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Mid infrared emission spectroscopy of carbon plasma

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ABSTRACT

Mid infrared time-resolved emission spectra were recorded from laser-induced carbon plasma. These spectra constitute the first study of carbon materials LIB spectroscopy in the mid infrared range. The carbon plasma was induced using a Q-switched Nd: YAG laser. The laser beam was focused to high purity graphite pellets mounted on a translation stage. Mid infrared emission from the plasma in an atmospheric pressure background gas was detected by a cooled HgCdTe detector in the range 4.4–11.6 μm , using long-pass filters. LIB spectra were taken in argon, helium and also in air. Despite a gate delay of 10 μs was used there were strong backgrounds in the spectra. Superimposed on this background broad and noisy emission bands were observed, the form and position of which depended somewhat on the ambient gas. The spectra were digitally smoothed and background corrected. In argon, for instance, strong bands were observed around 4.8, 6.0 and 7.5 μm . Using atomic spectral data by NIST it could be concluded that carbon, argon, helium and nitrogen lines from neutral and ionized atoms are very weak in this spectral region. The width of the infrared bands supports molecular origin. The infrared emission bands were thus compared to vibrational features of carbon molecules (excluding C_2) of various sizes on the basis of previous carbon cluster infrared absorption and emission spectroscopic analyses in the literature and quantum chemical calculations. Some general considerations are given about the present results.

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1. Introduction

Infrared absorption spectroscopy has been the mainstay in chemical structural analysis since a long time. Infrared emission has also been harnessed in chemistry, physics and especially in astronomy to study molecules in terrestrial and cosmic sources. Very good treatises may be found in the literature summarizing principles and applications of infrared emission spectroscopy [1–3]. In the past two decades Fourier transform spectroscopic methods have been extended to time-resolved studies of infrared emission (e.g. in plasma analysis [4]). This method however requires complicated equipment and has not been adopted on a large scale, especially not for field applications.

Following the initiatives of Alan C. Samuels at the Edgewood Chemical Biology Center between 2000 and 2002, in the past decade a new approach has been elaborated for the study of infrared emission spectroscopy from laser-induced breakdown (LIBS) plasmas [5–11]. The use of fast and sensitive cooled photo-conductive detectors such as InSb and HgCdTe (MCT) made it possible to apply this direct detection

method for stand-off field analysis of various materials using relatively simple optical constructs.

The main advantage of using infrared methods in LIBS analyses over traditional visible/UV spectroscopy is that molecular vibrational features may be observed. In conventional LIB spectroscopy electronic transitions are detected only up to a maximum of triatomic molecules. In the mid infrared (fingerprint) region on the other hand vibrational spectra of all molecules that possess infrared active vibrations are routinely found.

The science of carbon had a 'renaissance' following the chemical Nobel Prize winning (1996) discovery of the fullerenes in 1985 and their macroscopic preparation five years later [12–14]. A huge number of papers have been published in the following years on fullerenes and other carbon clusters. The size of this literature is far too large to reference it here. Some aspects of the field are surveyed in a review book published five years ago [15]. Conventional UV/visible LIBS analyses carried out for carbon plasmas so far have not yielded proof for the existence of large carbon molecules (the largest detected so far being the C_3 radical). Laboratory observation of larger carbon molecules in plasmas are of direct interest to nanomaterial science and infrared astronomy [16,17]. We have undertaken an exploratory study of mid infrared emission spectra obtained from laser generated carbon plasmas and report the results here. To our knowledge this is the first such study in the literature.

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2. Experimental

The measurements were conducted at pump energy of ~ 50 mJ using an actively Q-switched Nd:YAG pulsed laser (1064 nm) with 5 ns pulse width, 10 Hz repetition rate. The laser beam was focused with a lens (focal length = 5 cm) onto a high purity graphite pellet cut from rods (NAC Carbon Products: NAC-500 extruded graphite rod) leading to a beam diameter of ~ 0.2 mm (fluence ≈ 40 J/cm²). The pellet was affixed to a linear translation stage controlled by a stepper motor using motion controller. The stage was translated at a speed of about 1 mm/min to provide fresh surfaces for subsequent laser pulses. Two ZnSe lenses (focal length = 10 cm) were employed as collection optics to focus the infrared emission onto the entrance slit of a 0.15 m spectrometer. The emission was dispersed using a grating blazed at 8 μ m and a liquid nitrogen cooled single element MCT detector for detection in the 8–12 μ m region (then between 4.5 and 12 μ m). Scattered laser light and higher order spectra were removed by low-pass filters cutting at 4 and 7.4 μ m. The entrance and exit slits of the spectrometer were 2 mm wide. The spectral resolution was about 80 nm. The spectral range above was scanned at intervals 4400–5600, 5600–6800, 6800–8000, 8000–9200, 9200–10,400 and 10,400–11,600 nm using scanning speed 100 nm/min. The total scan was around 1 h. After one scan the sample mount was laterally displaced so that the next scan had new surface. Signals from ten spectra were averaged using a boxcar with 10 μ s delay and 16 μ s gate-width.

The infrared LIBS apparatus was placed in a plastic box taped up to stop environmental air and humidity getting into the box. The whole volume was purged, for instance, by ultra-pure grade 5.0 argon gas. Twenty minutes purging time was allowed before starting the LIBS

measurements. Fig. 1 shows the experimental setup of the mid IR LIBS emission.

3. Spectra

Figs. 2–4 show raw spectra using helium, argon or air as background gases in the wavelength range 8–11.5 μ m. The room temperature spectrometer background was obtained by recording emission from the spectrometer housing in the absence of the laser impulses. This background can be safely ignored as it is almost flat and nearly zero throughout the spectral range.

Fig. 5 shows a processed spectrum between 8 and 11.5 μ m in helium.

Processed spectra were obtained from the raw experimental spectra in Figs. 2–4 via a de-noising process using the astronomy software SPLAT from the website given in [18].

Using SPLAT one is able to apply various filters to re-bin or average a spectrum and correct for backgrounds. In Fig. 5, a Welch window was used that removed most of the noise and suppressed ‘channelling’ (interference fringes) arising from the presence of the long pass laser-light filter (see Fig. 1).

The spectral background in Figs. 2–4 increasing towards higher energies was fitted by a third-order polynomial and subtracted from the spectrum. (In Fig. 4 the spectrum in air was so much overlapped by the instrument background that processing was abandoned.) Possible sources for this background are discussed in Section 4. The correction for relative intensity effects due to the instrumental transfer function was neglected as we were not studying intensities. A similar processed spectrum taken in argon in the same spectral range is shown in Fig. 6.

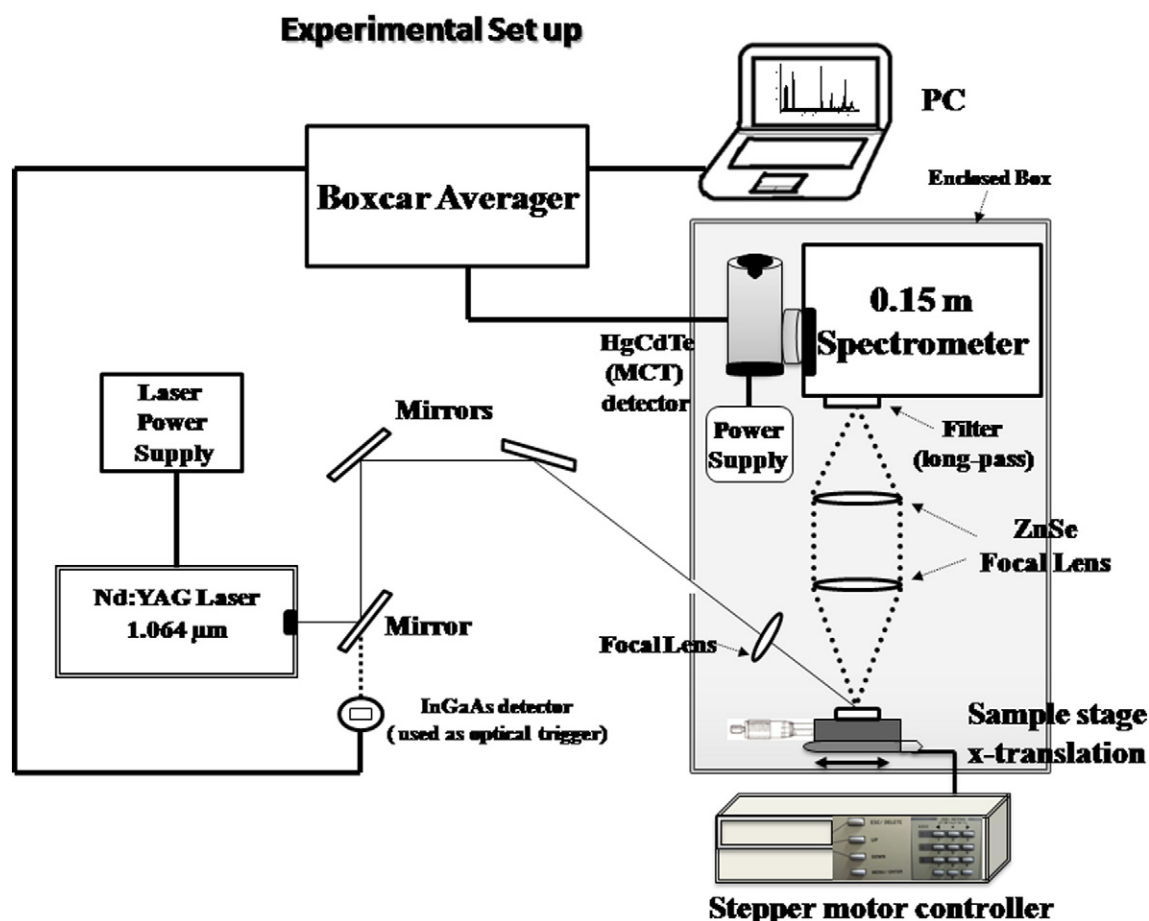


Fig. 1. Schematic diagram of the experimental setup for the infrared LIBS emission.

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