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Carbon nanowires generated by ion irradiation of hydrocarbon ices

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ABSTRACT

In this paper we present the formation of carbon nanowires (polyynes and polycumulenes) in the solid state by ion irradiation of frozen hydrocarbons (C_6H_6 and C_2H_2). Irradiations have been performed using H^+ ions in the 100's keV energy regime using fluences up to 5×10^{14} ions/cm^2. Beyond the intrinsic significance of these results in the field of material science, this work has been motivated by the fact that ion beam irradiation of hydrocarbon ices is one of the most important process thought to happen in several extraterrestrial environments where many spectroscopic features of polyyne molecules have been identified.

1. Introduction

The physics and chemistry of sp-coordinated all-carbon skeletons (carbynes) is actually a challenging topic in carbon science. Formed as linear chains of carbon atom pairs with alternating single and triple bonds, polyynes represent unique, truly one-dimensional molecular systems with intriguing optical and electronic properties [1,2].

There are a few ways to synthetically assemble polyyne chains by chemical routes, and the most popular method remains the electrochemical reductive carbonisation of poly(tetrafluoroethylene) and the $Cu^{I/II}$-catalysed oxidative homocoupling protocols [3,4]. While these techniques have been successfully used to form extended polyynes, one of the greatest problems remains the inability to produce and isolate significant quantities of the longest compounds, such as C_{16} and C_{20}. At the same time a number of physical methods have been employed, all of them characterised by the formation and manipulation of hot carbon vapour generated in different ways [5–10]. The interests in these last approaches are manifold.

First of all plasma generation methods allow to easy produce large amount of short and long chains (Carbon NanoWires, CNWs); hot plasma well reproduce the physical and chemical conditions of circumstellar environments, explaining the abundance in space of sp-hybridized carbon species variously end-capped [5,6]. Additionally, these methods represent a step towards the understanding in the formation of other carbon nano-phases, that is Single-Walled or Multi-Walled Carbon Nano-Tubes (SWNTs, MWNTs), fullerenes, carbon onions and others, bridging the gap between the olygomers (polyynes, $R–(–C{\equiv}C–)_n–R$ or polycumulenes, $(R_1,R_2){=}(C{=}C)_n{=}(R_3,R_4)$ and the structure of others allotropic forms of carbon. For instance, it has been demonstrated that carbon deposits containing a relevant percentage of polyynes species easily transform to nano-scale carbon tubules by heating and electron irradiation [11,12]. Recently the observation of CNW-CNT hybrid systems has been reported after arc discharge experiments [13,14] or by separate formation of CNTs and polyynes [15,16].

The existence of these linear structures in hot carbon vapour has been firstly observed by Kroto during the experiments leading to the observation of fullerene C_{60} [17]. Today it is quite clear that the formation of polyynes and polycumulenes happens when a hot carbon vapour is rapidly quenched in a low temperature environment such as in the case of cluster condensation sources [5,6] or in experiments conducted by ablating carbon targets in liquid environments [7,8] or by the ignition of arc discharges [9,10]. Recently Hu et al. have reported the first "all solid" formation of carbon chains by femtosecond pulsed laser deposition [18] in which carbon ion energies can be as high as 0.5–2 keV, one or two orders of magnitude larger than the energies involved during the ablation with nanosecond laser pulses.

In a previous study [19] we have shown that ion irradiation of hydrocarbon ices (namely C_2H_2, C_2H_4, and C_2H_6) in the inelastic collision regime leads to the formation of polyynes with definite lengths. This argument is particularly appealing in order to understand processes and materials of astrophysical relevance.

Radiolysis of hydrocarbons in solid, liquid and gaseous phase was in the past the subject of much investigation. A number of reactive species, including positive and negative ions as well as

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radicals in addition to electronically excited states have been identified, and several interconversion paths for the formation of unsaturated compounds were proposed [20–23].

Interestingly, favourable conditions for the formation of polyynes and polycumulenes occur near some carbon stars, in some objects in the Solar System (e.g. in comets), and interstellar clouds. Concerning the interstellar medium (ISM), the Infrared Space Observatory (ISO) observations (in the wavenumber range 220–4200 cm^{-1}) of the protoplanetary nebula CRL618 showed infrared absorption bands of two polyynes, C_4H_2 and C_6H_2, and two cyanopolyynes, HC_3N and HC_5N [24]. Furthermore, radio survey towards several molecular clouds revealed the presence of longer cyanopolyynes (H–(C≡C)$_n$–N) up to $HC_{11}N$ ([25]). Both infrared and radio observations strongly suggest the formation of longer polyynes in the ISM, although no direct evidence can be obtained by radio detection due to the absence of a permanent electric dipole [26].

Evans et al. [27] presented an observation of the very late thermal pulse object V4334 Sgr (Sakurai's Object) with the Infrared Spectrometer (IRS) on the Spitzer Space Telescope. They were able to attribute a number of features seen in absorption against the dust shell, to HCN and polyyne molecules. Polyynes have been also detected in Titan's atmosphere, where photolysis and radiolysis of mixtures containing methane and many other organic species lead to a rich organic chemistry [28].

Here we present new experiments of ion irradiation of simple hydrocarbons deposited on suitable substrates and analysed in situ after irradiation by infrared and Raman spectroscopy. Our specific motivation has been the search for linear carbon species generated by the ion-matter interaction.

2. Experimental methods and simulations

C_6H_6 and C_2H_2 ices have been deposited at 16 K under High Vacuum conditions (<10^{-7} mbar base pressure) onto a gold coated silicon (for the Raman analysis) and KBr (for the IR) substrates separately. The final film thickness has been measured using the interference fringes generated by a He–Ne laser beam reflecting at the vacuum-film and film-substrate interfaces, giving values around 2 μm. Ion irradiation has been performed with a 200 keV H^+ beam with ion current density around 0.1 μA/cm^2 and fluences up to 5×10^{14} ions/cm^2. Further details of the experimental set-up and procedures can be found elsewhere [29].

Simulations of ion-matter interaction (SRIM2008.04 code by James F. Ziegler, version available at http://www.srim.org) are reported in Fig. 1. The figure reports the energy loss suffered by the ions during their slowing down inside matter. It is quite clear that the energy loss by ionisations is predominant and nearly constant through the film thickness (full line, left scale), with the maximum values equal to 110 eV/nm. The energy loss by phonons creation into the sample is also reported (dashed line, right scale), showing values at least two orders of magnitude lower. The inset of Fig. 1 also shows a picture with the collision cascades for 100,000 ions during their slowing down into a C_6H_6 film. Traces represent the ion path inside the solid and account for the (few) produced recoils. From the figure it is possible to estimate that the average stopping power in a 2 μm thick sample is about 95 eV/nm which corresponds to 2.6×10^{-14} eV cm^2/16u where 16u is a small molecule [30]. In order to compare experimental results obtained with different ions and mixtures and to extend laboratory results to astrophysical environments the dose (eV/16u) is often used. In the present case a fluence of 1×10^{14} ions/cm^2 corresponds to a dose of 2.6 eV/16u.

Raman and infrared spectroscopies are techniques appropriate to observe the ice before and after irradiation. Indeed the Raman

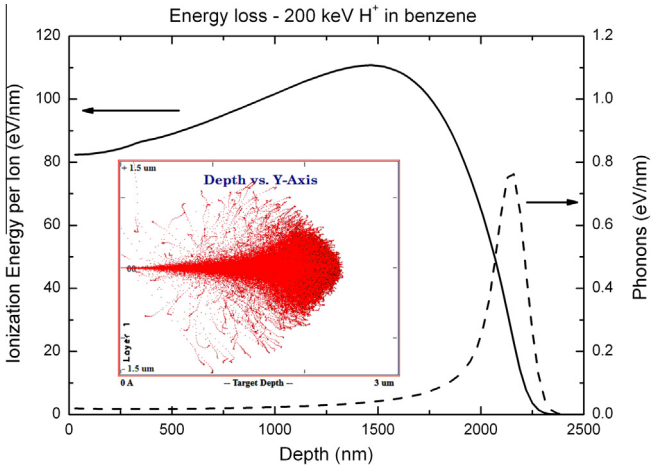

Fig. 1. Energy loss suffered by 200 keV protons in benzene (C_6H_6) by ionization and phonon creation as a function of the depth inside the sample. The inset shows a picture of the collision cascades for 100,000 ions.

cross sections for skeleton stretching in sp^2 and sp hybridized carbons are predominant under visible or near-infrared excitations [31–33]. Particularly interesting is the ability of Raman spectroscopy to directly observe the modes for the carbon backbone, to account for order/disorder features of the structure and to evaluate many geometrical parameters of a carbon nanostructure such as the radius of the tube in the case of the observation of CNTs or the length of the chain for polyynes or polycumulenes. On the other hand, IR absorption is able to give a clear indication about the presence of different functional groups from simple hydrogenation (CH signals) to complex functionalities and radicals.

The present experiments have been conducted with the acquisition of Raman and IR absorption spectra in situ during the irradiation at constant temperature and after annealing of the sample from 16 to 300 K.

In many previous studies a limiting factor for the application of Raman spectroscopy to irradiated frozen hydrocarbons has been the appearance of a strong luminescence after irradiation, when visible laser excitations (i.e. 514 nm) are used [34]. In this work this limit has been overcome by using a NIR 785 nm excitation wavelength which strongly reduces this effect.

3. Results and discussion

3.1. Evidences of polyynes formation by Raman spectroscopy

Fig. 2a shows the Raman spectra of C_6H_6 as deposited at 16 K (the band assignment can be found elsewhere [35]), after irradiation at 16 K with 200 keV H^+ and the spectrum taken after annealing at 180 K. Fig. 2b shows the Raman spectrum of C_2H_2 as deposited, after ion bombardment with 200 keV H^+ and after in situ annealing at 110 K [19]. As previously mentioned, a high background level has been observed for all the irradiated samples due to the formation of conjugated species with extended π electron systems. Nevertheless the irradiated samples before and after the annealing show a series of new features. These can be grouped into two regions: the sp^2 hybridized carbon vibrational field (1100–1600 cm^{-1}) and the sp hybridized carbon vibrational one (1800–2200 cm^{-1}).

As expected, the appearance of a broad signal between 1100 and 1600 cm^{-1} demonstrates the formation of amorphous carbon with a decreasing of the H/C atomic ratio as a function of ion beam fluence, as it has been shown in several other papers in which organic substances are subjected to particle irradiation [36].