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ACTIVATION OF AN ULTRAVIOLET RESONANCE IN HYDROGENATED AMORPHOUS CARBON GRAINS BY EXPOSURE TO ULTRAVIOLET RADIATION

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ABSTRACT

The results of an experiment aimed at simulating the UV processing of hydrogenated amorphous carbon grains that occurs in the interstellar medium are presented. UV exposure of these grains induces significant changes in the UV-visible spectrum and, in particular, activates a resonance at 215 ± 2 nm, very close to the position of the interstellar extinction bump. This is the first reported laboratory observation of the activation of a UV resonance in hydrogenated carbon grains irradiated by UV photons. The spectral variations depend on the UV dose deposited in the samples; as the dose increases, the band becomes more intense while its peak position remains stable.

We attribute the band to π–π^* electronic transitions in sp^2 ringed clusters that form the grains and interpret the spectral variations in terms of structural changes of the grains. This interpretation is confirmed by the behavior of the optical gap, which indicates an increase of the sp^2 clustering degree as a function of the grain processing. The results of the present experiment suggest that it is unlikely that hydrogenated amorphous carbon grains can be transformed into pure graphite grains by UV processing in a typical diffuse-cloud timescale.

The possibility that the interstellar bump is due to π–π^* transitions in graphitic clusters that form small carbon grains is analyzed. This hypothesis requires a definite internal structure for the bump carrier. A process able to determine the grain structure is briefly discussed.

Subject headings: dust, extinction — methods: laboratory — ultraviolet: ISM

1. INTRODUCTION

Thirty years after the discovery by Stecher (1965) of the strongest interstellar extinction feature, the bump at 217.5 nm, its physical origin and actual carrier or carriers remain a topic of controversy (see, e.g., Draine 1989). Among the possible carriers, much attention has so far been focused on carbonaceous materials. Graphite has long been a prominent candidate for the origin of the feature in the interstellar medium (Gilra 1972; Draine & Lee 1984; Mathis 1994). Several other carbon-based materials, such as amorphous carbons, coals, quenched carbonaceous composites, and polycyclic aromatic hydrocarbons (PAHs), have also been proposed (Bussoletti, Colangeli, & Orofino 1987; Joblin, Leger, & Martin 1992; Papoular et al. 1993; Sakata et al. 1994).

As far as the physical origin of the bump is concerned, two alternative explanations exist. The first is tightly related to the graphite hypothesis and assigns the interstellar feature to the absorption produced by π-plasmons in small graphitic grains (see, e.g., Gilra 1972; Draine & Lee 1984; Mathis 1994). The second explanation attributes the band to a different physical mechanism, electronic transitions (instead of collective excitations) of π-electrons (see, e.g., Joblin et al. 1992; Papoular et al. 1993; Mennella et al. 1995a).

At present, the proposed interpretations should be considered to some degree unsatisfactory, because the models either require very peculiar conditions of carrier population or do not fully satisfy observational constraints (Fitzpatrick & Massa 1986). As an example, in the case of the graphite hypothesis, the interstellar grains have been considered to be spherical or spheroidal homogeneous particles with smooth surfaces, and bulk optical constants have been adopted. On this ground, the constraints placed on interstellar graphite grains by astronomical observations have been studied by means of classical electromagnetic theory. The influence of size, shape, coatings, and coagulation on the bump profile have been analyzed. These results are strongly biased by the assumptions that the particles are homogeneous and have the same dielectric properties as graphite crystals. Draine & Malhotra (1993), on the basis of an extensive analysis of these effects, concluded that the basic model of spheroidal graphite grains cannot be reconciled with the observations. They invoked variations in the dielectric properties of graphite to explain the positional constancy and the width variations of the 217.5 nm band.

The nature and composition of carbon-based grains must be linked to the processes responsible for their formation and evolution. The difficulty of producing graphite particles in astronomical environments has been stressed by several authors (Czyzak & Santiago 1973; Donn et al. 1981; Hecht 1986; Mathis & Whiffen 1989). However, Hecht (1986) and Sorrell (1990) suggested that dehydrogenation and graphitization of small carbon grains take place whenever the hydrogenated particles undergo annealing by exposure to UV radiation. Specific experimental results on this subject are lacking.

Laboratory studies of cosmic analog materials and simulations of processes active in space can yield answers to specific questions and support theoretical models on an experimental basis. Recently, Mennella et al. (1995a, 1995b, 1995c) extensively studied the structural changes in both hydrogenated and dehydrogenated amorphous carbon grains produced by thermal annealing, a valid tool to study grain annealing in space.

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TABLE 1

RESULTS OF ACH2 EXPOSURE TO UV RADIATION

Sample	Irradiation Time (hr)	UV Dose (eV cm^{-2})	λ_p [a] (nm)	E_g [b] (eV)
ACH2.....	...	...	...	1.38
ACH2UV7	7	5×10^{20}	...	1.34
ACH2UV172.....	172	1×10^{22}	215	1.29
ACH2UV550.....	550	4×10^{22}	215	1.23

[a] UV peak position; uncertainties are ±2 nm.
[b] Optical gap; uncertainties are ±0.02 eV.

The main result was that the internal structure of single grains, having sizes similar to those proposed by Hecht (1986) and Sorrell (1990) as bump carriers ($a \simeq 5$ nm), controls the interaction with UV radiation. In particular, the electronic properties of the aromatic sp^2 clusters that form the single particles determine the extinction properties of carbon grains.

The aim of the present work is to improve the simulation of grain processing in space by studying the changes in the UV spectrum of hydrogenated amorphous carbon grains exposed to energetic UV radiation. In § 2, we describe the setup used to produce and irradiate grains and report the obtained results, which are discussed in terms of grain structural changes in § 3. The astrophysical implications of this experiment are reported in § 4.

2. EXPERIMENT AND RESULTS

The hydrogenated amorphous carbon (hereafter "ACH2") grains were prepared by condensation of carbon vapor that was obtained by striking an arc discharge between two carbon rods in an H_2 atmosphere at a pressure of 10 mbar. The carbon particles were collected on UV-grade fused silica substrates located 5 cm from the source. The resulting samples were characterized by a chainlike structure of spheroidal aggregates composed of three to five spherical grains with an average diameter of 11 nm. The optical properties of these carbon grains have been studied extensively in previous works (Blanco et al. 1993; Colangeli et al. 1995; Mennella et al. 1995a, 1995c), to which we refer the reader for details.

The processing by UV photons of ACH2 samples was carried out at room temperature in a chamber at a pressure of less than 10^{-6} mbar. A hydrogen flow discharge lamp with an MgF_2 window, operating at a pressure of 2 mbar and 100 V, was used as a source of UV radiation. Its spectrum is characterized by molecular and atomic Lyman emission, with the latter accounting for at most 30% of the total flux between 0.11 and 0.18 μm. The energy flux at the samples' position was $(2 \pm 1) \times 10^{15}$ photons cm^{-2} s^{-1}, with an average energy per photon of 10 eV (Mendoza-Gómez 1992; Jenniskens et al. 1993).

ACH2 grains were irradiated for different time intervals, from 1 to 550 hr. In the following, the samples are identified with labels that refer to the irradiation period, as reported in Table 1, where the irradiation doses corresponding to the exposure times are also listed. The uncertainty on the doses is ~50%. Before and after each irradiation, spectrophotometric measurements were performed in the range 0.19–2.5 μm with a resolution of 2 nm by using a dispersive double-beam spectrophotometer (Perkin-Elmer model Lambda 9). No spectral variations were noted up to 14 hr of irradiation, while changes were observed for the exposure times of 172 and 550 hr.

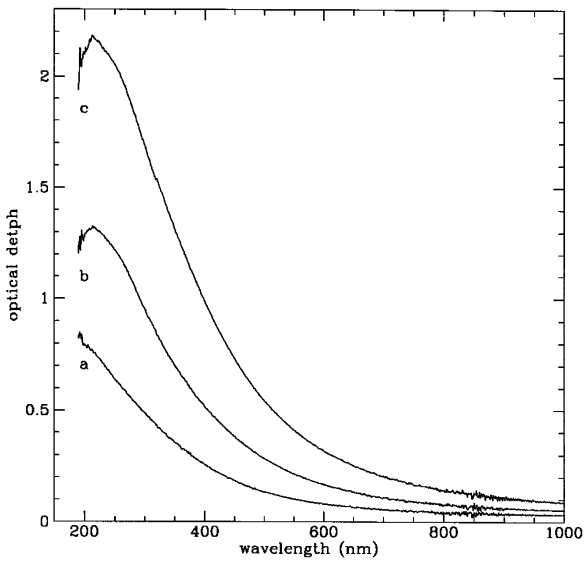

FIG. 1.—UV/near-IR optical depth of hydrogenated amorphous carbon grains, both not irradiated (a) and after UV doses of 1×10^{22} eV cm^{-2} (b) and 4×10^{22} eV cm^{-2} (c).

As one can see from Figure 1, a UV dose of 1×10^{22} eV cm^{-2} activates a UV resonance in the spectrum of ACH2 grains. The feature becomes more pronounced as the irradiation dose increases to 4×10^{22} eV cm^{-2}, while the peak position remains stable at 215 nm. Moreover, spectral changes take place at visible and near-IR wavelengths, where the spectral trend is characterized by a broad absorption edge that slowly changes as a result of the UV processing. These changes, linked to the sp^2 clustering degree within the grains (Robertson 1986; Mennella et al. 1995c), can be analyzed by considering the variation of the optical gap E_g. It was estimated from the optical data by using the "Tauc relation" between the absorption coefficient α and E_g: $(\alpha E)^{1/2} = B(E - E_g)$, where E is the energy and B is a constant (Tauc, Grigorovici, & Vancu 1966; see also Mennella et al. 1995c); the obtained values are listed in Table 1. The optical gap of the irradiated ACH2 grains slightly decreases as the UV dose increases. In particular, the data in Table 1 suggest that E_g is proportional to the logarithm of the UV photon fluence.

3. DISCUSSION

As shown in the previous section, UV irradiation produces significant changes in the spectrum of hydrogenated amorphous carbon grains. In particular, prolonged UV exposure activates a UV resonance at 215 ± 2 nm, very close to the position of the interstellar extinction bump. To obtain insight into this point, a comparison with the results of thermal annealing experiments on similar samples is useful. The main difference between the two processes is the uniformity of the sample processing. In the case of thermal annealing, the whole dust deposit is uniformly processed. On the contrary, the UV processing degree of the different layers varies according to the sample optical depth—the lower grain layers are less processed than the top layers. This effect is evidenced by the behavior of the Tauc slope B. While B is constant as a function of temperature (see Fig. 4 in Mennella et al. 1995c), it increases as a function of the UV dose. For the ACH2UV172 and

ACH2UV550 samples, we found, respectively, slope variations by factors of 1.35 and 1.79 with respect to the ACH2 sample. A similar behavior of the Tauc slope was found by Jenniskens (1993) for UV-processed organic residues.

Mennella et al. (1995a, 1995c) have studied the spectral variations of ACH2 grains caused by heat treatment in the range 250°C–800°C. Thermal processing activates a UV resonance that becomes more and more intense and shifts toward longer wavelengths, up to 259 nm at 800°C, as the annealing temperature increases. They assigned the resonance to π–π^* interband electronic transitions in sp^2 ringed clusters that form the grains and interpreted the shift of the UV band in terms of a dimensional growth of the graphitic islands, which is confirmed by Raman spectroscopy.

In the light of these results, we attribute the band of irradiated ACH2 grains to π–π^* electronic transitions in sp^2 clusters. The activation of the band shows that structural modifications take place in the grains as a result of energetic UV photons. This conclusion is further supported by the behavior of E_g as a function of the irradiation dose. The gap decrease indicates an increase of the sp^2 clustering sites in the grains. In particular, a small dimensional growth of the ringed clusters occurs. Since $E_g \simeq 6/M^{1/2}$, where M is the number of rings forming compact clusters (Robertson 1991), we find a small M variation, from 20 for ACH2 to 24 for ACH2UV550. Actually, these values refer to the largest clusters within the grains; when clusters of different sizes are present, the gap is determined by a concentration of a few percent of the largest clusters (Robertson & O'Reilly 1987). Moreover, the increase of the UV optical depth with the irradiation can be interpreted in terms of growth in number of the smaller clusters, which cannot be probed by the optical-gap variations (Robertson 1986, 1991; Mennella et al. 1995c).

As in the thermal annealing experiment, the structural changes are driven by the hydrogen loss during irradiation. The key role of C—H bond dissociation in photoinduced effects of hydrogenated amorphous carbon films was pointed out by Iida, Ohtaki, & Seki (1984); they estimated a photodissociation energy of ~3.6 eV. For aromatic C—H, a bond energy of ~5 eV is expected (Allamandola, Tielens, & Barker 1989). Therefore, when 10 eV photons break C—H bonds and hydrogen is removed, grain structure changes. In fact, in amorphous carbons, hydrogen primarily promotes the sp^3 bonding configuration by saturating π-bonds (Robertson 1986); the sp^3/sp^2 ratio is indeed ~3 for ACH2 grains (Mennella et al. 1995c). The effect of dehydrogenation on the electronic structure of the samples is indirect: the reduction in sp^3 bonds determines a decrease of the segregation of the graphitic clusters, which control the electronic properties, and thereby a decrease of the gap.

Finally, it is worth noting that a substantial degree of hydrogenation of the grains is still present after a UV irradiation dose of 4×10^{22} eV cm^{-2}. It is a well-settled result that a complete hydrogen effusion in amorphous carbons determines a delocalization of the π-bond and the closing of the optical gap, while E_g is 1.23 eV for ACH2UV550 sample. According to the optical-gap and hydrogen-content values measured in annealing experiments, we expect an H/C atomic ratio of ~0.3 for this last sample. Since H/C is 0.62 in ACH2 grains, half of the starting hydrogen has been removed by UV irradiation.

4. ASTROPHYSICAL IMPLICATIONS

To our knowledge, the result of the present experiment is the first reported laboratory observation of a UV resonance activation in hydrogenated amorphous carbon grains by UV irradiation. To analyze the implications on the interstellar bump interpretation, we first have to compare the laboratory grade of UV processing with that expected in space. To this end, according to Hagen, Allamandola, & Greenberg (1979), we assume that the interstellar radiation flux is $F \simeq F_0 \exp(-2A_v)$, where A_v is the visual extinction and $F_0 = 9.6 \times 10^8$ eV cm^{-2} s^{-1} is the unattenuated flux in the range 91–180 nm (Habing 1968; Mathis, Mezger, & Panagia 1983). Under diffuse-medium conditions ($A_v \simeq 0.6$), F is about 3×10^8 eV cm^{-2} s^{-1}; therefore, the total dose of UV photons deposited in amorphous carbon grains is 3×10^{23} eV cm^{-2} during the typical time of 3×10^7 yr that grains spend in the diffuse cloud medium (Jenniskens 1993). This fluence is a factor of 7 larger than that obtained in the laboratory. Extrapolating the dependence of E_g on the dose to the estimated fluence received by interstellar grains, we found $E_g = 1.19$ eV. This gap corresponds to graphitic clusters composed of ~30 sixfold rings. Similar values of the optical gap (0.6–1.2 eV) are expected for the hydrogenated amorphous carbon produced by UV irradiation in a diffuse cloud timescale starting from an organic refractory residue (Jenniskens et al. 1993). It is interesting to note that the optical gap of the residue is significantly larger than that of ACH2.

If our results are representative of the UV processing that occurs in space, then it is unlikely that hydrogenated amorphous carbon grains can be transformed into pure graphite grains in the diffuse medium. Processed carbon particles should form a disordered structure composed of sp^2 clusters and an sp^3 component whose relative abundance depends on residual hydrogenation. Moreover, the activation of a π-plasmon in carbon requires a delocalization of the π-bond, which is inhibited by the presence of hydrogen. Therefore, a revision of the interstellar bump interpretation in terms of π-plasmon in small carbon grains graphitized by UV radiation must be considered.

As is evident from laboratory results, π–π^* transitions determine the UV bump properties in small carbon grains. We suggest that the UV feature observed in space is due to these electronic transitions in graphitic clusters present within interstellar carbon grains. As typical of all models proposed so far (e.g., Draine & Lee 1984; Sorrell 1990; Joblin et al. 1992; Mathis 1994), this interpretation also puts strong constraints on the bump carriers. The observed constancy of the feature position requires a fixed value for the transition energy and thus for the peak of the cluster size distribution. In addition, the observed width variations of the bump must be tuned by width variations of the cluster size distribution.

In the diffuse medium, the evolution of hydrogenated amorphous carbon grains, both formed in hydrogen-rich stellar atmospheres and coming from the breaking off of processed organic refractory mantles in shock environments (Greenberg 1986, 1989; Greenberg, de Groot, & van der Zwet 1987; Jenniskens et al. 1993), into the carriers of the bump requires a physical process able to stop the peak shift at 217.5 nm. This process can be identified in a decrease of dehydrogenation efficiency by UV radiation, which prevents larger graphitic islands from a further dimensional growth. Duley & Williams (1988) analyzed the energy transfer between gra-

phitic islands in hydrogenated amorphous carbon grains. They found that, after the absorption of a UV photon, energy remains localized in clusters forming grains. Therefore, for the same internal energy, the smaller clusters loose hydrogen more efficiently than the larger ones. This effect is due to the lower excitation per vibrational mode in the larger clusters, in which cooling by radiation competes effectively with dehydrogenation relative to the smaller islands. A similar model has been proposed for PAHs and predicts no dehydrogenation for larger PAHs (Allamandola et al. 1989; Leger et al. 1989).

In conclusion, various problems have to be solved before the interpretation of the interstellar bump in terms of π–π^* transitions becomes more solid. Laboratory spectra obtained to date show UV bumps that are too wide and weak with respect to the interstellar feature. Much theoretical and experimental work remains to be done to completely account for the observational constraints. Higher UV fluxes are necessary in the laboratory, to confirm the extrapolation to the diffuse-medium values of the optical gap's behavior as a function of UV photon fluence and to check the actual bump position and profile. In addition, the effects on the electronic properties of rehydrogenation and ion irradiation must be analyzed. From the theoretical point of view, a quantum mechanical approach to the problem should be considered.

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