough experimental data have been accumulated for vibrational identification of C_{60} and C_{70} in various media and physical states. The C_{60} molecule has four infrared active bands at 1409, 1173, 570 and 528 cm^{-1} at about 1000 ^0C in the gas phase, whereas C_{70} has eight infrared bands at 1413, 1125, 1077, 793, 639, 576, 558, and 529 cm^{-1} between 930 and 1050 ^0C.

Using the temperature dependence of the vibrational bands of C_{60} it is possible to do a rough extrapolation to absolute zero temperature and the results agree among these extrapolated values and those observed in argon matrix isolation spectra [12]. Thus the data may be useful for the observation of very cold gas-phase fullerenes in astronomical sources. In fact these extrapolated values and matrix isolation data were used for the identification of fullerenes C_{60} and C_{70} in various stellar sources [13, 14] using the Infrared Spectrograph on board of the Spitzer Space Telescope [15].

Mid-infrared emission from laser-generated plasmas

Previous studies of time-resolved infrared emission from laser-induced breakdown spectroscopy of inorganic materials [3–6] led to the development of the necessary instrumentation and methodology. This is a significantly new extension of the traditional LIB methods. These studies were and are carried out for remote sensing of chemical, biological and explosive materials, such as various alkali nitrates, ammonium perchlorate and gunpowder [16], and various simple pharmaceuticals such as Tylenol and Aspirin, and compounds like dimethyl phosphate and methyl salicylate [17].

To detect infrared emission in the mid-infrared spectral range the latest instrumentation applied a flash-lamp pumped Q-switched Nd:YAG laser at its fundamental wavelength 1064 nm, and for spectral detection a cooled MCT linear detector array using time-resolved electronics [16, 17]. Linear detector arrays make it possible to run spectra in a few seconds. Previous experiments applied a single element MCT detector and a scanning grating spectrometer, thus were much slower.

These developments of mid-infrared LIBS created the possibility for observing time-resolved infrared emission from laser-generated carbon plasmas. These experiments are different from analogous remote-sensing studies on energetic materials and pharmaceuticals, as while the ablation laser evaporates or ablates existing molecules from the above inorganic and organic samples, in the carbon plasma experiments the only readily available molecular entities were laser-ablated graphite lattice fragments and macroscopic graphite particles while most of the vibrational signatures observed likely belong to laser-synthesized molecules.

Study of carbon plasmas by mid-infrared LIBS

In a recent paper the results of the application of the LIBS technique to study time-resolved infrared emission from carbon plasmas are described in details [7]. Here I summarize the observation of such spectra and outline some possible improvements and developments. The following is a short summary of experimental details, full experimental description is given in [7].

The infrared LIB spectra obtained for carbon were obtained at the Department of Physics, Hampton University, Hampton, Virginia, with contributions from Battelle Eastern Sciences and Technology Center, Aberdeen, Maryland. The spectra were run between 7.5 and 12 micron, and in a case between 4.5 and 11.5 micron. A grating spectrometer of 150 cm focal length was used, providing about 80 nm spectral resolution. Detection was made by a HgCdTe (MCT) detector at 77 K. The spectral sensitivity of the detector was at maximum at 10 micron, near 40% at 4 micron and near 70 % at 12 micron. The 1064 nm laser radiation from a Q-switched Nd: YAG laser was focused on a high purity graphite pellet on a linear translation stage that moved between subsequent pulses to provide fresh surface. Infrared radiation from target plasma was focused by ZnSe optics onto the 2 mm wide entrance slit of the spectrometer. Scattered laser light and higher-order spectra were cut using low-pass filters at 4 and 7.4 micron. Spectral ranges were scanned with a speed of 100 nm/min thus total spectral taking time was near 1 hour. The spectrometer was encased in a plastic box that was flushed by ultra pure grade N_2, Ar or He at atmospheric pressure.

The infrared spectra contained broad emission bands. The overall emission spectrum depended on the atmospheric pressure background gas used, and all spectra were characterized by strong continuous backgrounds. Spectra recorded in the 8–11.5 micron interval were weaker than those in the 4.5–8 micron region. The broadness of the emission bands is due partially to the limited spectral resolution (about 80 nm) and to the high plasma temperature; the fundamental source for their width is however their molecular origin. At plasma temperatures vibrational and rotational excitation are extensive leading to broad spectral envelops. Atomic lines would have been much narrower. In addition in the infrared region studied no neutral and/or ionic atomic lines are expected to appear with significant intensity [18].

The observed infrared emission did not show the room temperature blackbody emission from the spectrometer itself, and significant bands were only observed in atmospheric pressure rare gases. The fact that the spectra were different in argon and in helium suggests carbon molecule and cluster formation in the plasma. However not all spectral features may be due to molecule formation in the plasma, it is likely that the ablation laser removes graphene fragments from the graphite target. These are essentially dehydrogenated PAH (dPAH) molecules. Infrared bands of dPAH molecules computed using high level density functional methods were reported in the literature [19].

In addition the strong band observed between 4.4 and 5.4 micron do likely contain vibrational features of C_3, C_5, C_6, C_7 and C_9 linear carbon chain molecules, as expected from their matrix isolation infrared spectra [20].

An interesting possibility is that graphite target laser ablation plasmas contain the fullerenes C_{60} and C_{70}. The availability of laboratory hot carbon vapor infrared spectra and infrared astronomical observations provide comparisons. Such a comparison is shown in the Figure 1.

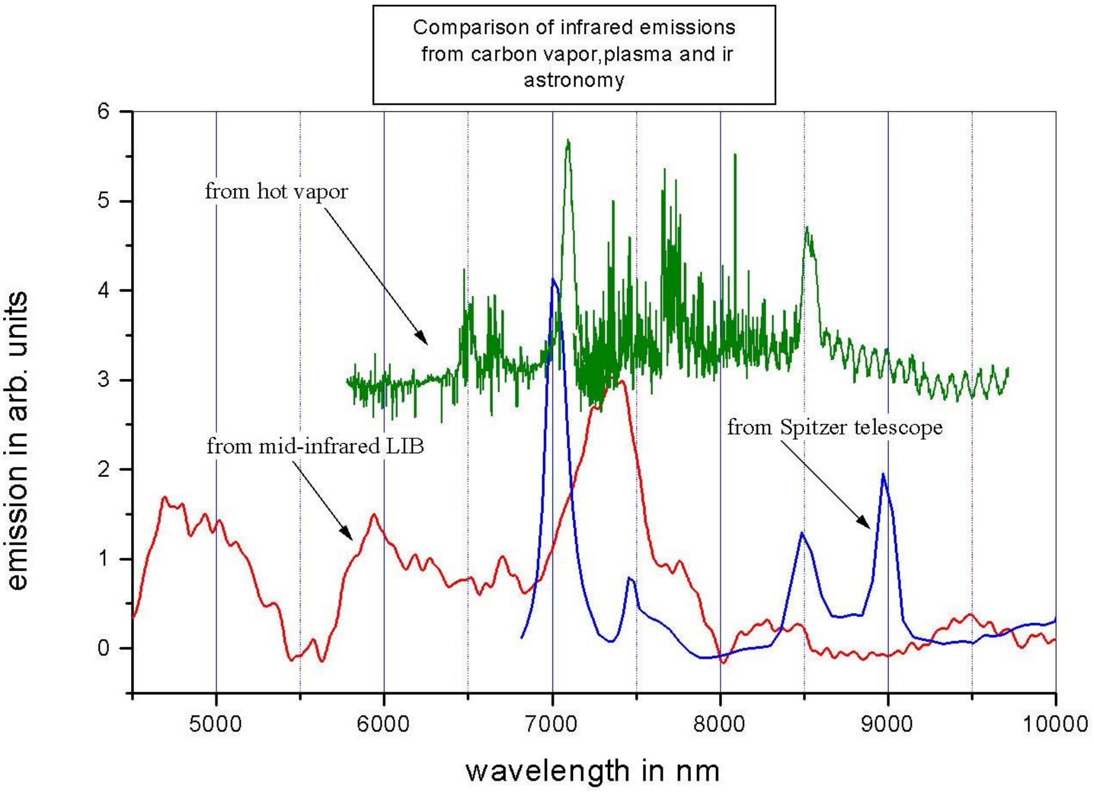

Figure 1. A comparison of different infrared emission spectra of carbon vapors and plasmas.

In the Figure 1 red denotes mid-infrared LIB spectra [7], blue denotes the spectrum from the Spitzer telescope [13], while green denotes infrared spectra from hot C_{60} vapor [9]. The plot is against nanometer wavelength (wl) scale, division by 1000 results in the usual micrometer scale. To turn micrometers to wavenumbers (cm^{-1}) 10^4 / wl (micron) should be used. As shown the ν_{25} and ν_{26} infrared modes of C_{60} at around 7 and 8.5 micron overlap between the laboratory C_{60} vapor and the Spitzer infrared spectra, but the mid-infrared LIB spectra do not show significant bands at those positions. On the other hand the LIB spectra contain strong emission bands at around 4.7, 6 and 7.4 microns.

DISCUSSION AND PROPOSITIONS

Infrared emission spectra observed by the mid-infrared LIBS (MIRLIBS) method are difficult to assign to known carbon molecules. As mentioned before, there are only two groups of molecules (linear carbon chains and dehydrogenated PAHs) for which previously obtained experimental data and high-level quantum-chemical calculations provide a tentative basis for identification. Fullerenes could not yet been positively identified in MIRLIB spectra and there are strong emission bands for which at present no molecular assignments could be given.

The present results from mid-infrared LIB spectra of carbon plasmas [7] are thus only preliminary as the experiments were performed using a setup for observing inorganic and organic molecular matter for remote-sensing applications.

In order to exploit this new analytical technique the experimental method should be extended and refined. Relative to the published spectra [7] obtained with a single element MCT (HgCdTe) detector/ scanning spectrometer requiring up to 1 hour of recording 10 spectra, the newly developed linear array MCT detector/grating based monochromator should provide fast acquisition of the infrared spectra (only 5 sec is needed to average 4 single-shot plasma spectra [16]). Thus with the linear array many spectra can be averaged resulting in significantly improved signal to noise ratio.

Another aspect is the time-resolved ability of the experimental arrangement. While in the previous experiments [7] time-delays up to 20 microseconds after the laser-pulse were used, in the experiments with the linear array were extended to 1 ms delay. This is important for observing fullerenes as their formation in the plasma requires time scales longer than 10 microseconds. In addition one would need warm background gases compared to the room temperature surrounding gas in previous experiments [7].

Increase of spectral resolution greater than 80 nm in further experiments would bring obvious advantages. An important extension of MIRLIB spectra of carbon and other substances would be the reduction of environmental gas pressure. For remote-sensing applications that often are carried out in ambient air, the necessity of using atmospheric (about 100 kPa) pressure is obvious, however to study the formation of atomic clusters much lower pressures are needed (maybe down to a few tens of Pascal).

The most significant advance of MIRLIB spectroscopy however would be a simultaneous use of the conventional LIB technique (in the visible and ultraviolet region) and the MIRLIBS method. As in the infrared range atomic lines of various ionization stages are not observed, whereas in conventional LIBS atomic lines are easily used to obtain electron temperature and electron volume density values (based on relative intensities and line widths), quantitative characterization of the plasmas in combined LIBS spectral ranges would be possible. The present state of infrared LIB spectroscopy and relevant technical aspects are reviewed in a recent paper [21].

With increased spectral resolution, better signal to noise ratios and available plasma electron parameters it might be possible to derive vibrational excitation conditions, molecular identifications and maybe molecular formation mechanisms (thus plasma chemistry) as well.

Such developments in the experimental techniques could provide important help for understanding carbon cluster formation which is a central theme in producing various carbon nanostructures. In addition the MIRLIBS technique could be extended to other cluster forming chemical elements, such as metals, alkali metals, semi-metals and some non-metallic elements (such as sulphur).

Infrared astronomy could also greatly benefit from carbon MIRLIB spectroscopy in identifying the molecular origin of cosmic infrared emitting sources, along the line of the Spitzer spectra of fullerenes [13, 14]. In particular with the coming of the James Webb Space Telescope’s mid-infrared observational possibilities between 5 and 28 microns [22] one may expect extensions of the Spitzer telescope’s spectroscopic studies.

Summarizing the conclusions and the above experimental propositions it appears that infrared emission spectroscopy of carbon and other plasmas has a great future.

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ИНФРАЦРВЕНА ЕМИСИОНА СПЕКТРОСКОПИЈА НА ЈАГЛЕРОДНИ ПАРЕИ И ПЛАЗМИ – КРАТОК ПРЕГЛЕД

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Даден е краток преглед на инфрацрвената емисиона спектроскопија на жешки јаглеродни пареи и плазми добиени со помош на Фуриеова трансформна инфрацрвена емисиона спектроскопија (FTIR) и со ласерски индуцирана разложувачка спектроскопија (LIBS) во средното инфрацрвено подрачје. Лабораториските емисиони спектри добиени со FTIR содржат вибрациони ленти од фулерените C_{60}, C_{70}, додека лабораториските спектри добиени со LIB во средното инфрацрвено подрачје покажуваат ленти што припаѓаат најчесто на неидентификувани јаглеродни молекули и кластери. Двата вида спектри се споредени со спектралните резултати од инфрацрвената астрономија. Спектрите се дискутирани од аспект на нивната примена во изучувањето на јаглеродната наноструктура, како и во инфрацрвената астрономија. Сугерирани се и можни проширувања за ласерски индуцираната разложувачка (плазма) спектроскопија.

Клучни зборови: Јаглеродна плазма; јаглеродна пареа; кластер; инфрацрвени емисиони спектри; FTIR; LIBS; ласерски индуцирано разложување; астрономија

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Original scientific paper

THEORETICAL VS. EXPERIMENTAL IR FREQUENCY SHIFTS UPON Π- HYDROGEN BONDING: COMPLEXES OF SUBSTITUTED PHENOLS WITH HEXAMETHYLBENZENE[•]

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The quality of theoretical prediction of O-H stretching frequency shifts upon π-hydrogen bonding is analyzed for series of ten complexes between monosubstituted phenols and hexamethylbenzene. Computed O-H frequencies from density functional theory computations at B3LYP/6-311++G(2df,2p) were compared with literature spectroscopic data. The results reveal that the applied theoretical method predicts with an excellent accuracy the O-H frequency shifts [Δν(OH)] upon π-hydrogen bond formation. Comparisons with analogous theoretical and experimental data for benzene complexes with substituted phenols reveal the magnitude of the methyl groups' hyperconjugative effects on interaction energies and frequency shifts. The induced by phenol substituents variations in bonding energies and Δν(OH) are rationalized using theoretically evaluated and experimental parameters.

Key words: π-hydrogen bonding; hexamethylbenzene; substituted phenols; O-H frequency; DFT computations

INTRODUCTION

Vibrational spectroscopy has provided rich experimental information on hydrogen bonding [1–5]. This method has also been instrumental in studies of π-hydrogen bonds [6–8]. The advances of computational quantum chemistry have opened possibilities for gaining deeper insights into the nature of this type of noncovalent interactions that are of key importance in biology, chemistry, and materials science [9–14]. The present study aims at examining properties for series of complexes of hexamethylbenzene with monosubstituted phenols by a combined application of computational and spectroscopic data. The O-H stretching frequency shifts upon complex formation provide an excellent basis for quantifying the effects of structural variations on the processes. The experimental data considered in the present research are taken from the work of Seguin et al. [15]. Our principal interest was in examining how well theoretical computations employing the widely applied B3LYP functional will perform in evaluating properties of the studied complexes. We also focus on analyzing the effects of substituents in the phenolic aromatic ring. By comparisons with previously obtained analogous computational and spectroscopic data for benzene [16], the role of the methyl hyperconjugative effects in hexamethylbenzene on the strength of π-hydrogen bonding is also assessed.

The usual interpretation of substituent effects in the proton-accepting aromatic ring considers their electron withdrawing and releasing effects on the π-electron system [17–19]. An alternative interprettation emphasized the direct interaction between the polar aromatic substituents and the approaching proton-donating molecule [20, 21]. Sherill et al. [21–23] and Lee et al. [24] have shown by using symmetry adapted perturbation theory (SAPT) [25] computations that the ratio between attractive (electrostatic, dispersion, induction) and repulsive (exchange) terms defines the effects of aromatic substituents.

Recent vibrational Stark spectroscopy studies of Saggu, Levinson and Boxer [26, 27] on the π-

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[•] Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

hydrogen bonded complex of phenol and benzene revealed a dominant role of the electrostatic interaction energy in complex formation. The experimentally determined electrostatic interaction energy compared well with the theoretically derived from DFT computations. Vibrational echo spectroscopy study on the same interaction revealed that the time constant of the complex was only 8 picoseconds [28, 29]. In a previous work, we presented results from an IR spectroscopic and theoretical investigation for a series of 20 π-hydrogen-bonded complexes of monosubstituted phenols and benzene [16]. Correlation analyses employing a number of experimental and theoretical quantities revealed a dominant role of the acidity of the proton donating phenols on complexation energies. Banerjee and Chakraborty [30] reached similar conclusions in their study of complexes of fluorosubstituted phenols with benzene. Zhou et al. [31] conducted a detailed theoretical study of the various geometries of phenol-benzene π-hydrogen bonded complexes.

In the present research, we examine the interaction of ten monosubstituted phenols with hexamethylbenzene. As mentioned, the selected molecules provide a possibility for analyzing the role of methyl hyperconjugative effects on the complex formation. In this respect, it was also of interest to assess how well different theoretical approaches will quantify the expected increased electron density over the aromatic ring in hexamethylbenzene. The theoretical analysis is validated by comparisons with the experimental IR O-H frequency shifts upon π-hydrogen bonding as determined by Saguin et al. [15] for CCl_4 solutions.

COMPUTATIONAL MEHTODS

DFT computations employing the B3LYP functional [32–34] combined with the 6-311++G(2df,2p) [35] basis set for a series of ten hydrogen-bonded complexes between monosubstituted phenols and hexamethylbenzene were performed. All computations employed the Gaussian09 program [36]. The optimized structures were verified to be minima of the potential energy surfaces with the aid of harmonic frequency computations. The interaction energies are corrected for basis set superposition error (BSSE) using the counterpoise procedure [37]. The computations employed the IEFPCM method [38] to simulate the experimental conditions (CCl_4 solvent) of the recorded infrared spectra [15]. A number of theoretical quantities were employed in rationalizing the effects of phenol substituents on interaction energies and shifts of O-H stretching frequencies. These included the NBO [39] and Hirshfeld [40] atomic charges as well as the electrostatic potential at nuclei (EPN). EPN was first introduced by Wilson in 1962 [41]. In a number of studies from our laboratory, we have established that EPN is a remarkably accurate descriptor of the abilities of specific atomic centers in molecules to form hydrogen bonds [42–47] and also in quantifying chemical reactivity [48–51]. In later years, EPN values have been successfully employed by other authors in examining reactivity trends [52–60]. Politzer and Thruhlar [61] defined the electrostatic potential at nuclei Y (V_Y) by Eqn. (1):

$$V_Y \equiv V(\mathbf{R}_Y) = \sum_{A(\neq Y)} \frac{Z_A}{\left|\mathbf{R}_A - \mathbf{R}_Y\right|} - \int \frac{\rho(\mathbf{r})}{\left|\mathbf{r} - \mathbf{R}_Y\right|} d\mathbf{r} \qquad (1)$$

In this relationship, the singular term for nucleus Y is excluded. Z_A is the charge of nucleus A at position R_A. and $\rho(\mathbf{r})$ is the electron density function. The electrostatic potential at nuclei is a rigorously defined quantum mechanical quantity.

RESULTS AND DISCUSSION

Figure 1 illustrates the computationally evaluated structure of the complex between phenol and hexamethylbenzene. All ten studied complexes are characterized by a T-shaped structure with nearly perpendicular orientation of the proton donor phenols with respect the hexamethylbenzene ring (Figure 1). As seen, two π-hydrogen bonds are simultaneously formed. The first is between the phenolic O-H bond and the π-electron system of hexamethylbenzene, while the second involves the *ortho* C-H bond. The O-H·····π-hydrogen bond is much stronger with distance from the O-H hydrogen to the nearest ring carbon of 2.45 Å. The distance from the C-H hydrogen to the nearest carbon is 2.95 Å. Comparisons with to the structure of analogous complexes of substituted phenols with benzene [16], reveals some distinct differences (Figure 1). Although the latter complexes also have T-shaped structure, the O-H and C-H bonds for the lowest energy isomers points toward the middle of the respective closest C-C bonds in the benzene ring (Figure 1). In the complexes with hexamethylbenzene, the two π-hydrogen bonds point toward ring edges (Figure 1).

As emphasized, it was of interest to examine how well the employed B3LYP DFT functional would perform in predicting properties of the investigated π-hydrogen bonded complexes. The availability of experimental $\Delta\nu_{OH}$ shifts for the systems studied provides an experimental verification of the theoretical results. The variations of C-H stretching frequencies, participating in π-hydrogen bonding, were only obtained from theoretical computations. These frequency shifts were determined for the respective tetradeutero phenols, in which the C-H bond participating in complex formation remains undeuterated. The theoretically estimated and experimental [15] frequencies for the studied complexes are shown in Table 1.

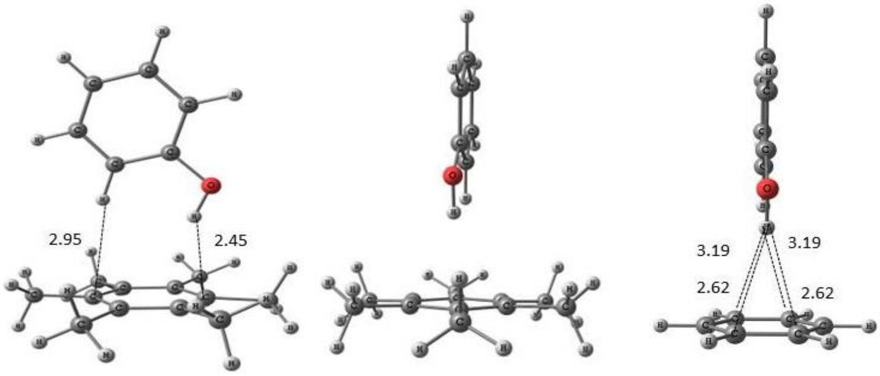

Figure 1. Optimized structures of π–hydrogen bonded complexes of phenol with hexamethylbenzene (left, center) and benzene (right) from B3LYP/6-311++G(2df,2p) computations.

Table 1. Interaction energies (kcal/mol) for π–hydrogen bonded complexes, experimental and computed O-H stretching frequency shifts (cm^{-1}), and computed C-H stretching frequencies (cm^{-1}) in substituted phenols and their complexes with hexamethylbenzene from B3LYP/6-311++G(2df,2p) calculations (CCl_4 solvent).

Substituent	ΔE	ν_{O-H} monomer	ν_{O-H} complex	$\Delta\nu_{O-H}$ theor.	$\Delta\nu_{O-H}$ [a] expl.	ν_{C-H} monomer	ν_{C-H} compl.	$\Delta\nu_{C-H}$ theor.
H (phenol)	–1.456	3824	3721	–104	–106	3155	3163	+8
m-CH_3	–1.265	3824	3726	–99	–102	3157	3161	+3
p-CH_3	–1.252	3827	3728	–99	–100	3153	3157	+4
m-OCH_3	–1.244	3825	3723	–102	–105	3162	3168	+6
p-OCH_3	–1.204	3831	3734	–97	–98	3163	3167	+4
m-$N(CH_3)_2$	–1.215	3828	3737	–92	–97	3177	3180	+2
m-Cl	–1.832	3825	3703	–122	–118	3168	3184	+16
p-Cl	–1.802	3827	3707	–120	–112	3166	3170	+4
p-F	–1.557	3829	3718	–111	–107	3167	3173	+6
m-NO_2	–2.193	3823	3682	–141	–136	3170	3171	+1
r, plot with $\Delta\nu_{O-H}$ (theor)[b]					**0.976**			
r,. plot with ΔE[b]				**0.985**	**0.956**			

[a] From Ref. [15]

[b] r, correlation coefficient

The red shifting of O-H stretching frequencies in the hydrogen-bonded complexes is quite significant. The experimental Δν(OH) from the study of Seguin et al. [15] vary from –98 cm^{-1} to –136 cm^{-1} for the differently substituted phenols (Table 1). It is remarkable that very similar range of variations (from –97 cm^{-1} to –141 cm^{-1}) is predicted by the B3LYP/6-311++G(2df,2p) computations. Along the entire series of π-hydrogen bonded complexes, the coincidence between theoretical predictions and experiment for the magnitude of frequency shifts is indeed very good. These results illustrate the power of the employed DFT method [B3LYP/6-311++G (2df, 2p)] in evaluating vibrational spectroscopic properties of the studied systems. Figure 2 illustrates the plot between theoretical and experimental $\Delta\nu_{OH}$.

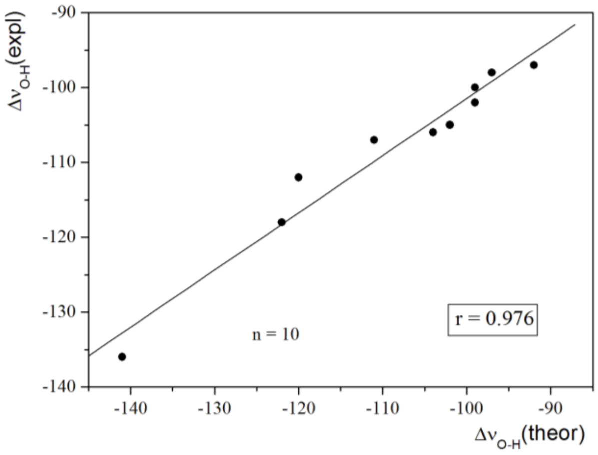

Figure 2: Plot of theoretically estimated O-H frequency shifts, $\Delta\nu_{O-H}$ (theor) vs. the experimental $\Delta\nu_{O-H}$ (expl) (the experimental data are from Ref. [16]).

The dependence is characterized by a good correlation coefficient (*r* = 0.976). It should, of course, be emphasized that the experimental frequencies include anharmonic effects. Thus, the obtained nice correspondence between observed and theoretical (harmonic) Δν(OH) may be regarded as somewhat fortuitous. Nonetheless, the anharmonic effects on the O-H stretching frequency are expected to be quite consistent along the investigated series of structurally closely related systems.

The trend for the C-H bond stretching frequency is reverse. For all studied complexes, the theory predicts blue shifts of the respective C-H frequencies upon complexation. These results are in accord with the previously reported data for the complexes of benzene with substituted phenols [16]. The weakening of the O-H bonds and strengthening of C-H bonds is well illustrated by the computed bond lengths (Table 2).

The O-H bonds are clearly elongated upon complexation. Literature studies [62] have shown that the process is accompanied by a transfer of electron density from the proton accepting π-system to the antibonding σ^* X-H orbital of the proton donor resulting in weakening of the bond. This also is reflected in the red-shifting X-H stretching frequency. The blue shifting hydrogen bonding is dominated by dispersive interactions resulting in shortening and strenthening of the respective X-H bonds [23, 62, 63]. Table 2 reveals a satisfactiory correlation (*r* = 0.966) between r_{OH} in the formed complexes and energies of hydrogen bonding.

The BSSE corrected interaction energies are also given in Table 1. Satisfactory coorrelations between ΔE and O-H frequency shifts are obtained (see the correlation coefficients in the last two rows of Table 1).

Table 2. BSSE corrected interaction energies (kcal/mol), O-H ($r_{O-H,}$ Å) and C-H ($r_{C-H,}$ Å) bond lengths for monomeric phenols and for π – hydrogen bonded complexes of phenol and hexamethylbenzene from B3LYP/6-311++G(2df, 2p) computations.

Substituent	ΔE	r_{O-H} reactant	r_{O-H} complex	r_{C-H} reactant	r_{C-H} complex
H (phenol)	–1.456	0.9624	0.9676	1.0835	1.0829
m-CH_3	–1.265	0.9625	0.9673	1.0833	1.0826
p-CH_3	–1.252	0.9623	0.9673	1.0836	1.0830
m-OCH_3	–1.244	0.9622	0.9675	1.0826	1.0820
p-OCH_3	–1.204	0.9620	0.9669	1.0832	1.0829
m-$N(CH_3)_2$	–1.215	0.9621	0.9667	1.0824	1.0819
m-Cl	–1.832	0.9626	0.9685	1.0828	1.0822
p-Cl	–1.802	0.9624	0.9682	1.0830	1.0825
p-F	–1.557	0.9622	0.9678	1.0828	1.0824
m-NO_2	–2.193	0.9629	0.9695	1.0828	1.0826
r,. plot with ΔE^b		**0.819**	**0.966**		

Comparisons of computed hydrogen bonding energies and O-H frequency shifts for complexes of substituted phenols with hexamethylbenzene and with benzene as proton acceptors are presented in Table 3. The experimental and theoretical (using the same level of theory) data for benzene are from our earlier study [16]. These comparisons reveal the effects of methyl hyperconjugation. Much higher hydrogen bonding energies characterize the complexes of phenols with haxamethylbenzene. In the case of the unsubstituted phenol as proton-donating species, the interaction energy is almost twice as high compared to the complex with benzene (Table 3). These observations clearly indicate a substantially increased electron density over the hexamethylbenzene ring, which facilitates the complex formation. Figure 3 compares the theoretically estimated EPN values and Hirshfeld atomic charges at the aromatic ring carbons in monomeric hexamethylbenzene and benzene. Contrary to expectations, Hirshfeld population analysis shows lower negative charges at the ring carbons in hexamethylbenzene compared to benzene. In contrast, the EPN values provide more accurate picture of the charge distribution in the two molecules. More negative electrostatic potentials at the point of the ring carbons indicates increased negative charges in the neighborhood, in harmony with the expected increased electron density. It should be emphasized that EPN values reflect complex influences of all negative and positive charges in the molecule (see Eqn. 1). Nonetheless, it was clearly demonstrated, that EPN at aromatic ring carbons reflects in a consistent way the effects of substituents in aromatic systems [51].

Table 3. Interaction energies (ΔE, kcal/mol) for π-hydrogen bonded complexes of substituted phenols with hexamethylbenzene and benzene, experimental and computed O-H IR frequency shifts (cm^{-1}) upon complexation from B3LYP/6-311++G(2df,2p) computations and experiment [16].

Substituent	Hexamethylbenzene			Benzene		
	ΔE	$\Delta\nu_{O\text{-}H}$ theor.	$\Delta\nu_{O\text{-}H}$[a] expl.	ΔE	$\Delta\nu_{O\text{-}H}$ theor.	$\Delta\nu_{O\text{-}H}$[b] expl.
H (phenol)	–1.456	–104	–106	–0.732	–65	–48
m-CH_3	–1.265	–99	–102	–	–	–
p-CH_3	–1.252	–99	–100	–0.845	–65	–45
m-OCH_3	–1.244	–102	–105	–	–	–
p-OCH_3	–1.204	–97	–98	–0.653	–60	–47
m-$N(CH_3)_2$	–1.215	–92	–97	–	–	–
m-Cl	–1.832	–122	–118	–1.061	–76	–55
p-Cl	–1.802	–120	–112	–0.970	–72	–53
p-F	–1.557	–111	–107	–0.990	–73	–48
m-NO_2	–2.193	–141	–136	–	–	–

[a] From Ref. [15]
[b] From Ref. [16]

Three theoretically evaluated parameters (NBO and Hirshfeld atomic charges, EPN values) were employed in rationalizing the effects of substituents in the proton-donating phenols on the energies of complex formation with hexamethylbenzene. In addition, the experimental pKa values for the different phenols were also considered. In our previous study on complexes between benzene and substituted phenols [16], the phenol pKa acidity constants best described the trend of interaction energy variations. Hydrogen bonding energies, pKa values, and the evaluated theoretical parameters are shown in Table 4. The correlation coefficients for the plots of ΔE with these quntitieas are given in the last row of Table 4.

Surprisingly, the pKa values do not provide a fully satisfactory description of the observed variations in interaction energies. The two types of atomic charges considered, do not perform well in explaining the trends of changes of π-hydrogen bonding energies. The best obtained correlation is with the EPN values at the phenolic O-H hydrogen in isolated phenols (V_H). The less negative V_H at the O-H hydrogen under the influence of electron-withdrawing substituents (NO_2, Cl, F) corresponds to greater ability of these hydrogen atoms to participate in hydrogen bonding. Inversely, the electron-donating substituents (CH_3, OCH_3) lead to more negative V_H values and lower strength of the formed π-hydrogen bonds. These results confirm the good predictive power of the electrostatic potential at nuclei as reactivity descriptor for the hydrogen bonding in series of related molecules [42–46]. The computed electrostatic potential at the O-H hydrogen provide best description of the ability of the monomeric phenols to form π-hydrogen bond with the hexamethylbenzene π-system.

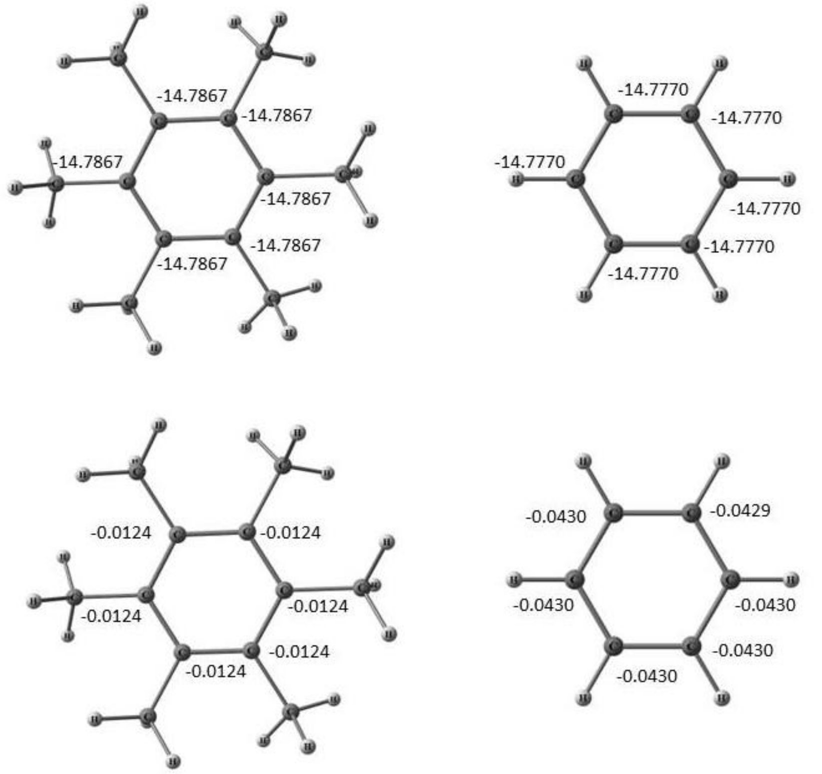

Figure 3: EPN values (top, in atomuic units) and Hirshfeld charges (bottom, in electrons) at aromatic ring carbons in hexamethylbenzene and benzene

Table 4. Interaction energies, experimental frequency shifts, electrostatic potential at nuclei (EPN), NBO and Hirshfeld atomic charges at O-H hydrogen atom in substituted phenol monomers from B3LYP/6-311++G(2df, 2p) computations

Substituent	ΔE kcal/mol	$\Delta\nu_{O\text{-}H}{}^{a}$ cm^{-1}	V_H a. u.	$q_H{}^{NBO}$ e	$q_H{}^{Hirsh}$ e	pKa^b
H (phenol)	–1.456	–106	–0.9691	0.4794	0.1746	9.99
m-CH_3	–1.265	–102	–0.9722	0.4790	0.1738	10.08
p-CH_3	–1.252	–100	–0.9733	0.4785	0.1731	10.19
m-OCH_3	–1.244	–105	–0.9705	0.4803	0.1747	9.93
p-OCH_3	–1.204	–98	–0.9752	0.4780	0.1721	10.21
p-$N(CH_3)_2$	–1.215	–97	–0.9330	0.4868	0.1871	9.88
m-Cl	–1.832	–118	–0.9569	0.4822	0.1791	9.02
p-Cl	–1.802	–112	–0.9580	0.4814	0.1780	9.38
p-F	–1.557	–107	–0.9622	0.4804	0.1762	9.95
m-NO_2	–2.193	–136	–0.9415	0.4846	0.1833	8.35
r, plot. with ΔE		**0.956**	**0.953**	**0.732**	**0.881**	**0.939**

[a] From Ref. [15]
[b] From Ref. [64]
[c,] r, correlation coefficient

CONCLUSIONS

Theoretical computations at B3LYP/6-311++G(2df,2p) predict quite accurately O-H stretching frequency shifts induced by π-hydrogen bonding between hexamethylbenzene and a series of substituted phenols. Comparisons with literature theoretical and experimental data for analogous T-shaped complexes of benzene with phenols provide an insight into the effects of methyl hyperconjugation on complex formation. Much stronger complexes with hexamethylbenzene are formed as reflected in computed energies as well as in observed and predicted Δν(OH) shifts.

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ТЕОРЕТСКИ НАСПРОТИ ЕКСПЕРИМЕНТАЛНИ ПОМЕСТУВАЊА НА ИНФРАЦРВЕНИТЕ ФРЕКВЕНЦИИ ПРИ π-ВОДОРОДНО СВРЗУВАЊЕ: КОМПЛЕКСИ НА СУПСТИТУИРАНИ ФЕНОЛИ СО ХЕКСАМЕТИЛБЕНЗЕН

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Анализиран е квалитетот на теоретското претскажување на поместувањата на O–H валентните фреквенции при π-водородно сврзување кај серија од десет комплекси помеѓу моносупституирани феноли и хексаметилбензен. Пресметаните O–H фреквенции со примена на методот на теоријата за функционал од електронската густина на B3LYP/6-311++G(2df,2p) ниво на теорија се споредени со спектроскопските податоци од литературата. Резултатите покажаа дека применетиот теоретски метод со одлична точност ги претскажува поместувањата на O–H валентните фреквенции [Δν(OH)] при формирање на π-водородно сврзување. Споредувањата со аналогните теоретски и експериментални податоци за бензенски комплекси со супституирани феноли ја даваат големината на хиперкоњугативниот ефект на метилните групи врз интеракционите енергии и фреквентното поместување. Индуцираните (од страна на фенолните супституенти) варирања на енергиите на врските и на Δυ(OH) се рационализирани со користење на теоретски евалуирани како и со експериментални параметри.

Клучни зборови: π-водородно сврзување; хексаметилбензен; супституирани феноли; O–H фреквенции; DFT пресметки

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Original scientific paper

VIBRATIONAL SCALING FACTORS FOR Rh(I) CARBONYL COMPOUNDS IN HOMOGENEOUS CATALYSIS[•]

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Metal carbonyl complexes are an important family of catalysts in homogeneous industrial processes. Their characteristic vibrational frequencies allow *in situ* tracking of catalytic progress. Structural assignment of intermediates is often hampered by the lack of appropriate reference compounds. The calculation of carbonyl vibrational frequencies from first principles provides an alternative tool to identify such reactive intermediates. Scaling factors for computed vibrational carbonyl stretching frequencies were derived from a training set of 45 Rh-carbonyl complexes using the BP86 and B3LYP functionals. The systematic scaling of the computed C=O frequencies yields accurate calculation and assignment of the experimentally obtained ν(CO) values. The vibrational scaling factors can be used to identify reaction intermediates of the industrially relevant Rh-catalyzed hydroformylation reaction. The absolute error between calculated and experimental spectra was significantly reduced and the experimental spectra were assigned successfully.

Key words: infrared spectroscopy; vibrational scaling factors; rhodium-carbonyl complexes; hydroformylation; DFT

INTRODUCTION

Hydroformylation of alkenes (also known as "oxo process") is one of the most important homogeneously catalysed industrial processes with a yearly production of more than 10 million metric tons of oxo chemicals [1]. The produced aldehydes from olefins and syngas (CO/H_2) are used as perfumes, surfactants, plasticizers and solvents. Owing to the milder process conditions, rhodium(I) carbonyl complexes are the predominant catalysts of choice [2]. For the purpose of achieving higher *n*/*iso* selectivity, rhodium carbonyl complexes are modified with bulky phosphine or phosphite ligands. Aryl diphosphite compounds are attractive modifying ligands offering high catalytic activity and selectivity on one hand, and ease of preparation in comparison to phosphines on the other [3]. Also being generally less sensitive to sulfur compounds and oxidizing agents, bulky aryl diphosphites are the first choice for selective production of large quantities of *n*-aldehydes. Phosphite ligands, such as BiPhePhos, provide 98–99% *n*-selectivity [4]. The ligand BiPhePhos and Rh(I)BiPhePhos precatalyst with two carbonyl and one hydride ligand are shown in Figure 1. In addition to hydroformylation purposes, rhodium carbonyl complexes are also important catalysts in a number of other large-scale homogeneously catalysed industrial processes, e.g. the production of acetic acid (the Monsanto process) [5].

Understanding the mechanism of the complex catalytic reaction networks and establishing structure-selectivity/reactivity relationships is incredibly valuable for the further development of catalysts and processes, as well as for tailoring new catalysts. Infrared (IR) spectroscopy plays a very important role in metal carbonyl chemistry for gaining mechanistic insight and the bands due to CO absorption, occurring around 2000 cm^{-1}, are especially informative. *Operando* IR spectroscopy

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[•] Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

is an advancing *in situ* methodology to monitor formation and disappearance of intermediate species in real time, under working conditions at elevated pressures and temperatures using time-resolved spectra [6].

For (carbonyl containing) Rh catalysts, the C=O stretching frequencies are of crucial importance to deduce structural information of intermediate complexes during the reaction. With CO being a strong π acceptor ligand, the strength of the Rh–CO bond and consequently frequency of vibration of the C–O bond will depend on the electron density at the rhodium atom.

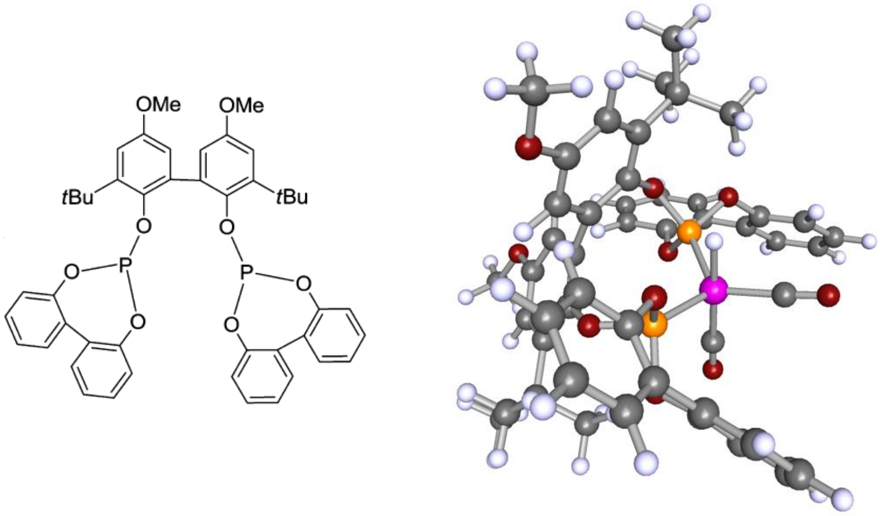


Figure 1. Structure of BiPhePhos ligand (left). DFT(BP86/def2-TZVP) optimized HRh(BiPhePhos)$(CO)_2$ hydroformylation pre-catalyst (right).

CO stretching vibrations are very sensitive to their chemical environment, give rise to sharp and intense bands well separated from other vibrations in the spectrum. All of this explains why IR is the most important technique for rationalizing the structure of CO complexes. Assignment of the resulting spectra, however, is almost never unambiguous. *Ab initio* calculated frequencies have been recognized as an inevitable tool in structural assignment and interpretation of complex vibrational spectra. For larger molecules and transition metal complexes, density functional theory (DFT) is the method of choice due to its computational efficiency [7, 8]. However, due to intrinsic biases of the theoretical models, the computed frequencies are shifted with respect to the experimental ones. This has its origins in approximating vibrational movements of a molecule to be harmonic. Other sources of error are the use of a finite basis set and the neglect of electron correlation. Further source of error is that the computed frequencies stem from isolated molecules (gas phase) whereas the measured spectra are usually done on liquid or solid samples where perturbations from solvent, counter ions or matrix environment are present. Thus the computed harmonic vibrational frequencies are typically larger than the experimentally observed fundamentals [9]. The discrepancies between computed and measured vibrational frequencies tend to be systematic. This makes it possible to correct *ab initio* frequencies by a scaling factor to compensate for the approximations so that they match the experimental outcome. Deriving scaling factors for harmonic frequencies has received a much of attention in the literature [10–14]. Derived scaling factors are specific to each level of theory used, but they also depend on the test set of molecules. In the literature usually global scaling factors are given for correcting the complete IR spectral range, although it is known that low and high frequencies are not equally affected by the deficiencies of the computational methods. When uniform scaling factors are used, large errors from the highly anharmonic low frequency modes enter in the scaling factors. Studies show the scaling factors for high and low frequencies can be very different which justifies the use of dual scaling [11]. There are published carbonyl frequency scaling factors for Fe-Fe complexes [15], or for diverse transition metal homoleptic carbonyls [16]. Nevertheless, the systematic errors arising from the basis sets of different transition metals are different. To the best of our knowledge, there is no systematic study for reliable and un-biased scaling of heteroleptic Rh-carbonyl complexes.

Here we derive vibrational scaling factors for two commonly used DFT functionals from a large number of experimentally characterized Rh(I) carbonyl complexes. The newly derived vibrational scaling factors can help to assign the structure of spectroscopically observed intermediates in complex reaction networks. A reliable assignment of complex *in situ* or *operando* vibrational spectra stemming from Rh-catalysed processes becomes possible.

COMPUTATIONAL DETAILS

A training set of 45 experimentally characterized Rh(I) carbonyl complexes was designed from chemical literature. All structures were optimized at the DFT level using two commonly used functionals: one generalized gradient approximation (GGA) functional (BP86 [17, 18]) and one hybrid functional (B3LYP [17, 19]). For all atomic orbitals, the def2-TZVP basis set was used [20] substituting previous Ahlrichs' basis sets [21]. This basis set was shown to give reliable vibrational CO frequencies for a number of metal complexes, see for example [22-24]. All final structures were characterized to be minima by calculating the Hessian matrices at the respective level and the absence of any imaginary eigenvalues. The frequencies corresponding to CO stretching vibrations were then used for comparison with experiment and derivation of a vibrational scaling factor. All calculations were done using TURBOMOLE V6.6 [25].

RESULTS AND DISCUSSION

A set of 45 carbonyl containing rhodium(I) complexes with available experimental IR spectroscopic data was selected from literature. The criteria for the selection were the formal oxidation state of rhodium to be +1 and the presence of one or two terminal carbonyl ligands. Complexes with bridging CO or clusters with more than one Rh atom were not included in the selection. It is beyond the scope of this study to individually discuss the CO stretching frequencies of each compound which span a range of 170 cm^{-1} (see below).

Both BP86 and B3LYP are known to generally reproduce structural parameters such as bond lengths and bond angles of transition metal complexes very well [26]. We here give one representative example complex from the test set, Rh(acac)(CO)$_2$, a precursor of the catalyst in hydroformylation (Figure 2). The calculated structural parameters are in excellent agreement with the experiment from X-ray structural analysis [27]. Both shown bond lengths (rhodium–CO and C–O) are better reproduced by BP86 (to within 0.01 Å), whereas B3LYP overestimates the Rh–C bonds by 0.3 Å, and underestimates C=O distances by 0.05 Å. This in turn yields higher C=O vibrational frequencies not only in this complex but observed in all B3LYP calculations.

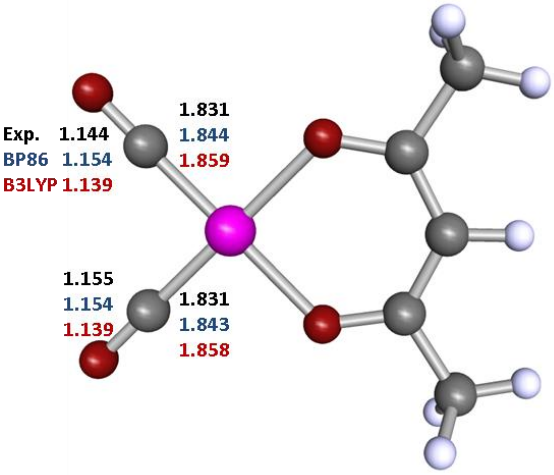


Figure 2. Comparison of experimentally obtained structure [27] of Rh(acac)(CO)$_2$ to the calculated ones on BP86/def2-TZVP and B3LYP/def2-TZVP levels of theory. Values given in Å.

These 45 complexes give a total of 69 CO vibrational frequencies resulting from the presence of multiple carbonyl ligands in some of the complexes. The test set of 45 molecules along with their experimental and computed frequencies are given in Table 1. Although all of the 45 complexes are formal Rh(I) complexes, the carbonyl stretching frequencies are in a range from 1920 to 2095 cm^{-1} thus spanning more than 170 cm^{-1}. This demonstrates that the CO stretching frequencies are subtle probes for the electron density at the central metal atom which is determined by the steric and electronic effects of the ligands. The 69 experimental frequencies are compared to the calculated ones with the BP86 and B3LYP DFT functionals. Although, it is known that the "exact" harmonic frequencies will always be greater than the true frequencies [28], our analysis shows that in the majority of cases BP86 underestimates CO experimental frequencies for the studied complexes. On the other hand, B3LYP being a hybrid functional including HF character, overshoots as expected in all of the cases. To precisely estimate the accuracy of the theoretical methods, the differences between the calculated unscaled and the experimental values are given in the 5th and 7th columns in Table 1 for

BP86/def2-TZVP and B3LYP/def2-TZVP, respectively. We give the deviation from experiment as a signed percentage error. The maximal absolute error for BP86 is 2.9% and 6.5% is for B3LYP. The average absolute error is 1% for BP86 and 3.5% for B3LYP.

Table 1. Set of molecules and the respective experimental and calculated C=O frequencies used in this study. The error of the calculated frequencies with respect to the experimental given as signed percent.

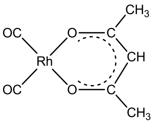
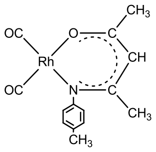
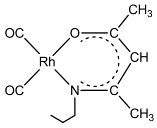
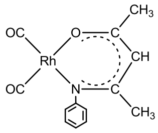
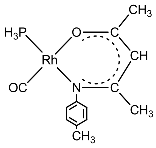
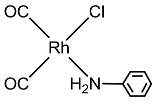
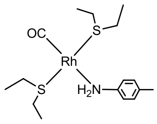
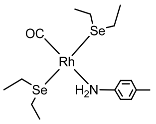
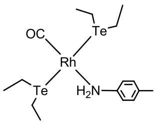
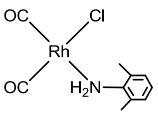
Molecular formula	Structural formula	$\nu(\mathrm{CO})$ [cm^{-1}]			$\nu(\mathrm{CO})$ [cm^{-1}]	
		Exp.	BP86	Error %	B3LYP	Error %
1	**2**	**3**	**4**	**5**	**6**	**7**
$Rh(CO)_2OOC_5H_7$ [29]		2084	2064.49	–0.94	2145.6	2.96
		2015	2001.52	–0.67	2084.8	3.46
$RhC_{14}H_{14}NO_3$ [30]		2068	2054.68	–0.64	2136.51	3.31
		2000	1992.98	–0.35	2075.39	3.77
$RhC_{10}H_{14}NO_3$ [30]		2070	2052.03	–0.87	2134.71	3.13
		2003	1983.27	–0.99	2064.68	3.08
$RhC_{13}H_{12}NO_3$ [30]		2065	2055.63	–0.45	2137.52	3.51
		2005	1994.04	–0.55	2076.59	3.57
$RhC_{31}H_{29}NO_2P$ [30]		1976	1982.55	0.33	2061.85	4.34
cis-$Rh(CO)_2(PhNH_2)Cl$ [30]		2070	2038.87	–1.50	2163.11	4.50
		2015	1969.44	–2.26	2085.53	3.50
$Rh(CO)(S(C_2H_5)_2)_2Cl$ [31]		1965	1958.35	–0.34	2034.45	3.53
$Rh(CO)(Se(C_2H_5)_2)_2Cl$ [31]		1961	1951.77	-0.47	2028.31	3.43
$Rh(CO)(Te(C_2H_5)_2)_2Cl$ [31]		1955	1948.97	–0.31	2021.33	3.39
$Rh(CO)_2(2,6\text{-}(CH_3)_2C_6H_3NH_2)Cl$ [30]		2081	2067.71	–0.64	2149.57	3.30
		2010	1995.42	–0.73	2078.49	3.41

Table 1. (Continuation)

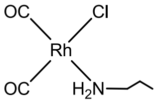
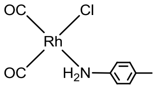
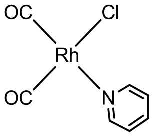
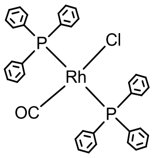
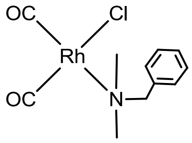
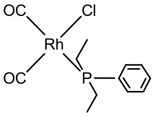
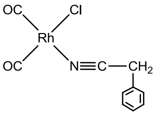
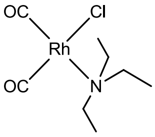
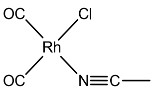
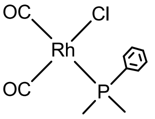
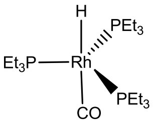
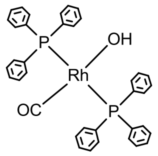
1	2	3	4	5	6	7
$Rh(CO)_2(n\text{-}C_3H_7NH_2)Cl$ [30]		2060	2044	–0.78	2158.58	4.79
		1985	1971.73	–0.67	2080.96	4.83
$Rh(CO)_2(p\text{-}CH_3C_6H_4NH_2)Cl$ [30]		2095	2067.21	–1.33	2149.03	2.58
		2035	1994.39	–2.00	2077.05	2.07
cis-$Rh(CO)_2$(Pyridine)Cl [32]		2089	2052.55	–1.74	2168.93	3.83
		2005	1983.67	–1.06	2091.77	4.33
trans-$Rh(CO)Cl(PPh_3)_2$ [33]		1965	1964.09	–0.05	2037.99	3.71
cis-$Rh(CO)_2$(DMBA)Cl [32]		2088	2066.26	–1.04	2147.93	2.87
		2004	1983.92	–1.00	2067.17	3.15
cis-$Rh(CO)_2(PEt_2Ph)Cl$ [32]		2096	2060.37	–1.70	2147.7	2.47
		2009	1988.11	–1.04	2068.04	2.94
cis-$Rh(CO)_2(PhCH_2CN)Cl$ [32]		2090	2069.95	–0.96	2151.28	2.93
		2038	2001.77	–1.78	2083.23	2.22
cis-$Rh(CO)_2(Et_3N)Cl$ [32]		2090	2037.96	–2.49	2140.89	2.43
		2002	1967.37	–1.73	2067.28	3.26
cis-$Rh(CO)_2(CH_3CN)Cl$ [32]		2090	2071.54	–0.88	2152.83	3.01
		2020	2002.26	–0.88	2083.81	3.16
cis-$Rh(CO)_2(PMe_2Ph)Cl$ [34]		2094	2063.39	–1.46	2151.51	2.75
		2003	1987.41	–0.78	2066.57	3.17
$HRh(CO)(PEt_3)_3$ [35]		1952	1970.29	0.94	2020.49	3.51
trans-$Rh(CO)(OH)(PPh_3)_2$ [35]		1948	1965.54	0.90	2050.52	5.26

Table 1. (Continuation)

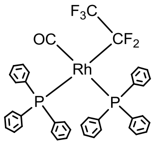
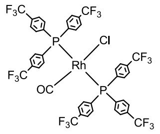
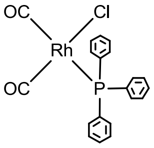
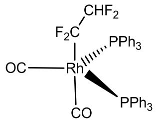
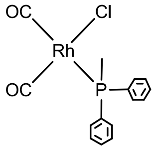
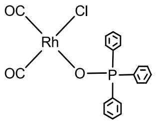
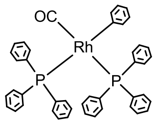
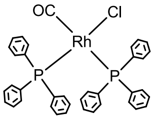
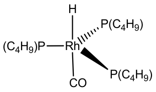
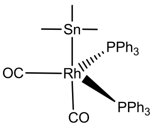
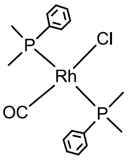
1	**2**	**3**	**4**	**5**	**6**	**7**
$Rh(C_2F_4H)(CO)(PPh_3)_2$ [36]		1995	1975.14	–1.00	2054.73	2.99
Rh(Cl)(CO)(P(p-$CF_3C_6H_4)_3)_2$ [37]		1985	1974.2	–0.54	2049.34	3.24
cis-$Rh(CO)_2(PPh_3)Cl$ [32]		2093	2061.82	–1.49	2149.03	2.68
		2009	1987.26	–1.08	2068.04	2.94
$Rh(C_2F_4H)(CO)_2(PPh_3)_2$ [36]		2005	2015.03	0.50	2101.14	4.80
		1958	1963.6	0.29	2047.14	4.55
cis-$Rh(CO)_2(PPh_2Me)Cl$ [32]		2092	2062.68	–1.40	2150.73	2.81
		2008	1985.5	–1.12	2064.73	2.83
$(Ph_3P)ORh(CO)_2Cl$ [32]		2084	2059.62	–1.17	2138.03	2.59
		2007	1988.04	–0.85	2070.21	3.25
cis -$Rh(Ph)(CO)(PPh_3)_2$ [36]		1978	1954.64	–1.18	2033.98	2.83
cis-$Rh(CO)Cl(PPH_3)_2$ [38]		2010	2008.27	–0.09	2089.84	3.97
$Rh(CO)_2(PPh_3)_2$(Sn $(CH_3)_3)$ [39]		1975	1947.47	–1.39	2026.93	2.63
		1930	1919.22	–0.56	1993.34	3.28
$HRhCO(P(n\text{-}Butyl)_3)_3$ [35]		1960	1966.06	0.31	2016.4	2.88
trans-$Rh(CO)Cl(PMe_2Ph)_2$ [34]		1964	1960.4	–0.18	2092.26	6.53

Table 1. (Continuation)

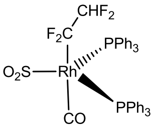
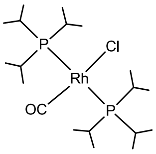
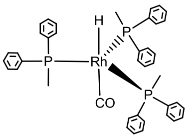
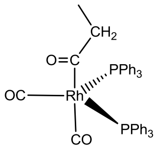
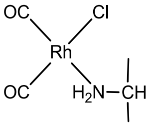
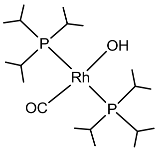
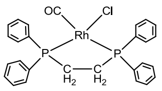
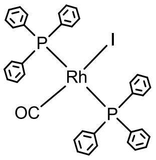
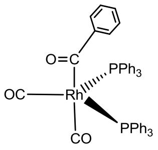
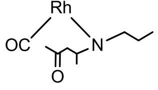
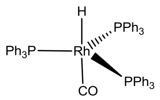
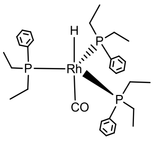
1	2	3	4	5	6	7
$Rh(C_2F_4H)(CO)(SO_2)(PPh_3)_2$ [36]		2055	2008.67	–2.25	2096.07	2.00
trans-Rh(CO)Cl(P(i-$C_3H_7)_3)_2$ [35]		1940	1977.67	1.94	2059.15	6.14
$HRh(CO)(PPh_2Me)_3$ [35]		1968	2015.85	2.43	2066.47	5.00
$Rh(COEt)(CO)_2(PPh_3)_2$ [36]		1990	1976.79	–0.66	2060.47	3.54
		1943	1928.52	–0.75	2008.32	3.36
cis-$Rh(CO)_2$(iso-$C_3H_7NH_2)Cl$ [30]		2086	2042.94	–2.06	2155.56	3.33
		2030	1971.2	–2.90	2079.02	2.41
trans-Rh(CO)(OH)(P(i-$C_3H_7)_3)_2$ [35]		1920	1944.59	1.28	2028.48	5.65
Rh(CO)(Diphos)Cl [32]		2010	2004.84	–0.26	2089.62	3.96
trans-$Rh(CO)I(PPh_3)_2$ [35]		1982	1990.59	0.43	2071.63	4.52
$Rh(COPh)(CO)_2(PPh_3)_2$ [36]		1980	1977.21	–0.14	2062.3	4.16
		1945	1926.8	–0.94	2009.68	3.33
cis-$Rh(CO)_2(C_8H_{15}NO)Cl$ [30]		2059	2052.35	–0.32	2170.82	5.43
		1994	1981.79	–0.61	2090.84	4.86
$HRh(CO)(PPh_3)_3$ [35]		2035	2011.54	–1.15	2063.54	1.40

Table 1. (Continuation)

1	**2**	**3**	**4**	**5**	**6**	**7**
HRh(CO)(PPhEt$_2$)$_3$ [35]		1970	1973.01	0.15	2026.18	2.85

The correlation between the experimental set of data and the two calculated sets of data was estimated and the fitting to a linear function shows a slope close to 6/8 for the BP86 values and a slope of 7/8 for the B3LYP values (Figure 3). This confirms the slightly better linear correlation of B3LYP to experiment in comparison with BP86 which was also observed in other studies [40].

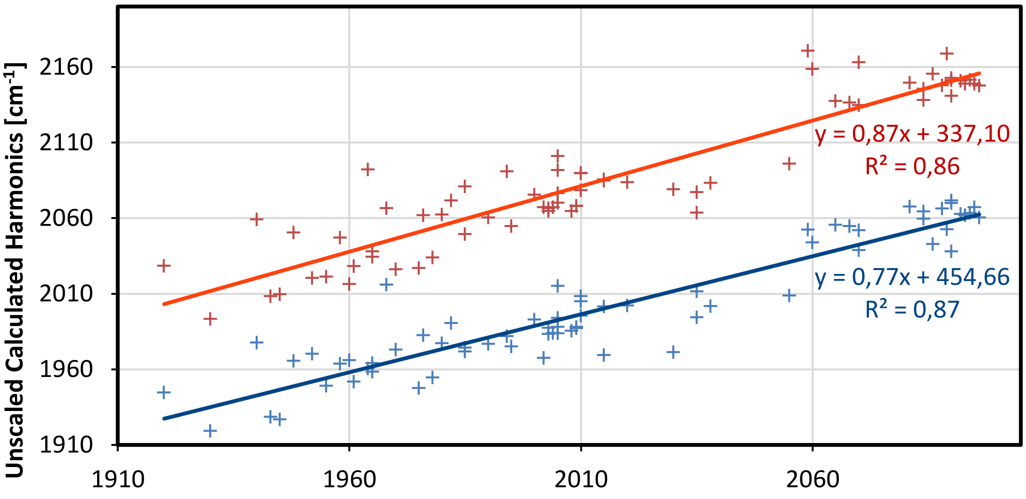


Figure 3. Comparison of experimental CO stretching frequencies for 45 Rh(I) complexes and computed with BP86/def2-TZVP (blue) and B3LYP/def2-TZVP (red) ones.

Using the experimental and calculated values from Table 1, vibrational frequency scaling factors for the both of the DFT methods were determined by minimizing the sum of the square of the errors (Equation (1)):

$$\Delta_{\mathrm{vib}} = \sum_i \left(\lambda(\mathrm{CO})\omega_i(\mathrm{CO}) - \nu_i(\mathrm{CO})\right)^2 , \quad (1)$$

where $\omega_i(\mathrm{CO})$ is the i-th calculated CO harmonic stretching frequency on the respective level of theory, whereas $\nu_i(\mathrm{CO})$ is the corresponding experimental fundamental carbonyl stretching frequency. The frequencies are given in cm^{-1}. The minimized residual for each analysed frequency was calculated as:

$$\Delta_{\min} = \left(\lambda(\mathrm{CO})\omega_i(\mathrm{CO}) - \nu_i(\mathrm{CO})\right)^2 \quad (2)$$

$\lambda(\mathrm{CO})$ is the scaling factor for carbonyl frequencies given by:

$$\lambda(\mathrm{CO}) = \frac{\sum_i \omega_i(\mathrm{CO})\nu_i(\mathrm{CO})}{\sum_i (\omega_i(\mathrm{CO}))^2} \quad (3)$$

Vibrational scaling factors of 1.0074 and 0.9662 were obtained for BP86/def2-TZVP and B3LYP/def2-TZVP, respectively. The results are summarized in Table 2.

Table 2. Frequency scaling factors derived for CO stretching vibrations and corresponding RMSE values

Method	Scale factor	RMSE before scaling/cm^{-1}	RMSE after scaling/cm^{-1}
BP86/def2-TZVP	1.0074	24.03	18.85
B3LYP/def2-TZVP	0.9662	72.99	18.80

The root mean squared error (RMSE) for both of the methods is calculated as a single measure of accuracy according to Equation (4). The values for the RMSE before and after scaling are presented along with the scaling factors in Table 2.

$$\mathrm{RMSE} = \left(\sum_1^n \Delta_{\mathrm{min}} / n_{\mathrm{all}}\right)^{1/2} \qquad (4)$$

where n is the number of all analysed frequencies.

Before scaling, BP86 shows RMSE of 24 cm^{-1} which is three times smaller than the RMSE for B3LYP (73 cm^{-1}). After the scaling, a RMSE of 18.8 cm^{-1} was obtained for both methods.

Our scaling factors are in line with those from Assefa et al. of 1.012 and 0.968 for BP86/def2-TZVP and B3LYP/def2-TZVP, respectively. These scaling factors were derived for different transition metal homoleptic carbonyl complexes but not for Rh complexes [16].

To better illustrate the effect of the scaling, the distribution of the deviations from experiment before and after scaling is shown in Figure 4. It can be seen that the unscaled B3LYP values are significantly dispersed around the experimental values (more than one third of the B3LYP errors are larger than 70 cm^{-1}) and using unscaled B3LYP frequencies can lead to possible difficulties in the interpretation or to misinterpretation of the experimental spectra. On the other hand, BP86 frequencies can even be used without scaling considering that they only might be slightly lower than the experimental ones. After scaling, both methods are equally good in reproducing the experimental CO frequencies.

Kershawani et al. were the first to derive a vibrational scaling factor for the Weigend-Ahlrichs basis sets for a benchmark set of small organic molecules [41]. Amongst others, they investigated the convergence of accuracy of calculated vibrational frequencies with basis set size. They obtained a RMSE for the BP86 exchange-correlation functional after scaling using SVP (38 cm^{-1}), def2-TZVP (26 cm^{-1}), def2-TZVPD (25 cm^{-1}), def2-TZVPP (24 cm^{-1}) to an extrapolated basis set limit CBSB7 (30 cm^{-1}). For B3LYP, the RMSEs were SVP (39 cm^{-1}), def2-TZVP (27 cm^{-1}), def2-TZVPD (27 cm^{-1}), def2-TZVPP (26 cm^{-1}) and CBSB7 (30 cm^{-1}). This demonstrates the appropriateness of the def2-TZVP basis set for calculation vibrational frequencies. A larger basis set does not necessarily improve the accuracy of calculated frequencies.

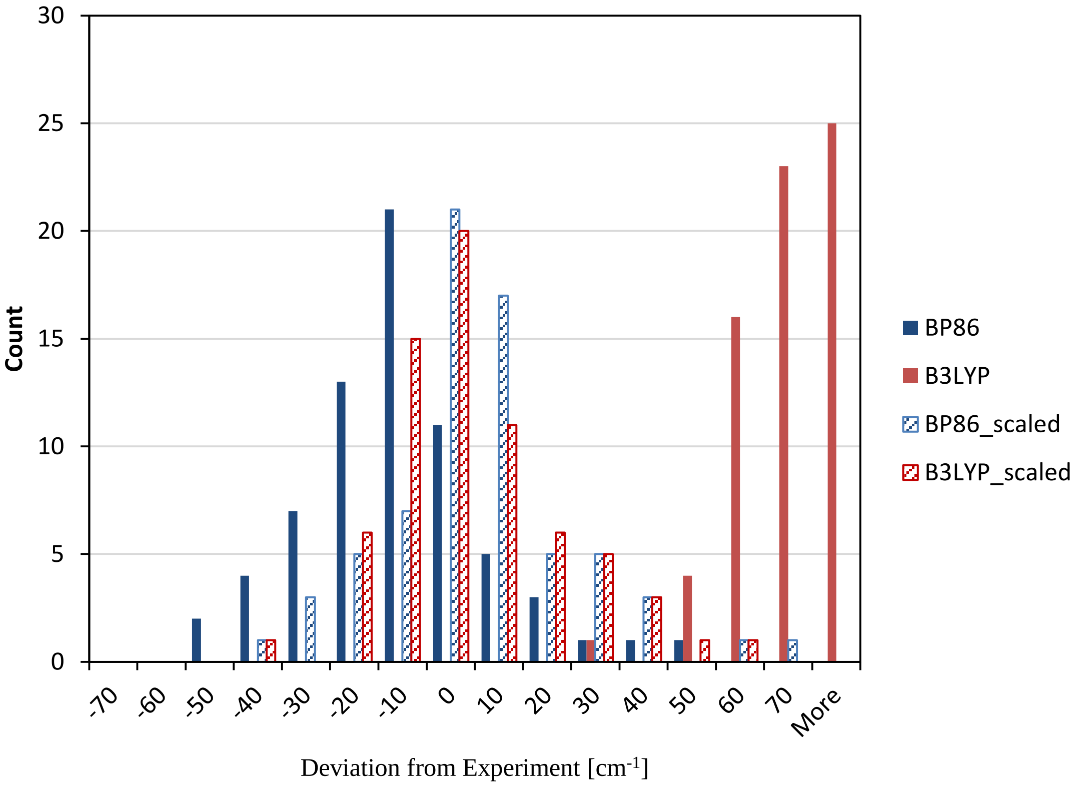


Figure 4. Histogram of CO stretching frequency differences between computed harmonics and observed fundamentals for unscaled and scaled BP86/def2-TZVP (blue) and B3LYP/def2-TZVP (red) level of theory.

One of the major concerns with quantum chemically calculated vibrational frequencies is the use of the rigid rotor harmonic oscillator (RRHO) approximation. For small molecules, the calculation of accurate anharmonic force fields is a practical option, see for example [42], but this becomes not feasible for larger molecules. For $Ni(CO)_4$, for example, the estimated anharmonicity constants from isotope experiments are between –3 and –11 cm^{-1} [43] and would bring calculated frequencies in even closer agreement with experiments. The use of a simple vibrational scaling factor aims to correct for (i) inherent deficiencies of the electronic structure methods, and (ii) the potential energy surface to be not harmonic.

In order to illustrate the usefulness of vibrational scaling factors on practical examples, we have chosen two Rh(I) catalyst complexes to assign experimental IR spectra.

$HRh(BiPhePhos)(CO)_2$ is a saturated 18-electron species with a trigonal bipyramidal structure and is supposed to give rise to a 3 bands pattern in the carbonyl stretching region. $HRh(BiPhePhos)(CO)_2$ is the "resting state" or "pre-catalyst" prior to hydroformlylation of long chain olefins. The "resting state" is activated by dissociation of one of the CO ligands. The bidentate phosphite ligand can coordinate around the Rh central atom in two different ways: the two phosphorous atoms may occupy two equatorial (e,e) positions or one equatorial and one axial (e,a). The equatorial-equatorial positioning can be discriminated from the equatorial-axial one according to the pattern in the carbonyl region originating from the two carbonyl groups and the hydride in the complex as shown in Figure 5. The comparison of both calculated spectra to the experimental one (compare Figures 5 and 6) led to successful assignment of the structure to the e,e configuration.

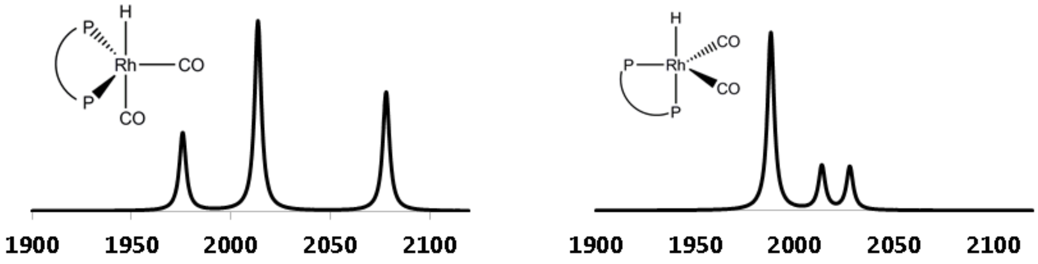


Figure 5. Two isomeric forms of a hydrido-dicarbonyl complex containing a bidentate ligand ($HRh(BPP)(CO)_2$) and their respective calculated IR spectra. Left: equatorial-equatorial (e,e) positioning. Right: equatorial-axial (e,a) positioning. Values are given in cm^{-1}.

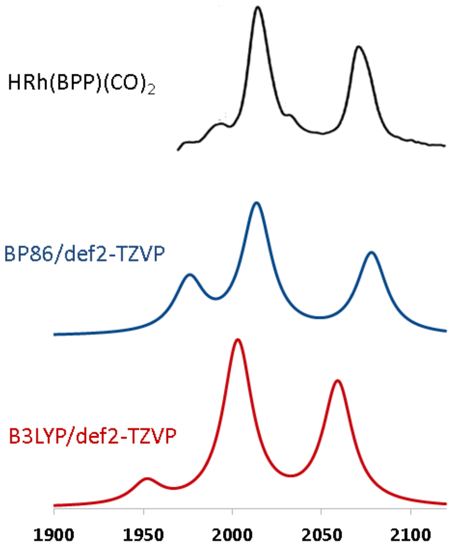


Figure 6. Comparison of the experimental spectrum of $HRh(BPP)(CO)_2$e,e and the spectra predicted by two DFT functionals using the vibrational scaling factors derived in this study. Values are given in cm^{-1}.

Figure 6 shows the experimental spectrum of this complex compared to the DFT calculated spectra for the e,e isomer. The weak absorption at 1993 cm^{-1} and the shoulder at 2033 cm^{-1} were assigned to a small moiety of the e,a isomer present in the mixture in the original work [44]. The weak absorption below 2000 cm^{-1} is commonly identified as Rh–H stretch. Nevertheless, such a band was not assigned in the original study. By means of first principles, we can thus reliably assign the vibrational peak. All three bands seen in the calculated spectra originate from coupling of the two Rh–CO and one Rh–H vibrational modes.

The calculated spectra are in good agreement with the experimental spectrum for both of the functionals in terms of peak positioning and, additionally, correctly reproduce the relative absorption intensities with the lower frequency band to be more intense. The exact position of the bands and the deviations from experiment are summarized in Table 3. The absolute deviation of 0.6 % (taken as arithmetic mean for both of the bands) for the unscaled values reduces to 0.2 % for BP86 and the deviation of 2.8 % for B3LYP reduces to 0.6 %.

Scaling CO stretches by uniform scaling parameters (applicable to the entire IR range) can lead to even larger deviations instead of correcting them. In this example, applying the global scaling factors of 1.0337 and 1.0044 for BP86/def2-TZVP and B3LYP/def2-TZVP respectively, derived by Kesharwani et al. [12] will blueshift both BP86 and B3LYP frequencies (Table 3). For BP86 it will be too high blueshifted than necessary (increase of the absolute deviation from 0.6 to 2.8 %) and for B3LYP no blueshifting is needed in the first place, but redshifting (increase of the absolute error from 2.8 to 3.3 %). This can be misleading for organometallic chemists who rely on the carbonyl spectral range in identifying carbonyl containing intermediates.

We bring a further example, $HRh(SX)(CO)_2$. The electron richer SulfoXantPhos (SX) ligand has the effect of weakening the C=O bond and redshifting its frequencies in comparison to its analogue BiPhePhos. The experimental [45] and the calculated frequencies for the e,e isomer of $HRh(SX)(CO)_2$ are given in Table 3. The higher vibration at 2032 cm^{-1} is one of the rare examples where BP86 yields a higher value than the experimental. Thus, scaling this frequency increases the deviation from experiment. This vibration originates from a coupled stretching motion of the axial hydride and axial carbonyl ligand. Given that the experiment was performed at a high pressure of CO and H_2 (HP-IR), we suggest that this vibration is most sensitive to increase in pressure. At high pressure, the Rh-H bond decreases in distance, the metal becomes more electron rich and this leads to a lower than expected C=O vibration. Nevertheless, the low frequency after scaling deviates only 1 cm^{-1} from the experimental value.

Table 3. Experimental and calculated CO frequencies and their absolute deviations for $HRh(BPP)(CO)_2$ and $HRh(SX)(CO)_2$. 3rd and 6th column – raw calculated frequencies; 4th and 7th column – scaled by the scale factors (sf) derived in this study; 5th and 8th column – scaled by a uniform scale factors.

	Exp	BP86	BP86 scaled	BP86 scaled by uniform sf [12]	B3LYP	B3LYP scaled	B3LYP scaled by uniform sf [12]
$HRh(BPP)(CO)_2$	[37]						
ν(CO) [cm^{-1}]	2071	2063	2078	2133	2129	2057	2138
	2015	1999	2013	2066	2073	2003	2082
$\Delta\nu$(CO) [cm^{-1}]		8	7	62	58	14	67
		16	2	51	58	12	67
$[HRh(SX)(CO)_2]^{2-}$	[38]						
ν(CO) [cm^{-1}]	2032	2041	2056	2109	2102	2031	2111
	1967	1951	1966	2017	2011	1943	2020
$\Delta\nu$(CO) [cm^{-1}]		9	24	77	70	1	79
		16	1	50	44	24	53

CONCLUSIONS

We derived vibrational scaling factors from a data set of 45 Rh(I) carbonyl complexes. Two representative DFT functionals (BP86 and B3LYP) were used. For reliable interpretation of experimental IR spectra, scaling of the frequencies by the here presented scale parameters for both of the methods is necessary. Global scaling factors found in literature are not recommended to be used for CO stretches in transition metal carbonyl complexes. If necessary, at least scaling factors for high frequencies should be employed. Comparing the computational times of both of the methods, BP86 is shown to be much more attractive requiring much less computational time and providing better accuracy without and same accuracy after scaling. As shown before [16] the scaling factors vary insignificantly with the basis set, which makes our derived scale factors also applicable to other basis sets.

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ВИБРАЦИОНИ СКАЛИРАЧКИ ФАКТОРИ ЗА Rh(I) КАРБОНИЛНИ СОЕДИНЕНИЈА ВО ХОМОГЕНАТА КАТАЛИЗА

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Метал карбонилните комплекси се важно семејство на катализатори во хомогените индустриски процеси. Нивните карактеристични вибрациони фреквенции овозможуваат *in situ* следење на каталитичкиот прогрес. Структурното асигнирање на интермедиери е често отежнато поради недостиг на референти соединенија. Пресметките *Ab inicio* на карбонилните вибрациони фреквенции нудат алтернативна алатка за идентификација на реактивни интермедиери. Скалирачки фактори за компјутерски пресметани карбонилни валентни фреквенции беа изведени од сет од 45 карбонилни комплекси на родиум користејќи ги функционалите BP86 и B3LYP. Систематичното скалирање на пресметаните C=O фреквенции овозможи веродостојно предвидување и асигнирање на експерименталните вредности на ν(CO). Овие вибрациони скалирачки фактори можат да послужат за идентификација на реакциони интермедиери во индустриски релевантната реакција на хидроформилација катализирана со родиумови комплекси. Апсолутната девијација помеѓу пресметаните и експерименталните спектри беше значително намалена и експериментални спектри беа успешно асигнирани.

Клучни зборови: инфрацрвена спектроскопија; вибрациони скалирачки фактори; карбонилни комплекси на родиум; хидроформилација; теорија на функционал од густина (ДФТ)

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Original scientific paper

THE EFFECT OF SODIUM DODECYL SULPHATE ON THE FORCED HYDROLYSIS of $FeCl_3$ SOLUTIONS•

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Precipitations by the forced hydrolysis of 0.2 M $FeCl_3$ aqueous solutions between 2 and 72 hours in the presence of 1% sodium dodecyl sulphate (SDS) were investigated. In the absence of SDS a direct phase transformation β-FeOOH → α-Fe_2O_3 *via* dissolution/recrystallization occured in the precipitation system. In the presence of SDS, α-FeOOH as an intermediate phase precipitated and, with a prolonged time of forced hydrolysis, also transformed to α-Fe_2O_3 *via* the dissolution/recrystallization mechanism. On the basis of Mössbauer spectra it was concluded that in the presence of SDS, α-Fe_2O_3 phase possessed a lower degree of crystallinity. In this precipitation process the competition between the stability of Fe(III)-dodecyl sulphate, on one side, and the formation of iron oxide phases, on the other, also played an important role. FE SEM revealed that the big α-Fe_2O_3 particles possessed the substructure. The elongation of primary α-Fe_2O_3 particles produced in the presence of SDS was noticed. This effect can be assigned to the preferential adsorption of dodecyl sulphate groups on nuclei and crystallites of FeOOH and α-Fe_2O_3 phase during the forced hydrolysis of $FeCl_3$ solutions.

Key words: $FeCl_3$ hydrolysis; sodium dodecyl sulphate; α-Fe_2O_3; Mössbauer; FT-IR; XRD; FE SEM

INTRODUCTION

Hematite (α-Fe_2O_3) particles have found different applications as pigments, photocatalysts, electrode materials, fine abrasives or cosmetic additives. α-Fe_2O_3 can also be used as an adsorbent for toxic elements or radioisotopes in wastewater treatment. In surface and colloid chemistry these particles are often used as model systems due to their excellent acido-basic surface properties. The investigation of colloid stability of α-Fe_2O_3 particles is important for understanding the nature of this phenomenon.

The simplest way to produce α-Fe_2O_3 particles is by forced hydrolysis in a boiling 0.01 M $FeCl_3$ solution [1], whereas at temperatures below 70 °C akaganéite (β-FeOOH) particles (spindle- or cigar-shaped) will precipitate. The synthesis and characterization of β-FeOOH and its decomposition products in vacuum were investigated [2]. Musić et al. [3] used Mössbauer spectroscopy to investigate the hydrolysis of 0.1 M solutions of $Fe(NO_3)_3$, $FeCl_3$, $Fe_2(SO_4)_3$ or $NH_4Fe(SO_4)_2$ at 90 °C. A proposal was made concerning the mechanism of formation of the oxides and hydroxides of Fe^{3+} ions in these precipitation systems. It is generally accepted that the phase transformation β-FeOOH → α-Fe_2O_3 in hydrolysing $FeCl_3$ solutions at elevated temperature is operated by a dissolution/recrystallization mechanism [4–6]. The application of Mössbauer spectroscopy in investigating the precipitation of iron oxides has recently been reviewed by Musić et al. [7].

The nano/microstructure of α-Fe_2O_3 plays a very important role in many applications of this iron oxide. For this reason many researchers investigated the conditions for the preparation of α-Fe_2O_3 with different properties. Katsuki and Komarneni [8] used the forced hydrolysis of the $FeCl_3$ solution under hydrothermal conditions to investigate the influence of morphology on the colour of

•Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

the red pigment (α-Fe_2O_3) for porcelain. Sugimoto et al. [9] noticed remarkably different effects of Cl^-, OH^-, SO_4^{2-} or PO_4^{3-} anions on the shape and internal structure of α-Fe_2O_3 particles. Hollow α-Fe_2O_3 spheres were produced by the forced hydrolysis of the $FeCl_3$ solution containing $H_3PW_{12}O_{40}$ [10]. Mesoporous α-Fe_2O_3 particles were produced by the forced hydrolysis of the $FeCl_3$ solution containing L-phenylalanine and N-(3-di methylaminoethylaminopropyl)-N-ethylcarbodiimide hydrochloride [11]. Kandori et al. [12] also investigated the effect of surfactants on the precipitation of colloidal particles by the forced hydrolysis of the $FeCl_3$-HCl solution. The hydrothermal transformation β-FeOOH → α-Fe_2O_3 in dense aqueous suspensions, prepared by a partial neutralization of the concentrated $FeCl_3$ solution with the concentrated NaOH solution, was investigated by Žic et al. [13]. Žic et al. [14] also investigated the precipitation of α-Fe_2O_3 from dense β-FeOOH suspensions with ammonium amidosulphonate added. The peanut-type α-Fe_2O_3 particles, as well as particles in the form of double cupolas interconnected with the neck were obtained. These particles showed the substructure. Double cupolas were porous and consisted of linear chains of small α-Fe_2O_3 particles (also interconnected) which were directed from the centre toward the surface of cupolas.

The aim of the present work was to obtain more data about the influence of sodium dodecyl sulphate on the crystallization kinetics, phase transformations and particle morphology in the precipitates formed by the forced hydrolysis of aqueous $FeCl_3$ solutions. This work is a continuation of our longtime investigations in the precipitation chemistry of iron oxides (group name for hydroxides, oxyhydroxides and oxides). In many cases the phase analyses of solid hydrolytical products of iron ions are a demanding task, specifically if iron oxide phases vary from amorphous to a well-crystalline nature. For this reason three complementary techniques, ^{57}Fe Mössbauer, FT-IR and XRD were used in the phase analysis. Generally, it is known that surface active agents act very differently on the precipitation processes in dependence on their characteristics (polar, nonpolar, chemical nature of the organic chain, pH).

EXPERIMENTAL

Sample preparation

AnalaR grade $FeCl_3 \cdot 6H_2O$ was supplied by Kemika. Sodium dodecyl sulphate (SDS) was supplied by Sigma Aldrich (Cat. No.: 151-21-3; ACS grade reagent). Twice distilled water was prepared in own laboratory and used in all experiments. The stock solution 2M $FeCl_3$ was prepared. The concentration of 0.2M $FeCl_3$ was adjusted in all precipitation systems. The experimental conditions for the preparation of samples are given in Table 1. The yellowish precipitate was formed by adding $FeCl_3$ solution into clear aqueous solution of SDS thus indicating the formation of Fe(III)-dodecyl sulphate. Thus obtained suspension was homogenized in ultrasound bath. The precipitation systems were autoclaved at 160 ^oC using a Teflon^R-lined, non-stirred pressure vessel manufactured by Parr Instruments (model 4744). The autoclaves were heated between 2 and 72 h in a DX 300 gravity oven (Yamato; temperature uniformity ±1.9 ^oC at 100 ^oC and ±3 ^oC at 200 ^oC). The autoclaving times were corrected for the time needed that the autoclave reaches the predetermined temperature. After a proper autoclaving time the autoclaves were abruptly cooled with cold water. The mother liquor was separated from the precipitate with the ultra-speed centrifuge (Sorvall model Super T21). The separated precipitates were subsequently washed with twice-distilled water and one time with C_2H_5OH, then dried.

Table 1. Experimental conditions for forced hydrolysis of 0.2 M $FeCl_3$ solution containing SDS

Sample	2M $FeCl_3$ / ml	SDS/ g	H_2O / ml	T / ^oC	Time of ageing
R1	4		36	160	2 h
R2	4		36	160	6 h
R3	4		36	160	24 h
R4	4		36	160	72 h
S1	4	0.4	36	160	2 h
S2	4	0.4	36	160	6 h
S3	4	0.4	36	160	24 h
S4	4	0.4	36	160	72 h

SDS = sodium dodecyl sulphate; h = hour

Instrumentation

^{57}Fe Mössbauer spectra were recorded at 20 ^{o}C in the transmission mode using a standard configuration by WissEl GmbH (Starnberg, Germany). The ^{57}Co/Rh Mössbauer source was used. The velocity scale and Mössbauer parameters refer to the metallic α-Fe source at 20 ^{o}C. Deconvolution of Mössbauer spectra was made using the MossWin program.

FT-IR spectra were recorded at RT with a Perkin-Elmer spectrometer (model 2000). The powders were mixed with KBr, then pressed into tablets using the Carver press.

XRD patterns were recorded with an APD 2000 powder diffractometer manufactured by Ital-Structures (GNR Analytical Instruments Group, Italy).

The samples were also inspected with a thermal field emission scanning electron microscope (FE SEM, model JSM-7000F) manufactured by Joel Ltd.

RESULTS AND DISCUSSION

The Mössbauer spectra of reference samples R1 to R4 as well as S1 to S4 produced in the presence of SDS surfactant are shown in Figures 1 and 2. The Mössbauer spectrum of sample R1 shows the superposition of two doublets with quadrupole splittings Δ_1 = 0.55 and Δ_2 = 0.99 mm s^{-1}. The parameters of this spectrum can be assigned to β-FeOOH (Table 2). The spectra of samples R2, R3 and R4 are characterized by one sextet with parameters corresponding to α-Fe_2O_3. The increase in hyperfine magnetic field (HMF) from 51.2 to 51.5 T with the autoclaving time prolonged from 6 and 72 h can be related to crystalline ordering in α-Fe_2O_3. Upon 2 h forced hydrolysis of the 0.2 M $FeCl_3$ solution containing SDS surfactant (sample S1) a central quadrupole doublet was recorded. This spectrum was fitted for one average doublet with Δ = 0.79 mm s^{-1} and can be assigned to β-FeOOH. The effect of SDS added to the phase composition of a solid hydrolytical product is well visible in the spectrum of sample S2. This spectrum was fitted as a superposition of the central quadrupole doublet and two sextets. The central quadrupole doublet (Δ = 0.75 mm s^{-1}) can be assigned to β-FeOOH (39 %), whereas two sextets with $HMF_{average}$ = 48.5T (~ 56 %) and HMF = 37.4 T (5 %) can be assigned to α-Fe_2O_3 and α-FeOOH (goethite), respectively. The spectrum of sample S3 showed two sextets, one corresponding to α-Fe_2O_3 ($HMF_{average}$ = 49.8 T) and the other of small relative intensity due to the presence of a small amount of α-FeOOH (outer peaks in the spectrum denoted with arrows). Sample S4 showed only the presence of the α-Fe_2O_3 phase characterized by $HMF_{average}$ = 50.7 T.

Table 2. ^{57}Fe Mössbauer parameters for samples R1 to R4 and S1 to S4

Sample	Line	δ / mm s^{-1}	Δ or E_q / mm s^{-1}	HMF / T	Γ / mm s^{-1}	A / %	Identification
R1	Q1	0.38	0.55		0.30	57	β-FeOOH
	Q2	0.37	0.99		0.33	43	
R2	M	0.37	– 0.21	51.2	0.34	100	α-Fe_2O_3
R3	M	0.36	– 0.21	51.5	0.29	100	α-Fe_2O_3
R4	M	0.37	– 0.21	51.5	0.34	100	α-Fe_2O_3
S1	Q^*	0.38	0.79		0.23	100	β-FeOOH
S2	Q^*	0.38	0.75		0.54	39	β-FeOOH
	M1	0.37	– 0.26	37.4	0.97	5	α-FeOOH
	M2	0.37	– 0.20	48.5	0.31	56	α-Fe_2O_3
S3	M	0.37	– 0.21	49.8	0.27	100	α-$Fe_2O_3^{**}$
S4	M	0.37	– 0.21	50.7	0.25	100	α-Fe_2O_3

All data are given relative to α-Fe standard.

Key: δ = isomer shift; Δ or Eq = quadrupole splitting; HMF = hyperfine magnetic field;
Γ = line width; A = area under the peaks

Errors: δ = ± 0,01 mm s^{-1}; Δ or Eq = ± 0,01 mm s^{-1}, HMF = ± 0,2 T

*Average quadrupole doublet

**Sample S3 also contains small amount of α-FeOOH, as denoted with arrows in Figure 2

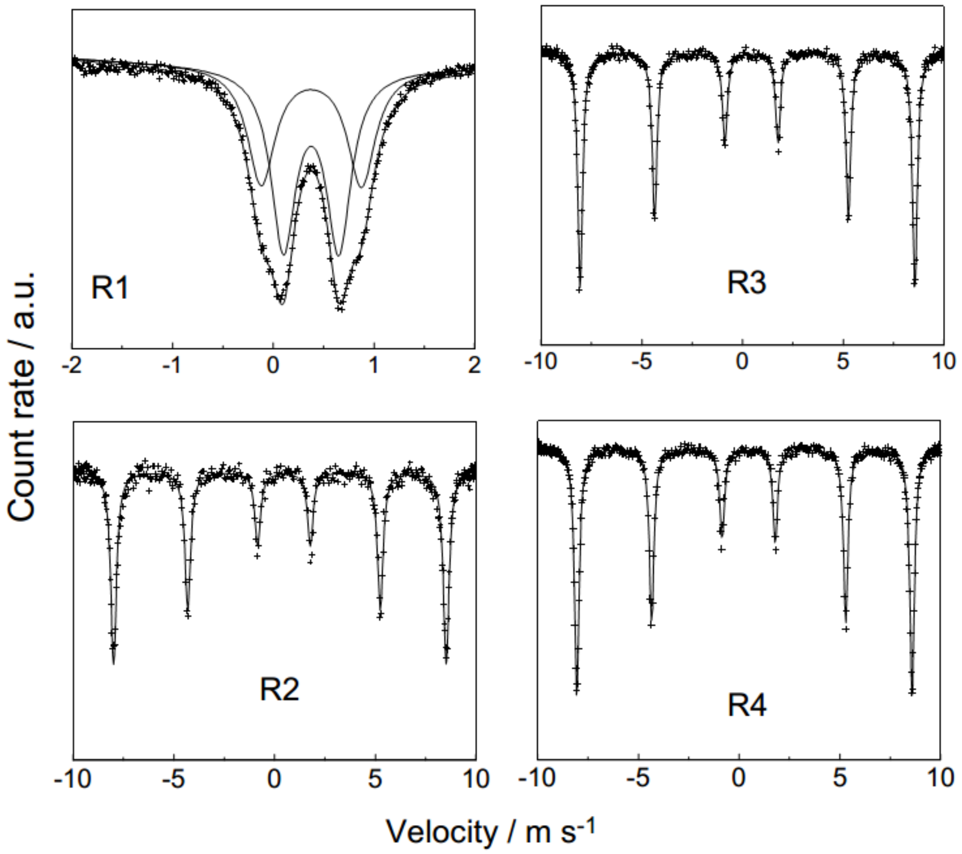

Figure 1. ^{57}Fe Mössbauer spectra of reference samples R1 to R4 produced by forced hydrolysis of 0.2 M $FeCl_3$ solution in the presence of 1% SDS.

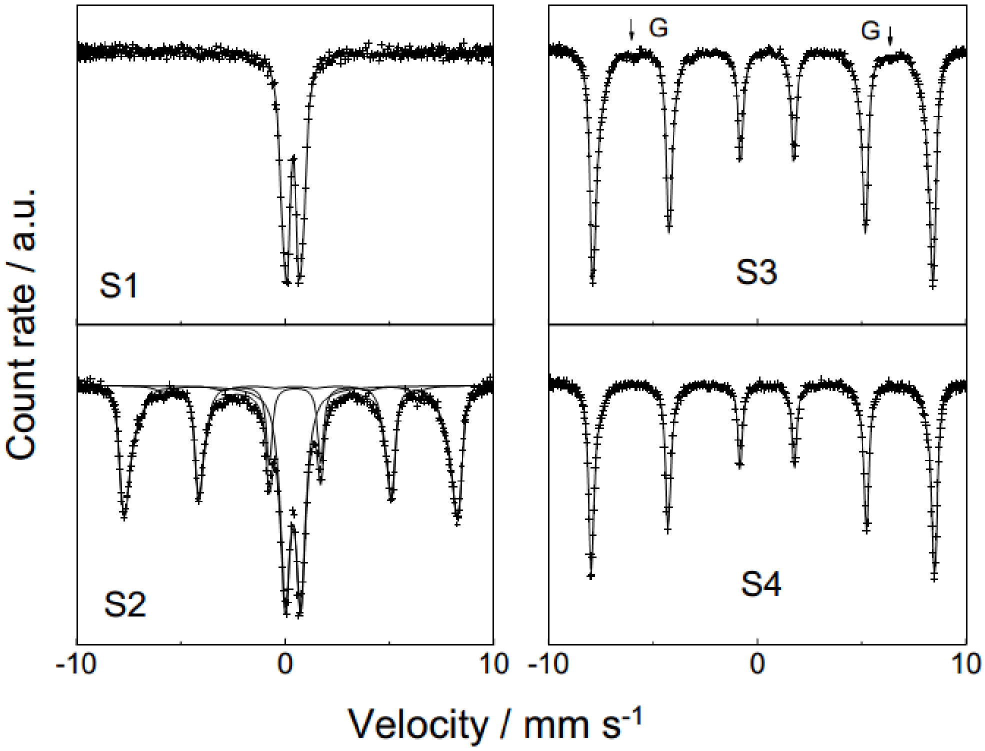

Figure 2. ^{57}Fe Mössbauer spectra of samples S1 to S4 produced by forced hydrolysis of 0.2 M $FeCl_3$ solution in the presence of 1 % SDS.

The Mössbauer spectra of samples S1 and S2 were recorded at extended velocity scale and for this reason the central quadrupole splitting subspectrum was fitted for one average spectrum which is assigned to β-FeOOH. The presence of β-FeOOH phase in samples S1 and S2 is confirmed with XRD as shown in Figure 3. The HMF values of α-Fe_2O_3 calculated for samples S2 to S4 increased from 48.5 to 50.7 T, which are lower values than those corresponding to α-Fe_2O_3 for reference samples R2 to R4. Evidently, this effect can be assigned to the presence of SDS. The XRD patterns of R and S samples are given in Figure 3.

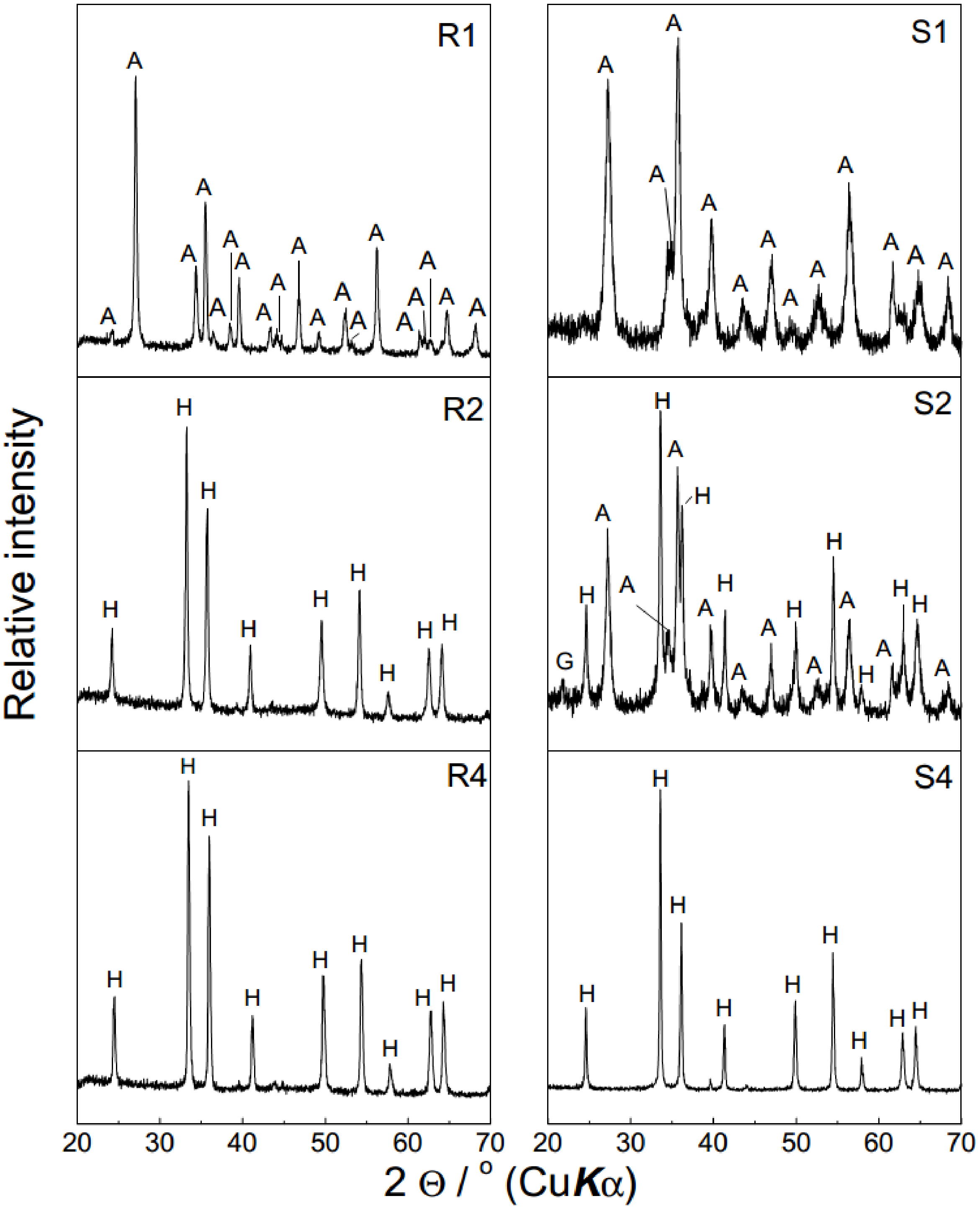

Figure 3. XRD patterns of reference samples R1, R2, R4 and samples S1, S2 and S4 produced in the presence of 1% SDS (A=Akagenéite; G=Goethite; H=Hematite).

The sharpness of XRD lines of sample R1 (Figure 3) is increased in relation to sample S1 and this can be related to better crystallinity or an increased crystallite size of β-FeOOH precipitated in the absence of SDS. However, sample S1 as well as S2 showed a higher relative intensity of the diffraction line 211 in relation to line 310, which could be related to the preferential adsorption of dodecyl sulphate groups on the selected crystallographic plane of β-FeOOH. The XRD pattern of sample S2 showed a small relative intensity XRD line 110 (denoted as G) due to the presence of a small amount of goethite, and this is in line with corresponding Mössbauer spectrum.

Figure 4 shows the FT-IR spectra of reference samples R1 to R4 and samples S1 to S4 prepared in the presence of SDS. The FT-IR spectra of samples R1 and S1 can be assigned to β-FeOOH. Sample R1 shows an IR band centred at 848 cm^{-1}, two shoulders at 700 and 640 cm^{-1} and two shoulders at 498 and 425 cm^{-1}. Sample S1 shows an IR band at 425 cm^{-1} with a shoulder at 491 cm^{-1}. According to earlier work [15] the band at 848 cm^{-1} and the shoulder at 700 cm^{-1} can be assigned to the deformation vibration of OH groups, whereas the intense shoulder at 640 cm^{-1} can be related to the interaction of Fe-OH groups with Cl$^-$ ions. Generally, β-FeOOH possesses a hollandite-type crystal structure and the structural channels in β-FeOOH produced from the $FeCl_3$ solution contain water and a small amount of Cl$^-$ ions [16]. These Cl$^-$ ions (less than ~ 2 %) in structural channels stabilize the crystal lattice of β-FeOOH and cannot be removed by simple washing. Weckler and Lutz [17] discussed two sets of vibrations at 847 and 820 cm^{-1}, and also those at 697 and 644 cm^{-1} in terms of two O-H...Cl hydrogen bonds present in β-FeOOH. The IR spectrum of β-FeOOH was also the subject of discussion by Murad and Bishop [18]. The FT-IR spectra of samples R2 to R4 can be assigned to α-Fe_2O_3. Wang et al. [19] tabulated optical parameters for bulk α-Fe_2O_3 and investigated the influence of the geometrical shape of α-Fe_2O_3 particles on the corresponding FT-IR spectrum. Generally, the IR spectrum of α-Fe_2O_3 shows six active vibrations, two A_{2u} ($E \parallel C$) and four E_u ($E \perp C$). The effect of SDS is clearly visible in the spectra of samples S2 to S3. In the FT-IR spectrum of sample S2 the IR bands at 850, 697 and 640 cm^{-1} are due to β-FeOOH and the IR bands at 574, 537 and 482 cm^{-1} are due to α-Fe_2O_3. Two IR bands at 895 and 796 cm^{-1} are typical of α-FeOOH and are assigned to the Fe-O-H bending vibration (δ_{OH} and γ_{OH}, respectively) [20]. The FT-IR spectrum of sample S3 shows only the presence of α-Fe_2O_3 and a small fraction of α-FeOOH, whereas the FT-IR spectrum of sample S4 can be assigned to α-Fe_2O_3 as a single phase. In the FT-IR spectra of samples produced in the presence of SDS additional bands are also noticed. For example, in the spectrum of sample S3 four IR bands at 1206, 1126, 1036 and 977 cm^{-1} are well visible. These IR bands can be related to the sulphate group. The $\nu_3(SO_4)$ fundamental vibration is split into 3 active IR bands due to the formation of a surface bidentate bridging complex between the sulphate group and surface iron atoms [21]. The presence of an IR band at 977 cm^{-1} is due to the $\nu_1(SO_4)$ vibration. It is generally known that the specific adsorption of oxyanions reaches its maximum at acidic pH values and decreases with an increase in pH values.

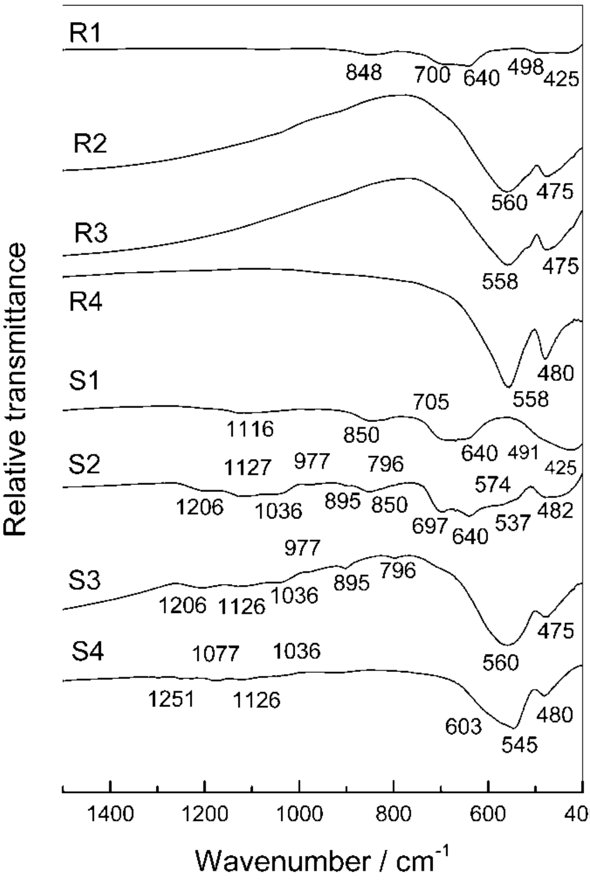

Figure 4. FT-IR spectra of reference samples R1 to R4 and samples S1 to S4.

Ocaňa et al. [22] precipitated spindle-shaped α-Fe_2O_3 particles by the forced hydrolysis of the $Fe(ClO_4)_3$ solution at 100 °C. The phosphate anions that could not be washed out were responsible for the formation of these particles morphology. The adsorbed phosphates were visible in the IR spectrum as evidence, with several peaks between 1036 and 934 cm^{-1}.

Mössbauer, XRD and FT-IR measurements showed a direct phase transformation β-FeOOH → α-Fe_2O_3 in reference samples (R) produced by the forced hydrolysis of the 0.2 M $FeCl_3$ solution. In the presence of SDS (samples S1 to S4) the kinetics of this phase transformation is retarded and in samples S2 and S3 produced between 6 and 24 hours of forced hydrolysis a small fraction of an intermediate phase α-FeOOH is detected. Kandori et al. [12] assigned the formation of α-FeOOH phase due to SDS addition in $FeCl_3$-HCl hydrolysing solutions (HCl concentration was fixed; log (HCl) = – 2.50). Musić et al. [23] investigated the effect of HCl additions on forced hydrolysis of $FeCl_3$ solutions. These authors found that under the certain conditions the forced hydrolysis of $FeCl_3$ solution containing only HCl additions may also produce α-FeOOH phase. Wang et al. [24] investigated the precipitation of α-Fe_2O_3 nanoparticles by the forced hydrolysis of $FeCl_3$ solutions with no additive presence. In dependence on the experimental conditions primary nanoparticles showed different morphologies. It was also reported that beside the β-FeOOH → α-Fe_2O_3 phase transformation there was also a direct phase transformation of the amorphous fraction into α-Fe_2O_3.

In the present work, the addition of SDS to the precipitation system caused the formation of a small fraction of α-FeOOH as an intermediate phase, and between 6 and 72 h of autoclaving the HMF value of α-Fe_2O_3 varied from 48.5 to 50.7 T. These values of HMF are significantly decreased in relation to 51.75 T measured for well-crystalline α-Fe_2O_3, as reported by Murad and Johnston [25]. It can be concluded that the presence of SDS lowers the crystallinity of precipitated α-Fe_2O_3.

The FE SEM image of sample R1 (Figure 5a) showed mainly the presence of β-FeOOH rods, but star- and X-shaped particles were also noticed. Sample R2 showed micron size α-Fe_2O_3 particles (Figure 5b) which consisted of primary α-Fe_2O_3 nanoparticles, as evidenced by Figure 5c. α-Fe_2O_3 particles produced upon 72 h of the forced hydrolysis of $FeCl_3$ solutions at 160 °C (sample R4) are shown in Figure 6a. These particles also showed the substructure (Figure 6b); however, the primary α-Fe_2O_3 particles increased in size. The agglomeration of β-FeOOH nanorods (sample S1) is visible in Figure 7a. Figures 7 b,c show big (micron size) particles of sample S4 of near spherical and peanut-type shapes, which possess the substructure and consist of fine, elongated (1D) primary α-Fe_2O_3 particles (Figure 7c).

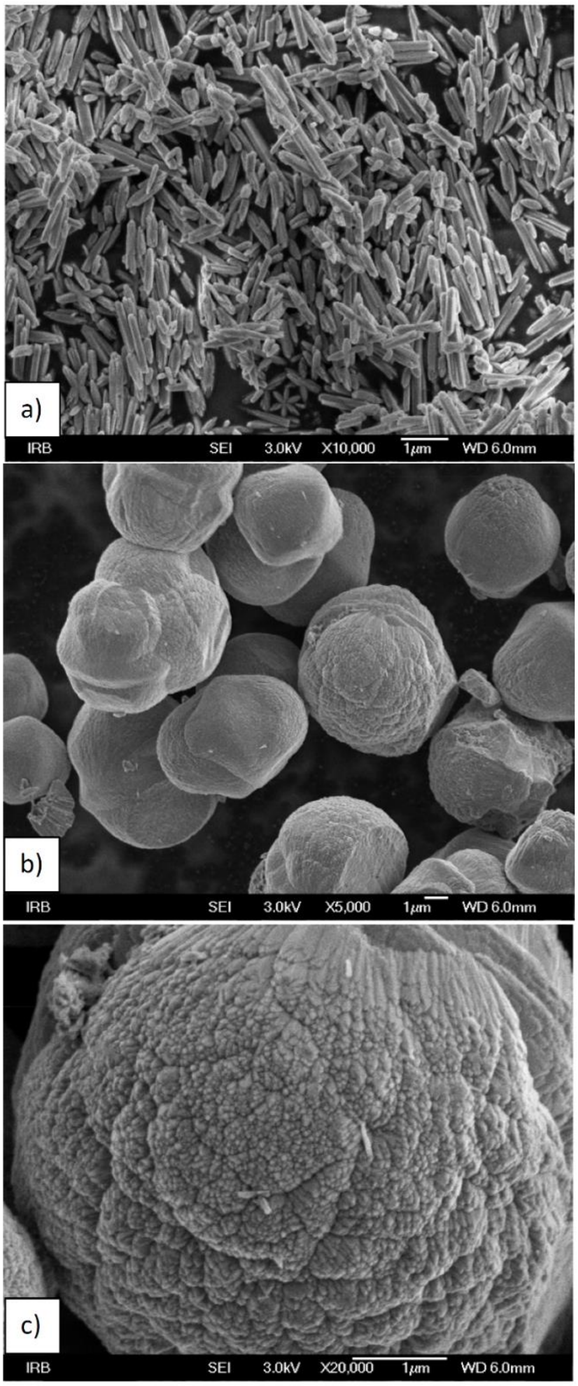

Figure 5. FE SEM images of samples: (a) R1 and (b, c) R2.

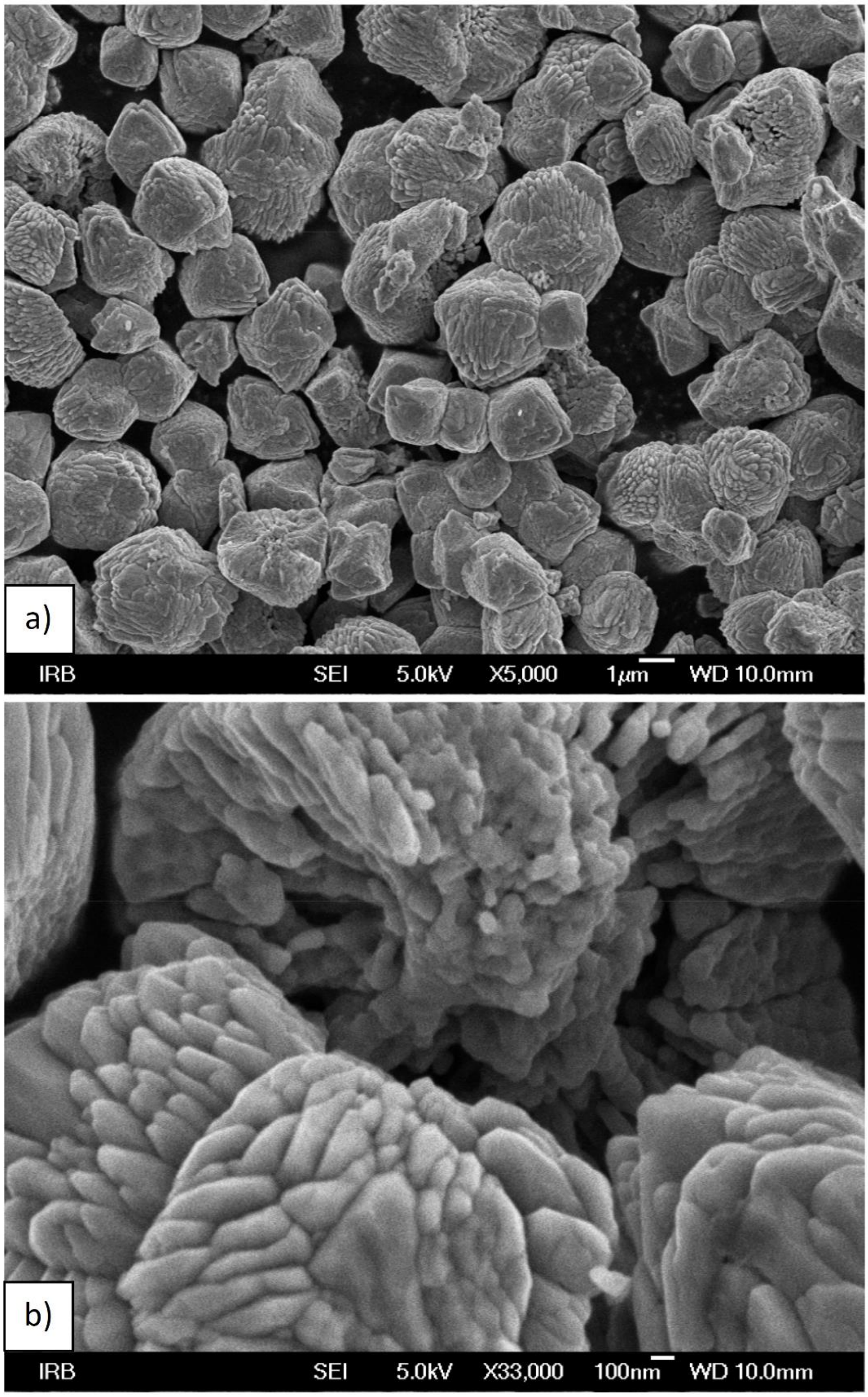

Figure 6. FE SEM images of reference samples R4 at different magnifications.

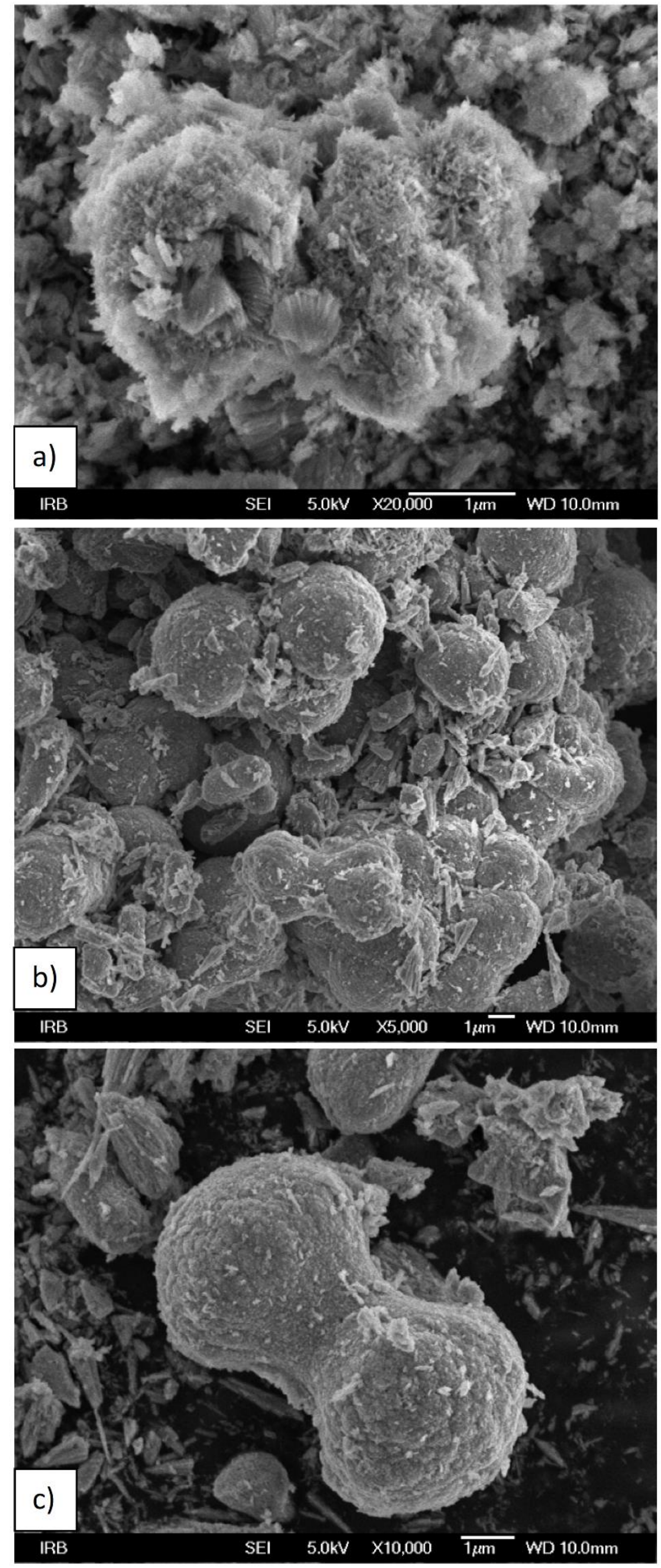

Figure 7. FE SEM images of samples: (a) S1 and (b, c) S4.
The samples were precipitated in the presence of SDS.

CONCLUSION

The effect of SDS (1 %) on the kinetics, phase composition and shape of the particles precipitated by the forced hydrolysis of the 0.2 M $FeCl_3$ solution was investigated. A direct phase transformation β-FeOOH → α-Fe_2O_3 *via* dissolution/recrystallization was present in the absence of SDS. In the presence of SDS a small fraction of α-FeOOH precipitated, which transformed to the end product α-Fe_2O_3 also *via* the dissolution/recrystallization mechanism. α-Fe_2O_3 particles precipitated in the presence of SDS showed lower crystallinity in relation to reference samples, as concluded on the basis of Mössbauer spectra. This effect was explained by the competition between the stability of Fe(III)-dodecyl sulphate on one side and the formation of iron oxide phases on the other side. Precipitated α-Fe_2O_3 particles showed the substructure, *i.e*., consisted of much smaller primary particles. The effect of SDS on the microstructure of α-Fe_2O_3 particles is noticed. The influence of SDS on the forced hydrolysis of $FeCl_3$ solutions can be related to the specific adsorption of sulphate groups on the nuclei and crystallites of FeOOH and α-Fe_2O_3 phases. The specific adsorption of dodecyl sulphate groups was evidenced by FT-IR.

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ЕФЕКТОТ НА НАТРИУМ ДОДЕЦИЛ СУЛФАТ ВРЗ ПРИСИЛНАТА ХИДРОЛИЗА НА РАСТВОРИ НА $FeCl_3$

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Изучувани се преципитациите при присилна хидролиза на воден раствор од 0.2 M $FeCl_3$ за времетраење од 2 до 72 часа во присуство на 1% натриум додецил сулфат (SDS). Во отсуство на SDS во преципитациониот систем доаѓа до директна фазна трансформација β-FeOOH → α-Fe_2O_3 преку механизмот растворање/прекристализација. Во присуство на SDS, α-FeOOH како интермедијарна фаза преципитира, а со продолжено време на присилна хидролиза исто така се трансформира во α-Fe_2O_3 преку механизам на растворање/прекристализација. Врз основа на Месбауеровите (Mössbauer) спектри е заклучено дека во присуство на SDS фазата на α-Fe_2O_3 поседува понизок степен на кристалност. Во овој преципитационен процес, важна улога игра и компетицијата помеѓу стабилноста на Fe(III)-додецил сулфатот, од една страна, и формирањето на фазите од оксидите на железото, од друга страна. FE SEM покажа дека крупните честички на α-Fe_2O_3 поседуваат супструктура. Забележано е издолжување на примарните честички на α-Fe_2O_3 добиени во присуство на SDS. Овој ефект може да му се припише на преферираната атсорпција на додецил сулфатните групи врз нуклеусите и кристалитите од FeOOH и фазата на α-Fe_2O_3 во текот на присилната хидролиза на растворите на $FeCl_3$.

Клучни зборови: $FeCl_3$ хидролиза; натриум додецил сулфат; α-Fe_2O_3; Месбауер (Mössbauer); FT-IR; XRD; FE SEM

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Review

LOW BENDING VIBRATIONS OF CRYSTALLINE WATER MOLECULES: AN ONGOING QUEST OR A FINAL WORD – TOPICAL REVIEW – A TRIBUTE TO ACADEMICIAN BOJAN ŠOPTRAJANOV–[•]

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The main aim of this topical review is to provide a concise but yet complete overview of the research that has been done in the field of low-lying crystalline water bending vibrations. Both theoretical and experimental work in the field is reviewed, and the most important dilemmas and obstacles hampering a direct explanation of the phenomenon are outlined. The present status in this field is also overviewed and clarified. While this topical review has mostly been focused on crystalline water molecules in crystalline hydrates and their vibrational properties, also some other interesting and exciting systems that have recently attracted the attention of the scientific community are covered. These included water absorbed on surfaces as well as water at the air-water interfaces.

Key words: crystalline water; crystalline hydrates; water bending vibrations; IR spectroscopy; quantum theory

INTRODUCTION

Water is, beyond any doubt, one of the most ubiquitous and at the same time one of the most widely studied substances across numerous scientific areas. It is perhaps impossible to overestimate its relevance to the very existence of life in the form that we know of. As a consequence of this, and also accounting for the fact that processes essential to life take place within the cells and subcellular fragments of the living organisms, to refer to the water confined within such micro- or nanosized spaces, the term "biological water" has been coined and, aside from its perhaps pretentious character, widely used in the literature [1–3 and references therein]. Properties of biological water could be rather different from the properties manifested by this substance when it appears in bulk form. In several hot-topic recent studies, the dynamics of water motions inside confining molecular cage-like systems (such as, e.g., C_{60}) has been thoroughly studied from both theoretical and experimental sides [4–9 and references therein]. Aside from all these cutting-edge research topics related to water embedded in small, nanosized systems, water is still an unresolved mystery even in its "conventional", *i.e.* bulk form, of appearance. The dynamics of hydrogen bond forming and breaking within liquid water is a subject of continual research interests. Behavior of the essential products of water autoprotolysis process, the H_3O^+ and OH^- ionic species, has also been a subject of continuing debates in the literature [10–17]. Even very essential issues, such as the ability of the OH^- ions to act as hydrogen-bond proton donors in bulk water, have been addressed from various viewpoints [10–17].

Aside from its relevance to biological systems, water is widely present in inorganic systems as well. It actually incorporates into the crystalline lattices of numerous inorganic compounds, (involv-

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[•] Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

ing minerals and their synthetic analogues), as crystalline water. Compounds containing crystalline water are known as crystalline hydrates [18, 19]. Investigations of the static and dynamical properties of such crystalline water can lead to a number of important information about crystalline surrounding and the dynamics of crystalline lattices in general. In the course of these investigations, numerous experimental techniques have been employed, among which, vibrational spectroscopy (both infrared and Raman) and diffraction techniques have been of particular interest. This review focuses on the former. However, especially in the course of both hardware and theoretical methodology developments, contemporary theoretical analysis of the experimentally observed spectral features has become a necessity in serious scientific publications, in certain cases shedding substantially more light on the issues in question. The most widely used vibrational spectroscopic techniques measure the energy differences between certain vibrational levels of complex molecular and solid state systems in the form of bands appearing in the absorption/transmission spectra. The surrounding in complex environments affects these energy differences in a rather complex manner and the overall effect enables one to use the molecular systems as a sort of probe to characterize the complex environment in which the molecule is embedded. In the course of studies related to these aspects, the O–H stretching vibrations of crystalline water molecules (as well as of hydronium and hydroxide ions) have been widely used as a very indicator of the existence of e.g. a hydrogen bonding or some other noncovalent interaction within the medium, involving the water molecule (or the corresponding ion) in question [20 and references therein]. This possibility has been much exploited using the advantage of the so-called isotopic isolation techniques. These techniques employ exchange of a rather small (or, on the other extreme, rather large) portion of the hydrogen atoms with deuterium ones, usually by a process of simple recrystallization from mixture of H_2O and D_2O. When only a small portion of hydrogen atoms is replaced by deuterium ones within the crystal (or other complex environment) one encounters a very small portion of HDO molecules within a vast majority of H_2O ones. In the opposite extreme, one encounters a very small portion of HDO molecules within a vast majority of D_2O ones. Within the HDO molecules, which are practically isolated among the other isotopomers, the intramolecular O–H and O–D oscillators are completely decoupled, due to the mass difference between hydrogen and deuterium. At the same time, intermolecular couplings between identical oscillators are eliminated as well, so that a rather clear spectral picture can be seen, within which numerous structural features can be elucidated, even such as the number of distinct O–H(D) oscillators within the crystal (or other medium), the nature and strength of the interactions involving a particular O–H(D) oscillator in question. For example, the involvement of an O–H(D) oscillator in an intra- or intermolecular hydrogen bond has been often judged by the direction of the shift in the O–H(D) stretching frequency. The magnitude of this shift, on the other hand, has often been found to be proportional to the interaction strength [10–17, 20]. Besides the effect of noncovalent interactions on the static and dynamical properties of the intramolecular O–H(D) oscillators, also the influence of in-crystal (or external) electrostatic fields on the statics and dynamics of the O–H(D) oscillators has been thoroughly addressed [21–24]. It has been actually shown that in certain cases (such as, e.g., in case of the $O–H^-$ ions placed within certain crystalline environments), in some cases the electric fields may dictate even the direction of the shift of the O–H(D) stretching vibrational frequencies [20]. Therefore, in such cases, observation of a blue- or red-shift of a given stretching mode can not be a priori attributed to the existence (or non-existence) a noncovalent intermolecular interaction (e.g. of a hydrogen bonding type) [20]. Due to all these reasons, O–H(D) stretching vibrations in crystalline water molecules have been studied a lot, and numerous spectra-structure correlations have even been established in the literature [e.g. 25–28].

Contrary to what has been previously concisely outlined about the water stretching vibrations, water bending vibrations have been studied much less. The δ(HOH) motion (or “scissoring” motion) of crystalline water molecules has often been thought of as being rather insensitive to the crystalline (or other) environments [29–31]. Such viewpoint has been supported by the early theoretical studies of water molecule dynamics as influenced by cationic and anionic species [32–36]. The bending vibrational motion of free water molecule gives rise to a band appearing at 1594.6 cm^{-1} [30, 31]. It has been long thought that in crystalline water molecules, the frequency of this mode is blue-shifted (*i.e.* shifted to higher frequencies) with respect to the gas phase value. Such belief was supported by the most of the available theoretical predictions based mainly on classical vibrational dynamics simulations, but also on *ab initio* calculations [32–36]. Concisely, theoretical calculations indicated that in the usually encountered structural patterns in solid state the water bending frequency should not be much affected by the presence of cations in the neighborhood of vibrating water. At the same time, presence of anionic species was expected to enlarge the HOH bending force constants, and the overall effect would be frequency blueshift. Both effects were, however, expected to be small, and the resulting overall perturbation of the energy difference between the ground and the first excited δ(HOH) levels would be of the order of just a few percents of the gas-phase value. More involved computations, including additional force constants due to both coordination and involvement in hydrogen bonding, have also shown that a frequency upshift is expected upon inclusion of an additional force constant in the vibrational force field of crystalline water [32–36]. All these theoretical findings actually correspond to the situation that has most frequently been encountered in practice.

However, in-depth spectroscopic and structural studies of a series of compounds of the type $MKPO_4 \cdot H_2O$, though at first sight inconsistent with the established opinion concerning these matters, have substantially changed the situation and opinion in the field [37–45]. The main aim of this review paper is to point out the development of scientific thought related to the problem of water bending vibrations appearing at significantly lower frequencies than the gas phase values. Academician Šoptrajanov has invaluable contribution to this field, and therefore with great pleasure we dedicate this topical review to him, on the occasion of his 80th birthday.

EXPERIMENTAL TECHNIQUES

Essentially all of the experimental literature data referred to in the present paper have been obtained with infrared spectroscopic techniques. In references [41–45], Fourier-transform infrared spectra have been recorded on a Perkin-Elmer System 2000 FT-IR interferometer. Spectra have been collected at both room temperature as well as at liquid nitrogen boiling temperature (actually, at about –174 °C), using a Graseby-Specac variable temperature cell coupled with a controller. To achieve a good signal-to-noise ratio, often at least 32 spectra have been collected and averaged (or even more in certain cases, when required – in some cases even up to 128). Further processing of the spectra in the sense of determination of band maxima position, half-widths and general band shapes has been done with Grams32 program package [46]. For this purpose, usually standard non-linear curve fitting procedures were implemented, using either linear combinations of Gaussian and Lorentzian model band shape functions, or Voigt model functions.

A SURVEY OF EXPERIMENTAL FINDINGS

In this context, we will overview the experimental spectroscopic proofs for the appearance of bands demonstrating significantly red-shifted water bending (scissoring) vibrations in certain crystalline hydrates, as well as for water molecules adsorbed on some surfaces. In cases when structural data are known as well, we will discuss the local geometric specificities related to the in-crystalline water molecules that could be a possible source for the observed peculiar (or, at least, unusual) vibrational behavior.

The first notification concerning the existence of IR spectral bands due to water bending motions is present in the paper by Falk [28]. However, the lower frequency limit for this mode noted in the mentioned paper (1582 cm^{-1}) is only slightly below the gas phase value. Though such slight red-shifts were related to the presence of metal cationic species with smaller radii possessing higher charge in the crystal structure of the studied compounds (and therefore it was implied that electrostatics has to be intrinsically related to this observation), the situation was not clarified in detail.

Very recently, as a matter of fact, another interesting example of water exhibiting low bending vibrations has been presented in the literature. It refers to water adsorbed on TiO_2 surface [47]. Experimental studies of water adsorption on titanium dioxide surface are rather important in the context of materials chemistry and physics in general as well as in surface science. Experimental IR spectroscopic data (as described and cited in Ref. [47]) have unequivocally shown that a defined band (appearing as a shoulder in the IR spectral patterns) at ~ 1560 cm^{-1} could be attributed to water ν_2 (δ(H–O–H)) mode, strongly red-shifted by about 85 cm^{-1} as compared to the liquid water bending appearing at 1645 cm^{-1}. In [47], such assignment was supported by DFT study of finite-clusters mimicking the adsorption of water molecules on nanocrystalline TiO_2. The authors have found out that the red-shift of water bending mode does not correlate with the Mulliken charges of the surface exposed Ti-cationic sites, but such a correlation seems to exist with the natural bond orbital (NBO) charges. This is in a sense expected, if one keeps in mind the lack of exact physical significance of the Mulliken charges. Though widely used in the literature, the

Mulliken charge partitioning scheme was actually never intended to be used for atomic charge assignments, but rather for other purposes. This point has been discussed in numerous studies by our and other groups [48, 49 and references therein]. We have even clearly demonstrated the rather counterintuitive results that could be brought about by straightforward usage of "Mulliken charges" [48, 49]. Atomic charges derived on the basis of natural bond orbital theory by Weinhold and Carpenter [50 and references therein] have certainly much clearer physical meaning, although one has to keep in mind that since the only exact physical observable is the electronic density itself, no scheme for its partitioning into "atomic charges" should be regarded as unambiguous. However, NBO charges obviously necessarily describe better the electrostatic field generated by the surface exposed titanium ionic centers and the effects that this field exerts on the water bending frequencies. Note, however, that the mentioned correlation even in the case of NBO charges has been found only in the case of simultaneous absorption of five water molecules. No such correlation has been found to exist in the case of absorption of a single water molecule on the titanium dioxide surface. Such findings, though certainly emphasizing the significance of electrostatics for the discussed phenomenon, also strongly imply a rather complex, cooperative nature of the overall water bending frequency shifts induced by surface absorption or by inclusion of water molecules into crystalline hydrates.

In a series of papers coauthored by the members of the group around academician Šoptrajanov, numerous examples of the appearance of rather significantly red-shifted water bending vibrations in crystalline hydrates have been presented [37–45]. In the first paper more widely circulated paper of a series devoted to this phenomenon [41], Šoptrajanov has briefly reviewed the awareness concerning the very existence of “low water bending modes”, and he has also referred to two particular examples of compounds (crystalline hydrates) in which crystalline water molecules exhibit such pronounced red shift of the water bending mode. The two particular examples considered were two members of the series of compounds with a general formula $MKPO_4 \cdot H_2O$, where $M \in \{Ni, Mg\}$. In the case of $NiKPO_4 \cdot H_2O$ the band due to water bending mode was found to appear at 1478 cm^{-1}, while in the case of $MgKPO_4 \cdot H_2O$, the corresponding frequency is 1470 cm^{-1}. It is worth noting at this point that the phenomenon of low water bending in crystalline hydrates has actually been discovered much earlier by Šoptrajanov and collaborators [37–40], but the first studies devoted to its presentation and clarification had not been more widely circulated. Therefore, reference [41] may be regarded as a first attempt to bring the awareness of the red shift of crystalline water bending modes to a wider audience. In [41], the assignment of the 1478 cm^{-1} band in the case of $NiKPO_4 \cdot H_2O$ to the crystalline water bending vibration was based on a detailed and thorough spectroscopic study of a series of protiated and partially deuterated samples at both room temperature and at liquid nitrogen boiling temperature. The spectral region from 1900 – 1300 cm^{-1} in the case of $NiKPO_4 \cdot H_2O$ is obviously dominated by a single band of appreciable IR intensity (Fig.1. in Ref. [41]) which is directly attributable to fundamental vibrational transition. Subsequent studies of partially deuterated analogues of this compound have been undertaken in order to confirm that it is indeed a crystalline hydrate. This has been demonstrated by following the evolution of the relevant spectral bands upon partial deuteration of the parent compound. Concerning the previously mentioned 1900 – 1300 cm^{-1} region, it has been unequivocally demonstrated that the band appearing in this area in the case of protiated compound completely disappear upon complete deuteration. Actually, in the spectra of partially deuterated analogue with low deuterium content, a new band has been shown to appear at 1315 cm^{-1} which initially gains in intensity upon deuterium content increase (at up to 50 % D), but further gradually disappears and is completely absent in the spectra of fully deuterated sample. This, in conjunction with the behavior of the region of the HOH, HOD and DOD stretching bands, has been used as a strong argument confirming that one deals with crystalline hydrates and further confirming the initial empirical assignment of the δ(HOH) band at 1478 cm^{-1}. Other spectral features in the case of protiated and deuterated sample of this compound have further implied that the HOH angle is probably close to 90 °, which could have significant implications in relation to appearance of the HOH bending mode at rather low frequencies. Unfortunately, this implication could not be confirmed by X-ray structural investigations, as the positions of hydrogen atoms could not be determined.

In subsequent combined experimental and theoretical studies [42, 43], Šoptrajanov, Jovanovski and Pejov have focused on two further members of the series of compounds of the type $MKPO_4 \cdot H_2O$, those in which $M \in \{Co, Mn\}$. In this study, both RT and LNT spectra of protiated and partially, as well as practically fully, deuterated samples of the mentioned compounds have been recorded and analyzed in detail. In the case of Co compound, no band of appreciable intensity has been found to appear in the region where bands due to the δ(HOH) mode are expected (above 1600 cm^{-1}). Instead, a rather intensive band has been found to appear at 1464 cm^{-1} in the LNT FT IR spectrum. Analogously as in the case of $MKPO_4 \cdot H_2O$, however, two much weaker satellite bands have been found to appear at 1708 and 1614 cm^{-1}. All of the mentioned bands (the intense one and the two satellite) were found to be deuteration-sensitve and are completely absent in the spectra of fully deuterated analogue. This has been taken as an unequivocal proof of the relation of these bands to the crystalline water vibrational motions. However, only the most intensive band could be attributed to fundamental (first order, *i.e.* |0> → |1>) vibrational mode. It is exactly this band that the authors have attributed to the δ(HOH) mode. The satellite bands have, on the other hand, been attributed to the second-order vibrational transitions involving lower-frequency fundamentals. One such candidate that the authors have pointed at is the band at 828 cm^{-1} originating from water librations. On the basis of the results of the factor-group analysis, this mode has actually been found to posses the right symmetry (A_1) to interact with a component of the δ(HOH) |0> → |1> fundamental transition. Comparison between the estimated and observed overtone frequency in this case have, however, indicated a rather weak anharmonic vibrational coupling. The situation with the crystalline water vibrations in the case of $MnKPO_4 \cdot H_2O$ has been found to be rather different than in the cobalt counterpart. In the context of the current review, we will focus on the spectral region of the δ(HOH) fundamental modes. In this region, now two bands with almost equal IR intensities have been found to appear, at 1661 and 1433 cm^{-1}; these are accompanied with a much weaker band positioned at 1525 cm^{-1}. All these bands have been found to be notably sensitive to deuteration and they completely disappear upon complete deuteration. Comparing the regions of appearance of bands due to δ(HOH) fundamental modes as well as the regions of appearance of water rocking librational modes in the series of $MKPO_4 \cdot H_2O$-type compounds, where M is Ni, Co and Mn, the authors of [43] have concluded that the frequency of water librational band follows the order Mn < Co < Ni. At the same time, the authors have noticed that the closer the position of the direct overtone of this rocking mode (ρ(H_2O) |0> → |2> vibrational transition) is to the position of the strongest band in the δ(HOH) region, the closer the intensities of the bands in this region become. On the basis of these experimental observations, the authors of reference [43] have concluded that actually nearly-accidental degeneracy of vibrational modes takes place, involving the fundamental δ(HOH) and overtone ρ(H_2O). As the conditions for Fermi-like resonance become fulfilled, intensity redistribution between the δ(HOH) fundamental and ρ(H_2O) overtone bands occurs, the later gaining in intensity as compared to the case in which no vibrational coupling takes place. Further indication of such vibrational mode mixing was the additional shift of the δ(HOH) fundamental mode to lower frequencies in the case of $MnKPO_4 \cdot H_2O$ as compared to the Co and Ni counterparts. This is attributed to the mutual repelling of the interacting vibrational levels (δ(HOH) first excited vibrational state |1> and ρ(H_2O) second excited vibrational level |2>). This is schematically presented in Figure 1.

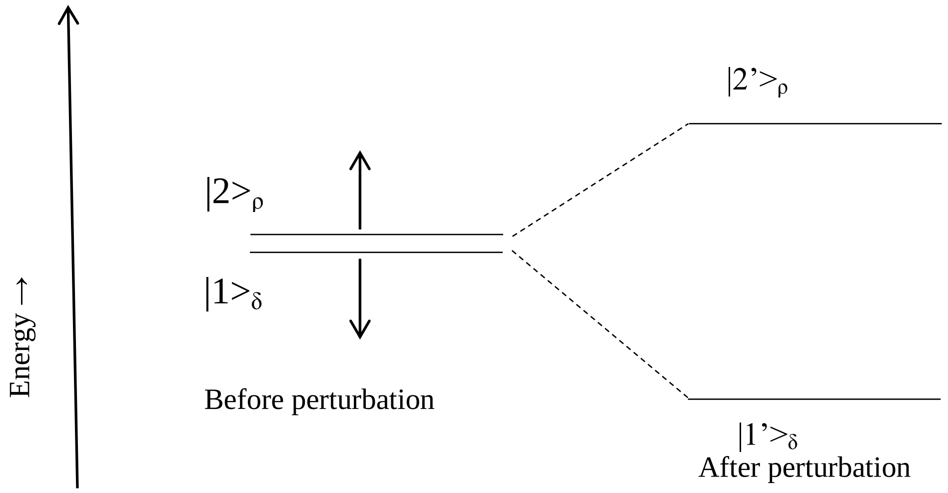

Figure 1. A schematic presentation of the mutual repelling of the interacting vibrational levels (δ(HOH) first excited vibrational state |1> and ρ(H_2O) second excited vibrational level |2>) due to vibrational mode mixing as a consequence of accidental near-degeneracy.

Further work by Šoptrajanov and collaborators [44] in the field has been devoted to a series of ammonium phosphate compounds with general formula $MNH_4PO_4·H_2O$ (where M ∈ {Mg, Co, Ni, Mn, Cd}) which have been found to be isomorphous to the potassium analogues $MKPO_4·H_2O$. Although the spectra in this series of compounds appeared to be much more complicated with respect to assignment of vibrational modes due to crystalline water, as a consequence of the presence of ammonium ions, the careful and thorough analysis of the experimental spectra at RT and LNT of the protiated as well as of a series of deuterated analogues of $MgNH_4PO_4·H_2O$ (the synthetic analogue of mineral dittmarite) carried out by the authors, have led them to rather significant conclusions and thorough reassignments of bands in this case. It is worth noting that besides their fundamental significance, the compounds of the mentioned series contain ammonium ions involved in strong intermolecular interactions of hydrogen bond type within the crystal, and are therefore of certain applicative importance, as potential proton conductors. The bands that are in the focus of the present review (due to the water bending fundamentals) fall in the same spectral region as the bands due to the two of the NH_4^+ ion bending modes (usually denoted as ν_2 and ν_4). All these bands are, of course, expected to be deuteration-sensitive. Indeed, the authors of [44] have found several intensive, deuteration-sensitive bands in the spectral region from 1700 to 1400 cm^{-1} in the FT IR spectra of $MgNH_4PO_4·H_2O$. Due to the bands originating from ammonium cations, an exact and unequivocal assignment of bands due to water bending fundamentals in this region would most probably be hampered, if there was not a strong evidence for the isomorphism between the currently studied compound and its potassium counterpart. Careful inspection of spectra of both samples enabled the authors to precisely locate the position of δ(HOH) $|0\rangle \rightarrow |1\rangle$ fundamental band and to make substantial revision of the assignments of bands offered in an earlier study [51], most of which are directly related to the appearance of the fundamental δ(HOH) band at frequencies significantly lower than the gas phase value. In the δ(HOH) (and $\delta(NH_4)$) spectral region at LNT, as many as five bands appear at 1663, 1536, 1482, 1432 and 1472 cm^{-1} (the last one being of lowest intensity, *i.e.* appearing as a shoulder). Closer inspection of the evolution of appearance of this region upon deuteration has revealed that the band at 1316 cm^{-1} appearing in the spectra of slightly deuterated analogue of $MgNH_4PO_4·H_2O$ most probably originates from the δ(HOD) mode. The authors have, however, found it rather hard to clarify completely the spectral picture upon further increase of the deuterium content due to the formation of various species of partly deuterated ammonium ionic species [44]. It is worth noting that the situation here actually suffers from an additional complication related to the possible Fermi resonance between ν_4 mode of ammonium species and ν_2 of crystalline water. Two components of the former vibrational modes are, under the site-group approximation, of the same symmetry as the water bending mode and therefore appreciable vibrational mode mixing could take place. The authors have, however, in this context also provided a further indirect proof that the HOH bending mode gives rise to a band at appreciably lower frequency than the gas phase value. This proof has been based on the observed trend in the series of $MNH_4PO_4·H_2O$ – type compounds upon change of the M cationic species. Namely, the mentioned shift on going from Ni to Mn has been found to closely resemble the situation encountered in the series of (presumably isomorphous) series of $MKPO_4·H_2O$ – type compounds.

Although mentioned in the final segment of this part devoted to experimental evidence related to appearance of low-lying bands due to crystalline water bending modes, the aspect that we will address now appeared to be a key one for thorough understanding of the spectroscopic data. Aside from enabling the researchers to apply group theoretical formalism and therefore to make definite conclusions concerning e.g. vibrational couplings between the modes, as well as the very appearance of bands due to particular modes, the insight into the in-crystalline environment around the "peculiar" crystalline water molecules have also enabled further theoretical insights into the reasons behind unusual spectral features to be gained. The aspect in question is the experimental determination of the structure of $MgKPO_4·H_2O$ by single-crystal X-ray diffraction technique. In [52], Jovanovski, Pocev and Kaitner have determined the crystal structure of this prototypical compound of the series $MKPO_4·H_2O$. This has been done by the single-crystal X-ray diffraction technique, at room temperature, using 246 independent reflections for the structure determination. Refinement of coordinates of all non-hydrogen atoms has been done up to final $R = 0.064$. The compound has been found to crystallize in the orthorhombic space group $Pmn2_1$, with $Z = 2$. The structure of this molecular crystal is composed by PO_4 tetrahedral species, K and Mg ions, as well as H_2O molecules. Mg ions are coordinated to as many as 5 oxygen atoms belonging to phosphate groups and one crystalline water oxygen atom. The potassium ion is, on the other hand, surrounded by as many as eight oxygen atoms (both from water molecules and phosphate groups). Perhaps the most important structural feature (at least in the context of low water bending modes) is the fact that water molecules were found to form bifurcated hydrogen bonds. However, the exact hydrogen bonding pattern was difficult to establish with a high degree of certainty, as the hydrogen atom positions in the structure have not been determined. Crystalline water molecules are surrounded by four phosphate ion oxygen atoms and by single Mg and single K ions.

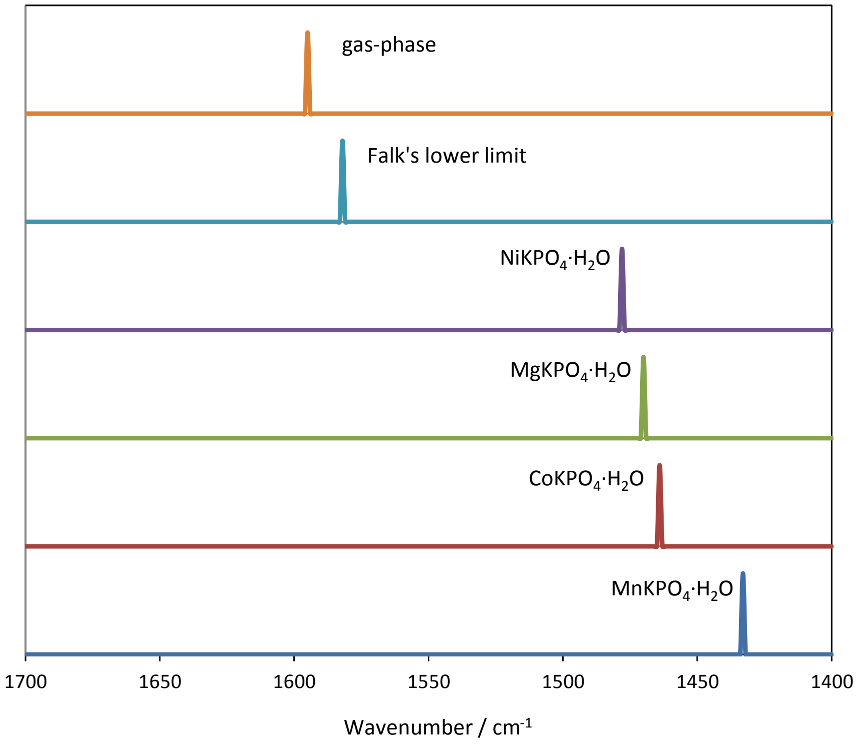

Figure 2. A schematic presentation of the positions of δ(HOH) bands in the IR spectra of the mentioned compounds, compared with the position of the δ(HOH) band in the case of gaseous water and the "Falk's lower limit".

To summarize in a pictorial way the previously outlined survey of experimental data related to the title issue, in Figure 2 we have schematically presented the positions of δ(HOH) bands in the IR spectra of the mentioned compounds, compared with the position of the δ(HOH) band in the case of gaseous water.

As an unambiguous conclusion, aside from the discussed peculiarities and intricacies of band assignments which seem to be a necessity in the case of the studied series of compounds, it can be stated that the bands due to crystalline water HOH bending (scissoring) modes in all of these cases appear at *significantly* lower frequencies that the Falk's low limit. This is a rather uncommon situation and such observations impose a quest towards a more in-depth insight into the reasons responsible for such notable red-shifts of the water bending modes in particular solid-state environments. Theoretical modeling tools seem to be invaluable in this context.

CHOSEN SYSTEMS AND GENERAL METHODOLOGY ASPECTS

A wide variety of theoretical/computational approaches has been applied to approach the problem dealt with in this topical review, *i.e.* the problem of low-lying bending vibrations. The main aim of essentially all theoretical studies was to get an in-depth insight into the physical reasons behind the observed vibrational frequency red-shifts, and, at the same time, to become aware of the particular segment/fragment of the environment (e.g. in-crystal) that induces such red-shift. The simplest approaches involved semiempirical methods e.g. with PM3 Hamiltonian, as used in Refs. [41, 42], Hartree-Fock method [41, 42], and Density functional theory (DFT) approaches [43–45] using various combinations of exchange and correlation functionals. Various basis sets have been used for orbital expansion in the course of solving the HF or Kohn-Sham equations in an iterative manner, ranging from the rather popular LANL2DZ, which is a combination of D95 on first row elements and Los Alamos effective core potential (ECP) plus DZ on Na-Bi [53, 54], up to the rather flexible, Pople-type 6-311++G(3*df*,3*pd*) basis of triple-zeta quality. In the studies performed within our group, in the course of all DFT computations, special attention has been paid to the SCF convergence-related issues. Thus, in all our studies relying on the DFT approach, the Kohn-Sham (KS) SCF equations were solved iteratively for each particular purpose of this study, with an "ultrafine" (99, 590) grid for numerical integration (99 radial and 590 angular integration points). In the case of free water molecule, we have located the stationary points on the potential energy surface (PES) employing Schlegel's gradient optimization algorithm [55], that relies on analytical computation of the energy derivatives with respect to nuclear coordinates. The character of the stationary points located on the corresponding PES was further tested by subsequent computation and analysis of the Hessian matrices. The absence of negative eigenvalues of the second-derivative matrix indicated the true minimum character of the particular stationary point on the PES.

In cases when geometry and vibrational spectroscopic properties of water molecule embedded in a fragment (cluster) mimicking the actual crystalline environment in the studied class of compounds were explored, only the intra- and intermolecular geometry parameters related to crystalline water were allowed to relax (*i.e.* partial geometry optimizations were carried out), while keeping all other parameters within the cluster fixed at their experimental values.

To simulate the influence of purely electrostatic contributions to the changes in geometry and vibrational frequencies, also finite-field calculations were carried out by our group [42, 43, 45]. Sequentially, electrostatic fields with various strengths (ranging from 0.020 to 0.060 a.u.) were applied along *x*, *y* and *z* axes of a local coordinate system fixed to water molecule (Fig. 3) and the changes in electron density distributions and other molecular parameters relevant to the presently studied phenomenon were monitored. This was done by explicit inclusion of the electrostatic field $\vec{F}$ in the many-particle Hamiltonian, *i.e.* by iteratively solving the Schrödinger equation:

$$\left[\hat{H} + \vec{F}\cdot\vec{r}\right]\Psi = E\Psi \qquad (1)$$

in an SCF manner.

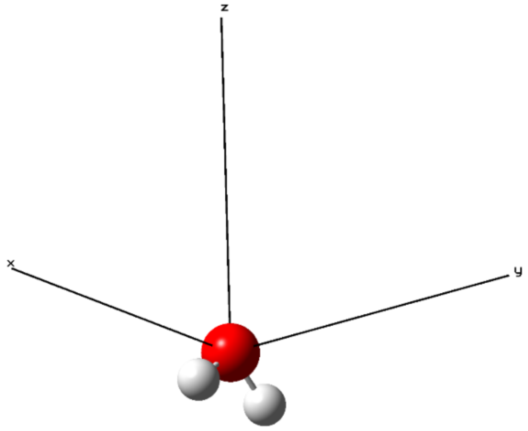

Figure 3. Orientation of the local coordinate system fixed to water molecule used in the computations.

For a more in-depth and in a sense more pictorial and chemically intuitive description of the fundamental bonding features encountered in the studied cases, both Weinhold's Natural bond orbital (NBO) analyses [50] and Bader's atoms in molecules (AIM) approaches were implemented to analyze the electronic density, in particular in the noncovalent bonding region (characterized with low density values and, at the same time, high gradient) [56].

All quantum chemical calculations were carried out by GAUSSIAN 03 series of computer codes [57].

INFERENCES FROM THEORETICAL CALCULATIONS

In our early theoretical studies devoted to possible clarifications of the reasons behind the appearance of pronouncedly low HOH bending frequencies in crystalline hydrates we have applied an exact approach to compute those values [41-43]. We have, namely, scanned the one-dimensional cut through the complete vibrational potential energy hypersurface of free and in-crystal water molecule corresponding to the δ(HOH) motion. This has been done by a series of pointwise energy calculations, varying the HOH angle with a step of 2 °. The resulting function $V = f(\alpha)$ was subsequently fitted to a fourth – order polynomial in $\Delta\alpha$ ($\Delta\alpha = \alpha - \alpha_e$, α_e being the equilibrium value of α) of the form:

$$V(\Delta\alpha) = V_0 + \frac{1}{2}k_{\alpha\alpha}\, r^2_{\mathrm{OH,\,e}}(\Delta\alpha)^2 + k_{\alpha\alpha\alpha}\, r^3_{\mathrm{OH,\,e}}(\Delta\alpha)^3 + k_{\alpha\alpha\alpha\alpha}\, r^4_{\mathrm{OH,\,e}}(\Delta\alpha)^4 \qquad (2)$$

The resulting Schrödinger equation has subsequently been solved with the second-order perturbation theoretical (SOPT) approach. It has been actually shown that the SOPT leads to values of the |0> → |1> transition energies that are rather close to those obtained e.g. by the linear variational technique in cases with small anharmonic corrections (as is the presently studied case). To model the in-crystal water molecule, two approaches have been adopted in our initial study [41, 42]. Within the first one, the in-crystal water molecule was embedded in an environment composed by only the nearest neighbors within the crystal, while in the second one, the water molecule has been immersed in a homogeneous electrostatic field with different orientations. These initial studies have been, however, based on the semiempirical PM3 Hamiltonian and, in parallel, on the *ab initio* Hartree-Fock theory (HF), using either the rather large, triple-zeta quality 6-311++G (3*df*,3*pd*) basis set for orbital expansion, or the LANL2DZ basis. Although these initial attempts to model the title phenomenon have led to excellent agreement of the free water anharmonic HOH bending frequency computed at HF/6-311++G (3*df*,3*pd*) level of theory with the experimental one (1605.6 *vs.* 1594.6 cm^{-1}), the computed in-crystal values with explicitly included nearest neighbors have been found to be higher than the free-water values, which is contrary to the experimental findings. On the other hand, it has been found in this study that external homogeneous electrostatic field could have significant influence on the HOH bending frequencies. If the electric field was directed parallel to the water molecule dipole moment (*i.e.* parallel to the z-axis coinciding with the C_2 axis) a very small δ(HOH) frequency upshift (blue-shift) has been found. On the other hand, when the field is directed oppositely to the water dipole moment vector, then the frequency exhibited a remarkable downshift (red-shift). For example, a field with magnitude of 0.060 a.u. applied parallel to the water dipole leads to frequency upshift of about only 10 cm^{-1} with respect to the value for free water. A field of the same magnitude, but oriented antiparallel to the water dipole moment, would lead to frequency downshift with appreciable magnitude of approximately 200 cm^{-1}. Downshift of the order of 100 cm^{-1} has been obtained for field strengths of about 0.030 a.u. These findings opened the possibility that the frequency of the HOH bending mode could exhibit red shift as a consequence of vibrational Stark effect (under an assumption that the crystalline field is "properly" oriented), *i.e.* that the observed spectral features could be due to long-range electrostatics effects; of course, all this provided that the results obtained with explicit inclusion of the in-crystal neighbors are correct. Interestingly enough, however, contrary to the HF SCF level of theory, the PM3 results gave qualitatively correct trends even upon inclusion of the first-order in-crystal neighbors of the crystalline water molecules. However, since the description of Mg^{2+} and K^{+} ions by the PM3 Hamiltonian is hardly much different form point charges, it is possible that PM3 level of theory actually also predicts electrostatically-induced red shift of the δ(HOH) mode. Perhaps the only exact and unequivocal conclusion that could be derived from the outlined theoretical approaches was that the frequency shift is due to the δ(HOH) mode to lower frequencies could appear due to "flattening" of the δ(HOH) vibrational potential, *i.e.* due to changes of the harmonic force constant. In contrast, the anharmonic contributions to the overall shift have been found to be negligible in [42].

All in all, having in mind the rather modest level of theory implemented in these initial theoretical attempts to solve the problem in question, one cannot guarantee the sufficiency of the implemented theoretical level for the mentioned purposes. For these reasons, more elaborate theoretical studies have been undertaken recently after publication of [42] in order to address the problem in a more thorough manner. These further studies [43–45] have been based on combined application of HF as well as Density functional theory approach (DFT), based on combination of Becke’s three-parameter adiabatic connection exchange functional [58] with the Lee-Yang-Parr [59] correlation functional (usually denoted with the acronym B3-LYP). The modest size, but still sufficient in the sense of providing convergency of the results, 6-31++G(*d,p*) basis set has been used for orbital expansion in the course of seeking iteratively for the solutions of the HF or Kohn-Sham (KS) equations. In this study, the problem of explicit inclusion of the in-crystal environment of the water molecule has been addressed in a much more systematic manner. Thus, several finite clusters that have been aimed to represent, *i.e.* mimick the crystalline surrounding of the vibrating water molecule have now been considered (Fig. 4). The first one was the $\text{Mg}^{2+}\text{K}^{+}(\text{H}_2\text{O})$ cluster, which includes only the nearest-neighboring metal cations. The second one, aside from the closest cationic species, also included the nearest phosphate anions as well, *i.e.* is of the form $\text{Mg}^{2+}\text{K}^{+}(\text{PO}_4^{3-})_2(\text{H}_2\text{O})$, while the largest cluster involved the second neighboring phosphate anions as well: $\text{Mg}^{2+}\text{K}^{+}(\text{PO}_4^{3-})_4(\text{H}_2\text{O})$. To discriminate between the purely electrostatic effects and the influence of short-range intermolecular interactions, also the "charge-field" analogues of the previously described clusters have been considered. These "charge-field" clusters have been constructed simply by exchanging the ionic species with the point charges of the corresponding magnitude placed at the corresponding centers of mass of the realistic species.

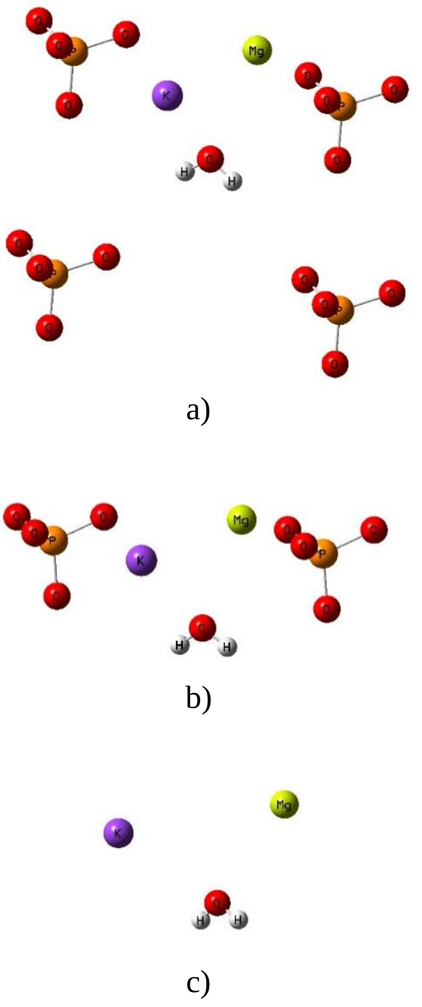

Figure 4. A schematic presentation of the finite clusters used to model the δ(HOH) frequencies in the studied series of compounds: **a**) $Mg^{2+}K^{+}(PO_4^{3-})_4(H_2O)$, **b**) $Mg^{2+}K^{+}(PO_4^{3-})_2(H_2O)$, **c**) $Mg^{2+}K^{+}(H_2O)$.

Such charge field perturbational-like (CFP) approach for modeling the electrostatic + polarization influence on the δ(HOH) vibrational frequencies accounts completely for all terms in the perturbation-theory expansion of the energy as a function of the field:

$$-\Delta E\left(\vec{F}\right) = \vec{\mu}^{0}\cdot\vec{F} + \frac{1}{2!}\overline{\overline{\Theta}}\cdot\nabla\vec{F} + \frac{1}{3!}\overline{\overline{\Omega}}\cdot\nabla^{2}\vec{F} + \frac{1}{4!}\overline{\overline{\Phi}}\cdot\nabla^{3}\vec{F} + \cdots + \frac{1}{2!}\overline{\overline{\alpha}}\cdot\vec{F}^{+} + \cdots \qquad (3)$$

In the previous equation, $\overline{\overline{\Theta}}, \overline{\overline{\Omega}}, \overline{\overline{\Phi}},\ldots$ are the quadrupole, octupole, hexadecapole tensor functions of second, third, fourth etc. order, while $\vec{\mu}^{0}$ and $\overline{\overline{\alpha}}$ are the dipole moment vector of the free molecule and the dipole polarizability function, respectively. The last quantity is actually a second order tensor.

The geometry of the “in-crystal” water molecule embedded within the mentioned clusters has been fully optimized at the mentioned levels of theory. Subsequently, the δ(HOH) vibrational frequency has been computed by diagonalization of the mass-weighted Hessian matrix computed for the minima on the corresponding potential energy hypersurfaces (PESs). Adopting the double-harmonic approximation as a method of choice for the currently studied system has been fully justified by the previously mentioned preliminary-like results [41, 42] in which we have demonstrated that the contribution of anharmonicity to the overall trends and even to absolute frequency values when the δ(HOH) mode is in question are indeed minor ones.

Inclusion of only the nearest Mg^{2+} and K^{+} ions to the vibrating in-crystal water molecule, practically regardless on the implemented level of theory have led to a δ(HOH) frequency upshift (blue-shift) of approximately 70 cm^{-1} (with respect to the free water value). One can therefore safely conclude that interaction with these two ionic species that reside in the immediate vicinity of the crystalline water in $MgKPO_4{\cdot}H_2O$ can not be regarded as being responsible for the *observed* significant frequency downshift (red-shift). Moreover, it has been further shown in [43-45] that purely electrostatic interaction with these two ions (as computed by the charge field perturbational approach) would lead to only a small frequency upshift, contrary to the full-wavefunction value (less than about 26 % regardless on the employed theoretical level). This observation would certainly not be expected if one is led by a purely "chemical" reasoning. It has been, however, argued in [44, 45] that the exchange component of the interaction energy (*i.e.* the “Pauli repulsion” term) could be regarded as responsible for such trend. Further addition of two nearest-neighboring phosphate ions to the initial $Mg^{2+}K^{+}(H_2O)$ cluster (*i.e.* building it up further to the $Mg^{2+}K^{+}(PO_4^{3-})_2(H_2O)$) readily leads to a significant flattening of the δ(HOH) potential, and, consequently, a too large frequency red shift (as large as 350 cm^{-1}). It could be concluded that placement of phosphate ions on the oxygen side of crystalline water molecule ("above" the hydrogen atoms) imposes a strong influence on its deformation mode, resulting in drastic reduction of its harmonic force constant. Within the framework of the NBO theory, one would actually expect significant charge transfer (CT) interaction occurring e.g. from PO_4^{3-} nonbonding states to the OH antibonding ones. As shown by the CFP analysis of this cluster, the purely electrostatic interaction between the crystalline water molecule and its neighbors in the described cluster would cause an even larger flattening of the δ(HOH) vibrational potential. The CT term, thus, most probably counteracts the classical electrostatics with this respect. Finally, expanding further the $Mg^{2+}K^{+}(PO_4^{3-})_2(H_2O)$ cluster with additional two phosphate ions placed "below" water hydrogen atoms (*i.e.* building up the $Mg^{2+}K^{+}(PO_4^{3-})_4(H_2O)$ cluster) seems to nicely balance everything at HF level of theory, leading to an overall frequency red-shift of about 150 cm^{-1}, in good agreement with the experimental data. B3LYP shift was, however, shown to be significantly smaller (~ 26 cm^{-1}). All in all, if one analyzes the dependence of δ(HOH) frequencies on the equilibrium values of the HOH angle, a very good correlation between the later two quantities. To get a further insight into the direction and magnitude of the charge transfer interactions (CT) within the studied clusters, NBO analyses have been carried out in [43–45]. More precisely, second-order perturbation theory analysis of the Fock matrix (or its Kohn-Sham analogue) within the NBO basis had actually been carried out in [45], at HF level of theory. The energetic effects due to these interactions have been estimated by the second-order perturbation theoretical (SOPT) expressions of the form [60]:

$$\Delta E^{(2)}_{\psi\text{donor}\to\psi\text{acceptor}} \approx -2\cdot\frac{\left\langle \psi^{*}_{\text{don}}\middle|\hat{F}\middle|\psi_{\text{acc}}\right\rangle^{2}}{\varepsilon_{\text{acc}}-\varepsilon_{\text{don}}} \qquad (4)$$

In (4), ε_{i} is a diagonal NBO matrix element of the Fock operator $\hat{F}$ (or, in the case of the DFT formalism, the Kohn-Sham one-electron analog $\hat{h}_{\text{KS}}$). The quantities of transferred charge from a given donor to a given acceptor orbital have been, on the other hand, estimated using elementary perturbation theory arguments. The following approximate formula has been obtained on the basis of SOPT treatment [60]:

$$q_{\psi\text{donor}\to\psi\text{acceptor}} \approx 2\left(\frac{\left\langle \psi^{*}_{\text{don}}\middle|\hat{F}\middle|\psi_{\text{acc}}\right\rangle}{\varepsilon_{\text{acc}}-\varepsilon_{\text{don}}}\right)^{2} \qquad (5)$$

It has been found out that the most significant CT occurs in the direction from water oxygen atom nonbonding orbital to the extra-valence (Rydberg) states of the Mg^{2+} ion. This particular interorbital interaction appeared to be the strongest CT interaction within the cluster. In this manner, the differences between full-wavefunction and CFP results related to the δ(HOH) frequency shifts in the case of smallest clusters considered, becomes clearly understandable. Considering the water → K^{+} CT interaction, it has been shown to be negligibly small, *i.e.* one could safely state that no significant CT has been found to occur between water oxygen nonbonding states to the potassium ion virtual states. CT in the direction phosphate → water has been found to be essentially unidirectional. Most of it occurs from the nonbonding orbitals of the phosphate ions oxygen atoms to the water molecule O–H antibonding states. All of the four phosphate ions appeared to be equivalent in the sense of CT interaction with the “central” water molecule. It is also worth noting that though the overall charge transfer has been found to be small on an absolute scale, it is still rather significant in a chemical sense.

CONCLUSIONS

One of the classical paradigms related to spectroscopy of crystalline water in solid state hydrates has been related to the spectral area of appearance of the water bending mode; this mode has been expected to give rise to bands at frequency values that are higher (blue-shifted) or only slightly lower (*i.e.* red-shifted) as compared to the free-water value. In the early works of academician Šoptrajanov and his group and collaborators, however, this paradigm has been questioned and further on confirmed not to be true in a general case. Subsequent developments in the field have further propelled this idea, expanded the knowledge of systems in which this apparent "unusual" behavior has been experimentally detected, and also enabled certain theoretical insights to be gained. All these aspects have been overviewed in this topical review, following the temporal development of ides, as well as the conceptual methodological development. Our current level of fundamental understanding of the phenomenon itself has been considered in detail, carefully pinpointing the weak sides and the possibilities for further developments. On the basis of currently available experimental and theoretical data, the following general conclusions related to the phenomenon may be outlined:

- Carefully collected experimental data for protiated and deuterated samples of $MKPO_4{\cdot}H_2O$, where

M∈{Ni, Mg, Co, Mn}, as well as $MNH_4PO_4·H_2O$ (where M ∈ {Mg, Co, Ni, Mn, Cd}) have unambiguously implied the existence of "low-bending crystalline water modes", *i.e.* bands due to water scissoring mode appearing at significantly *lower* frequencies than even the lowest "Falk's" limit reported before.

- Low frequencies of the HOH bending mode in crystalline water molecules may be in principle induced if the effective local crystalline field vector at the in-crystal water site is directed oppositely to the water dipole moment vector.

- Homogeneous field with magnitude of 0.060 a.u. applied parallel to the water dipole leads to frequency upshift of about only 10 cm^{-1} with respect to the value for free water, while a field of the same magnitude, oriented antiparallel to the water dipole moment, would lead to frequency downshift with appreciable magnitude of approximately 200 cm^{-1}. Downshift of the order of 100 cm^{-1} could be obtained for field strengths of about 0.030 a.u.

- More explicit inclusion of the in-crystal neighborhood around the "peculiar" water molecules enables more light to be shed on the reasons behind the appearance of low-lying δ(HOH) modes.

- The nearest-neighboring phosphate groups around the crystalline water are positioned such that a notable "flattening" of the δ(HOH) vibrational potential occurs, manifested as a significant reduction in the harmonic force constant value. The effect is much more pronounced if only the PO_4^{3-} groups lying above the water are accounted for; those placed below in part counteract it and make a suitable balance in the overall δ(HOH) mode.

- Anharmonic contributions to this shift were found to be of minor importance whatsoever.

Despite the outlined points, one could not say that the story of low-bending crystalline water molecules ends here. This is mostly due to the fact that the crystalline structure of most compounds in which this effect is manifested are yet unknown in details. At the same time, more rigorous periodic DFT computations could be applied to the problem, where all of the crystalline environment would be integrally accounted for. If combined with the finite-cluster approach, such studies could certainly shed much more light into each of the individual contributions to the overall experimentally observed shift of this mode. Such preliminary studies are actually in progress. Of course, last but not least, if more experimental spectroscopic data become available, much more and also finer details of the trends encountered in a series of structurally similar or distinct compounds could be involved in the forthcoming analyses.

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НИСКИ ДЕФОРМАЦИОНИ ВИБРАЦИИ НА КРИСТАЛНИ МОЛЕКУЛИ ВОДА: ТЕКОВНО ТРАГАЊЕ ИЛИ КОНЕЧЕН ЗБОР – ТЕМАТСКИ ПРЕГЛЕДЕН ТРУД – ОМАЖ ЗА АКАДЕМИК БОЈАН ШОПТРАЈАНОВ –

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Целта е, во овој тематски прегледен труд, да се даде концизен и комплетен преглед на извршените истражувања од областа на ниските деформациони вибрации на кристалните молекули на водата. Направен е преглед на досега добиените теоретски и експериментални резултати на ова поле, со посветување на посебно внимание на појавените најважни дилеми и пречки кои го оневозможуваат директното објаснување на забележаниот феномен. Направен е, исто така, обид да се разјаснат моменталните состојби на ова поле на истражување. Иако во овој преглед главниот акцент е фокусиран на кристалните молекули вода кај кристалохидратите, како и на нивните вибрациони својства, посочени се, исто така, и некои други интересни системи кои неодамна го привлекоа вниманието на научната јавност. Тие вклучуваат вода апсорбирана на површините како и на меѓуповршините воздух-вода.

Клучни зборови: кристална вода; кристалохидрати; деформациони вибрации на водата; ИЦ спектроскопија; квантна теорија

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Educational review

ON THE 'TRUE POSITION' OF HYDROGEN IN THE PERIODIC TABLE[•]

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Several attempts are known lately intending to point to 'the proper place' for hydrogen (sometimes also helium) in the Periodic Table of the elements. There are altogether five different types of arguments that lead to the following conclusions: (1) Hydrogen should be placed in Group 1, above lithium; (2) Hydrogen should be placed in group 17, above fluorine; (3) Hydrogen is to be placed in group 14, above carbon; (4) Hydrogen should be positioned above both lithium and fluorine and (5) Hydrogen should be treated as a stand-alone element, in the center of the Periodic Table. Although all proposals are based on arguments, not all offered arguments sound equally convincing. An attempt is made, after critical reexamination of the offered arguments, to hopefully point to the best possible choice for the position of hydrogen. Few words are also mentioned on the structure of the Periodic Table and the (novel) attempts to reorganize it.

Key words: hydrogen; position of; Periodic Table; trends; hydrogen bonding

PROLOGUE

In addition to the numerous works in molecular spectroscopy (mostly hydrogen-bonded systems, particularly crystalline hydrates) it has to be recognized that our laureate was the first one that introduced modern courses of chemistry education for chemistry majors (in the early 1990’s)at the Ss. Cyril and Methodius University. In thinking about a suitable topic that would reflect his main interests of study, it seemed more than appropriate to discuss, once again, the ‘true position’ of the element *hydrogen* in the Mendeleev’s Periodic Table.

INTRODUCTION

In the beginning of the new millennium, several authors made attempts to answer the question that persists for many decades: what is the true position of hydrogen in the Periodic Table (PT) of the elements?

Let us mention in the very beginning that we understand perfectly that:

- this question is a difficult one;
- depending on the arguments offered, various choices may appear to seemingly lead to the ‘best possible choice’, and
- people are usually biased/predetermined to one of the possible choices.

The latter necessarily leads to non-objectiveness, meaning that people put ‘high weights’ on their own arguments while being in the same time highly critical to arguments offered by others.

For several years we followed with interest the discussions (sometimes monologues) of various authors, heavily based on their own arguments. We ourselves were not particular supporters of any of the offered proposals that is (perhaps) kind of an advantage that allows judging the offered arguments more critically and objectively than the authors themselves.

[•]Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

Let us rephrase slightly the task that is to be completed: the problem is, how to classify hydrogen? In other words, to which group(s) in the PT should it be properly assigned?

Hydrogen is the first element in the PT. It seems obvious (without offering a formal proof) that *if it is to be classified* to some group, it should be one of the eight groups, formerly called ‘main groups’ of the PT, i.e. groups 1–2 and 13–18, and not groups 3–12 (containing transition metals).

The italicized text in previous paragraph is intended to point to an important issue that is often forgotten: every classification is a human activity. It is not just a mere indisputable fact that exists in nature waiting to be discovered. Classifications are (or might be) more or less arbitrary. Indeed, there are many criteria according to which the elements of a given set could be classified. The above holds especially when speaking about chemical elements: chemical elements might be classified according to the state of aggregation, boiling and melting temperatures, color, electrical conductivity etc., etc. It may not be quite clear why would someone classify the elements on the basis of their electrical conductivity, unless it is done for a very specific (hence limited) interest. Yet, even such a classification is possible.

The standard approach nowadays (and for many decades back) is to list the elements in a series of ascending atomic numbers, and then search for similarities. This approach is today somewhat different from the original Mendeleev’s [1], but has the advantage of being on a better scientific ground. The result is the well-known classification of the elements in the PT, comprising 7 periods and 18 groups, accounting for all *s*-, *p*- and *d*-elements, but hydrogen and (to a lesser extent) helium. Other approaches exist too, resulting in somewhat different schemes of the elements in the PT and will be briefly mentioned in what follows.

A word on the literature used: we listed all references [1–40] chronologically, and then refer to each of them simply by its number in the list.

Brief review of previous work

In the somewhat extensive literature sources that were available to us, there are those devoted to the discovery of the PT [1, 6, 8, 11, 26, 36], its reception [8], the contribution of physics to the periodic law [4, 27], the definitions of the term element [10, 11, 15, 20, 25, 28] and jubilees (centennial) of the death of Mendeleev [17]. The definition of **element** is in, a way, dual: it relies on a concept of element as an observable (elemental, or simple substance), but also on a concept of element as "*a 'basic substance,' something that can survive chemical change and is the common component of different compound substances.*" [11]. It is the latter notion, of elements as basic substances, that is more important. It seems that the distinction between the two concepts was known as early as the discovery of the PT [15].

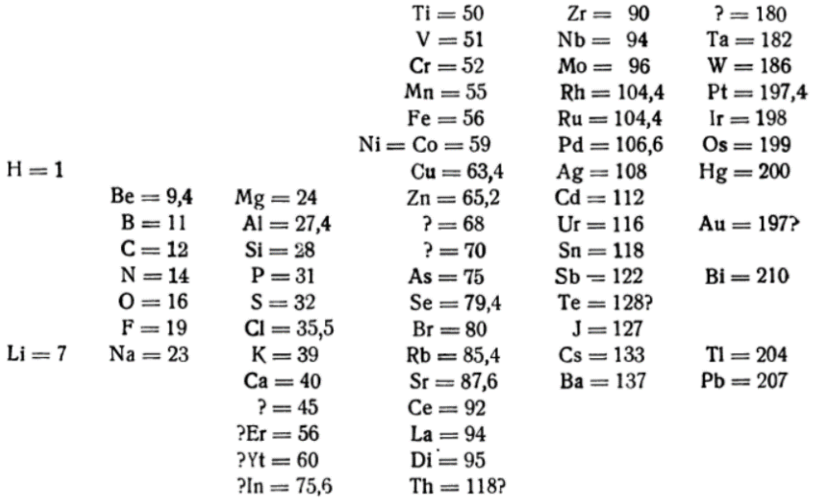
Closely related to the previous are publications aimed (among other things) at the best possible demonstration of the periodicity (including triads) and the periodic law selecting “the best possible choice of a PT” [5, 12, 18, 22, 23, 29, 30]. Regarding the possible formats/presentations of PT, we will mention only few (let’s call those ‘typical representatives’) of the huge number of possibilities (Figures 1–5).

The above format presentations will be discussed in relation to the central question of the present contribution: what is the true (if any) place of the element hydrogen, in the PT? For that reason, primarily the references devoted to this question [7, 9, 10, 13, 14, 16, 19, 31, 32, 34, 37, 39] will be reviewed in the next heading.

Three references were devoted to noble gas chemistry: that of Ar [2, 3] (HArF was synthesized in 2000 and was proven to be stable at very low temperatures [2]) and the brand new publication reporting the synthesis of Na_2He under extreme pressures of some 100 GPa [38]. Reference 21 is about the notion of isoelectronic series, isodiagonality and diagonal relationships between the elements in PT [24], the order in which the 3*d* and 4*s* energy levels are populated [33] and the eka- elements and chemical pure possibilities [35].

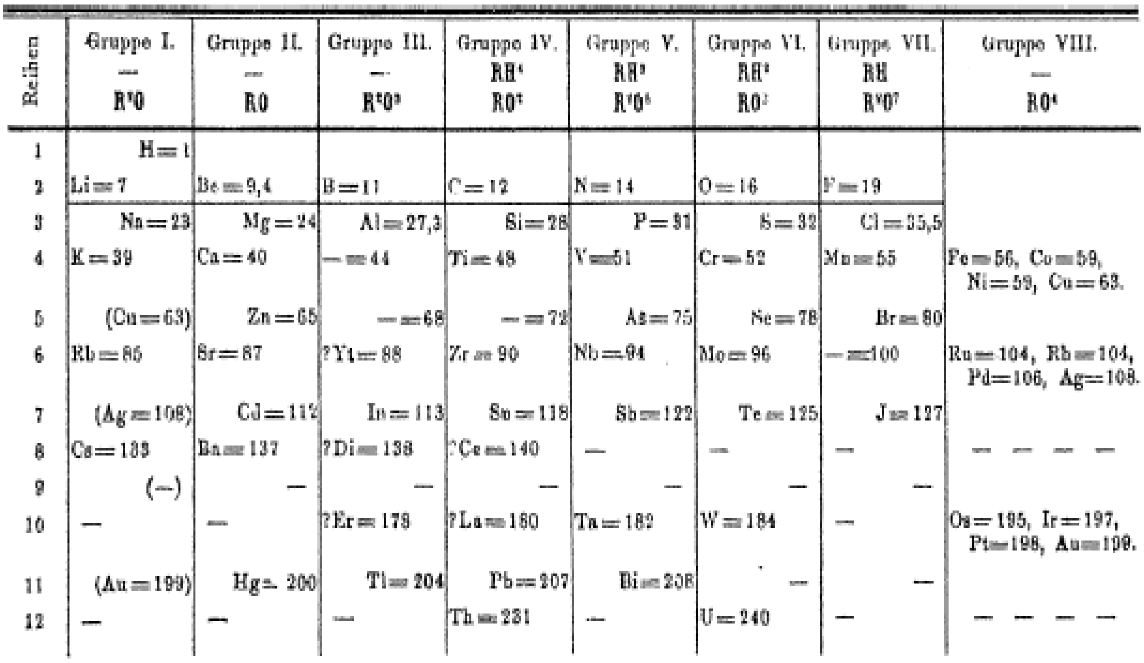
WHERE TO PLACE HYDROGEN IN THE PT?

The first one that assigned hydrogen in the PT was, of course, Mendeleev [1]. In 1869 he originally positioned it (cf. Figure 1 a) in the same group (row) with copper, silver and mercury. In view of his excellent knowledge of the chemical properties which weighed so much on the positioning of the elements it is reasonable to allow that he meant it to be separated from all other elements. In two years (1871) he placed it in the first group, next to the alkali metals [14]. True, since this is the short format of PT, this group contained also Cu, Ag and Au (but arguments could be offered even for such similarities [30]). Group 1 is even nowadays the most ‘popular’ place for H [5, 10, 13, 16, 18], as demonstrated by the most common ‘shape’ of the PT (cf. Figure 2). The arguments stem from the fact that H is univalent (exactly as the alkali metals), and forms compounds with the same general formula. Further, from the point of view of physics, the atomic term of hydrogen ($^2S_{1/2}$) is identical with that of alkali metals. One more reason would be that under very high pressures (≈ 500 GPa) there are strong experimental indications that metallic hydrogen is formed [39]. If this is proven to be true, that would be a serious argument for those inclined to put H above Li. The trends of electronegativities is qualitatively correct, albeit the value for H is much higher (the variation of the electronegativity from Li to Cs is in much smaller steps). On the other hand, there are really strong arguments against this assignment. We would only like to mention here that no alkali metal forms M^- anions (unlike the stable H^-, the hydride anion). Also, all MX salts (where M is an alkali metal, and X is halogen) are ionic solids. All HX compounds are covalent and gaseous. More arguments will be offered in the subsequent paragraph.



			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104,4	Pt = 197,4
			Fe = 56	Ru = 104,4	Ir = 198
			Ni = Co = 59	Pd = 106,6	Os = 199
H = 1			Cu = 63,4	Ag = 108	Hg = 200
	Be = 9,4	Mg = 24	Zn = 65,2	Cd = 112	
	B = 11	Al = 27,4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210
	O = 16	S = 32	Se = 79,4	Te = 128?	
	F = 19	Cl = 35,5	Br = 80	J = 127	
Li = 7	Na = 23	K = 39	Rb = 85,4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87,6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75,6	Th = 118?		

(a)



Reihen	Gruppe I. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—	—	
12	—	—	—	Th = 231	—	U = 240	—	— — — —

(b)

Figure 1. (a) The original Mendeleev’s PT [1] and (b) his short-period table (source: Lang [12]).

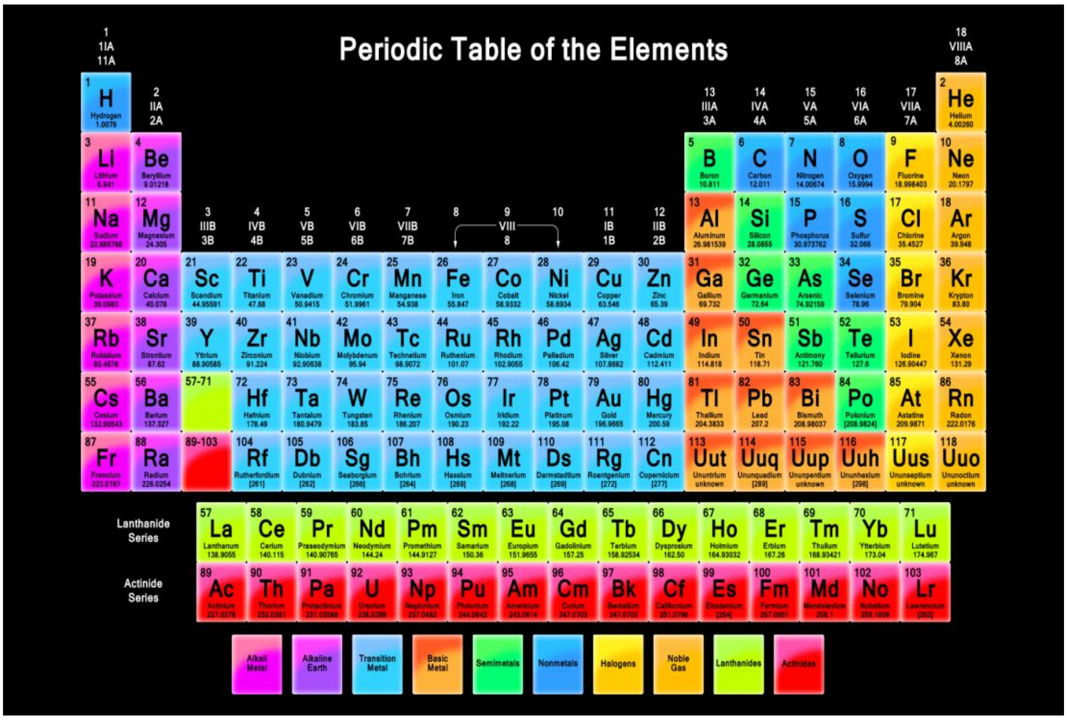


Figure 2. The standard medium-long PT format with the *f*-elements shown separated from the main body of the table [40].

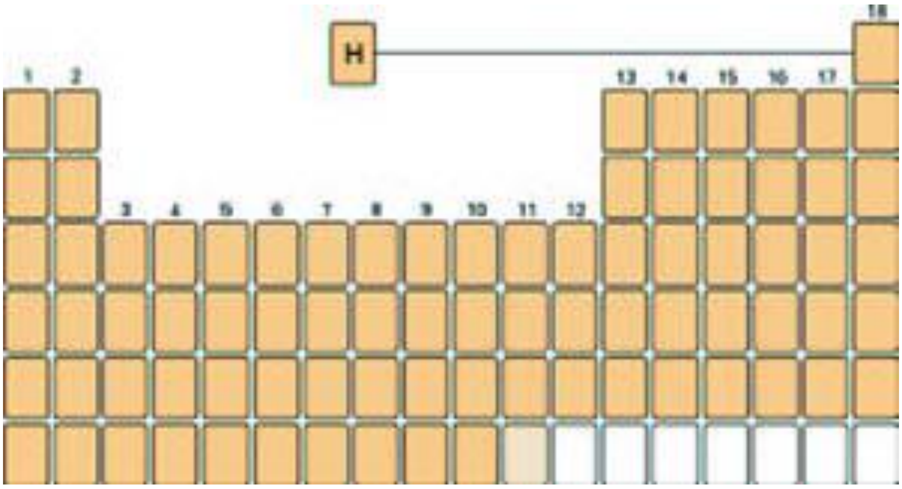
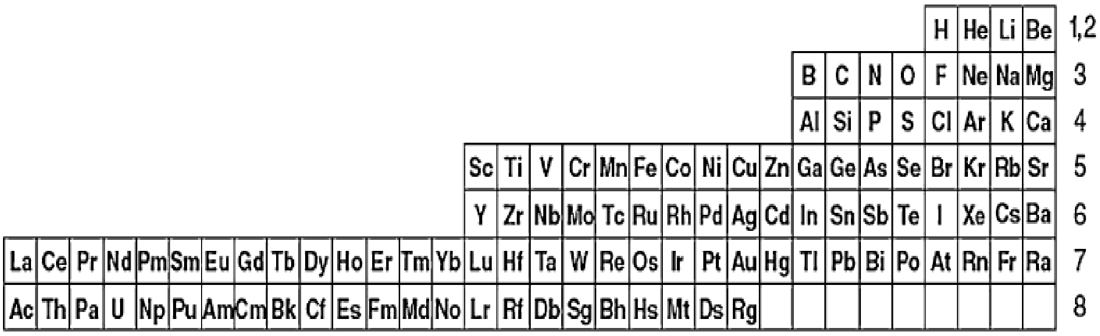


Figure 3. PT proposed by Kaesz & Atkins [7].



																												H	He	Li	Be	1,2
																								B	C	N	O	F	Ne	Na	Mg	3
																								Al	Si	P	S	Cl	Ar	K	Ca	4
														Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	5
														Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	Cs	Ba	6
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	7
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg										8

Figure 4. PT proposed by Scerri [22].

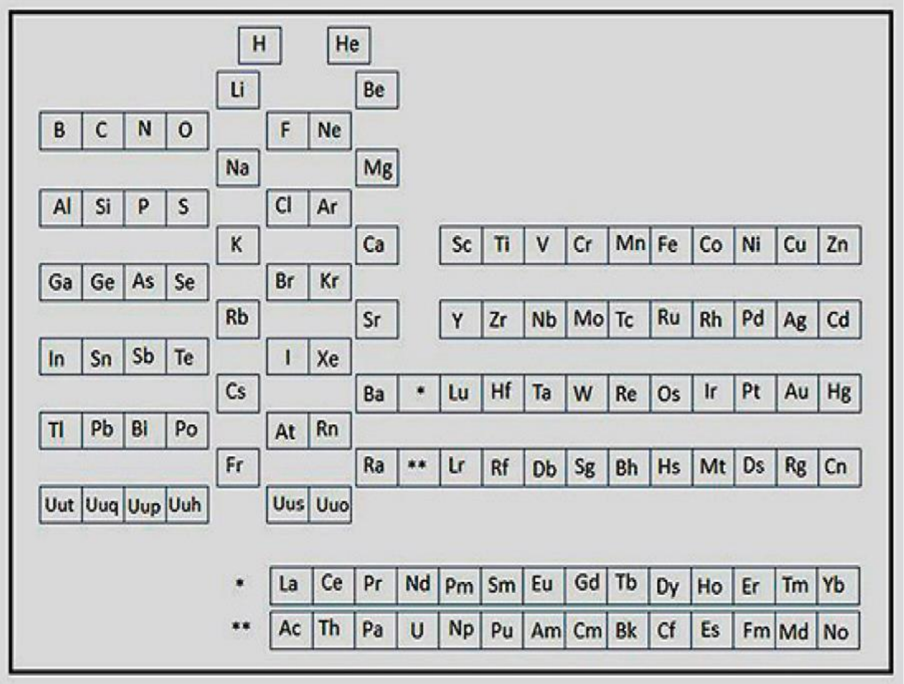


Figure 5.The Labarca & Srivaths PT [34].

Hydrogen could be placed in Group 17 (halogens) above F (cf. Figure 4). A solid argument for this is that it forms covalent compounds with all nonmetals, but ionic compounds with alkali metals and most of alkaline earths (exactly as the halogens). Hydrogen as a simple substance, just like the halogens, exists in the form of diatomic molecules. It cannot form free H^+ ions, due to the extremely high polarizability of the naked proton. Invoking Sacks [14], "*A Coulombic model, in which all compounds of hydrogen are treated as hydrides, places hydrogen exclusively as the first member of the halogen family and forms the basis for reconsideration of fundamental concepts in bonding and structures. The model provides excellent descriptive and predictive ability for structures and reactivities of a wide range of substances... Although unique in many respects, both physical and chemical properties of the element conform best – if not perfectly – with other halogens*". Scerri [22] has also supported this view (in contrast to his previous opinion [10, 18]), first of all as a result of treating the elements as basic (and not simple) substances, but also because if such a scheme is adopted, PT benefits with one more perfect triad (triad of atomic numbers). Hernández & Novaro [32] also give arguments against placing hydrogen in Group 1, but they are not saying explicitly that it should lead the halogens group.). Although H above F seems a better option than H above Li, it too suffers from several shortcomings. The atomic term of all halogen atoms is $^2P_{3/2}$, and this is a compelling argument against its assignment to this group, at least for physicists. Also, the trend of electronegativities in the series H, F, Cl, Br, I is counterintuitive (one would expect the first element in a group to be the one with highest value for the electronegativity and this is true for all groups of *s*- and *p*- elements, providing hydrogen is left aside). Further, all alkali metals react vigorously (some of them even explosively) with water, giving MOH and hydrogen gas. The products with the analogous X_2O are MX and M_2O, if an excess alkali metal is used. It would not be possible to prevent the formation of MOH under similar experimental conditions, for if that was possible, Davy could not generate potassium and sodium by electrolysis of molten MOH! Alkali hydrides are hydrolized in water giving H_2 and MOH. No reaction is possible between MX and X_2O, at least for X = F, Cl! Finally, considering the ionization energies one comes to the conclusion that hydrogen is 'incompatible' with both Group 1 and Group 17.

Hydrogen has also been placed in group 4, above carbon [9, 13], on the basis of several arguments: a) Its valence electron shell ($1s^1$) is half filled, as is the shell of carbon ($1s^22p^2$); b) Its electronegativity is between the electronegativities of C and Si; c) The types of compounds hydrogen forms are closely related to the compounds with methyl (CH_3) instead of H; d) The H–H and C–H bonds are of comparable strengths etc. While the above is true, it is highly unusual to put a univalent element in a group of tetravalent ones. Neither the atomic terms of the elements in the carbon family ($^3P_1$) have anything in common with the term for hydrogen ($^2S_{1/2}$). In our opinion, this is the weakest proposal of all offered so far.

A step forward is the PT of Labarca & Srivaths [34] (cf. Figure 5), where H is positioned above both Li and F, thus pointing to a resemblance of H with both Group 1 and Group 17. To further advocate this approach, one should be aware that there are no real arguments, apart from a belief, that ‘every element in PT belongs to *one and one only* of the existing groups of elements’. Simplified, that would read: ‘Every *s*- or *p*- element in the PT belongs to one of the eight groups headed by the elements of period 2’. Yes, the latter works perfect for all *s*- and *p*- elements except for hydrogen! In relation to this, the Labarca & Srivaths approach is a real success. The questions are: can one do better than that? Namely, within the frame of Labarca & Srivaths PT scheme, the problems with the trends (electronegativity, ionization energy) discussed above remain. Also, there are pure peculiarities about hydrogen, specific for this element only. That is the phenomenon of hydrogen bonding (HB), where a hydrogen atom is shared between two (or, very seldom, three highly electronegative atoms). This unique type of bonding may vary in strength continuously: on one end, it may approach the ‘bonding strength’ of Van der Waals contacts; on the other, it may be indistinguishable from a true covalent bond, like in the case of $(F–H–F)^-$, where both FH and HF bonds are identical by symmetry. A whole continuum of HB strengths is possible. This has remarkable consequences on the XH stretching frequencies of a HB species X–H···Y (with X being proton donor and Y being proton acceptor): from some 3700 cm^{-1} for a ‘free’ O–H stretching, to some 500^{-1} for very strong O–H–O hydrogen bonds. No other element in the PT spans such a wide range of stretching vibration wavenumbers.

Having in mind the above, it might be understandable why we agree with Kaesz & Atkins [7], that H should be placed at a stand-alone position within the PT. As the authors say: ‘*We do not support the duplication of hydrogen in the periodic table. Instead, we believe the symbol should appear only once in the table, in Period 1 but centered between the alkali metals and the halogens as illustrated in the figure. This position is consistent with the elements at the head of each group being significantly different from their congeners: hydrogen lies at the head of the entire table and as such can be expected to be strikingly different from all the elements, as is in fact the case*’ (cf. Figure 3). However, the reasoning of Kaesz and Atkins was criticized by Scerri: “*Our current inability to place hydrogen in the periodic table in an unambiguous manner should not lead us to exclude it from the periodic law altogether, as Atkins and Kaesz seem to imply in removing hydrogen from the main body of the table. I suggest that hydrogen is as subject to the periodic law as all the other elements are*”. Now, the latter conclusion isn’t quite true. Of course, hydrogen was not ‘excluded’ from the PT. It is well within it. However, it is *not* placed in any of the groups in this table. We do not see why such an approach would not be a legitimate one? Especially, when one recalls that the leading elements (Li, Be, B, C, N, O and F) show a certain extent of ‘exotic behaviour’, when compared with those below them in the group. The diagonal relationships in the PT [24] (i.e. similarities between Li and Mg; Be and Al; B and Si, and to a lesser extent of C and P) are well known for a long time. These similarities might be, at least in part, related to the fact that atoms of the elements of the second period do not have (empty) *d*-orbitals of energy comparable to that of the valence electrons, unlike their heavier analogues. A similar, but much more pronounced ‘exotic behaviour’ could then be a priori expected for hydrogen, being a first period element (and thus having no energetically close *p*-orbitals). If the former is true, the logical consequence would be to give it a special position in the PT, exactly as Kaesz & Atkins did!

To end this discussion, we will very briefly point to the similar dilemma about the true position of He in the PT [19, 23, 31, 34]: shall it be put above Be or above Ne? Actually, it is only the electron configuration and the atomic spectra of He that matches those of alkaline earths. The atomic term of helium is equal to both terms of the alkaline earths and noble gases, namely $^1S_0$. However, there is a lack of real chemistry of He (with a single exception, the synthesis of Na_2He under some really extreme experimental conditions, that has just recently been published [38]). The former is in line with the properties of noble gases (showing, once again, a pronounced trend of increasing reactivity when going from He to Xe). Chemically, helium has nothing in common with typical metals, as are alkaline earths and the latter fact fully justifies its position in the PT as the first noble gas (and the least reactive element in PT).

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ЗА 'ВИСТИНСКОТО МЕСТО' НА ВОДОРОДОТ ВО ПЕРИОДНИОТ СИСТЕМ

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Во последно време се познати неколку обиди чија амбиција е да се укаже на "вистинското место" на водородот (понекогаш и хелиумот) во периодниот систем на елементите. Постојат вкупно пет различни вида аргументи кои доведуваат до следните заклучоци: (1) Водородот треба да се стави во првата група, над литиумот; (2) Водородот треба да се става во 17-тата група, над флуорот; (3) Водородот треба да се стави во 14-тата група, над јаглеродот; (4) Водородот треба да биде поставен над литиумот и флуорот и (5) водородот треба да се третира како уникатен елемент и да се смести централно во периодниот систем. Иако сите предлози се засноваат на аргументи, не сите понудени аргументи звучат подеднакво убедливо. По критичкото преиспитување на понудените аргументи, направен е обид да се избере најдобрата можна позиција за водород. Се споменуваат и неколку зборови и за структурата на Периодниот Систем маса и за обиди за неговото реорганизирање.

Клучни зборови: водород; местоположба; периоден систем; трендови; водородна врска

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Original scientific paper

VERY LOW H–O–H BENDING FREQUENCIES. VI. VIBRATIONAL SPECTRA OF $CdCl_2·H_2O$[•]

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The infrared and Raman spectra of $CdCl_2·H_2O$ as well as those of a series of its partially deuterated analogues were recorded at room and at liquid-nitrogen temperature (RT and LNT, respectively). The combined results from the analysis of the spectra were used to assign the observed bands. In the difference IR spectrum of the compound with low deuterium content (≈ 4 % D) recorded at RT, one broad bands is observed at around 2590 cm^{-1} while in the LNT spectrum two bands appear (at 2584 cm^{-1} and 2575 cm^{-1}). The appearance in the LNT spectrum of these two bands which are due to the stretching OD modes of the isotopically isolated HDO molecules points to the existance of two crystallographically different hydrogen bonds and is in accordance with the structural data for this compound. In the LNT infrared and Raman spectra of the protiated compound, one band, at 1583 cm^{-1}, is observed in the region of the bending HOH vibrations with a frequency that is decreasing with lowering the temperature. An interesting finding related to this band is that its frequency is lower than that for the water molecule in the gas phase (1594 cm^{-1}). In the RT and LNT IR spectra, only one strong band (at 560 cm^{-1}) is observed in the region of the librations of water molecules (700 cm^{-1} – 400 cm^{-1}).

Key words: cadmium chloride monohydrate; infrared spectra; Raman spectra

INTRODUCTION

Various types of aquahalogeno complexes have been studied in the last decades by the structural chemistry group at the Institute of Chemistry, Faculty of Natural Sciences and Mathematics in Skopje. Continuing our research in studying the vibrational spectra of aquahalogeno complexes [1–16], in this work we report the results from the analysis of the infrared and Raman spectra of the protiated cadmiun chloride monohydrate ($CdCl_2·H_2O$) and its deuterated analogues recorded at room temperature (RT) and at the liquid nitrogen boiling temperature (LNT). To the best of our knowledge, the IR and Raman spectra of this compound and its deuterated analogues recorded at RT and LNT have not been previously studied and reported.

The structure of $CdCl_2·H_2O$ has been determined by single-crystal X-ray diffraction [17]. It was found to crystalize in the orthorhombic space group *Pnma* with a = 925(2) pm; b = 377.6(8) pm; c = 1189(2) pm and four formula units in the unit cell. The crystal structure consists of m-symmetrical $[CdCl_5(H_2O)]$ octahedra sharing edges to form $[Cd_2Cl_{10}(H_2O)_2]_n$ columns along [010], the columns being connected by O–H···Cl bonds of the H_2O molecules. There is only one type of water molecules in the structure. The positions of the hydrogen atoms have not been found, but

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[•]Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday from the surrounding of the oxygen atoms, it may be deduced that the water molecules are trigonally coordinated and oriented in the mirror planes of the structure forming two different weak and strongly bent hydrogen bonds of the O–H···Cl type to two different but symmetry related Cl atoms (Cl_1 and Cl_1') with O···Cl distances of 330(3) pm and 321(3) pm. The Cd–O distance is 232(2) pm. It should be noted here that the hydrogen bond acceptor angle Cl_1–O_w–Cl_1' is 132.6(8)° and is among the highest angles of this type found in solid hydrates [18].

EXPERIMENTAL

Synthesis of $CdCl_2{\cdot}H_2O$ and its deuterated analogues

The monohydrate of cadmium chloride used in the study was a commercial compound from Merck (Darmstadt, Germany) with a pro analysis purity. It is soluble in water, so that recrystallization was performed from water and well shaped crystals were obtained. To check its identity, an X-ray diffractogram of a powder sample was obtained and analyzed, which corresponded to the one for $CdCl_2{\cdot}H_2O$ – JCPDS (PDF-00-027-0073).

The deuterated analogues were prepared by dissolving a small amount of the protiated compound in H_2O–D_2O mixtures of appropriate composition. The crystallization of these solutions was carried out in a vacuum desiccator over silica.

Recording of spectra and X-ray diffractograms

The infrared spectra were recorded of oil suspensions in Nujol and Fluorolube using the infrared interferometer Perkin-Elmer System 2000 in the spectral range from 4000 cm^{-1} to 370 cm^{-1} by accumulating 32 scans with a resolution of 2 cm^{-1} and 4 cm^{-1}. The spectra were recorded at room temperature (RT) and the liquid nitrogen boiling temperature (LNT). The low temperature measurements were made in a specially designed cell P/N 21525 (Graseby Specac). For collecting and processing the Fourier-transformed infrared spectra the software packages GRAMS ANALYST 2000 [19] and GRAMS 32 [20] were used.

The Raman spectra were recorded at room temperature using the LabRam 300 (Horiba Jobin-Yvon) micro-Raman spectrometer with a He–Ne laser (red) at 633 nm and a Nd:YAG laser (green) at 532 nm. Olympus MPlanN microscope with an enlargement factor 50 was used for focusing the laser. The spectra were recorded in the region from 4000 to 100 cm^{-1} by accumulation of 15–30 spectra with a resolution of 2 cm^{-1} using a grating with 1800 lines/mm. The low temperature Raman spectra were recorded in glass capillaries using the Fourier-transforme Raman spectrometer RFS 100/S (Bruker) with Nd:YAG laser excitation at 1064 nm (resolution of 2 cm^{-1}). The software packages GRAMS ANALYST 2000 [19] and GRAMS 32 [20] were used for collecting and processing the Raman spectra.

The X-ray diffractograms of powdered samples (XRPD) were obtained using a Rigaku Ultima IV diffractometer with CuKα radiation with a generator with 40 kV voltage and 40 mA current. The powdered sample was placed on a silicon sample holder and data were collected at room temperature using a D/tex detector in the 2θ region from 5 to 70° with a recording speed of 10°/min.

RESULTS AND DISCUSSION

The infrared spectra of $CdCl_2{\cdot}H_2O$ recorded in Nujol mull (N) at room temperatute and at the boiling temperature of liquid nitrogen are shown in Fig. 1, and the Raman spectra recordet at RT and LNT are presented in Figure 2.

Internal vibrations of water molecules

Group theory considerations suggest that three IR and three Raman active internal vibrations of the water molecules are expected due to the existence of a static field (Table 1). If the correlation field is also taken into consideration, the number of bands would significantly increase.

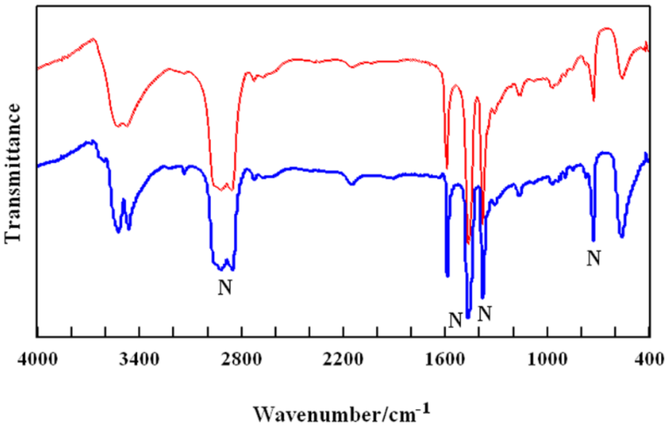


Figure 1. Infrared spectra of $CdCl_2{\cdot}H_2O$ recorded in Nujol (N) at RT (upper curve) and at LNT (lower curve).

Stretching vibrations of water molecules

In the IR spectra of $CdCl_2·H_2O$ recorded at RT, two intensive bands, at 3525 cm^{-1} and 3470 cm^{-1}, appear in the region of the OH stretching vibrations (Fig. 1, upper curve). In the same region, four intensive bands are observed at 3540 cm^{-1}, 3520 cm^{-1}, 3475 cm^{-1} and 3462 cm^{-1} in the LNT spectrum (Fig. 2, lower curve) as a result of correlation splitting of the antisymmetric and symmetric stretching HOH modes (Table 1). In the same region of the IR spectrum, one low intensity band is observed at 3133 cm^{-1} what might be attributed to a second order transition of the bending HOH modes. In the Raman spectrum recorded at RT, the corresponding bands in this region appear at around 3470 cm^{-1} and 3139 cm^{-1} (Fig. 2, lower curve) whereas in the LNT spectrum, they are found at 3520 cm^{-1}, 3467 cm^{-1} and 3130 cm^{-1} (Fig. 2, upper curve).

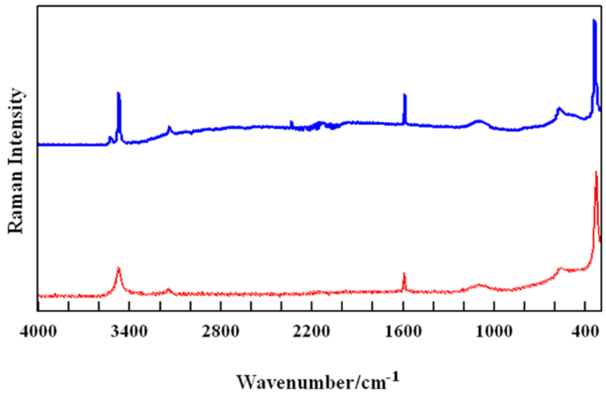


Figure 2. Raman spectra of $CdCl_2·H_2O$ recorded at RT (lower curve) and at LNT (upper curve).

In the difference IR spectrum of the compound with low deuterium content (≈ 4 % D) recorded at RT, one broad band is observed at around 2590 cm^{-1}, and two bands (at 2584 cm^{-1} and 2575 cm^{-1}) appear in the LNT spectrum which are due to the uncoupled O–D stretching modes of isotopically isolated HDO molecules (Fig. 3). The presence of these two bands in the LNT spectrum is in accordance with the structural data of this compound [17], i.e. with the existence of two non-equivalent hydrogen bonds. The slight frequency difference between these two bands indicates that the force field for these two OD stretching vibrations is almost identical. This conclusion is strenghted by the spectral picture in the region of OD stretching modes for the series of partially deuterated analogues of the studied compound (Fig. 4). To be exact, in this region of the spectra of the deuterated analogues, the increase of the deuterium content leads to the appearance of new bands symmetrically distributed around the two bands at 2584 cm^{-1} and 2575 cm^{-1}. These new bands, found at 2628 cm^{-1} and 2535 cm^{-1}, certainly originate from modes of isolated HDO molecules and can be attributed to the antisymmetric and symmetric stretching vibrations of the D_2O molecules. In the Raman spectrum of the analogue with the highest deuterium content recorded at LNT, the corresponding bands appear at 2635 cm^{-1} and 2543 cm^{-1}, respectively (Fig. 5).

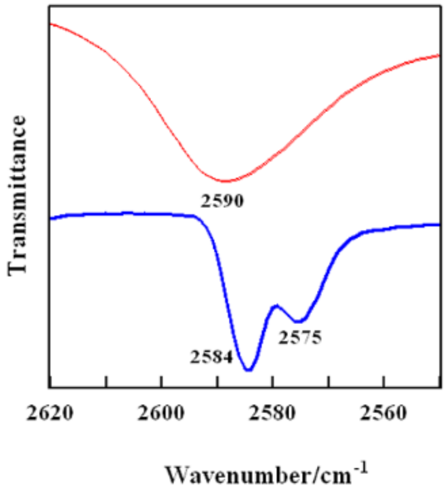


Figure 3. Deconvoluted difference infrared spectra recorded at RT (upper curve) and at LNT (lower curve) in the region of the ν(OD) vibrations, obtained by subtracting the respective spectrum of the protiated sample of $CdCl_2·H_2O$ from the spectrum of the analogue with low deuterium content (≈ 5 % D).

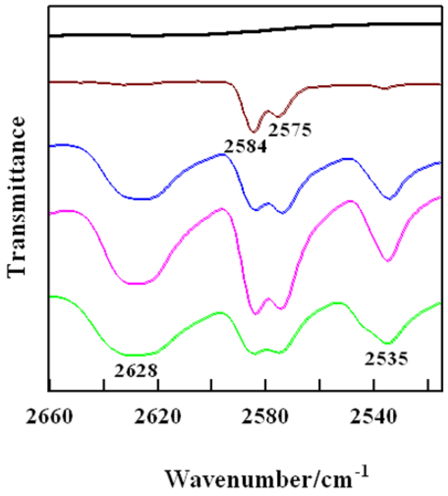
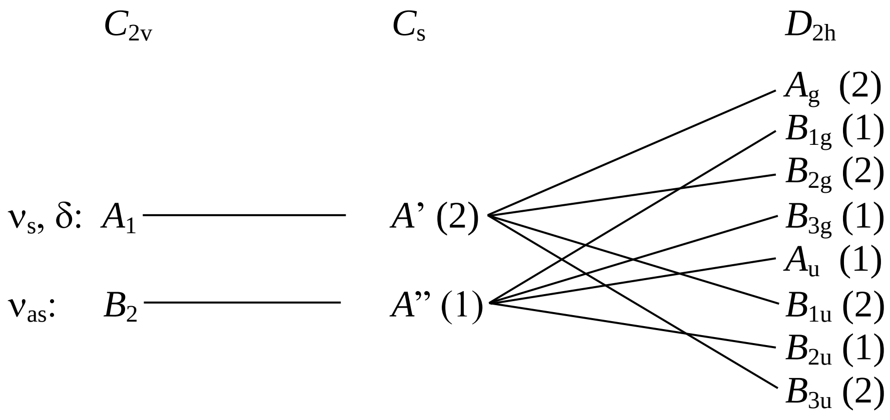


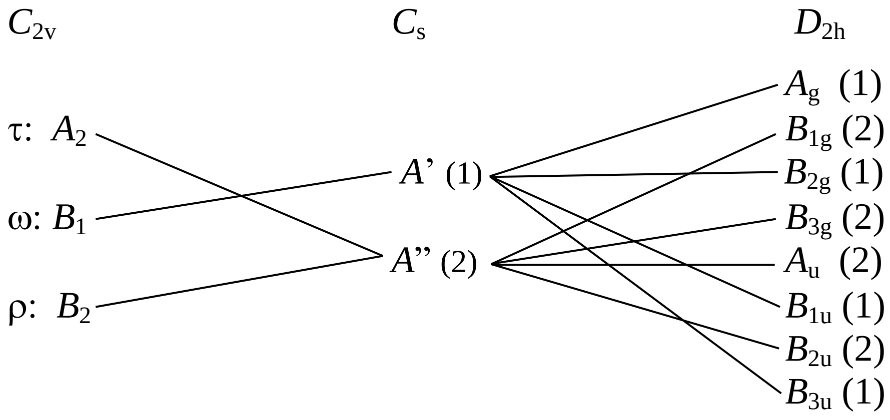
Figure 4. Infrared spectra of $CdCl_2·H_2O$ and its partially deuterated analogues recorded at LNT in the region of the OD stretching vibrations (the content of deuterium increases from top to bottom, offset spectra are presented).

Table 1. The unit-cell group analysis for the internal and external vibrations of the water molecules in $CdCl_2 \cdot H_2O$

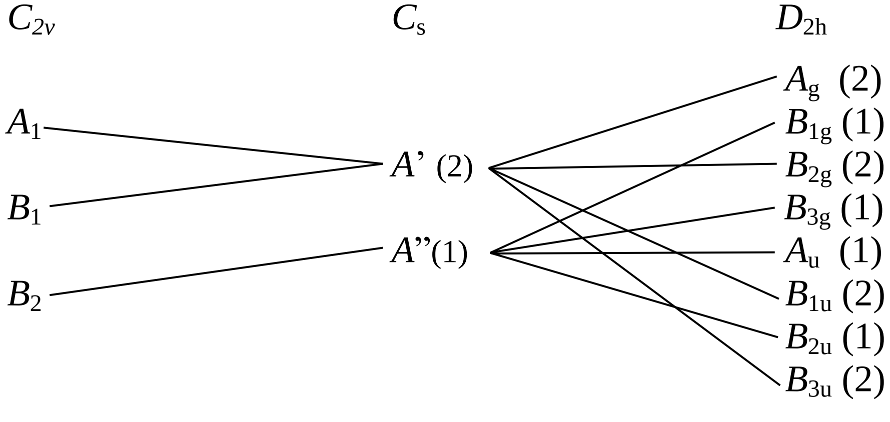
Internal vibrations



Librations



Hindered translations



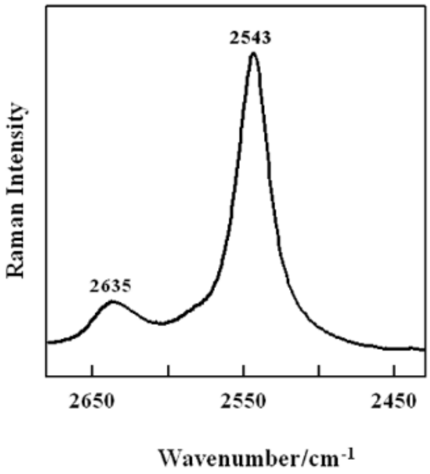


Figure 5. Raman spectrum of the nearly fully deuterated analogue of $CdCl_2{\cdot}H_2O$ recorded at LNT in the region of the OD stretching vibrations.

The temperature shift of the OD stretching mode frequencies of the isotopically isolated HDO molecules (see Fig. 3) is *positive*, i.e. $d\nu/dT > 0$. According to Falk et al. [21], this would point to linear hydrogen bonds. Contrary to that, the X-ray diffraction data [17], require strongly bent O–H···Cl hydrogen bonds since the hydrogen bond acceptor angle $Cl_1–O_w–Cl_1'$ is 132.6(8)°. A similar behavior has been found for *trans*-$[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$ [12]. This means that the finding of Falk et al. [21] is not applicable in these cases.

It should be mentioned that in the case of the alkaline earth halide monohydrates $MX_2{\cdot}H_2O$ (M = Sr, Ba; X = Cl, Br, I), the temperature dependence of the OD stretching mode frequencies of isotopically isolated HDO molecules is negative ($d\nu/dT < 0$) [22]. In these hydrates, the water molecules are positioned in a three-dimensional $[M{\cdots}O{\cdots}M{\cdots}O]_n$ framework showing the same crystallographic symmetry of H_2O and its atoms as found for $CdCl_2{\cdot}H_2O$ forming also weak but this time bifurcated hydrogen bonds to the surrounding halide ions with O···Cl distances between 310.4(3) pm and 344.6(3) pm [23], i.e. the temperature dependence of the OD stretching mode frequencies of the isotopically isolated HDO molecules for the alkaline earth halide monohydrates $MX_2{\cdot}H_2O$ (M = Sr, Ba; X = Cl, Br, I) is in accordance with the finding of Falk et al. [21].

A more thorough explanation of the temperature dependence of the OD stretching mode frequencies of isotopically isolated HDO molecules of $CdCl_2{\cdot}H_2O$ and *trans*-$[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$ could be given if comparison would be made on the basis of the respective structure data determinated by neutron diffraction analysis at room and low temperature. Unfortunately, the crystal structures of these two chloride hydrates have been determined by X-ray diffraction and only at room temperature.

Bending vibrations of water molecules

The region of the bending vibrations of water molecules in the vibrational spectra is very interesting as the subtitle of the paper suggests. In the RT and LNT infrared and Raman spectra of the protiated compound (4 % D_2O, Fig. 6 a and b), one band is observed in the region of the H–O–H bending vibrations with a frequency that is decreasing with lowering the temperature.

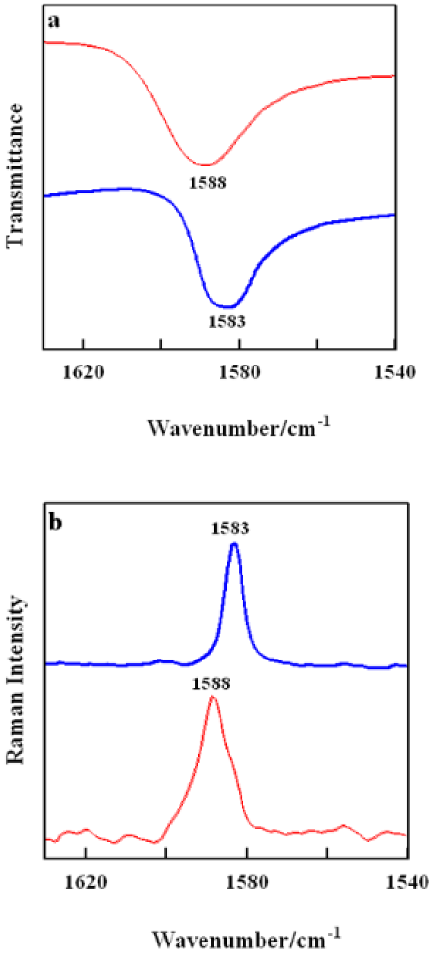


Figure 6. Infrared (a) spectrum of $CdCl_2{\cdot}H_2O$ recorded at RT (upper curve) and at LNT (lower curve) and Raman (**b**) spectrum of $CdCl_2{\cdot}H_2O$ recorded at RT (lower curve) and at LNT (upper curve) in the region of the HOH bending vibrations.

In the RT spectra, this band appears at 1588 cm^{-1}, and in the LNT spectra it is found at 1583 cm^{-1}. The appearance of a single band at 1583 cm^{-1} in both the IR and Raman LNT spectra (Fig. 6

a and b) of the protiated analogue is in accordance with the existence of one crystallographically different type of water molecules in the structure. The fact that the frequencies in the two types of spectra coincide indicates an absence of the correlational splitting of modes. An interesting finding related to this band is that its frequency is lower than that for the water molecule in the gas phase, which is 1594 cm^{-1} [24], whereas in solid hydrates these frequencies are most often higher [25–27]. The appearance of the bending HOH modes at such a frequency corresponds to the existence of a very large $Cl_1 \cdots O \cdots Cl_1'$ angle, which is 132.6(8)° [17]. Šoptrajanov [28, 29] has explained the differences of the frequencies of the bending vibrations between those of water molecules in the gas phase and those in solid hydrates with the respective differences of the structural features of water molecules.

In the region of the HDO and DHO bending vibrations, only one band is observed (at 1397 cm^{-1}) in the LNT IR and Raman spectra of the compound with low deuterium content instead of the expected two (Fig. 7). Similar to the case of the two OD stretching vibrations of the isotopically isolated HDO molecules, this suggests that the force fields for the HDO and DHO modes are practically identical. This means that the stretching and bending vibrations are like those of a symmetric water molecule, rather than the asymmetric one indicated by the available crystal structure data [17].

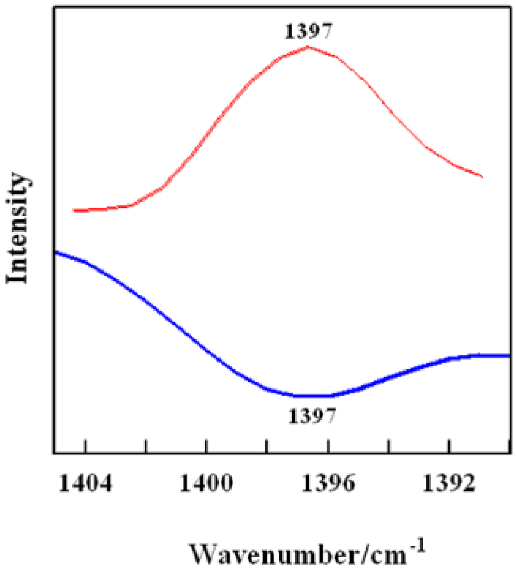


Figure 7. Infrared spectrum (lower curve) and Raman spectrum (upper curve) of $CdCl_2 \cdot H_2O$ analogue with low deuterium content (≈ 5 % D) recorded at LNT in the region of the HDO and DHO bending vibrations.

External vibrations of water molecules

By incorporation of the water molecules in a crystal, the rotational and translational modes of the free water molecules become vibrational modes. To distinguish these modes from the modes of free water molecules they are referred to as hindered rotations and hindered translations. Hindered rotations are also called librations and the three librational modes of water molecules are denoted as: *rocking*, *wagging* and *twisting*. Bands from librational modes in the vibrational spectra are often found in the region between 1000 cm^{-1} and 300 cm^{-1} [30]. As a rule, the bands from these modes are with higher intensity in the IR spectra than in the Raman spectra (see e.g. [31]).

Besides rotations that become librations in a crystal, the three translations of the structural units also become vibrations i.e. external vibrational modes. For coordinated water molecules, these latter vibrations have the character of metal-water modes. Hindered translations of water molecules that are not coordinated to a metal usually appear below 300 cm^{-1}, whereas for coordinated water molecules they appear in the region between 500 and 300 cm^{-1} [25].

The librational modes have been reviewed and results from systematic studies are published in the works of Falk and Knop [24], Tayal et al. [30] and Lutz [27]. In spite of the thorough studies, there are still unresolved questions related to the nature of the three librational modes, their expected frequencies, criteria for their exact assignment as well as the expected intensites of the bands from the librations of the water molecules in the IR and Raman spectra.

The librations are very sensitive to the effects related to the environment of the water molecules. Thus, changes in the structural features from one solid hydrate to another, as well as changes in temperature or isotopic substitution, have more pronounced effects on the frequency, halfwidth and intensity of the librational bands than on the bands from internal vibrations of water molecules.

The results for the vibrations of the primitive cell of the investigated compound (Table 1) show that, in absence of correlation field, the expected number of bands due to librations of water molecules in the IR and Raman spectra is three. If there is a correlation field, four bands are expected in the IR spectra and six bands due to librational HOH modes are expected in the Raman spectra.

The location of the bands from librations is facilitated by studying the isotopic H_2O/D_2O and the H_2O/HDO frequency shifts in the vibrational spectra [32, 33] as the following discussion will show.

In the RT and LNT IR spectra, only one strong band at 560 cm^{-1} is observed in the region of the librations of water molecules and, surprisingly, it is not temperature sensitive (Fig. 1). In the LNT Raman spectrum, one broad band with lower intensity is found at 568 cm^{-1} (Fig. 3). The appearance of only one intensive band suggests that all three librational modes (pure or mixed) have approximately the same frequency. In fact, the model calculations of Eriksson and Lindgren [34] have shown that in the case of C_s (σ_{xz} – plane) local symmetry (as is the case with cadmium chloride monohydrate), there is an intensive mixing of the *wagging* and *twisting* modes.

Considering the existence of weak hydrogen bonded water molecules, water librational bands could be expected below 400 cm^{-1} (see e.g. [30] and [35]). However, since we have studied the infrared spectra in the region only down to 400 cm^{-1}, such bands could not be observed in our infrared spectra. Thus we shall limit our dicussion to bands appearing above 400 cm^{-1} .

In the LNT IR spectra of the partially deuterated analogues, new bands, not present in the spectra of the protiated compound, appear at around 480 cm^{-1} and 427 cm^{-1} with intensities increasing as the deuterium content increase (Fig. 8), the frequency factors for the H_2O/D_2O and H_2O/HDO isotopic shifts being 1.32 and 1.16, respectively. Such values are sufficient to assign the observed bands to librations, the higher-frequency band attributable to HDO librations and that at 425 cm^{-1} to D_2O librations.

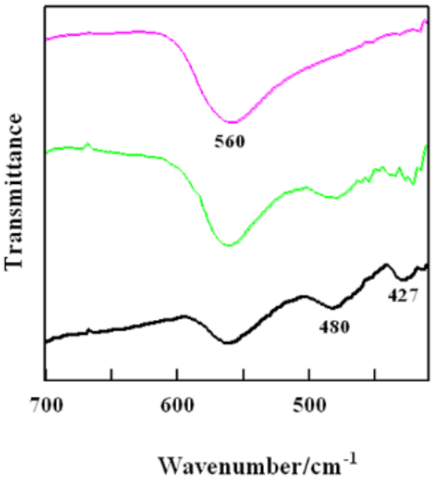


Fig. 8. IR spectra of $CdCl_2·H_2O$ and its partially deuterated analogues recorded at LNT in the region of the HOH external vibrations (the content of deuterium increases from top to bottom, offset spectra are presented).

In the LNT Raman spectra of the protiated compound and the compound with the highest deuterium content (Fig. 9) bands are observed at 334/323 and 173/164 cm^{-1} (the first value refers to the protiated species and the second to the isotopomer with the highest deuterium content) that may be attributed to vibrations with a significant $M–OH_2/M–OD_2$ character, whereas the corresponding bands at 223 cm^{-1} and 205 cm^{-1} should be attributed to M–Cl modes. It is, of course, possible that some librational character could be present in the corresponding vibrational modes.

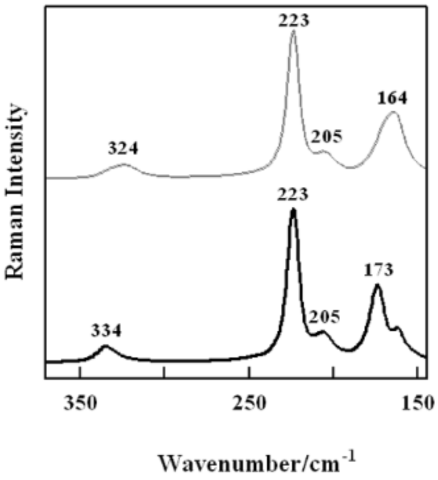


Fig. 9. Raman spectra of $CdCl_2·H_2O$ (lower curve) and its almost completely deuterated analogue (upper curve) recorded at LNT in the region of the HOH external vibrations.

CONCLUSION

This paper presents a detatiled interpetation of the vibrational spectra of crystalline cadmium chloride monohydrate, $CdCl_2·H_2O$, and its deuterated analogues. The analysis of the infrared and Raman spectra shows good agreement with the structural data. In the LNT infrared and Raman spectra of the protiated compound, one band, at 1583 cm^{-1}, is observed in the region of the bending HOH vibrations. An interesting finding related to this band is that its frequency is lower than that for the water molecule in the gas phase (1594 cm^{-1}), whereas in solid hydrates these frequencies are most often higher. Appearance of a band at such a low frequency in the region of HOH deformations can be correlated to the specific structural features of the water molecules in this compound.

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МНОГУ НИСКИ H–O–H ДЕФОРМАЦИОНИ ФРЕКВЕНЦИИ. VI. ВИБРАЦИОНИ СПЕКТРИ НА $CdCl_2·H_2O$

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Инфрацрвените и раманските спектри на $CdCl_2·H_2O$ и на неговите парцијално деутерирани аналози беа снимени на собна температура и на температурата на вриење на течен азот. Севкупните резултати од анализата на спектрите беа користени за асигнација на соодветните ленти. Во диферентниот инфрацрвен спектар на соединението со ниска содржина на деутериум (≈ 4 % D), снимен на собна температура, во подрачјто на валентните O–D е најдена една широка лента на околу 2590 cm^{-1}, додека во спектарот снимен на ниска температура се појавуваат две ленти (на 2584 cm^{-1} и 2575 cm^{-1}). Појавата на овие две ленти од валентни OD модови на изотопски изолираните HDO молекули укажува на постоење на две кристалографски различни водородни врски што е во согласност со структурните податоци. Во инфрацрвените и во раманските спектри на протираното соединение снимени на ниска температура, една лента, при 1583 cm^{-1}, е најдена во областа на деформационите HOH вибрации, чија фреквенција се снижува со намалување на температурата. Интересно е што фреквенцијата на оваа вибрација е пониска од онаа на молекулата вода во гасна фаза (1594 cm^{-1}). Во инфрацрвениот спектар снимен и на собна и на ниска температурата во областа на либрациите на молекулите вода (700 cm^{-1} – 400 cm^{-1}) се појавува само една многу интензивна лента на 560 cm^{-1}.

Клучни зборови: кадмиум хлорид монохидрат; инфрацрвени спектри; рамански спектри

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Short communication

THE LANGUAGE REQUIRES RESEARCH•

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This paper focuses on some of the more serious issues faced by the Macedonian language. One of them, is certainly the lack of a serious scholarly Macedonian grammar that shall be up-to-date with the development of the language which, like all other languages, is a complex adaptive system. Consequently, there is a lack of a historical grammar and modern language grammar. Another serious issue identified is the unfinished work on the Macedonian dialect dictionary and, in general, the inadequate care for dialectology. In the first part of the paper, we highlight the link between the need for greater linguistic research and the fact that this volume of the journal *Contributions* is dedicated to the marking of the 80th birthday of academician Bojan Šoptrajanov, our "honorary linguist".

Key words: Macedonian language, history of Macedonian language research, dialectology, historical grammar

Having the opportunity to take part in the celebration of the 80th birthday of academician Bojan Šoptrajanov, I would like to take advantage of it to also discuss the issues stated in the title of this paper.

Years ago, right after the establishment of the Research Center for Areal Linguistics at MASA (Macedonian Academy of Sciences and Arts), we the "centrists" bestowed the title of an honorary linguist to academician Bojan Šoptrajanov because we were impressed by his understanding of the tasks of linguistics, his real interest in the matters of our language, his publications dedicated to the scientific and professional terminology of his discipline – chemistry [1–10], as well as his frequent attendance and active participation in our linguistic events.

However, regretfully, this dedication to his language is not a typical attitude either for most Macedonians, or for his colleagues at the University or at MASA.

RESEARCH IS REQUIRED

On one occasion, when I was trying to explain the pressing need to publish a contemporary grammar of the Macedonian language, I heard a colleague commenting: "Grammar! We already have a grammar! I studied grammar… "

Macedonians, or rather Macedonian intellectuals, usually share a conviction that the established structure of the standard language, fixed down over 70 years ago, is a heritage that we need to nurture and to preserve its purity and inviolability. It never occurs to them that language is a living dynamic structure, with the best proof of the success of its standardization is the fact that this very same structure has shown to be resilient and capable of further development. The language is capable of evolving and adapting to the dynamic world which we live in, while the task of the linguists is to document and interpret the new phenomena and incorporate them in the new editions of the Macedonian Grammar… That is why, when I received the invitation to contribute to the volume dedicated to our honoree, I saw it as an opportunity to explain to our readers the extent to which the Macedonian linguistic library is impoverished and outdated.

HISTORICAL BACKGROUND

The primary scholarly grammar of the Macedonian language is the authorial monograph by

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•Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

Blaže Koneski [11], which has last been revised more than 40 years ago. To reiterate: an authorial monograph, an original work written by a genius poet and a linguist with a rarely seen intuition. It is a work that lends itself to new discoveries at every reading, while at the same time brings back memories of the many times when I came to Blaže with linguistic inquiries only for him to refer me to his Grammar where he had already resolved the issue in question. However, this is not a grammar intended for work with students, let alone younger children, because much of the information is implicitly incorporated in the text of the book. On top of that, during the past 40 years our world has undergone rapid change, intensive development and transformations, while linguistic theory has been upgraded and new theories have been developed bringing new interpretations. Parallel to this, Macedonian standard language has also been evolving, constantly being enriched and adapting to the changes in the society it lives and serves to. The language as it is, represents a so-called "complex adaptive system" – a working concept utilized by many exact sciences, one of which is linguistics.

The foundations of Macedonian linguistics during the early years of the young Republic were planned and laid with great thought and care, the process being lead and decisions made by specialists full of passion and love for their language and profession. Yet, in due time as they started to leave us, the awareness about the linguistic priorities got lost along the way. We have a series of monographs dedicated to specific components of grammar, such as syntax, word formation, idiomatic expression, yet they are harmonized neither from a theoretical, nor from a terminological point of view. Though, what is most evident is that their authors are not up to date with the developments in linguistic theory that are happening abroad, nor do they always follow or read each other's work, let alone discuss it publicly. The guidelines for lecturers and proofreaders have not been changed for the past 70 years, failing to take into account the changes that have occurred in the language itself. Our general care for the language which is declared at every possible occasion represents *de facto* a care for the immutability of the language, in other words it comes down to blocking its natural evolution.

Our Macedonian library lacks works which would illustrate the continued development of the Macedonian language system from its distinction from the old Slavic community until today. Unlike the customary practice in the Slavic northern countries where students are handed both a descriptive grammar and a historical grammar that depicts the history of the evolution of the grammatical system, the university curricula here only includes, unfortunately less and less, dialectology. This is understandable considering the fact that the standardization occurred quite late in the whole Slavic South, while dialects have remained quite alive and vibrant to this very day, containing the overall information about the pre-standard, mostly oral history of the language. Still, this aspect of dialectology as a linguistic branch of science is not sufficiently evaluated. In the work of B. Vidoeski [12–16], the Macedonian dialect complex is covered in its entirety and its evolution is presented along the main lines with a special focus on the western dialect as the basis for standardization. Yet, most readers, predominantly student readers, do not comprehend Vidoeski's works as a veritable history of the Macedonian language, while the existing studies on the history of the language by B. Koneski [17] or by P. Ilievski [18] only concern the so-called external history of the language, its contact with other languages, its presence in written documents, its social status, etc. The only exception (initiated by an outside scholar, Shevelov who was the driving force behind the series!) is the "Historical Phonology" by Koneski [19], which has recently been published in Macedonian to the satisfaction of all of us.

It is regretful that all the preparations for the development of a Macedonian dialect atlas which Vidoeski almost saw through to the end [15] (questionnaire with a rounded network of reference points, completed exploration, drafted demographic descriptions of the villages) were shelved after his death and the passing of Dr. Ubavka Gajdova. Even the card index is still to be digitalized, while its old discolored cards are slowly deteriorating.

If a linguist interested in Macedonian would come to visit us from abroad, we wouldn't be able to offer him or her either a descriptive or a historical grammar, let alone an atlas or a dictionary which meets any of the modern standards. Let's not even talk of "items of luxury" such as etymological dictionaries, terminological dictionaries or the like.

Fortunately (?!), we rarely have visits from foreign colleagues because our linguists have very limited contacts within international professional circles. So much for the promotion of the Macedonian language worldwide!. Yet, we need to point out that a comprehensive linguistic analysis of the Macedonian standard language and its dialects could offer a great deal of interesting information to all interested parties, not only about Slavic and Balkan linguistic relations, but also regarding the natural language itself and the directions of its evolution. The long centuries of mainly oral communication without any intervention from the norm have allowed the old and inherited – some even from ancient Slavic times – developmental tendencies to take further shape and evolve, while at the same time enabling the system to adapt to the multilingual Balkan environment.

The language is supposedly the most ideal incarnation of our thoughts, it is one of the essential keys to the understanding of the mechanisms of the functioning of the human brain… We can learn quite a lot, only if we allow it to develop spontaneously.

LOOKING TO THE FUTURE

Unfortunately (or maybe not...), we cannot import textbooks for learning Macedonian from Harvard or Oxford – they have to be developed here, by ourselves. For that to be achieved, we need a) societal support and b) human resources... Slowly, but surely, there is an ever growing group of young people who enjoy to read and think, and whose main interest is the Macedonian language. There is also ever growing support and understanding by the general public about the importance of the language for all of us and what our language needs and expects from us.

Our honoree should be given great credit for his contribution in the achievement of all of the above, for which I am deeply grateful to him. I hope that with his and the help of all that share his ideas and principles we shall be able to ensure that our scientific community, MASA, the universities, as well as the media are up to the task and overcome in a dignified manner all the challenges they face.

SUMMARY

This paper focuses on some of the more serious issues faced by the Macedonian language. One of them, certainly is the lack of a serious scholarly Macedonian grammar that shall be up-to-date with the development of the language which, like all other languages, is a complex adaptive system. Consequently, there is a lack of a historical grammar and modern language grammar. Another serious issue identified is the unfinished work on the dialectological dictionary and, in general, the inadequate care for dialectology. In the first part of the paper, we highlight the link between the need for greater linguistic research and the fact that this volume of the journal *Contributions* is dedicated to the marking of the 80th birthday of academician Bojan Šoptrajanov, our "honorary linguist".

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ЈАЗИКОТ БАРА ИСТРАЖУВАЊЕ

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Во трудот се набележани некои од сериозните проблеми со кои се среќава македонскиот јазик. Еден од нив секако е недостатокот на сериозна научна граматика на македонскиот јазик којашто ќе го следи развојот на јазикот кој, како и другите јазици, е комплексен адаптивен систем. Оттаму, недостасува *историска грамат- ика*. Како сериозен проблем е наведена недовршената работа на дијалектниот речник и, воопшто, недостатната грижа за дијалектологијата. Во првиот дел од трудот се посочува врската меѓу потребата за истражување на јазикот и фактот дека овој број на списанието *Прилози* е посветен на одбележувањето на 80-тиот роденден на академик Бојан Шоптрајанов, наш „почесен лингвист“.

Клучни зборови: македонски јазик; историјат на истражувањата на македонскиот јазик; дијалектологија; историска граматика

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Short communication

THE ROLE OF WHITESPACE IN NOTICING IN SCIENTIFIC DIAGRAMS•

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Scientic diagrams are one of the tools of explanation, alongside text. The paper is a part of research on the role of diagrams in learning, here focusing on what is known as whitespace. Whitespace, which is not always white, is often seen as empty space, that is space without content. However, many diagrams have active whitespace, such the green background in safety diagrams which indicates action to be taken, and is a positive colour. Some have red 'whitespace' indicating the danger of undertaking an action. These all promote 'noticing', that is, drawing features to the observers' attention as part of the diagram purpose. The paper explores two clear examples on safety diagrams (signs) and one where observers were unclear about what was whitespace and what was active content.

Key words: scientic diagrams; whitespace; empty space

INTRODUCTION

The role of diagrams in learning in science education is too often second place to text (words), even to the point of being central and dominant in many external assessment programmes. The PALAVA teacher researcher group (www.palava.wikispaces.com), physically located in the UK but having a virtual international membership, has been engaged in investigating representations (models) in science education for two decades. More recently PALAVA has targeted diagrams in science education. Our aims have been:

1. To characterise the distinguishing features of scientific explanatory and descriptive diagrams, as separate from the general category of illustrations and graphs;
2. To explore what observers notice in diagrams and, concurrently, develop the role of the Think Aloud Protocol as an investigative tool (e.g. Topsakal and Oversby 2012a, 2012b and 2013). By notice, we specifically refer to an active form of seeing that clarifies which features attract attention in the context of scientific explanation. The Think Aloud Protocol has been designed to probe tacit thinking by asking participants to share aloud this thinking with the researcher. Thinking Aloud contemporaneously seems to slow down the thinking processes, and often to stray into episodes of explanation, but is one of the best methods of exposing thinking. Recalled and stimulated Thinking Aloud Protocols are also used but can be subject to both forgetfulness and to rationalisation of immediate thinking.
3. To explore construction of diagrams by individuals and groups for creating a scientific explanation or description. PALAVA has continued to use the Think Aloud Protocol in these studies.
4. To investigate the role of tactile diagrams

I will use examples to indicate some of the issues involved. Much of the written material around whitespace comes from marketing and design contexts. We have so much to learn from other disciplines.

The Chinese Food Guide Pagoda

The Chinese Food Guide Pagoda (Food and Agriculture Organisation of The United Nations, 2007) below serves as a suitable diagram to demon-

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•Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

strate a typical diagram used in science education. It has elements of icons (pagoda shapes and a male person), diagrams of different kinds of food, and significant quantities of text, alongside important matters such as location.

Apart from the active components there is much space that is simply there but intended to be ignored. Traditionally, this space was white (the colour of the paper) and was termed whitespace. It indicates a part of a page that is not covered by print or graphic matter. However, in the food pagoda a part that is intended to be un-noticed is grey so that we can say that the whitespace is grey. In this article, 'noticing' is used in the sense of attracting definite attention, worthy of letting the mind dwell on its meaning in some way. The food pagoda diagram has other areas that I believe are not intended to be noticed. Each of the four pagoda levels has a background of a different colour. These do not appear to be significant, so could be treated as whitespace.

Salt	<6g
Cooking oil	25~30g
Milk and dairy products	300g
Soybeans and nuts	25~35g
Lean meats	40~75g
Fish	40~75g
Eggs	40~50g
Vegetables	300~500g
Fruits	200~350g
Cereals, tubers and legumes	250~400g
Whole grains and legumes	50~150g
Tubers	50~100g
Water	1500~1700ml

Active whitespace – safety signs that are diagrams

The ubiquitous safety sign indicating where to go in the event of a fire breaking out has a background of green (right). The green is not only whitespace but is a positive statement to carry out an action at a specific time. A group of science teacher educators 'noticed' the text, the arrow, the icon of the person, and the door, as prominent features. The green space was a sub-conscious feature. There is a green icon, the person, that is intended to be noticed. So, perhaps there are two kinds of green in this diagram. One is the green of an icon, and the other green is active whitespace.

The second safety sign (below) is also one that has active whitespace, red. This indicates danger.

When is it whitespace?

Finally, for this paper, the diagram below, of ground-source heat extraction, has a clear section of whitespace at the top, which can be termed passive whitespace. This kind of whitespace is simply a background on which the truck is imposed. There are two other spaces, which might be considered as whitespace by some, and not by others (as judged by some members of the PALAVA teacher researcher group). The light brown space that seems to be a background but could be a kind of rock, was seen by some to be whitespace. Similarly, the grey to the bottom and left was contentious. It may be that the notion of whitespace could act as a provocation for discussion about diagrams.

CONCLUSION

In this paper, I have attempted to illustrate some research thinking about diagrams, particularly about whitespace in diagrams. Firstly, whitespace is not so obvious, as intended, but when it is recognised as a significant part of a diagram, it may help us to understand the diagram better. Secondly, whitespace can be contentious, with the resulting arguments enabling researchers to drill deeper into the issue.

The whitespace research may eventually lead into a clear typology of various kinds of space in diagrams that could help in data analysis. At this stage, initial thinking is that macro-whitespace (space that is not simply the gap between text letters or lines of text) may be of three kinds:

- Whitespace that is non-contentious to most observers, being simply space that is not occupied by any content. Some designers call this passive whitespace.
- Whitespace that is not occupied by content but influences the observer, such as the green in the exit sign which is a go-colour. Designers often call this active whitespace.
- Whitespace that seems to be contentious, such as the grey and brown spaces in the last diagram. Using the Think Aloud Protocol on this kind of whitespace may be valuable in unearthing the subtle ways in which a diagram can be interpreted.

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УЛОГАТА НА БЕЛИОТ ПРОСТОР (WHITESPACE) ВО КРЕИРАЊЕ НАУЧНИ ДИЈАГРАМИ

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Научните дијаграми се едни од алатките за објаснување на текстот. Овој труд е дел од истражувањата за улогата на дијаграмите при учењето, со посебен осврт, во овој случај, на тоа што претставува белиот простор (whitespace). Белиот простор, којшто не секогаш е бел, често се гледа како празен простор, што претставува простор без содржина. Меѓутоа, многу дијаграми имаат активен бел простор, како што е, на пример, зелена позадина во сигурносни дијаграми која индицира преземање на акција и претставува позитивна боја. Некои имаат црвен 'бел простор' кој укажува на опасност од преземање на акција. Сите тие промовираат некој вид предупредување, односно сликовни карактеристики за привлекување на внимнието на набљудувачите како дел од целта на дијаграмот. Трудов истражува два чисти примера на сигурносни дијаграми и еден каде на набљудувачите не им било јасно значењето на белиот простор, односно активната содржина.

Клучни зборови: научни дијаграми; бел простор (whitespace); празен простор

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Original scientific paper

CONCEPTUAL UNDERSTANDING OF SOLUBILITY CONCEPTS AMONG FIRST-GRADE HIGH-SCHOOL STUDENTS[•]

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A study was conducted to inspect conceptual understanding of solubility concepts among first-grade students and to identify the potentially present misconceptions. A total of 122 high-school students (15–16 years old) were involved in the study and a solubility concept test was administered in order to get insight into their conceptual knowledge. Students were divided into two groups: control group and an experimental one. Only the experimental group was subjected to a conceptual change intervention program.

Descriptive statistics and significance testing were used to analyse and summarize data. Independent-samples *t*-test was used to test the differences in the scores between the control group and the experimental one and between male and female students involved in the study. For multiple-choice questions, four areas of conceptual understanding have been set: satisfactory conceptual understanding, roughly adequate performance, inadequate performance and quite inadequate performance. Furthermore, the findings revealed six misconceptions present in students' minds.

Key words: solubility; secondary- and high-school chemistry education; misconceptions; intervention program, conceptual understanding.

INTRODUCTION

Chemistry is a conceptual subject based on a number of abstract concepts. Thus, it is possible that students may not fully understand such concepts. Moreover, the chemical knowledge is acquired at three levels [1]: the macroscopic, the microscopic and the representational (symbolical) level. In many teaching practices, the microscopic level is neglected and students are being lead from macroscopic directly to symbolical level. Thus, it is likely that some misconceptions appear due to the fact that students do not distinguish between macroscopic and microscopic explanations [2–4]. Many misconcepttions concerning various science topics have been documented [5, 6] and many other investigations on misconceptions regarding solutions and solubility are known [7–9]. Still, not all erroneous notions are classified as school-made misconceptions [10]. Sirhan [11] claims that the development of misconceptions may originate from previous knowledge of students [12], the usage of everyday or specific scientific terminology etc.

This study was aimed to get insight into students' understanding of some solubility concepts and to check their capability to transfer their knowledge through the three levels of thinking as well as the ability to use graphs to plot the data. Another important segment in the study was to detect any misconceptions students may have regarding solutions and solubility. An integral part of the investigation was an implementation of the instructional program. Namely, this study was conducted to evaluate the effectiveness of intervention program on cognitive achievement towards solubility concepts of high-school students. The intervention program (that included deepened explanations, drawings, experiments and discussions) was implemented during instruction to facilitate understanding of solubility concepts among students.

[•] Dedicated to academician Bojan Šoptrajanov on the occasion of his 80th birthday

METHODOLOGY

Objectives of the study

The main objective of this study was to inspect the conceptual understanding of solubility concepts of first-grade students and to determine whether there are some misconceptions present. Also, students' ability to apply the microscopic level in their explanations and the ability to represent data graphically were tested. Furthermore, the study was aimed at evaluating the effectiveness of an intervention programme on students' achievements.

The following research questions were investigated:

1) Are the differences in the mean scores between the control and the experimental group statistically significant?
2) Is there a difference between male and female students in the testing?
3) Are there any misconceptions present in students' thinking (and what are they)?

Design

The study consisted of three parts: (1) information on the students' previous achievements in chemistry; (2) applying a conceptual change intervention program (CCIP) and (3) administration of the solubility concept test (SCT). CCIP included deepened explanations, discussions and simple experiments. Also, students were actively involved by writing and drawing what they see and what they think happens at microscopic level. The experiments carried out together in the class consisted of dissolving salt and sugar in water at different temperatures.

Research sample

The research sample comprised 122 first-grade high-school students from one high-school in Skopje, Macedonia (15-16 years old) in the 2015/16 school year. Students were divided into two groups: control group (CG) and experimental group (EG). Only the EG was subjected to the intervention program. Details concerning participants involved in the study are given in Table 1.

Table 1. Participants involved in the study

Group	Number of participants		
	Male	Female	Total
CG	22	35	57
EG	33	32	65
Total	55	67	122

Research instrument

The solubility concept test (SCT) was administered to both CG and EG approximately ten days after all class activities were finished in both groups. The test consisted of ten questions, two of which asked for microscopic level of understanding of the dissolution process, five were multiple-choice questions regarding solubility concepts, one involving the usage of graphs and two open-ended conceptual questions.

Data analysis

Maximum points for questions 1 and 2 was 1.5 each (0.5 for each correct drawing), multiple-choice questions (questions 3–7) were scored by 1 point for correct answer and 0 points for wrong one, and for other questions students could receive 1, 0.5 or 0 points for correct, partially correct and wrong answer, respectively. The maximum score for the SCT was 11. The test scores ranged from 0 to 9 points.

Means, standard deviations (SD) and significance testing were used to analyse and summarize data. Independent-samples *t*-test was used to test the differences between CG and EG and between male and female students involved in the study.

According to the literature [13] the percentage of students who correctly answered the question can serve as an indicator of conceptual understanding. Thus, for the multiple-choice questions, four areas of conceptual understanding have been set:

1) satisfactory conceptual understanding (SCU) if the correct answer is given by 75 % of the students or more;
2) roughly adequate performance (RAP) if this percentage is in a range 50–74 %;
3) inadequate performance (IP) for percentage range 25–49 % and
4) quite inadequate performance (QIP) if obtained frequency is less than 25 %.

Furthermore, a distractor (wrong answer) chosen by more than 20 % of the students has been considered a misconception [14].

RESULTS AND DISCUSSION

In this section several aspects are considered. Firstly, the analysis of each question will be given having in mind the potential misconceptions (research question 3), and then the research questions 1 and 2 will be investigated in more details.

The questions 1 and 2 test the students' understanding of microscopic level. Students were required to make drawings of particles of particular substances when dissolving table salt (question 1) and sugar (question 2) in water.

Table 2. Information of the percentage of students' answers in questions 1 and 2

	Question 1		Question 2	
Points	EG	CG	EG	CG
1.5	18	0	37	0
1	31	0	17	2
0.5	37	0	34	0
0	14	100	12	98

It seems obvious that little attention is paid on microscopic level in the teaching process. This level of teaching in chemistry is crucial in understanding the behavior of substances and many chemical phenomena. Thus, it is important to introduce activities and teaching methods to increase the students' achievements in this area. The results in the EG are not very satisfying, but improvement is unambiguously noticeable.

Questions 3–7 are multiple-choice questions and information on students' answers regarding these questions is given in the next table. The correct answer (or two accepted answers) is given in bold, and options that represent misconceptions are marked with asterisk.

From the table above it can be noticed that there is sound understanding of the tested knowledge in the third question in both groups, which is denoted as SCU (satisfactory conceptual understanding). Furthermore, no misconceptions have been identified in this question. Therefore, it can be concluded that students don't seem to have any problem classifying the solutions according to their saturation.

In the questions 4 and 5 the effect of temperature on solubility of solids (Q4) and gases (Q5) is considered. As a general rule, the increased temperature causes an increase of the solubility of solids in water, but there are some exceptions in which the substance is more soluble in cold than in hot water. Therefore, both options "a" and "d" were taken as correct ones. In both question 4 and 5 the performance of EG-students was higher than the one of CG-students. This is most likely due to the intervention program applied in the EG.

Two misconceptions were located in the question 5. Namely, the idea that solubility of gases increases as the temperature increases (option "a") were common in both CG and EG. Students seem to think that all substances (regardless of the state of matter) are more soluble at higher temperatures. There was another misconception present only in CG. Namely, 30 % of CG-students thought that the solubility of gases is independent of temperature (option "c").

The analysis of the questions 6 and 7 reveals two interesting notions. The first one is that students from EG and CG had diametrically opposite points of view about the effect of pressure on solubility of solids (question 6). CG-students thought that increased pressure leads to increasing solubility, and EG-group students' opinion was that solubility will decrease in this case. Both statements can be considered as misconceptions as more than 20 % of students have chosen the given distractor.

The second notion that should be mentioned is that CG-students were more successful in question 7 than the EG-students. There are also two misconceptions found in this question: 1) increased pressure leads to decreasing solubility of gases – 34 % of EG-students, and 2) the pressure doesn't affect the solubility of gases – 25 % of EG-students and 23 % of CG-students. Apparently, concepts tested in the last two questions are not well understood by students and more emphasize should be paid in the learning process.

Table 3. Information of students' answers in questions 3–7

		Percentage of students' answers		Area of conceptual understanding	
Question	Option	EG	CG	EG	CG
Q3	**a**	**98**	**91**	SCU	SCU
	b	0	2		
	c	2	7		
	d	0	0		
Q4	**a**	**82**	**61**	SCU	RAP
	b	11	7		
	c	5	19		
	d	**3**	**11**		
Q5	a	29*	42*	RAP	IP
	b	**62**	**26**		
	c	5	30*		
	d	2	0		
Q6	a	17	35*	IP	IP
	b	31*	11		
	c	**38**	**44**		
	d	11	7		
Q7	**a**	**37**	**60**	IP	RAP
	b	34*	11		
	c	25*	23*		
	d	2	3		

The findings of the last three questions in the test are rather interesting. CG-students were more efficient in giving full answer to the eighth question, which tested students' graphical interpretation of solubility. However, it should be pointed out that 62 % of EG-students have answered the question 8 (although partially) in comparison to total of 35 % of CG-students (giving full or partial answer). It can be concluded that generally EG-students were more successful in drawing a solubility graph to display solubility at different temperatures. Still, more effort is needed to obtain firm knowledge and sound concept understanding.

Questions 9 and 10 were designed as open-ended conceptual questions. EG-students performed well only in question 10. The reason for this is double. Namely, this question is somewhat related to the question 4, which tested the capability of understanding the correlation of solubility of solids and the temperature change. EG-students showed satisfactory conceptual understanding in question 4, and seem to being able to transfer this knowledge and give correct answer to question 10. Furthermore, this question has some similarities with one of the experiments that were carried out during the lesson, thus students found it more familiar and easier to answer. The percentage of students' answer to these questions is given in Table 4.

The list of misconceptions found as a result of implementing the solubility concept test to students is given in Table 5.

Next, regarding research question 1, an independent-samples *t*-test analysis was conducted to determine if there was any significance difference between achievements of CG-students and EG-students. The analysis revealed significant difference between these two groups of students (Table 6), which means that the intervention program had a positive effect on the learning process of this particular topic.

Table 4. Information of the percentage students' answers in questions 8–10

	Question 8		Question 9		Question 10	
Points	EG	CG	EG	CG	EG	CG
1	0	26	26	24	62	16
0.5	62	7	12	3	11	5
0	38	67	62	30	28	63

Table 5. The list of misconceptions detected by the solubility concept test

Misconception	Percentage of misconception found in EG	Percentage of misconception found in CG
Solubility of gases increases as the temperature increases (option 5a)	29	42
The solubility of gases is independent of temperature (option 5c)	Not found	30
Increased pressure leads to increasing solubility of solids (option 6a)	Not found	35
Increased pressure leads to decreasing solubility of solids (option 6b)	31	Not found
Increased pressure leads to decreasing solubility of gases (option 7b)	34	Not found
The pressure doesn't affect the solubility of gases (option 7c)	25	23

Table 6. Independent-sample *t*-test analysis results for intervention program effect on test scores

Group	*N*	Mean	SD	*t*	*p*
CG	57	4.07	1.47	–8.17	0.00
EG	65	6.46	1.72		

At this point, it is important to mention that the two groups were identical according to their previous achievements in chemistry. Namely, the results from the independent *t*-test analysis on students' grades given by their teacher indicate that there isn't any significance difference between EG and CG previous achievements, as can be seen from the Table 7.

Table 7. Independent-sample *t*-test analysis results for students' previous achievements

Group	*N*	Mean	SD	*t*	*p*
CG	57	3.19	1.27	–0.03	0.97
EG	65	3.20	1.61		

An independent-sample *t*-test was also run to investigate the gender effect on test scores (research question 2). The analysis did not yield any significant difference at 0.05 level between the mean scores of the responses by the females and those of the male participants in the study. The results are presented in the Table 8.

Table 8. Independent-sample *t*-test analysis results for gender effect on test scores

Gender	*N*	Mean	SD	*t*	*p*
Male	55	5.33	2.06	0.08	0.93
Female	67	5.36	1.97		

Having in mind the test results of the students, several points need to be addressed concerning this study. The higher scores in the EG showed that the intervention program was successful in facilitating understanding of solubility concepts, enabling students to gain more scientific explanations. Still, some misunderstandings and difficulties seem to be present among students that caused several misconceptions to emerge in both CG and EG.

There are two things that could be considered in teaching chemistry: 1) the "cognitive conflict" strategy [15] and 2) carefully introducing the new material (ideas or concepts) using visualization techniques (models, animations or computer software) [16, 17]. The latter is valid especially when three level of thinking are discussed. Although, some drawings and models are presented in the textbooks, it is the teachers' creativity to enrich the lesson using different teaching techniques.

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КОНЦЕПТУАЛНО ЗНАЕЊЕ ВО ВРСКА СО РАСТВОРЛИВОСТА КАЈ УЧЕНИЦИ ОД ПРВА ГОДИНА ГИМНАЗИСКО ОБРАЗОВАНИЕ

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Целта на ова истражување е испитување на концептуалното разбирање на концептот на растворливост кај ученици од прва година и идентификација на евентуално присутните мисконцепции. Во истражувањето беа вклучени вкупно 122 ученика од гимназиско образование (15–16 години) на кои им беше зададен тест на знаење од областа на раствори и растворливост за да се провери нивното концептуално знаење. Учениците беа поделени во две групи: контролна и експериментална. Само учениците од експерименталната група беа подложени на специјално дизајнирани упатства (инструкции) во текот на поучувањето.

За обработка на добиените резултати беше користена описна статистика и статистички тестови. За испитување на разликата во освоените бодови меѓу учениците од контролната и од експерименталната група, како и меѓу постигнувањата на момчињата и на девојчињата вклучени во истражувањето, беше искористен *t*-тест за парови независни примероци. Кај прашањата со повеќечлен избор беа идентификувани четири области на концептуално разбирање: задоволително, нецелосно, слабо и недоволно. Понатаму, врз основа на наодите од истражувањето беа откриени шест мисконцепциикај учениците.

Клучни зборови: растворливост, средно образование, мисконцепции, специјално дизајнирани упатства, концептуално разбирање.

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Found: C 81.63; H 9.36; O 9.01 %.
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Journals:

[1] J. Zhang, X. Wang, H. Xie, Phonon energy inversion in graphene during transient thermal transport, *Phys. Lett.* A, **377** (2013), pp. 721–726.

[2] G. Jovanovski, P. Makreski, B. Šoptrajanov, B. Kaitner, B. Boev, Minerals from Macedonia, *Contributions, Sec. Math. Tech. Sci*., MANU, **XXVI**, 1 (2005), pp. 7–84.

[3] A. Čarni, M. Kostadinovski, V. Matevski**,** Species composition and syntaxonomic consideration of two communities of the Drabo-Cardaminion hirsutae in the southern part of the Republic of Macedonia, *Acta Bot. Croat*., **62** (2003), pp. 47–56.

[4] D. Dimovski, A geometric proof that boundary links are homotopically trivial**,** *Topology Appl.*, **29** (1988), pp. 237–244.

[5] F. C. Oliveira, Á. C. Collado, L. F. C. Leite, Autonomy and sustainability: An integrated analysis of the development of new approaches to agrosystem management in family-based farming in Carnaubais Territory, Piauí, Brazil, *Agr. Syst.*, **115** (2013), pp. 1–9.

Books:

[1] J. A. Roels, *Energetics and Kinetics in Biotechnology*, Elsevier Biomedical Press, Amsterdam, New York, Oxford, 1983.

[2] H. Chum, M. Baizer, *The Electrochemistry of Biomass and Derived Materials*, ACS Monograph 183, American Chemical Society, Washington, DC, 1985, pp. 134–157.

[3] J. W. Finley, G. A. Leveille, Macronutrient substitutes, in: *Present Knowledge in Nutrition*, E. K. Ziegler, L. J. Filer Jr. (Eds), ILSI Press, Washington DC, 1996, pp. 581–595.

[4] Gj. Filipovski: *Characteristic of the Climatic and Vegetational Soil Zones in the Republic of Macedonia*, Macedonian Academy of Sciences and Arts, Skopje, 1996.

Scientific meetings:

[1] M. S. Steel, Creating woodlands for wildlife and people in Scotland, *18th Commonwealth Forestry Conference; Restoring the Commonwealth's Forests: Tackling Climate Change*, Edinburgh, Scotland, 2010, Book of Abstracts, p. 3.

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