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Infrared studies of swift heavy ion irradiated C_{60} thin films

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Abstract

The modification of fullerenes vibrational properties by energetic ion irradiation is investigated, using Fourier transform infrared (FTIR) spectroscopy . The C_{60} thin films have been irradiated with 200 MeV Au ions at fluence from 1×10^{12} to 1×10^{13} ions/cm^2. It is observed that 577 cm^{-1} mode is the most sensitive but 527 cm^{-1} IR active mode is more resistive for swift heavy ion irradiation. To understand change in the molecular structure of fullerene molecule under swift heavy ion (SHI) irradiation, we determined damage cross-section for all four T_{1u} (527, 577, 1183, 1428 cm^{-1}) IR active modes. It is observed that damage cross-section (σ) is different for different vibrational modes. The effective radii (r) of the damage cylindrical zone are also evaluated.

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Keywords: Fullerene; Ion irradiation; Infrared and Raman spectroscopy

1. Introduction

The discovery of C_{60} has developed a completely new field for physical, chemical and material researches. This new material exhibits potential applications as superconductor and semiconductor [1–3], etc. As a result, in recent years, a great number of theoretical and experimental investigations have been reported on these exciting molecules. One of the most important topics of studies is the structure of solid C_{60} and the way it is affected by different type of treatments [4,5].

Fullerene has a closed "soccer-ball" type structure similar to a geodesic dome constituted of 20 hexagons and 12 pentagons, in which each carbon is sp^2 bonded to its neighbours, leaving one electron per carbon for conduction. Even in the solid form the C_{60} molecules are well separated and are only weakly bonded to each other by Van der Waals forces. As a consequence, despite the presence of sp^2 bonds, the material as a whole is electrically insulating. When crystallized, fullerene displays a cubic structure with a lattice constant of 1.417 nm with a C_{60}–C_{60} nearest-neighbours distance of 1.002 nm and density of 1.72 g/cm^3.

In solid fullerenes, the intermolecular forces are much weaker than the intramolecular forces, so the vibrational modes are classified into two distinct groups: external and internal vibrations. The external vibrations involve either translational or rotational motion of the molecules. The internal vibrations involve changes of the bond distances or bond angles of the carbon atoms in the fullerene molecule. These are classified on the basis of observations modes involving primarily carbon atom displacements in the radial direction and others in the tangential one. The energies of radial modes and tangential modes are determined by bond angle bending and bond stretching stiffness, respectively. Therefore, typical radial modes and typical tangential modes are found at the lower and at the higher end of the spectrum, respectively [6]. Both the theoretical and experimental studies [6,7] show that C_{60} molecules have many internal vibrational modes, out of which there are four IR active (T_{1u}) and 10 Raman active (A_g, H_g). These vibrational modes shift when the molecule is subjected to external perturbations including intermolecular

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interactions. Infrared and Raman spectroscopy studies showed obvious shifts of the four fundamental IR modes and 10 fundamental Raman modes of C_{60} at high pressures or at high temperatures, which suggested a decrease in intermolecular spacing and the existence of intermolecular interaction [8] at there extreme condition. Because of the high symmetry of C_{60} molecules, the investigations of their vibrational properties are, particularly, of interest. In the present work we have studied the infrared properties of the vibrational mode in irradiated fullerene thin films by Fourier transform infrared spectroscopy.

2. Experimental

Fullerene thin films were deposited on Si(1 0 0) substrate in a vacuum of 1×10^{-6} Torr by resistive heating of commercially available 98% pure C_{60} in a Ta boat. The thickness of the film, as measured by quartz crystal thickness monitor, was 500 nm. The samples were irradiated with 200 MeV Au ion beam ($S_e = 16.2$ keV/nm, $S_n = 109.4$ eV/nm [9]) from NSC Pelletron with fluences of 1×10^{12}, 3×10^{12} and 1×10^{13} ions/cm^2.

Fourier transform infrared measurements were performed on the as deposited and Au ion irradiated C_{60} films. The FTIR spectra were obtained with a Nexus 670 FTIR spectrometer. The spectra were recorded in the range of 400–4000 cm^{-1}. The data were collected using a spectral resolution of 4 cm^{-1}. For each spectrum an averaging over 200 scans effected noise reduction.

3. Results and discussion

The infrared spectra of unirradiated and irradiated fullerene films are shown in Fig. 1. The peaks observed are fundamental IR active modes consistent with those previously reported in literature and are attributed to the internal modes of the C_{60} molecule [6]. With increase in the fluence, the intensities of the peaks decrease. This decrease in peak intensity is due to the breaking of fullerene molecules.

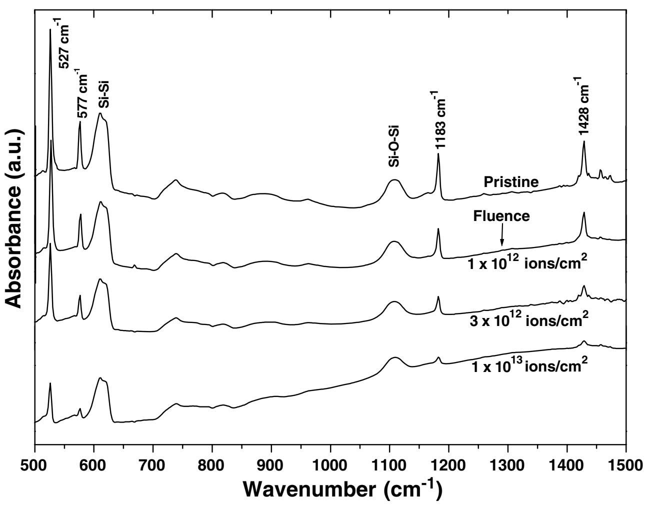

Fig. 1. Fourier transform infrared spectra of pristine and irradiated fullerene films with 200 MeV Au ions at indicated fluences.

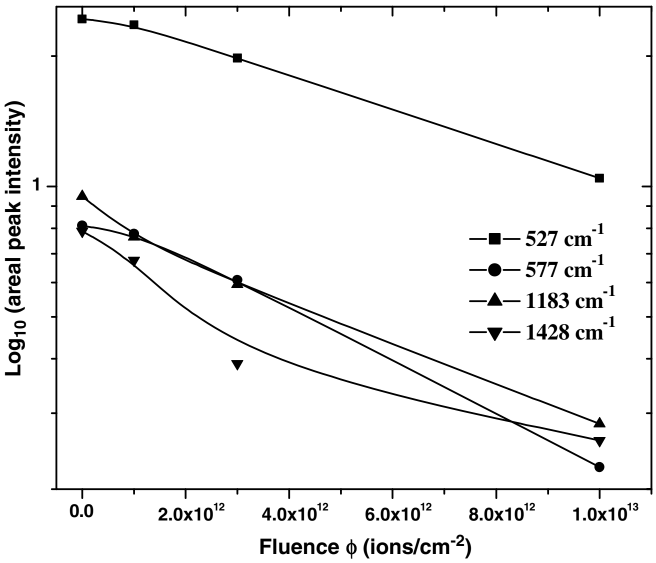

Fig. 2. Variation of area under IR active peaks with indicated fluence of 200 MeV Au ions.

The areas under the IR active peaks decreases exponentially with the ion fluence as shown in Fig. 2. The decreasing rate is different for the different peaks. It means that different modes have different sensitivities to ion irradiation.

The peak positions do not change significantly with ion irradiation as shown in Fig. 3. The width of modes at 527 and 576 cm^{-1} remains almost constant but the width of 1183 and 1428 cm^{-1} modes increase with the fluence and the mode at 1428 cm^{-1} shows the most broadening. This result indicates that cross-linking of fullerene balls occur due to by new cycles formed by the breaking of π bonds in two neighbouring molecules. It is the signature of polymerization of fullerene, because the polymerized fullerene is known a IR mode at 1424 cm^{-1} [10].

It is noticed that there are no new peaks in the ion irradiated fullerene spectra. The lack of new peaks and the peak shifts give a strong evidence that no substantial amount of intermediate fragmentations of C_{60} occurs. This is in contrast with the results of low energy ion irradiation and other energy deposition mechanisms [11]. It would be better to mention that to the best of our knowledge IR sensitivity of such fragments are not very well reported in literature. There is no new feature in the region 400–1600 cm^{-1} in irradiated fullerene films, which is similar to the observation in low energy ion irradiation of fullerene [12].

The cross-section for the damaging process of the C_{60} molecules under ion irradiation can be deduced from the decrease in the IR peak intensities with fluence as shown in Fig. 4. The analysis suggested [12] that the areal density, $N(\phi)$, of the fullerene molecules remaining after irradiation with an ion fluence (ϕ), is given by