Macromol. Symp. **2005**, *220,* 165-175

Vibrational Spectroscopy of Ion Irradiated Carbon Containing Macromolecules

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Summary: A large variety of carbon rich macromolecules has been studied in our laboratory, before, during, and after ion irradiation (3-60 keV ions), by *in situ* IR and Raman spectroscopies. In this paper we present results obtained on: (a) Films of frozen H_2O:CH_4:N_2 mixtures that have been deposited at low temperature (12 K) on a silicon substrate, and irradiated with fast ions. Irradiation causes the formation of organic refractory residues whose spectra have been recorded and studied also after further irradiation at room temperature. (b) Pentacene (a Polyciclic Aromatic Hydrocarbon, PAH) whose Raman spectra have been studied also during ion irradiation at room temperature. (c) Thin samples of fullerene (C_{60}) films also irradiated at room temperature.

Here we discuss some of the most relevant results and compare the spectra of the very different samples that after prolonged irradiation, evolve towards amorphous carbons that have common spectral characteristic. The results are discussed in terms of their astrophysical relevance. It is demonstrated that frozen hydrocarbons, PAHs and fullerenes are rapidly converted to amorphous carbon in space. Amorphous carbon has to be a widespread material in many astrophysical environments.

Keywords: fullerenes; ices; infrared spectroscopy; ion irradiation; PAHs; Raman spectroscopy

Introduction

A large variety of carbon rich macromolecules has been studied in our laboratory, before, during, and after ion irradiation (3-60 keV ions), by *in situ* IR and Raman spectroscopies. The studied materials include: films of frozen hydrocarbons (benzene, methane, butane, acetylene, etc.) pure or mixed with O and/or N bearing species, that have been deposited at low temperature on a substrate, and irradiated with fast ions. Irradiation causes the formation of an organic refractory

DOI: 10.1002/masy.200550213

residue.[1,2] Commercially available graphite[3] and amorphous carbon[4] grains prepared by arc discharge in controlled atmospheres. PAHs (coronene, pentacene, etc.) whose IR and Raman spectra have been studied also during ion irradiation.[5] Thin samples of fullerene (C_{60} and C_{70}) films obtained by depositing some drops of a fullerene-CS_2 diluted solution on a substrate and allowed to evaporate to leave a uniform microcrystalline fullerene film.[6,7]

Here we present recent results obtained on: (a) films of frozen H_2O:CH_4:N_2 mixtures that have been deposited at low temperature (12 K) on a silicon substrate, and irradiated with 30 keV He^+ ions. Irradiation causes the formation of an organic refractory residue whose spectra have been recorded and studied also after further irradiation at room temperature. (b) Condensed pentacene whose Raman spectra have been studied also during ion irradiation at room temperature. (c) Thin samples of fullerene (C_{60}) films also irradiated at room temperature.

We discuss some of the most relevant results and compare the spectra of the very different samples that after prolonged irradiation, evolve towards amorphous carbons that have common spectral characteristic. The results are discussed in terms of their astrophysical relevance. It is demonstrated that frozen hydrocarbons, PAHs and fullerenes are rapidly converted to amorphous carbon in space. Amorphous carbon has to be a widespread material in many astrophysical environments.

Experimental

Infrared or Raman spectroscopy have been performed in a stainless steel vacuum chamber facing an FTIR spectrometer (Bruker Equinox 55) or a Raman spectrometer.[8] For Raman analysis a continuous (514.5 nm) Ar^+ ion laser beam enters a confocal optical system arranged in such a way that any parallel beam incident along the optical axis in the opposite direction of the laser is focalized onto the entrance slit of the spectrometer (Triplemate SPEX). Two flat mirrors are used to reflect the laser beam towards the vacuum chamber, where it is focused on the sample. The Raman scattered light is collected by the same objective and it is collimated into a parallel beam reflected back along the same path of the laser, in the optical axis of the confocal illuminator.

Inside the vacuum chamber pressure is below 10^{-7} mbar and a silicon crystal substrate is placed in thermal contact with a cold finger whose temperature can be varied between 10 K and 300 K. The vacuum chamber is interfaced to an ion implanter (Danfysik 1080-200) from which ions with energy up to 200 keV (400 keV for double ionizations) can be obtained. The ion beam produces a 2x2 cm^2 spot on the targets and currents in the range of 100 nA cm^{-2} to tens of μA cm^{-2}. A needle valve is used to admit pre-prepared gas mixtures into the chamber, where they freeze on the substrate. Solid samples are simply mounted in contact with the cold finger.

The substrate holder is mounted at an angle of 45° both with the ion beam and with the incoming Raman laser beam (or the IR beam), so that spectra can be easily taken *in situ*, even during irradiation, without tilting the sample.

Frozen hydrocarbons

Ion irradiation of frozen mixtures containing carbon bearing species leads to the production of new species, among which a not-volatile refractory residue. Residues are made of carbon suboxide polymers if the only constituents the icy mixtures are C and O bearing molecules[9,10] and of an organic cross linked "polymer like" macromolecular material if the carbon bearing ice is an hydrocarbon or the mixture contains H and C bearing molecules with or without N and O bearing species.[1,8,11,12]

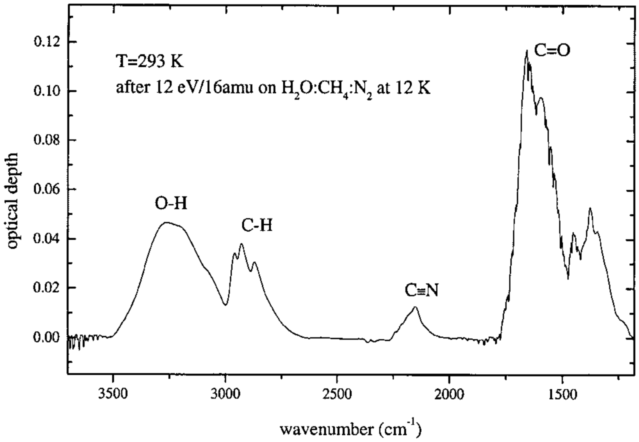

Figure 1. Infrared spectrum of the residue left over at room temperature after ion irradiation of a mixture H_2O:CH_4:N_2 with 30 keV He$^+$ (12 eV/16amu) at 12 K. The spectrum has been taken after the sample has been left at room temperature under vacuum overnight.

Figure 1 shows the IR spectrum in the 3700-1200 cm^{-1} region of the residue left over after ion irradiation of a mixture H_2O:CH_4:N_2 (=1:1:1) irradiated at 12 K with 30 keV He$^+$ ions. The amount of energy released by ions to the target molecules was 12 eV/16amu. This spectrum has been taken after the sample has been left under vacuum overnight at room temperature. The absorption features due to O-H, C-H, C≡N and C=O groups which are part of a polymer-like solid are easily identified.

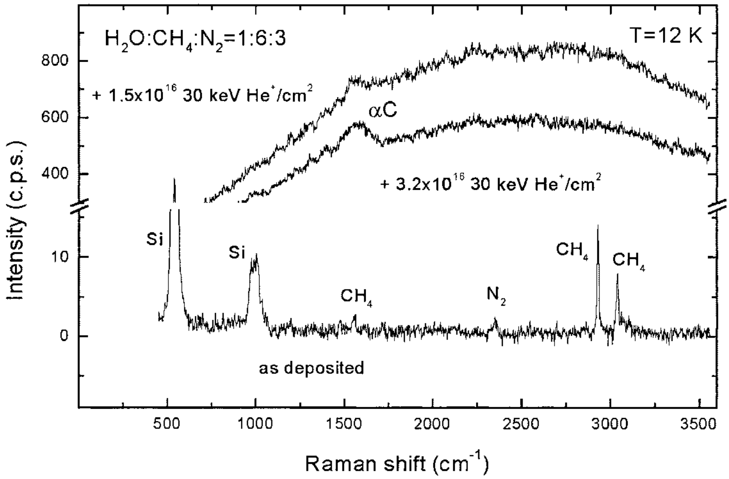

Figure 2. Raman spectra of a mixture H_2O:CH_4:N_2 as deposited at 12 K and after irradiation with 30 keV He$^+$ ions at two different fluences.

Further irradiation of organic residues exhibiting spectra similar to the one shown in Figure 1 causes a progressive carbonization with loss of H, N, and O. At high doses an amorphous carbon that we call IPHAC (Ion Produced Hydrogenated Amorphous Carbon) is left over[1,8]. Amorphous carbon has no easily detectable IR bands. Thus the question arises to see if amorphous carbon is already produced at low T or if it is formed during the warm-up of the target to room T. Raman spectroscopy is a technique capable to answer that question. In the bottom of Figure 2 the Raman spectrum of a mixture H_2O:CH_4:N_2 (1:6:3) as deposited at 12 K on a silicon substrate is shown. The thickness of the deposited layer is about 5 microns such that the laser light reach the silicon substrate that exhibits, in the Raman spectra, two bands. Bands due to frozen methane and nitrogen are also detected. It is interesting to note that nitrogen, an omonuclear molecule, has not IR active vibrations (although in the solid phase a very weak band can in some instances be detected because of the loss of the symmetry) but it is more easily detectable in the Raman spectrum. Viceversa water ice, that has a very intense band at about 3200 cm^{-1} in the IR (O-H stretching), is not detectable in the Raman spectrum of Figure 2 due to its low intrinsic strength. In the same Figure 2 two more spectra are shown as obtained after irradiation with 30 keV He$^+$ ions at two different fluences. The top spectrum, obtained after 1.5 x 10^{16} ions/cm^2, exhibits an intense photoluminescence continuum that masks all of the Raman bands but one newly formed at about 1550 cm^{-1} and easily attributed to amorphous carbon. This is a proof of the formation of IPHAC already at low T, a general result that has been also found for a variety of irradiated hydrocarbons and that has important astrophysical consequences[1, 8]. It has been in fact inferred that the suggested formation of a cometary crust by cosmic ion irradiation does not requires a passage of the comet near the Sun (i.e. heating) but can occur during the long time (4.6 x 10^9 yrs) spent by a comet, at low T, far from the Sun.[13]

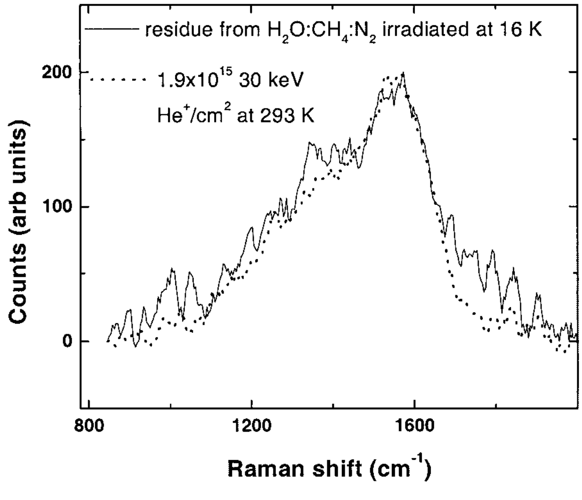

Figure 3. Raman spectra of the residue left over at room temperature after ion irradiation of a mixture $H_2O:CH_4:N_2$ (see Figure 2) and further irradiation with 30 keV He$^+$ ions. The shape of the feature due to amorphous carbon observed in the two spectra is compared, after normalization.

Further irradiation at low T (see the spectrum in the middle of Figure 2) produces a decrease of the photoluminescence continuum and an increase in the intensity of the band due to the amorphous carbon.

In Figure 3 we show the Raman spectra of the residue left over at room temperature after ion irradiation of a mixture H_2O:CH_4:N_2 (see Figure 2) and after further irradiation with 30 keV He^+ ions. The shape of the feature due to amorphous carbon observed in the two spectra is compared, after normalization. We can see that the two spectra, although slightly different, are both representative of high disordered amorphous carbon.

Fullerenes and PAHs

Some drops of fullerene (C_{60} or C_{70}) dissolved in CS_2 solutions have been deposited over a substrate of polished monocrystalline silicon and allowed to evaporate to leave a uniform microcrystalline films with thickness that varies between about 1 and about 4 micrometers. The obtained films have been irradiated, at room temperature, with 30 keV He^+ ions and the induced effects studied by Raman and IR spectroscopies.[6,7] Because those samples are sensitive to the laser beam used for the Raman spectroscopy, the Raman spectra have been recorded under Ar atmosphere at low laser power (15 mW). Thus for each Raman measurement, the ion irradiation has been stopped and Ar has been admitted into the chamber to record the spectrum. Then the irradiation was re-started after having restored the original vacuum conditions.

The penetration depth of 30 keV He^+ ions in carbons (assuming a density of 2.6 g cm^{-3}) is of about 3500 Angstrom i.e. lower than the thickness of the samples. This means that only a fraction of the film has been irradiated. However Raman spectroscopy is a surface analysis and sounds the sample to depth lower than the penetration depth of the ions i.e. at depths where the laser light penetrates. Moreover, as the irradiation proceeds, the irradiated sample become more absorbing as demonstrated by IR spectroscopy.[6] In Figure 4 we show the Raman spectra obtained for an as prepared C_{60} sample and that obtained after irradiation at different fluences of He^+ ions: $0.1 \times 10^{15}/cm^2$, $0.5 \times 10^{15}/cm^2$, $3.0 \times 10^{15}/cm^2$. Spectra have been offset for clearness. We note that, already at the lowest doses the photoluminescence continuum, evident in the unirradiated sample at Raman shifts higher than 2000 cm^{-1}, is strongly reduced and disappears at the higher fluences.

The spectral difference between the pristine C_{60} and the irradiated one at the lowest dose involve mainly the shift of the pentagonal-pinch mode band originally located at 1476 cm^{-1} to 1464 cm^{-1}; a similar shift toward shorter wavenumbers can be observed also for the band originally located at 1444 cm^{-1} which shifts to 1438 cm^{-1}. These spectral changes have been be interpreted in terms of oligomerization, that occurs for C_{60} also during UV photolysis[14,15] and γ radiolysis.[16] Such an oligomerization has not been noticed for C_{70}.[7] From Figure 4 we can also see a progressive decrease of the original bands that results in the production of amorphous carbon.

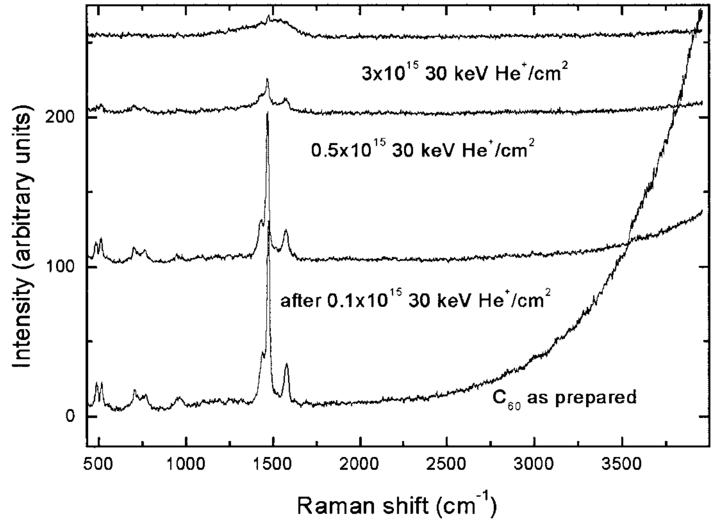

Figure 4. Raman spectra of the as prepared C_{60} sample and those obtained after irradiation at different fluences. Spectra have been offset for clearness.

Samples of Polyciclic Aromatic Hydrocarbons (PAHs) targets have been irradiated with 3 keV He ions. The penetration range of these ions is only few x 10^{16} molecules/cm^2. Targets were prepared in vacuum, on silicon substrata, by putting the chosen PAHs dust inside a "broken" bulb of a tungsten lamp. When the lamp is switched on, the dust sublimates and condense on the substratum. In this way films as thick as few hundredths of angstroms can be obtained.

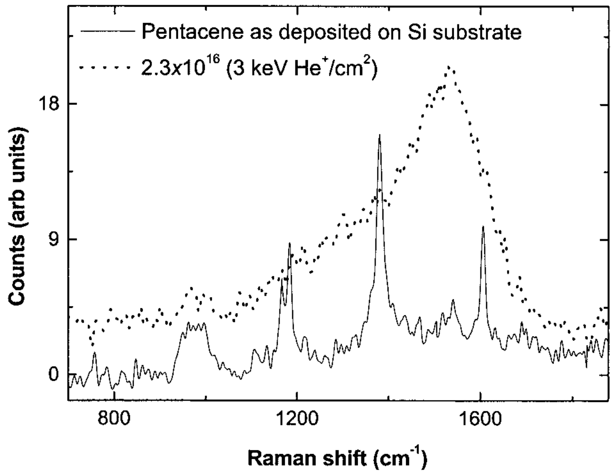

Figure 5. Raman spectra of an as prepared pentacene sample and that obtained after irradiation at the given fluence.

In Figure 5 we show the Raman spectra of pentacene ($C_{22}H_{14}$) before and after irradiation with 3 keV He$^+$ ions at a fluence of 3 x 10^{16} ions/cm^2. The thickness of the sample was about 1.5 x 10^{16} molecules/cm^2 so that the ion beam travels the sample. We can say that the as deposited sample exhibits bands attributed to aromatic C-C stretching (at Raman shifts greater than 1300 cm^{-1}) and to C-H bending and rocking modes. Cannia et al[5] demonstrated that already at the lowest dose the spectrum changes: an intense fluorescence continuum appears, typical of disordered carbons containing large quantity of hydrogen. As radiation goes on, hydrogen is lost, the sample is carbonized and at the highest dose (shown in Figure 5) the spectrum is typical of an amorphous carbon.

In figure 6 the Raman spectra of the amorphous carbons obtained after ion irradiation of pentacene and C_{60} fullerene are compared. The spectrum of fullerene still exhibits a peak at about 1400 cm^{-1} probably because the original sample has not been fully irradiated. We can however clearly see that the amorphous carbons obtained from so different materials, by ion irradiation, are quite similar and are characteristic of very disordered material with a low hydrogen content.[1]

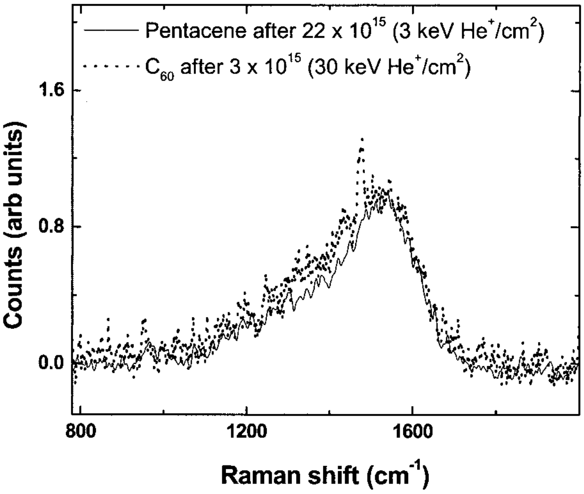

Figure 6. Raman spectra of the amorphous carbons obtained after ion irradiation of pentacene and C_{60} fullerene.

Astrophysical consideration

To apply the results of ion irradiation experiments to astrophysical scenarios it is necessary to have an idea of the amount of energy deposited by cosmic ions on astrophysical targets. As a matter of fact the amount of energy deposited in the samples (eV/C-atom) has to be compared to that suffered by atoms and molecules on grains in the interstellar medium (ISM).

The experiment here shown have been performed by using 30 keV He^+ ions (3 keV in the case of pentacene). A single 30 keV He^+ ion interacting with a carbon target releases about 7 x 10^{-15} eV cm^2/C-atom. Thus, as an example, after a fluence of 10^{16} ions/cm^2 the sample adsorbed a dose of about 70 eV/C-atom. Such a dose is delivered by cosmic ions on time scales of about 2.5 x 10^7 yr and 2.5 x 10^8 yr on grains in diffuse and dense clouds respectively.[17] These times are within the estimated lifetimes of interstellar clouds.[18] Thus we are confident that the results obtained in the laboratory are effective in the interstellar medium.

As a consequence, fullerenes and PAHs in space, if condensed on the surface of solid grains and exposed to cosmic radiation, cannot survive as such but are converted to amorphous carbons. Frozen hydrocarbons can exist as such only in frozen mantles on grains in dense clouds. A fraction of them is converted to a carbonaceous refractory residue that is re-cycled to a diffuse phase where it is further irradiated and converted to amorphous carbon as simulated in the laboratory.

Conclusion

We have shown that very different materials such as C-containing frozen gases, fullerenes, and PAHs, if ion irradiated at dosages that are compatible with those suffered by materials in diffuse or dense clouds in the ISM, are efficiently converted to disordered amorphous carbons with a low hydrogen content.

In astrophysical environments, amorphous carbon is likely produced in the atmosphere of C-rich evolved stars and released to the interstellar medium. Amorphous carbon grains expelled from stars have been well simulated in the laboratory by grains produced by arc discharge between two carbon electrodes in an inert Ar atmosphere.[19] The so produced amorphous carbon exhibits a degree of order that is however progressively lost after ion-irradiation.[20]

Indubitably amorphous carbon, more or less hydrogenated, produced in the atmosphere of evolved stars and injected in the ISM or produced in the ISM by cosmic ion irradiation of many carbon bearing species as those discussed in this paper, is an important constituent of the interstellar dust.

Also in the Solar System, interplanetary dust (IDP) and meteoritic materials, contain carbon species that could reflect, at least partially, the composition of pre-existing (interstellar) grains. In fact dense molecular clouds, after further contraction are the places where stars and planetary objects are born. Interstellar grains may also be “reprocessed” in the solar nebula. Some Raman studies have shown that most of IDPs exhibit the characteristic amorphous carbon Raman feature. Different degrees of order have been measured testifying either different origin or different processing. Recently a comparison between Raman spectra of amorphous carbons produced by ion-irradiation of frozen ices and those obtained for interplanetary dust particles and meteorites demonstrated that those laboratory residues do not reproduce the IDPs spectra.[2] A comparison between the amorphous carbon Raman features of IDPs, and those of carbon dust analogues obtained in the laboratory by ion irradiation of amorphous carbon obtained by arc discharge is more promising. In fact it has been suggested that amorphous carbon with different degrees of order could be indicative of different irradiation doses by solar wind particles and fast solar protons, suffered by IDPs in the interplanetary medium before collection in the Earth atmosphere.[21]

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