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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 $^{\circ}C$ 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 $^{\circ}C$.

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 devel-

opment 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 N₂, 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 envelopes. 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 C₃, C₅, C₆, C₇ and C₉ 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 C₆₀ and C₇₀. The availability of laboratory hot carbon vapor infrared spectra and infrared astronomical observations provide comparisons. Such a comparison is shown in the Figure 1.

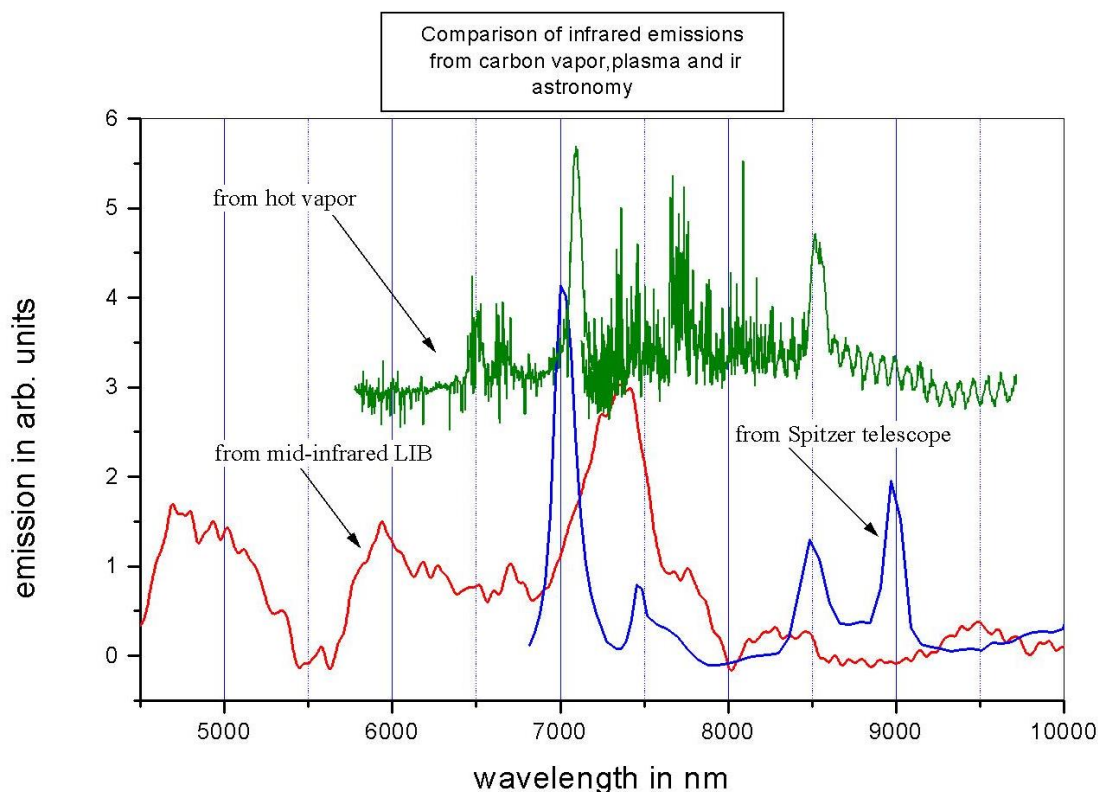


Figure 1. A comparison of different infrared emission spectra of carbon vapors and plasmas.

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 пари 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 C₆₀, C₇₀, 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 пара; кластер; инфрацрвени емисиони спектри; FTIR; LIBS; ласерски индуцирано разложување; астрономија