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An apparatus for *in situ* Raman spectroscopy of ion-irradiated frozen targets

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A novel experimental apparatus designed to study, using *in situ* Raman spectroscopy, chemical and structural modifications induced by ions impinging on frozen gases and solids at low temperatures (10–300 K) is described.

I. INTRODUCTION

We developed an experimental apparatus for Raman spectroscopy of frozen gases and solids during their irradiation with ions having energies in the keV range.

For several years many experimental results have been obtained on the chemical and physical changes induced by ion and electron irradiation of materials with a view to their astrophysical relevance.[1–6] Among the studied effects, one of particular interest is the formation of an organic refractory residue left over after ion irradiation and warming up at room temperature. At energy depositions greater than $\simeq 50$ eV/carbon atom, this residue evolves towards what we call ion-produced hydrogenated amorphous carbon (IPHAC).[1] However, although *in situ* infrared spectroscopy points out the formation of new molecular species during bombardment at low temperature[7] it is not clear if IPHAC is already formed or if its formation is triggered by temperature increase during warming up of the irradiated target.

Raman spectroscopy could, in principle, give valuable information on the effects induced by ions impinging on solids at low temperature. Indeed this technique has both the ability to distinguish between chemical species and can provide valuable evidence on the structural properties of materials and, in particular, of carbonaceous materials.[8] Raman spectroscopy has been used in fact to obtain insight in the structural lattice damage of solids resulting from ion bombardment.[9,10]

II. EXPERIMENTAL APPARATUS

A. Spectrometer

A schematic block diagram of the experimental apparatus is shown in Fig. 1. The Raman spectrometer is a SPEX 1488 double monochromator equipped with two holographic gratings (1800 grooves/mm) to which an OMA III (EG&G Princeton Applied Research) intensified reticon was faced as detector. The monochromator has a spectral dispersion of $\simeq 1.333$ nm/mm corresponding (one diode is 25 μm wide) to $\simeq 0.0333$ nm/channel. The maximum spectral resolution of this system (obtained for a width slit less than 100 μm) is 4–5 cm^{-1}. The exciting laser is a 300-mW multilines Ar laser.

In the nominal operation of the detector, the diode-array chip was cooled to -5 °C by a Peltier cooler to reduce the dark current of the diode array; dry N_2 gas was used to purge the cold detector to avoid frost. Using this system about 20 photons at 500 nm correspond to "one count."

We wrote a base code spectrometer driver by using the programming keystroke facility available on the OMA III computer console. This code drives the gratings allowing both direct positioning in Raman shift, and data acquisition on the spectral region covered by the multichannel (limited to 330 pixels, approximately 10 nm, by an intermediate monochromator slit, in order to reduce the straight light level). The code also provides data acquisition in contiguous spectral regions (approximately 2 nm wide overlapping region), the data are stored in RAM memories as intensity versus pixel position number. Furthermore the code automatically provides background subtraction, for each grating position, by switching off the laser beam with a shutter.

The data-acquisition procedure is controlled by a basic program written on a master computer constituted by an IBM PC/AT connected to the OMA one via a standard RS-232 input/output interface. The basic program yields flat-field correction and assembling of the contiguous spectral regions by converting the pixel position numbers, on each gratings position, to Raman shifts. Exposure time, number of scans and spectral range (Raman shift) are all programmable parameters.

B. Scattering chamber

The scattering chamber, a stainless-steel cube with sides of 7.5 cm, was designed to allow both easy mounting to the vacuum system through two DN 40 standard flanges, as well as its setting in the 1439 sample compartment of the 1488 Spex monochromator. The chamber has been mounted to our vacuum system using one of those flanges with an ion gun (3-keV Varian ion gun) facing it; the closed-cycle helium cryostat has been attached to the other flange. On the remaining four faces of the cube we have mounted glass windows: One transmits the laser light to the sample, another transmits the Raman-scattered light to the detection system.

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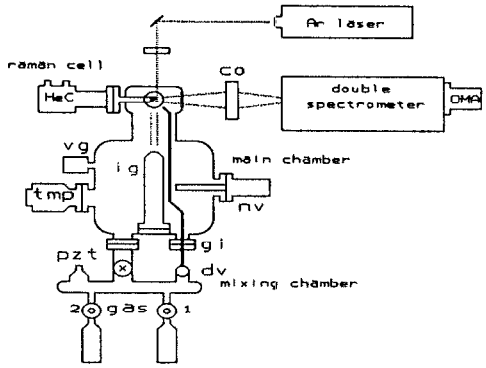

FIG. 1. Schematic view of the experimental apparatus. co: collecting optics; dv: dosing valve; gi: gas inlet; He c: Helium cryostat; ig: ion gun; nv: nitrogen vessel; pzt: piezo electric transducer; tmp: turbomolecular pump; vg: vacuum gauge.

A schematic view of the scattering chamber is shown in Fig. 2. We use a 90° scattering geometry. The direction of incident and collected light, as well as the direction of the ion beam, are mutually perpendicular. The studied species are condensed, by admitting a single gas species or mixtures prepared in a mixing chamber (see Fig. 1) into the scattering chamber through a needle valve, on a substratum (silicon). The substratum is in thermal contact with a copper cold finger attached to the tail section of a closed-cycle helium cryostat, whose temperature can be varied in the range 10–300 K. The cold finger has been designed to avoid the collection of laser light reflected in the specular direction by the monochromator collimating lenses; for this reason, the surface where the substratum is placed, has been oriented at 30° with respect to the incident

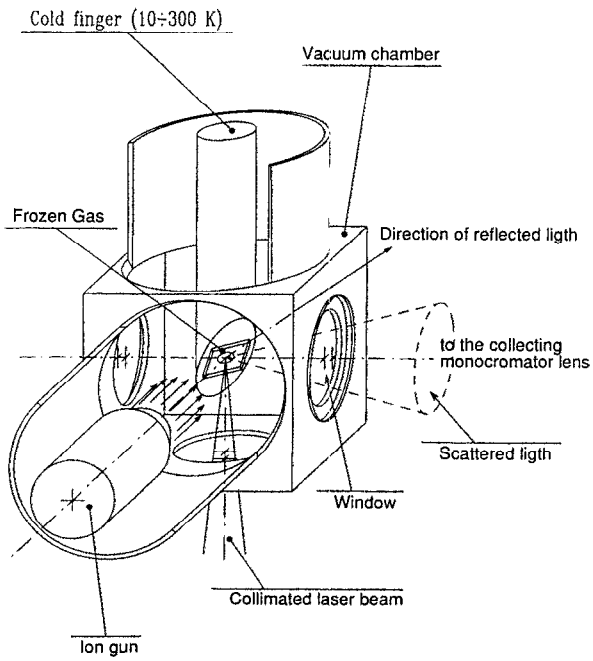

FIG. 2. Schematic view of the scattering chamber.

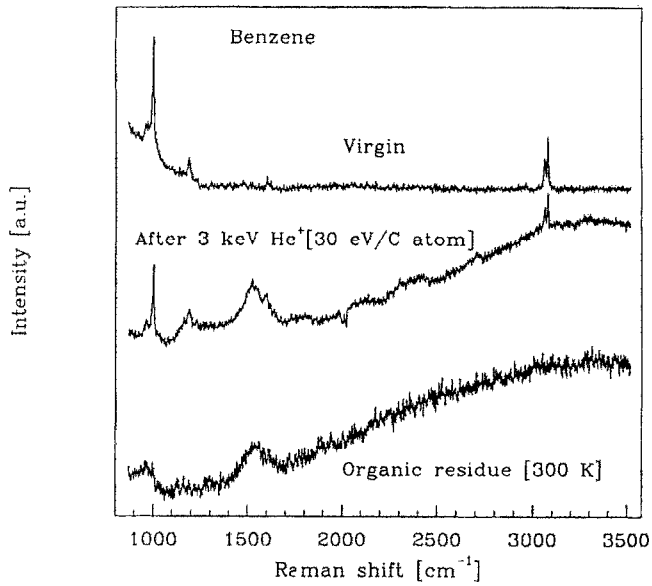

FIG. 3. Raman spectra of frozen benzene: as deposited (77 K), during irradiation with 3-keV He ions (77 K) and the organic residue (300 K) left over after ion irradiation.

laser light, and it is azimuthally rotated (around the cold finger vertical axis) 45° with respect to the ion-beam direction (see Fig. 2).

The vacuum system ($P < 10^{-7}$ mbar), the scattering chamber, and the ion gun have been assembled on a movable rack in order to allow a preliminary positioning in the monochromator sample compartment. The final alignment is obtained through a fine x-y adjustment in a plane orthogonal to the direction of the collected light, by maximizing the signal from the 525-cm^{-1} Raman peak of the clean silicon substratum.

III. RESULTS AND DISCUSSION

The performance of the apparatus was investigated by collecting Raman spectra during irradiation of frozen benzene and highly oriented pyrolytic graphite (HOPG).

A benzene film (about 2 μm thick) obtained by slow-rate deposition ($\simeq$0.11 μm/min) on the substratum (T=77 K), was irradiated with 3-keV He$^+$ ions. Some spectra are reported in Fig. 3: (from top to bottom) as deposited, after 30 eV/carbon atom, and after warming up at room temperature. All of the spectra in the figure were obtained by using the 514-nm argon laser line, with an output power less than $\simeq$40 mW. The incident light was with the electric vector orthogonal to the plane of scattering; the scattered-light polarization was not analyzed. The entrance slit width was 0.1 mm, corresponding to a resolution of about 5 cm^{-1} and the exposure time was 3 s$\times$ 30 scans = 90 s in each spectral region (see Sec. II). It is interesting to note that in the irradiated sample a newly formed broad band at $\simeq$1600 cm^{-1}, typical of amorphous carbon or hydrogenated amorphous carbon,[8,11] appears in addition to the benzene ones. The appearance of such a

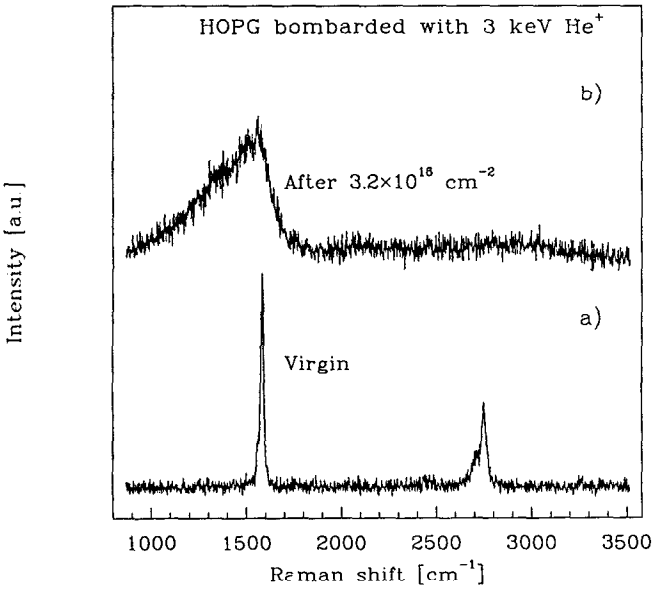

FIG. 4. Raman spectra of highly oriented pyrolytic graphite: (a) as prepared and (b) after irradiation with 3-keV He ions.

structure points out that IPHAC had been already formed during bombardment at low temperature.

In Fig. 4 Raman spectra of HOPG graphite before and after ion bombardment (3-keV He^+; total fluence 3.2×10^{16} cm^{-2}) are shown. The spectra were obtained by using the 488-nm argon laser line (20 mW output power). The entrance slit width was 0.2 mm, corresponding to a resolution of $\simeq 10$ cm^{-1}. The remaining acquisition parameters were the same as above. The peak in spectrum 4(a) at $\simeq 1585$ cm^{-1} is the symmetry-allowed E_{2g} Raman active mode in crystalline graphite. Upon bombardment this band evolves into a broad asymmetric band [spectrum 4(b)] that has been interpreted as being a distinct indication of amorphous graphite resulting from ion-bombardment-induced lattice damage.[9]

The results here illustrated confirm that the system is able to detect, in a very simple way, the Raman signal of frozen gases and solids at low temperature during ion bombardment. Solid targets (e.g., graphite, silicon, etc.) can be investigated usefully; for instance, since the system enables one to obtain Raman spectra from the same scattering surface of the sample, at different fluences, lattice damage versus fluence can be studied in a very quick and reliable way.

We plan to improve the apparatus by using a triple monochromator (with a double-filter stage) instead of the double one. Indeed, owing to the relative large width of the "modified" intermediate slit (see Sec. II), the straight light rejection is not always satisfactory enough in the double monochromator; this is particularly true at the low Raman shifts and for samples with strong and extended continua (e.g., fluorescent materials).

ACKNOWLEDGMENT

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