# ULTRAVIOLET SPECTRAL CHANGES IN AMORPHOUS CARBON GRAINS INDUCED BY ION IRRADIATION

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## ABSTRACT

Small carbon grains, processed by UV radiation and cosmic rays, have been proposed as carriers of the 217.5 nm bump present in the interstellar extinction curves (Hecht 1986; Sorrell 1990). In this paper, we present the results of an experiment aimed at simulating, in a first approximation, the cosmic-ray irradiation active in space.

We have studied the effects induced by 3 keV  $He^+$  ions on the UV spectrum of small cosmic analog carbon grains. Two different kinds of grains have been analyzed. They were produced by vapor condensation in hydrogen and argon quenching atmospheres.

Spectrophotometric measurements have been carried out on grains as they were produced and after ion irradiation in the spectral range  $0.19-2 \mu m$ . Relevant UV spectral changes are observed after ion irradiation: while the UV absorption band shifts from 203 to 215 nm in hydrogenated amorphous carbon grains, an opposite trend is observed for the samples produced in the argon atmosphere. In this case the UV band moves from 240 to 218 nm. These spectral changes are well correlated with the optical gap variations and are therefore interpreted in terms of grain microstructure changes induced by the interactions with ions. At the highest ion fluence considered, the two carbons tend to have a similar microstructure, as testified by the UV peak position and optical gap values because of a saturation effect of the two competitive processes, amorphization and graphitization, which occur in carbon samples during ion irradiation (Compagnini & Calcagno 1996).

The results of the present experiment suggest that hydrogenated amorphous carbon grains cannot be transformed into graphite grains by cosmic-ray irradiation. Moreover, the efficiency of ion irradiation in destroying well-ordered aromatic structures poses the problem of the survival itself of polycrystalline or pure graphite particles in the interstellar medium.

Subject headings: cosmic rays - dust, extinction - methods: laboratory - ultraviolet: ISM

## 1. INTRODUCTION

Among the proposed interpretations of the ubiquitous bump at 217.5 nm in the extinction curves of the diffuse interstellar medium, the models by Hecht (1986) and Sorrell (1990) are the only ones that discuss the problem in the framework of an evolutionary scenario for the carriers of the interstellar feature. With the exception of the attribution by Steel & Duley (1987), which proposed that the bump might be produced by  $OH^-$  ion in low coordination sites in silicate grains, several kinds of carbonaceous grains have been considered as being responsible for the 217.5 nm band. However, because of the difficulties of satisfying the observational constraints, there is no unanimous agreement on the physical properties of the carbonaceous carriers.

In order to obtain a best fit of the bump, many authors have indeed focused their attention on parameters such as size, shape, and coatings by using the optical constants of bulk graphite (e.g., Gilra 1972; Draine & Lee 1984; Mathis 1994; Aannestad 1995). This approach shows at least two main difficulties: (1) the use of bulk graphite optical constants to describe the optical properties of small interstellar grains and (2) the existence of such small graphite grains in the interstellar medium. Only by invoking variations of the bulk dielectric properties of the grain material, due to surface effects, crystallinity degree, or impurity content, might it be possible to reconcile the graphite hypothesis with the observations (Draine & Malhotra 1993). Moreover, laboratory results on carbon vapor condensation suggest that graphite particles are unlikely to form in carbon-rich astrophysical environments such as evolved star outflows or supernova ejecta (Czyzak & Santiago 1973).

On the other hand, the nature of any grain species invoked to explain the bump must be related to the origin and evolution of such particles in the interstellar medium. A theoretical evolutionary scenario for carbon grains has been outlined by Hecht (1986) and Sorrell (1990). Both authors have attributed the interstellar feature to a  $\pi$  plasmon in a separate population of small hydrogen-free carbon particles and stressed the importance of hydrogen in their formation and evolution. They suggest that hydrogenated carbon grains may not show the 217.5 nm extinction bump because of the presence of hydrogen, which inhibits the delocalization of the  $\pi$  bond and, consequently, the  $\pi$  plasmon. The feature in the interstellar extinction is interpreted in terms of dehydrogenation and graphitization due to annealing caused by shock process and exposure to strong UV radiation and cosmic-ray bombardment. It is implicitly assumed that these processes are equivalent and can graphitize hydrogenated carbon grains. To validate the interpretation of the UV bump as being due to carriers obtained from such processes, some basic questions have to be answered. Do the above-mentioned processes have the same efficiency

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in determining dehydrogenation and graphitization of carbon particles? Do they induce the same effects in grains with different starting properties?

Only recently have specific laboratory simulations been carried out to address part of these questions on an experimental basis (Blanco et al. 1993; Mennella et al. 1995a, 1995b, 1995c). A first step was the thermal annealing of small carbon grains, with sizes similar to those considered by Hecht (1986) and Sorrell (1990) as carriers of the interstellar feature. When hydrogenated amorphous carbon grains whose extinction spectrum lacks any evident UV extinction feature are heated, a band appears in the spectrum. As long as the temperature rises in the range 250-800° C, it becomes more intense, and its peak position shifts to longer wavelengths. A similar behavior was observed in amorphous carbon grains, produced in Ar atmosphere, annealed up to 780° C (Mennella et al. 1995b). The spectral variations were attributed to  $\pi$ - $\pi$ \* electronic transitions in  $sp^2$  ringed clusters, which determine the UV to visible spectral properties in carbons (Robertson 1986), and the UV peak shift was interpreted as being due to their growth in size (Mennella et al. 1995a, 1995c). The microstructure of the carbon particles, rather than size or shape effects, controls the electronic properties and, consequently, the absorption in this spectral region.

In view of a more realistic carbon grain processing simulation, the spectral behavior of similar hydrogenated particles irradiated by UV radiation was analyzed (Mennella et al. 1996). After irradiation the  $\pi$ - $\pi$ \* resonance is activated and remains stable at 215 nm, while its intensity increases as a function of the dose deposited in the samples. The results obtained indicate a difference between thermal and UV annealing and suggest that it is unlikely that hydrogenated amorphous carbon grains can be transformed in pure graphite grains by UV annealing in a typical diffuse cloud timescale.

With this paper, we continue our effort to simulate grain processing in space. The aim is to study the modifications induced in the UV spectrum of amorphous carbon grains by ion irradiation. In § 2 we give a description of the grain production method and of the setup used to perform the experiment and report the results. They are discussed in terms of grain structural changes in § 3. Finally, the astrophysical implications of the experiment are presented in § 4.

#### 2. EXPERIMENT AND RESULTS

Two different kinds of amorphous carbon grains are considered in this work. Both were produced by condensation of carbon vapor obtained by striking an arc discharge between two carbon electrodes and were collected on quartz substrates. Samples with different spectral and structural properties were obtained by using hydrogen and argon quenching atmospheres at a pressure of 10 mbar. In the following they will be identified as ACH2 and ACAR, respectively. Both the samples are characterized by a fluffy structure of spheroidal aggregates composed of three to five spherical grains with an average diameter of 11 nm. The morphological, optical, and structural properties of these carbon grains have been studied extensively in previous works, to which we refer the reader for more details (Colangeli et al. 1995; Mennella et al. 1995a, 1995b, 1995c; Rotundi et al. 1996).

The ion bombardment of ACAR and ACH2 samples was carried out at room temperature in a chamber at a pressure

of less than  $10^{-7}$  mbar. A Varian ion gun was used as a source of 3 keV He<sup>+</sup>. The ion beam was spread homogeneously on a sample area of about 1 cm<sup>2</sup>. The current was kept at only 1.5  $\mu$ A cm<sup>-2</sup> in order to avoid heating effects in the samples. The grains were irradiated at different fluences, from  $10^{15}$  to  $10^{17}$  ions cm<sup>-2</sup>; the corresponding energies deposited in samples are reported in Table 1. The penetration depth of the used ions is of the order of 60 nm. The amount of deposited energy (dose in eV C atom<sup>-1</sup>) has been evaluated by the knowledge of the specific energy loss (eV cm<sup>-2</sup> C atom<sup>-1</sup>) of 3 keV He ions.

Spectrophotometric measurements on grains as they were produced and irradiated samples were performed in the spectral range  $0.19-2 \mu m$ , with a spectral resolution of 2 nm, by using a dispersive double-beam spectrometer (Perkin Elmer model Lambda 19) equipped with a Labsphere accessory (model RSA-PE-19). The latter is essentially an optical bench that includes double-beam transfer optics to a 15 cm diameter integrating sphere and detectors. The used configuration allowed us to perform absorption rather than extinction measurements. It has to be noted that a freshly produced sample was used for each irradiation.

The absorption spectra are shown in Figures 1 and 2 for ACH2 and ACAR samples, respectively. Two distinct behaviors are observed for the two kinds of carbon grains. Unlike the extinction spectra previously reported (Blanco et al. 1993; Colangeli et al. 1995; Mennella et al. 1995a), in which no band was clearly evident in the UV spectral range, the absorption spectrum of hydrogenated carbon grains shows a band at about 203 nm. This feature shifts only slightly toward longer wavelengths for fluences up to  $10^{16}$ ions  $cm^{-2}$ , and then it moves to 215 nm and becomes more pronounced for the highest used fluence (see Table 1). On the other hand, the 240 nm band, which characterizes the UV spectrum of as-prepared ACAR samples, shifts down to 218 nm and becomes less pronounced as the irradiation energy deposited in the sample increases, except for an irradiation of  $10^{15}$  ions cm<sup>-2</sup> when an opposite trend is observed.

To link the spectral variations to the microstructure modifications induced by ion irradiation, we studied the variations of the optical gap,  $E_g$ , as a function of the deposited energy.  $E_g$  is a very useful parameter for the characterization of semiconducting samples such as ACAR and ACH2. It was extracted from the energy dependence of the optical absorption edge via the Tauc relation (Tauc, Grigorovici, & Vancu 1966):  $(\alpha E)^{1/2} = B(E - E_g)$ , where  $\alpha$  is the

 TABLE 1

 Results of ACH2 and ACAR Bombardment with 3 keV He<sup>+</sup> Ions

Label	Fluence (ions $\text{cm}^{-2}$ )	Dose (eV C atom <sup>-1</sup> )	$\lambda_p^{a}$ (nm)	$E_g^{b}$ (eV)	L <sub>a</sub> ° (Å)
ACAR			240	0.52	15
ACARI15	$1 \times 10^{15}$	6.6	245	0.42	18
ACARI16	$1 \times 10^{16}$	66	219	0.52	15
ACARI17	$1 \times 10^{17}$	660	218	0.62	12
ACH2			203	1.32	6
ACH2I15	$1 \times 10^{15}$	6.6	205	1.23	6
ACH2I16	$1 \times 10^{16}$	66	206	1.11	7
ACH2I17	$1 \times 10^{17}$	660	215	0.69	11

<sup>a</sup> UV peak position; uncertainties are  $\pm 2$  nm.

<sup>b</sup> Optical gap; uncertainties are  $\pm 0.02 \text{ eV}$ .

<sup>c</sup> Aromatic coherence length derived from the optical gap.



FIG. 1.—Evolution of the UV absorption spectrum of ACH2 samples due to  $3 \text{ keV He}^+$  ion irradiation. Curves b, c, and d are upper shifted with respect to the ordinate scale by 0.1, 0.2, and 0.3 units, respectively.



FIG. 2.—Evolution of the UV absorption spectrum of ACAR samples due to  $3 \text{ keV He}^+$  ion irradiation. Curves b, c, and d are upper shifted with respect to the ordinate scale by 0.12, 0.24, and 0.36 units, respectively.

absorption coefficient, E is the energy, and B is a constant (see also Mennella et al. 1995c). The obtained values are reported in Table 1.

While the optical gap of the irradiated ACH2 samples decreases, from 1.32 to 0.69 eV, as the ion dose increases, a different behavior is observed for ACAR samples: starting from a value 0.52 eV,  $E_g$  decreases to 0.42 eV for a fluence of  $10^{15}$  ions cm<sup>-2</sup> and then increases up to 0.62 eV for the highest fluence considered in the experiment.

#### 3. DISCUSSION

The results obtained in the present experiment show that two distinct behaviors are observed for ACH2 and ACAR samples because of 3 keV He<sup>+</sup> ion irradiation. To get insights into these results, one has to take into account the physical origin of the UV spectrum in amorphous carbon grains and the different microstructure of the two samples.

The physical properties of amorphous carbons, which can contain  $sp^3$  and  $sp^2$  carbon sites, and hydrogen in variable proportions, depend on the prevalent bond type and on the topological configuration. The link between electronic properties and microstructure is one of the most interesting physical aspects of these materials. Analysis of the energetics of  $\pi$  bonding suggests that the  $sp^2$  sites form graphitic clusters embedded in a  $sp^3$ -bonded matrix instead of random configurations (Robertson & O'Reilly 1987). The clustering of the  $sp^2$  sites arises from the nonlocal character of their  $\pi$  bonding, which determines medium-range order, unlike  $\sigma$  bonds, which drive short-range order. Since the  $\sigma$ - $\sigma$ \* energy spacing is larger than  $\pi$ - $\pi$ \* spacing, the edges of electronic density of states (DOS) are  $\pi$ -like (i.e., the valence and conduction bands are determined by  $\pi$  states) in both hydrogenated and hydrogen free amorphous carbons. The widths of  $\pi$  peaks in the DOS depends on the size of the  $sp^2$ clusters, with larger clusters giving rise to closer  $\pi$ - $\pi$ \* band edges. In fact, Robertson (1986) found that the optical gap,  $E_a$ , varies inversely with the aromatic coherence length of the  $sp^2$  clusters:  $E_g$  (eV)  $\approx 7.7/L_a$  (Å). Moreover, Mennella et al. (1995a, 1995c) found a correlation between the graphite cluster size and the position of the UV bump: the larger the clusters, the lower the  $\pi$ - $\pi$ \* transition energy.

Previous measurements performed on similar samples (see Mennella et al. 1995a, 1995c) have shown that as prepared ACH2 grains are characterized by a low  $sp^2$  clustering degree as testified by Raman, UV and IR spectroscopy, optical gap, and hydrogen content measurement; the H/C atom ratio is 0.62 and the largest graphitic islands have a size  $\approx 6$  Å. Such a structure is formed as a consequence of the presence of hydrogen in carbons, which favors the  $sp^3$  carbon bonding configuration and, hence inhibits the clustering of  $sp^2$  sites. On the other hand, the UV peak position (at 240 nm), the optical gap value (0.53 eV), and the intensity ratio of the D and G first-order Raman bands indicate that the ACAR sample has a higher  $sp^2$  clustering degree (Baratta et al. 1996). Compact aromatic clusters with sizes up to 15 Å are present in this sample (see also Table 1).

In view of interpreting our results for the two kinds of studied carbons, which are different in their microstructure, it is useful to highlight the main aspects of the interaction between ions and carbon samples. An exhaustive discussion of this subject is reported in the review paper by Compagnini & Calcagno (1996), to which we refer the reader for more details. The interaction between a fast colliding ion and a solid target produces several effects, such as material removal from the target (sputtering) and alteration of its chemical and structural properties. These effects are a consequence of the ion energy loss due to both elastic collisions with target nuclei and excitation and ionization of target atoms and/or molecules. In the case of ion irradiation of carbons, two main competitive processes must be considered: graphitization and amorphization. The first one can be related to the energy release in form of heat (thermal spikes) inside the collision cascade which transforms  $sp^3$ into  $sp^2$  sites with or without hydrogen loss (Compagnini & Calcagno 1996). It should be noted that the characteristic relaxation time of ion excitation is of the order of 1 ps or less: thus, equilibrium processes such as thermal annealing are not possible (Kalish & Adel 1989). The second process, amorphization, is caused by the so-called displacement collisions, and its efficiency depends on the  $sp^2$  cluster size: it becomes more and more important as the structural order increases (Compagnini, Calcagno, & Foti 1992).

The UV spectral variations observed in our samples after ion irradiation are evidence of changes in the  $\pi$  electronic structure and, consequently, of the  $sp^2$  clustering degree induced by colliding 3 keV He<sup>+</sup>. In ACH2 samples, the shift of the UV peak up to  $215 \pm 2$  nm and the decrease of the optical gap as a function of the ion dose are interpreted in terms of an increase of the  $sp^2$  clustering degree. Therefore, graphitization, accompanied by hydrogen loss, is the driving process for structural modifications. Contrarily, ion irradiation induces a declustering of the atomic configuration of the  $sp^2$  carbon component in ACAR samples, as testified by the shift of the UV peak and the increase of  $E_a$  in the irradiated samples. The shift from 240 to 245 nm, correlated to a decrease of  $E_a$ , after a ion fluence of  $10^{15}$  ions  $cm^{-2}$ , must be due to the loss of the small hydrogen fraction present in the sample (Colangeli et al. 1995; Baratta et al. 1996). The amorphization process prevails on graphitization in this case because of the relatively high  $sp^2$  clustering degree in the starting material.

In ACAR samples, the previous conclusions are supported by Raman spectroscopy, which provides information about the microstructure of carbons (e.g., Robertson 1991; Mennella et al. 1995b). Raman spectra, measured in situ during irradiation of these samples, were reported by Baratta et al. (1996). The evolution of the first-order Raman spectrum as a function of the ion fluence indicates that a reduction of the  $sp^2$  clustering degree takes place in the sample.

We stress that ACH2 and ACAR samples have similar values of the optical gap (0.62 and 0.69 eV) and of the UV peak position (215 and 218 nm) after high ion fluences. This result indicates that ion irradiation tends to produce an amorphous structure with defined physical properties independently of the starting sample. Similar experimental evidence was reported by Compagnini et al. (1992). These authors irradiated with a 300 keV Ar<sup>+</sup> beam two different carbon samples: a hydrogenated amorphous carbon film and a high-temperature (900° C) annealed amorphous carbon, characterized by optical gaps of 1.5 and 0.1 eV and  $sp^2/sp^3$  ratios of 0.3 and 0.8, respectively. After an irradiation of  $10^{16}$  ions cm<sup>-2</sup>, the two samples showed similar  $sp^2/sp^3$  ratios (0.7) and optical gaps (0.5 eV). Following Compagnini et al. (1992), we conclude that the stable microstructure configuration in amorphous carbon, obtained after keV ion irradiation, is a consequence of a saturation

effect of the competition between the graphitization and the amorphization processes.

Finally, we note that this process shows some similarities with the thermal annealing treatment. In this last case, disordered carbons tend to reach a stable configuration, i.e., graphite, independently of the original structure. The graphitization degree depends on parameters such as temperature and pressure (i.e., Oberlin 1984; Robertson 1986; Papoular et al. 1996). Actually, the first stage of this process is observed for our ACH2 and ACAR annealed at 800° C (Mennella et al. 1995a, 1995b). According to the previous discussion, ion bombardment also tends to produce a "stable," but disordered, configuration, which results from the two above-mentioned competitive effects.

#### 4. ASTROPHYSICAL IMPLICATIONS

To our knowledge, the present results are the first reported laboratory data on UV spectral changes in carbon grains induced by ion irradiation. They can have important implications on the interpretation of the observed UV bump extinction properties in terms of amorphous carbon grain processing. To discuss the astrophysical implications, we have to compare the energy received from the samples irradiated in the present simulation with that deposited in interstellar carbon particles by cosmic rays. To this end, we will consider low-energy (1 MeV) protons, which dominate grain processing in space. Heavy cosmic-ray ions are indeed a factor of  $10^3$  less abundant in the interstellar medium, even if their stopping power is higher (10–100) than that of 1 MeV protons (Simpson 1983).

When a 1 MeV proton interacts with a carbon grain, it passes through the particle depositing part of its energy. In fact, for organic materials with a density  $\rho = 1 \text{ g cm}^{-3}$ , the range of a cosmic proton is of the order of  $10^{-2}-10^{-3}$  cm (Ziegler 1980), much larger than the typical interstellar grain size. The energy release during the interaction is characterized by the specific energy loss, which for 1 MeV protons and grains composed of atoms such as C, N, O, and Si is of the order of  $10^{-14}$  eV cm<sup>-2</sup> atom<sup>-1</sup> (Strazzulla & Baratta 1992).

To calculate the dose deposited in carbon grains, it is necessary to know the flux of cosmic rays in the interstellar medium, which actually is a rather uncertain quantity. Following Strazzulla & Baratta (1992), we assume a 1 MeV proton flux of 3 cm<sup>-2</sup> s<sup>-1</sup>, which gives an energy deposition rate by cosmic rays in a carbon particle of  $3 \times 10^{-14}$  eV s<sup>-1</sup> atom<sup>-1</sup>. Therefore, the total energy received by these grains due to the interaction with fast colliding charged particles, during the typical time of  $3 \times 10^7$  yr they spend in the diffuse interstellar medium, is about 30 eV atom<sup>-1</sup>.

If our laboratory results are representative of the cosmicray bombardment of carbon grains in space, we can infer some interesting hints about the influence of this process on the evolution of carbonaceous particles in the interstellar medium. It has to be noted that 3 keV He<sup>+</sup> ions, used in our experiment, have a stopping power similar to that of 1 MeV protons (Jenniskens et al. 1993). The comparison of our data (see Table 1) with the interstellar dose previously estimated suggests that, in a typical diffuse cloud timescale, the effects of cosmic rays on hydrogenated amorphous carbons should not be important (see Table 1). They can significantly contribute to the polymerization of these grains only on a timescale similar to the estimated lifetime of grains,  $5 \times 10^8$  yr (Seab 1987; McKee 1989), which corresponds to several diffuse to dense cloud cycles (Greenberg 1989). Alternatively, the same result could be obtained for a cosmic-ray flux a factor of 20 larger than that assumed. Moreover, we recall that UV irradiation of ACH2 samples at a dose 7 times lower than that expected in  $3 \times 10^7$  yr in the diffuse medium is already sufficient to produce the same effects observed for a ion dose of 660 eV C atom, which should correspond to residence time of  $7 \times 10^8$  yr in the diffuse cloud medium. These elements bring us to the conclusion that UV photons dominate the polymerization of carbon grains in the interstellar medium. Our findings agree with the result by Jenniskens et al. (1993) obtained on the basis of irradiation experiments of organic refractory residues.

On the other hand, ion irradiation must be very efficient in reducing the aromatic clustering degree in carbon grains on a timescale of one or two diffuse to dense cloud cycles. As a consequence, the possibility that carbon grains can be transformed in pure graphite grains by particle irradiation has to be ruled out. Actually, the high efficiency of fast colliding ions in destroying ordered aromatic structures poses the problem of the survival itself of pure graphite particles or polycrystalline graphitic grains in the interstellar medium.

As discussed above, both UV and particle irradiation are able to block the evolution of carbon grains towards graphite and to determine a defined disorder degree, i.e., a welldefined size distribution of graphitic islands within grains. In the case of the UV processing, the physical mechanization was identified in a decrease of the dehydrogenation efficiency by UV photons, which prevents large graphitic clusters from further growth (Mennella et al. 1996). Instead, the increase in importance of displacement collisions as  $sp^2$ structures become more ordered is the driving factor in ion irradiation. Thus, according to the correlation between structural and electronic properties, this implies a welldefined bump position as a spectroscopic counterpart.

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Even if experiments aimed at simulating grain processing in space give, at present, UV bumps centered very close to the interstellar feature, the problem of a too-wide UV peak with respect to the interstellar one remains. This drawback can be partially due to the experimental limitation of working on agglomerated grains rather than on isolated particles. Recently, Schnaiter et al. (1996) showed that clumping is indeed responsible for a broadening of the UV features measured on soot particles. These authors studied the extinction behavior of matrix-isolated primary soot grains extracted by a molecular beam technique from an acetylenic flame. The most striking result is a width decrease of the band and a peak shift from 263 to 253 nm for grains isolated in argon ice with respect to the soot samples collected directly on a substrate. This finding is not in contrast with our general conclusion that the grain microstructure is the major driving factor to determine their optical properties and, in particular, the UV peak position. Thus, despite grain agglomeration, our results, obtained by differently processing (thermal annealing, UV irradiation, and ion bombardment) similar samples, may be a valid tool in understanding the grain processing of the bump carriers.

Before a definite answer can be given about the attribution of the UV bump in the interstellar extinction curves to  $\pi$ - $\pi$ \* electronic transitions in graphitic clusters forming carbon grains, a careful quantitative check of the cosmic carbon abundance, required to match observations, has to be performed, on the basis of revised values of carbon available in the interstellar medium for the formation of grains (e.g., Snow & Witt 1995, 1996; Cardelli et al. 1996).

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