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FULLERENES AND BUCKYONIONS IN THE INTERSTELLAR MEDIUM

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ABSTRACT

We show that photoabsorption by fullerenes and buckyonions (multishell fullerenes) explain the shape, width, and peak energy of the most prominent feature of interstellar absorption, the UV bump at 2175 Å. The predicted optical and near-infrared transitions for these molecules also offer a potential explanation for the long-standing problem of the identity of the diffuse interstellar bands. The implied ubiquitous distribution of fullerenes may also account for the anomalous galactic microwave emission detected by cosmic microwave background experiments. Comparing theoretical cross sections and astronomical data, we estimate a density of fullerenes in the diffuse interstellar medium of 0.1–0.2 parts per million, consistent with the findings in meteorites. Fullerene-based molecules appear to be a major carbon reservoir in the interstellar medium.

Subject headings: dust, extinction — ISM: lines and bands — ultraviolet: ISM

1. INTRODUCTION

The presence of fullerenes in the interstellar medium (ISM) was suggested soon after the discovery of this new allotropic form of carbon (Kroto et al. 1985; Kroto & Jura 1992). However, the lack of spectroscopic data and the poor knowledge of the photoabsorption spectrum of these complex molecules have prevented us from making any firm conclusion. The detection of fullerenes C_{60}–C_{400} in meteoritic material (Becker et al. 1993, 1999; Pizzarello et al. 2001) and the tentative identification of some diffuse interstellar bands (DIBs) as carriers (Foing & Ehrenfreund 1994) has renewed interest in this possibility.

Fullerenes can adopt multilayered configurations in which one is encapsulated inside another, like layers of an onion. In his experimental study, using electron-bombarding techniques on carbon dust, Ugarte (1992) observed the transformation of polymeric particles of carbon into others with multiple spheric layers. Diverse laboratory experiments have proved that these groups of carbon, commonly known as buckyonions, can be formed with tens of layers. Electronic microscopy has determined that the separation between layers is of the order of 3.4–3.5 Å, which is approximately the separation between sheets of graphite. The buckyonions have also been synthesized, exposing carbon dust to thermal treatments (Cabioc'h et al. 1995). Laboratory experiments have shown that fullerenes and buckyonions are highly stable molecules that can survive the harsh conditions of interstellar space more easily than other carbon aggregates. Within the fullerene family, buckyonions composed of concentric spherical shells are the most stable (Tománek et al. 1993; Tomita et al. 1999). They can be part of two icosahedral families $60n^2$ and $180n^2$ with $n = 1, 2, \ldots$. Experiments support the existence of the first of these families with examples of such molecules up to $N \sim 100$ shells. Processes leading to the formation of fullerenes and buckyonions in the laboratory (Ugarte 1995; Kuznetsov et al. 1994) may also take place in the circumstellar envelopes of evolved stars and other astrophysical environments.

The most prominent feature in the ISM extinction curve is the UV bump at 2175 Å. The carrier of this band was soon associated with some form of carbonaceous material, but the exact physical nature of this material that was ultimately responsible for the band is still unknown (see, e.g., Draine 2003). The increase of interstellar extinction at shorter wavelengths and the existence of the mysterious, much weaker DIBs in the optical and near-infrared are also some of the intriguing observational properties of the interstellar material (Jenniskens & Désert 1994; Herbig 1995). The DIBs are believed to arise from gas-phase organic molecules (rather than from dust grains) in the ISM, but in spite of more than 80 years of research since the discovery of the first DIB, the nature of the carriers remains unknown.

The relationship of the interstellar UV bump with carbon spheres and carbon onions has been explored using classical dielectric models and graphite dielectric properties with promising results (see, e.g., Mathis 1994 and Henrard et al. 1997). However, this continuum approach neglects important quantum effects at the smaller scales (Iglesias-Groth et al. 2002; Iglesias-Groth 2003). A more refined modeling of the photoabsorption spectra of fullerenes and buckyonions is required if we want to ascertain their presence in space by comparison with the observed features of interstellar extinction.

2. THE PHOTOABSORPTION SPECTRA OF FULLERENES AND BUCKYONIONS

Very little is known about the electronic structure of fullerenes and buckyonions. Ab initio computations of the electronic structure are available only for fullerenes with small numbers of atoms and shells. Given the complexity of these models, other approximations have to be followed in the study of larger fullerenes. Semiempirical Hückel (tight minus binding) and Pariser-Parr-Pople (PPP) types of models have been successfully used in the study of the electronic structure of C_{60} (Cioslowski 1995). We use these PPP models to predict the electronic photoabsorption spectra of icosahedral fullerenes and buckyonions, taking into account the screening effects in these highly correlated electronic systems. Model parameters are first fixed by fitting the laboratory spectrum (Berkowitz 1999) of C_{60} in the energy range 1–30 eV, and then they are properly adjusted for larger fullerenes. Adopting the same approach and theoretical model as in previous work on the first five stable fullerenes of the icosahedral family (Iglesias-Groth et al. 2002), we have obtained spectra for icosahedral fullerenes containing up to 6000 atoms. For C_{1500} and smaller fullerenes, we use the PPP approach. For larger molecules, we use a Hückel approximation that assumes a hopping energy of -2.57 eV between π-like orbitals belonging to neighbor C atoms and of -8 eV for σ-electrons. All the theoretical spectra show a prominent band associated with the π-π^* plasmon transition at energies in the range 5.5–6 eV, which is close to that of the UV bump (5.7 eV).

We have also performed calculations of photoabsorption spectra in the range 1–15 eV for buckyonions of the $60n^2$ family up to C_{3840}. We have considered fullerenes with a complete number of shells. In order to obtain dynamic polarizabilities and photoabsorption cross sections, we adopted the formalism used to compute the static dipole polarizabilities of buckyonions in Iglesias-Groth et al. (2003), where an effective one-electron model and the screening effects are treated within the random phase approximation. The dipole moment on each shell is obtained in terms of either screened or unscreened polarizabilities of the isolated shells. The dynamic polarizability of a buckyonion formed by n concentric spherical shells is given by

$$\alpha(\omega) = \alpha^0(\omega)[1 + \alpha^0(\omega)/R^3]^{-1}, \tag{1}$$

where α^0 is the unscreened polarizability, R is the effective fullerene radius, and ω is the frequency. The photoabsorption cross sections of buckyonions (plotted in Fig. 1) have been computed using the imaginary part of the polarizability according to the relationship $\Gamma(\omega) = 4\pi c^{-1}\omega \,\mathrm{Im}\, \alpha(\omega)$. A prominent π-π^* band is predicted for each buckyonion. Peak energies result in the narrow range 5.6–5.8 eV. In buckyonions with a large number of shells ($N \geq 5$), the peak energy progressively converges to the value of the UV bump.

3. THE UV BUMP

The photoabsorption cross sections of individual and multishell fullerenes resemble the UV bump (see Fig. 1*a*). Since it is unlikely that extinction is related to fullerenes of just one size, we have considered different power-law size distributions $n(R) \propto R^{-m}$ for both fullerenes and buckyonions. We obtained via a least-squares fitting to the observed extinction curves what index m reproduces better, i.e., the characteristics of the UV bump: (1) the profile; (2) the stability of the peak energy (better than 0.5%); and (3) the range of variation of the bump width ($\pm 6\%$ at 1 σ) along different lines of sight (Cardelli et al. 1989; Fitzpatrick 1999). In the fits, we take into account the absorption by silicates conventionally described by a lineal function of energy (Mathis 1994). In all these models, we assumed the same abundance for the smallest fullerenes in the sample (C_{60} and C_{180}), as suggested by the measurements in meteorites. In Figure 1*b*, we compare some of our models with the extinction curve $A(\lambda)/A(V)$ for the diffuse ISM (characterized by the dimensionless optical parameter $R_V = A(V)/[A(B) - A(V)] = 3.1$) taken from Fitzpatrick (1999). The best-fit model was obtained for a mixture of fullerenes and buckyonions ranging from C_{60} to C_{3890} (with a radius between 3.5 and 28 Å) with a power-law size distribution of index $m = 3.5$. Molecules with a radius larger than 30 Å produced bumps that were too broad, and therefore they were finally discarded from the mixture. In this model, each buckyonion has the same abundance as its most external single fullerene. However, it is also possible to find good fits to the bump with mixtures that do not include buckyonions (see Fig. 1*b*).

The range of bump widths observed in different lines of sight can be explained in terms of small variations of the power-law index. Values of m in the range 3–4 satisfy the requirement on peak energy stability while providing a range of widths consistent with the observations. Reducing the value of m increases the width, as can be seen in Figure 1. The photoabsorption cross sections also show increased extinction toward higher energies (10 eV and beyond), in good agreement with observations (Sassen et al. 2002).

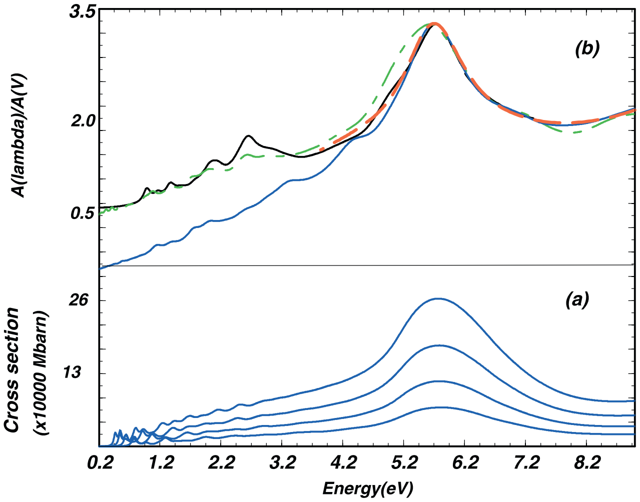

FIG. 1.—(*a*) Predicted cross sections for buckyonions of the $60n^2$ family with a complete number of shells. From bottom to top, the curves are plotted for buckyonions with external shells formed by the fullerenes C_{1500}, C_{2160}, C_{2940}, and C_{3840}. (*b*) Predicted absorption curves for fullerene and buckyonion mixtures in comparison with observations of the UV 2175 Å bump (5.7 eV) in the diffuse ISM (*dashed red line*). *Solid blue line*: Best-fit model to the UV bump obtained for a power-law size distribution $n(R) \propto R^{-m}$ of buckyonions and individual fullerenes ranging from C_{60} to C_{3840}, with index $m = 3.5$. *Dot-dashed green line*: Example of extinction curve for a distribution of fullerenes and buckyonions from C_{60} to C_{3840} adopting a power-law index $m = 2.5$ to illustrate how sensitive the peak position and width of the UV bump are to the characteristics of the distribution. *Solid b lack line*: Best-fit obtained for an index of the power-law size distribution of $m = 3.5$ using only single-shell fullerenes up to C_{1500}.

Comparison between the theoretical cross sections and the UV bump data allows us to estimate the density of fullerenes and buckyonions in the diffuse ISM. Using the parameters of the best-fit model and the well-known relationship between the excess color index and the hydrogen column density (Bohlin et al. 1978), which gives $A(V)/N(\mathrm{H}) = 5.3 \times 10^{-22}$ mag cm^2 for the diffuse ISM, we find values of 0.1–0.2 molecules per million hydrogen atoms for the smallest fullerenes, remarkably similar to the values found in meteoritic material. According to the preferred distribution law, the density decreases significantly as the size of the fullerene increases, reaching densities as small as 0.0001 parts per million (ppm) for the largest fullerenes under consideration. Such small densities for very large fullerenes may also explain why they have not yet been detected in meteorites.

For a mixture based on single fullerenes and a power-law index of $m = 3.5$, we estimate that 80 carbon per million hydrogen atoms would be locked in these molecules. If, as expected, the cosmic carbon abundance is close to the solar atmosphere value $N(\mathrm{C})/N(\mathrm{H}) = (350 \pm 50) \times 10^{-6}$ (Grevesse & Noels 1993), individual fullerenes may lock up 20%–25% of the total carbon in the diffuse ISM. In our best-fit model, fullerenes and buckyonions of the same size have the same abundance. In such cases, the fraction of interstellar carbon in fullerene-based molecules could reach 50% of the cosmic abundance. This fraction is smaller in regions of the ISM with larger values of R_V. A large fraction of carbon in fullerene-based molecules does not conflict with current estimates of the interstellar carbon budget that allocate about 40% of carbon in the form of atomic gas (Cardelli

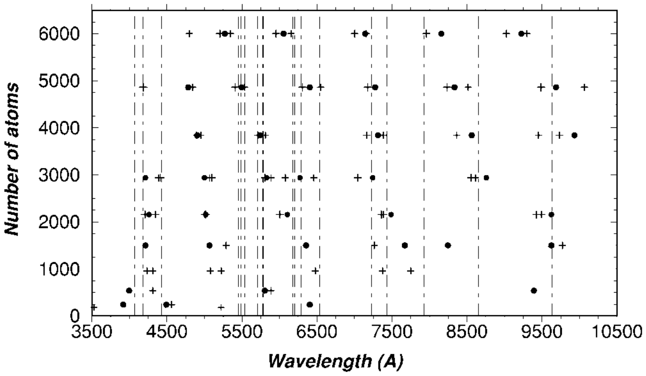

FIG. 2.—Predicted wavelengths for optical bands of fullerenes and buckyonions. The different molecules are denoted by the number of atoms in the case of single-shell fullerenes (*crosses*) or the number of atoms in the most external shell for buckyonions (*filled circles*). The vertical dashed lines indicate wavelengths of the most intense DIBs.

et al. 1996) and less than 10% in polycyclic aromatic hydrocarbons (PAHs; Désert et al. 1990).

4. DIFFUSE INTERSTELLAR BANDS

Unlike other proposed carriers for the UV bump, we predict for fullerenes and buckyonions a large number of weak bands in the optical and near-infrared (see the ripples at low energy in the cross sections plotted in Fig.1*a*). These bands have strengths consistent with those of the strongest DIBs, and their number per wavelength interval appears to decrease toward longer wavelengths, as is the case for the DIBs. In Figure 2, the predicted wavelengths for these transitions are compared with the positions of the 40 stronger DIBs known (Herbig 1995). At least 20% of these DIBs coincide (within the precision of the model ∼10 Å) with a theoretical transition of a fullerene or buckyonion, leading to a tentative association of these molecules with the DIBs carriers. Almost all the fullerenes and buckyonions considered here present a relatively strong band at energies close to the DIB at 4430 Å. Interestingly, it has been noticed that a positive correlation (Désert et al. 1995) exists between the strength of the UV bump and the strength of various DIBs. Hydrides of the fullerene C_{60} have also been investigated as potential DIB carriers (Wester 1993a, 1993b, 1995). No specific identification has been suggested, but it should be noted that the conjugated systems of π-electrons are predicted to have transitions in the visible range.

Remarkably, the longest wavelength band predicted by our models is at 3.37 μm and corresponds to the largest molecule considered in this Letter, i.e., to the buckyonion containing 6000 atoms in the most external layer. Our computations show a tendency for larger fullerenes to produce longer wavelength bands (see Fig. 3), so we cannot exclude that some of the ubiquitous infrared emission bands at 3.3, 6.2, 7.7, 8.6, and 11.3 μm observed in many astronomical objects (including emission and reflection nebulae, and the ISM of our Galaxy and other galaxies) may be partially associated with fullerenes of large size. However, the density of such large molecules in the ISM would be very small according to the power-law size distribution found in the previous section. Thus, it seems implausible that they are major carriers of these rather strong IR emission features. PAH molecules have been proposed as carriers of these IR bands (see, e.g., Leger & Puget 1984 and Allamandola et al. 1989). The optically active vibrational modes produced when hydrogen atoms are bounded to carbon atoms in aromatic rings may provide a natural explanation for these bands. The vibrational excitation would result from the absorption of UV or visible photons. Ionized PAHs absorb in the visible and near-IR and are also potential carries of the DIBs (Salama et al. 1996, 1999). A large effort is devoted to laboratory measurements of the UV-visible-NIR absorption spectra of PAHs (see, e.g., Ruiterkamp et al. 2002). The potential of fullerenes and buckyonions as carriers of the UV bump and DIBs is remarkable, and therefore we urge extensive laboratory experiments and more refined theoretical studies aimed at a precise determination of their spectroscopic properties in the optical and near-infrared.

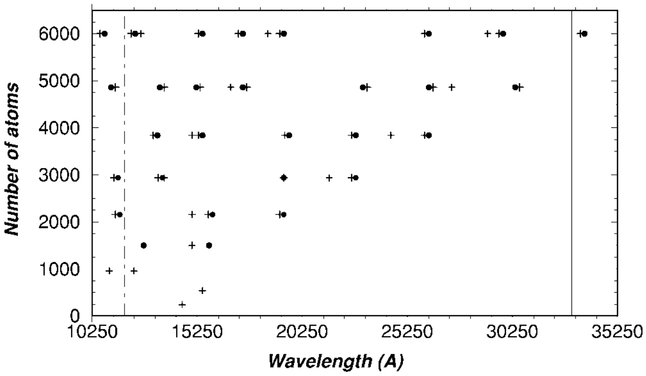

FIG. 3.—Predicted wavelengths for near-infrared bands of fullerenes and buckyonions. Symbols are the same as in Fig. 2. The vertical solid line indicates the infrared emission band at 3.3 μm.

5. DIFFUSE MICROWAVE EMISSION

Recent experiments dedicated to the study of the anisotropy of the cosmic microwave background have found evidence of microwave emission in the range 10–100 GHz correlated at high galactic latitudes with thermal emission (DIRBE 100 μm map) from interstellar dust (Kogut et al. 1996; Leitch et al. 1997; de Oliveira-Costa et al. 2004). An explanation for this anomalous dust-correlated microwave emission based on electric dipole emission from fast-rotating carbon-based molecules has been proposed (Draine & Lazarian 1998a, 1998b). We note that fullerenes and buckyonions fit the basic characteristics of the grain carriers of this emission proposed in some of the Draine & Lazarian models, particularly the spherical shape and a number of atoms in the range 30–1000 (which dominate emission in the 10–100 GHz region). According to the above results, fullerenes and buckyonions are broadly distributed in the Galaxy and lock a large fraction of interstellar carbon, probably higher than the 5% assumed in the Draine & Lazarian models. The same mixture of fullerenes that is able to explain the UV bump is also expected to produce microwave emission with a maximum at 30–35 GHz according to the pure spheres model considered by these authors. The vibration spectrum of multishell fullerenes may also display bands (Iglesias-Groth & Bretón 2000) in the range 100–500 μm that would correlate with emission at lower frequencies. Future space missions like *Planck* and *Herschel* will obtain high-sensitivity maps in a frequency range suitable to prove the distribution of fullerenes in the ISM.

6. CONCLUSIONS

The cross sections obtained for single fullerenes and buckyonions reproduce the behavior of the ISM UV extinction curve. We have found that a power-law size distribution $n(R) \propto R^{-m}$

with $m = 3.5 \pm 1.0$ for these molecules can explain the positions and widths observed for the 2175 Å bump and, partly, the rise in the extinction curve at higher energies.

We infer ISM densities of 0.2 and 0.1 ppm for small fullerenes and buckyonions (very similar to the densities of fullerenes observed in meteorites ~0.1 ppm). For a mixture based on single fullerenes and a power-law index of $m = 3.5$, we estimated that ~80 carbon per million hydrogen atoms would be locked in these molecules. If as expected the cosmic carbon abundance is close to the solar atmosphere value, individual fullerenes may lock up 20%–25% of the total carbon in diffuse interstellar space. Slightly better fits are obtained when buckyonions are also considered in the mixture. In our best-fit model, fullerenes and buckyonions of the same size have the same abundances. In such cases, an even higher fraction of interstellar carbon in fullerene-based molecules is obtained but is still consistent with current estimates of the interstellar carbon budget that allocate about 40% carbon in the form of atomic gas and less than 10% in PAHs.

Our computations also show that fullerenes and buckyonions present weaker transitions in the optical and near-infrared, with their number decreasing toward longer wavelengths. These transitions may be responsible for some of the known but unexplained DIBs. It would be very important to obtain high-sensitivity, high-resolution laboratory spectra of these molecules in the optical and near-infrared for a more precise comparison with the very detailed observations of DIBs already available.

Finally, fullerenes and buckyonions are expected to produce rotationally based electric dipole microwave radiation under the conditions of the diffuse ISM. These molecules are potential carriers for the anomalous Galactic microwave emission recently detected by several cosmic microwave experiments. Their precise contribution to this emission should be fully investigated.

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