

Research Note

On the far infrared bands associated to the vibration of multishell fullerenes

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Abstract. Multishell fullerenes could be produced in the circumstellar envelopes of rich carbon giants as proposed by Ugarte (1995) and could be carriers of diffuse interstellar bands. Here, we investigate a potential way to detect these molecules through the far infrared bands related to their vibrational spectra. Based on a surface continuum spherical description of the carbon shells, we have derived analytic expressions for their interaction potential and determined the vibrational frequencies of fullerenes in endohedral configurations. We find that their harmonic frequencies of oscillation lie in the range $20\text{--}65\text{ cm}^{-1}$. The associated bands could be observed with the spectroscopic facilities planned for the Far Infrared and Submillimeter Telescope (FIRST) providing a new way to confirm the existence of fullerenes in space. Suitable astronomical targets to search for these molecules are their likely sites of formation: carbon stars, post-AGB stars, protoplanetary nebulae, and dusty regions in the Galaxy.

Key words: molecular processes – stars: AGB and post-AGB – ISM: lines and bands – ISM: molecules – submillimeter

1. Introduction

Laboratory experiments aimed to achieve a better understanding of the physical conditions of the atmospheres of giant stars and to probe whether carbon-chains could explain some of the diffuse interstellar bands (DIBs) led to the discovery of the fullerene C_{60} , a new allotropic very stable form of carbon (Kroto et al. 1985). Further experiments have revealed the formation of larger molecules of the fullerene family C_{70} , C_{84} , C_{240} , etc. (see e.g. Iijima 1991, Ebbesen & Ajayan 1992). These molecules, created at very high temperatures, can survive under intense ultraviolet radiation and are highly resistant to destruction by collisions. Thus it was soon postulated their existence in meteorites (Heymann, 1986) and in the interstellar medium (Kroto & Jura 1992).

The first searches for fullerenes in meteorites have produced negative or controversial results. Tingle et al. (1991) and De Vries et al. (1993) did not find evidence for their presence in the

carbonaceous chondrites of the Allende and Murchison meteorites. More recently, Becker et al. (1994) have reported a detection of C_{60} in the Allende C3V condrite, however Heymann (1986, 1997) have not obtained an independent confirmation of these results and thus, the existence of fullerenes in meteorites cannot be definitively concluded. Similarly, evidences for the presence of fullerenes or other molecular analogues (ionized and hydrogenated fullerene species) in the interstellar medium have been reported in connection with the outstanding astronomical problem of the nature of the DIBs carriers. There are more than 150 DIBs in the visible, ultraviolet and infrared spectrum of stars observed through dusty regions of our Galaxy (Herbig, 1995). Given the interstellar ubiquity of these bands, their carriers have to be rather abundant and widely distributed in space. Some of the proposed candidates are associated to small dusty particles or to molecules containing a large number of carbon atoms: carbonated chains, polycyclic aromatic hydrocarbons (PAHs), hydrogenated amorphous carbon, carbon rings, fullerenes and fullerene-based molecules. Kroto et al. (1985) already pointed out that fullerenes should be considered as possible carriers for DIBs. The advantages of fullerene-based species, in this respect, have been described by several authors (Léger et al. 1988, Ballester et al. 1990, McIntosh & Webster 1993, Edwards & Leach 1993). So far, the available observations do not appear to support C_{60} and C_{70} as likely carriers of DIBs (Bensasson et al. 1995, Coheur et al. 1996), but there is increasing evidence that ionized fullerenes and hydrides of fullerenes could be the carriers for some of them. This appears to be the case of C_{60}^+ for the DIBs at 957.7 nm and 963.2 nm seen by Foing & Ehrenfreund (1994) towards several stars (see also Ehrenfreund & Foing 1997). Hydrides of fullerenes ($C_{60}H_m$, $m=1,2,\dots,60$) and their ions could be the carriers for the $21\ \mu$ feature seen in the spectra of some carbon-rich objects (Webster, 1991, 1993, 1995).

Another family of fullerene-based molecules which could be relevant to clarify the origin of the DIBs and the unidentified infrared emissions in astronomical objects are the so-called buckyonions or multishell fullerenes. These molecules suggested by Kroto & McKay (1988) were first synthesized in laboratory by Ugarte (1992, 1993) and show a higher stability than single fullerenes (Tománek et al. 1993, Lu & Yang 1994, Maiti

et al. 1994). Ugarte (1995) has proposed a model to explain the growth of these hyperfullerenes from nanodiamonds in the circumstellar envelopes of rich carbon giant stars. The process of nanodiamond annealing has been observed in the laboratory (Kuznetov et al. 1994) and the conditions that could make it feasible in space and its implications on the 217.5 nm band have been discussed by Ugarte (1995). In this process, nanodiamonds form by vaporization and subsequently lead to graphitic particles and multishell fullerenes. The latter author has shown that carbonaceous material irradiated with high energy electrons results transformed in particles with spherical multishell structure. On the other hand, the transformation of the inner region of buckyonions into nanodiamonds under electron irradiation has been reported by Banhart & Ajayan (1996). Molecules with up to hundreds of graphitic spherical shells have been observed by transmission electron microscopy (Ugarte 1992). Multishell fullerenes are therefore a new interesting molecular complex whose astrophysical implications deserve further investigation.

Henrard et al. (1997) have numerically studied the properties of multishell fullerenes in the ultraviolet, more precisely, in the region of the excitation of the π plasmon of carbon. They considered carbon onions with a void interior, and with interior filled by a dielectric material, in both cases incorporating adsorbed water molecules. According to their work the optical properties of multishell fullerenes with adsorbed water are consistent with those of the interstellar ultraviolet band at 217.5 nm yielding additional support to the idea that these kind of fullerenes could play a relevant role in the astronomical contexts mentioned above.

In this paper we present results of a simple model aimed to investigate the vibrational spectrum of fullerenes in endohedral (and exohedral) configuration, and determine their harmonic frequencies of oscillations. Details of the calculations have been published in Iglesias-Groth et al. (1997). Here we summarize them for completeness. The vibrational spectrum offers a potential way for identification of these molecules in the interstellar medium or in the circumstellar envelopes of carbon-rich stars using the spectroscopic facilities planned for the Far Infrared and Submillimeter Telescope (FIRST) of the European Space Agency.

2. The vibration of endohedral fullerenes

2.1. The model

We will consider here two spherical fullerenes with masses M_1 and M_2 , radii R_1 and R_2 containing N_1 and N_2 atoms, respectively, with their centres separated by a distance r . In Fig. 1 we display the endohedral configuration which will be considered in what follows. We have done a systematic analysis of the equilibrium configuration, stability conditions and confinement criteria adopting a surface continuum spherical description of the carbon shells (Iglesias-Groth et al. 1997). Our approximation is just a generalization of the Girifalco model (Girifalco 1992) for the van der Waals interaction between two C_{60} molecules. This continuum approximation has been successfully used in the calculation of the adsorption energy, equilibrium distances and

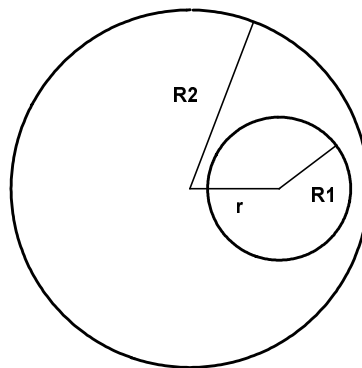


Fig. 1. Schematic representation of endohedral fullerenes.

atomic and molecular motions inside spherical and cylindrical fullerenes (Bretón et al. 1993, 1994), as well as in numerical simulations aimed to determine the stability of clusters of C_{60} (Rey et al. 1994, Wales 1994) and also to predict the potential energy of spherical fullerenes near a graphitic surface (Ruoff & Hickman 1994).

The interaction potential V_0 between the two spherical layers, mainly van der Waals, can be described as

$$V_0 = \sum_n \frac{N_1 N_2 c_n}{4(n-2)(n-3)R_1 R_2 r} \times \left\{ \frac{1}{A^{n-3}} + \frac{1}{B^{n-3}} + \frac{1}{C^{n-3}} - \frac{1}{D^{n-3}} \right\} \quad (1)$$

where $n=6, 12$ ($c_6=19.975 \text{ eV}\text{\AA}^6$, $c_{12}=3.4813 \text{ eV}\text{\AA}^{12}$) and,

$$\begin{aligned} A &= R_2 - R_1 - r, \\ B &= R_2 - R_1 + r, \\ C &= R_2 + R_1 + r, \\ D &= R_2 + R_1 - r. \end{aligned}$$

Using the reduced variables $s = \frac{r}{R_1}$ and $b = \frac{R_2}{R_1}$, the interaction potential becomes

$$V_0(R_1, b, s) = \sum_{n=6,12} R_1^{(4-n)} D_n b \times \{F_n(b+1, s) - F_n(b-1, s)\} \quad (2)$$

where $D_n = (4\pi)^2 \rho_s^2 c_n$, (ρ_s being the atomic density of carbon atoms $N_k/(4\pi)^2 R_k^2$) characterizes a Hamaker-like coefficient and the function F_n is expressed as:

$$F_n(\alpha, s) = \frac{1}{4(n-2)(n-3)s} \times \{(\alpha+s)^{3-n} - (\alpha-s)^{3-n}\} \quad (3)$$

where α can take values $b+1$ or $b-1$. The endohedral situation corresponds to $s \leq b-1$ and the exohedral one to $s \geq b+1$. In Fig. 2 we show interaction potential energy curves for some of the buckyonions considered in our work. The position at $r=0$ is unstable for $b \geq 2$ (systems with off-centred equilibrium positions). For $b \leq 2$, the equilibrium position is at $r=0$. Note that

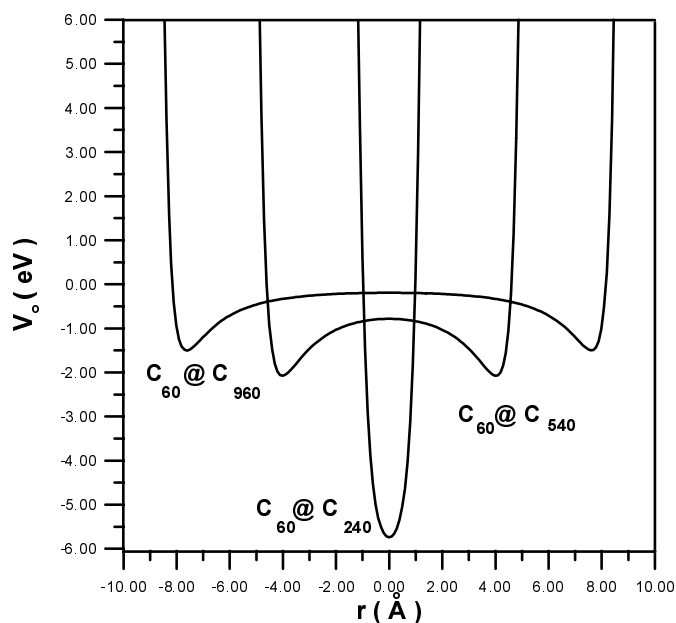


Fig. 2. Interaction potential of some examples of endohedral fullerenes against the separation of their centres.

the radial barriers $\Delta V_0 = V_{min} - V_0(r=0)$, i.e the difference between the minimum potential and the value of the potential at $r=0$ are -1.307, -1.290, and 0.0 eV for $C_{60}@C_{960}$, $C_{60}@C_{540}$ and $C_{60}@C_{240}$, respectively.

2.2. Harmonic frequencies of oscillation. Far infrared emission

We define the reduced mass of the two fullerene system as:

$$\mu = M_1 \frac{b^2}{b^2 + 1} \quad (4)$$

which is valid within the approximation of constant atom density in the fullerenes. The corresponding mode frequency for the relative vibration of the two fullerenes is then

$$\omega(b) = \frac{1}{2\pi c R_1 \mu^{1/2}} \left(\frac{d^2 V}{ds^2} \right)^{1/2} \quad (5)$$

where c is the speed of light.

We give in Table 1 our results for several endohedral fullerenes. We list the value of the radius of the inner fullerene (Column 1) and the corresponding relative radius (Column 2) with respect the external one (both molecules assumed spherical). These radii are a good approximation to the correct ones (see Tománek et al. 1993). The equilibrium distances (r_0 , Column 3) were obtained by minimizing the interaction potential $V_0(R_1, b, s)$ given in Eq. (2) and the harmonic frequencies of oscillation resulting from Eq. (5) are given in the last column.

In Fig. 3 we plot the behaviour of the frequency of the relative vibration mode against the ratio of the radii of two endohedral fullerenes. As it can be seen, for endohedral fullerenes containing a C_{60} with $b \geq 2.5$ the frequency of vibration progressively decreases converging to a value $\omega(b=\infty) = 32.6 \text{ cm}^{-1}$

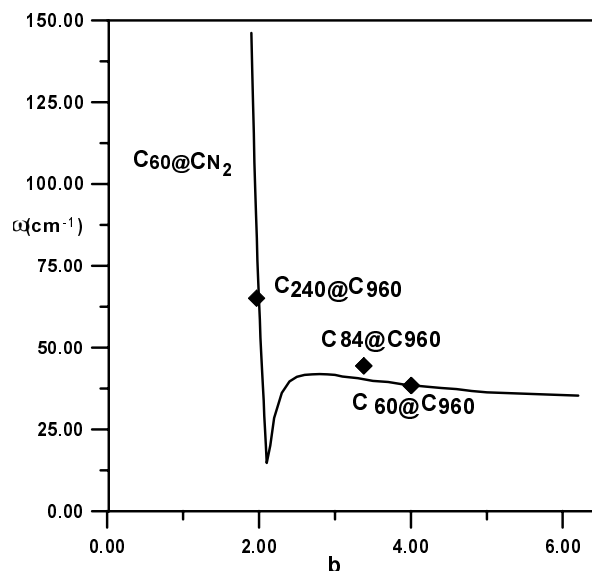


Fig. 3. Behaviour of the harmonic frequency of oscillation, ω , versus $b = \frac{R_2}{R_1}$ for endohedral fullerenes formed by the C_{60} molecule and a fullerene with N_2 carbon atoms (solid thick line). Diamonds denote the location of the labelled endohedral fullerenes.

Table 1. Equilibrium characteristics for endohedral fullerenes $C_{N_1}@C_{N_2}$.

Complex	R_1 (Å)	b	r_0 (Å)	ω (cm^{-1})
$C_{60}@C_{240}$	3.55	2.0	0.004	64.2
$C_{60}@C_{540}$	3.55	3.0	4.026	41.6
$C_{60}@C_{960}$	3.55	4.0	7.620	38.4
$C_{84}@C_{960}$	4.19	3.4	6.970	44.3
$C_{240}@C_{540}$	7.10	1.5	0.001	42.3
$C_{240}@C_{960}$	7.10	2.0	4.026	66.4

which corresponds to that of the interaction of the C_{60} with a graphitic plane. The harmonic frequencies are considerably smaller than the intramolecular vibrational frequencies of the fullerenes ($273\text{--}1469 \text{ cm}^{-1}$ for the C_{60} molecule, Bethune et al. 1991). Note in passing, that only the 527, 577, 1183 and 1415 cm^{-1} are infrared actives (Taylor et al. 1990, Mejer & Bethune 1990). The curve shows a minimum at $b \sim 2.1$. Remember that $b \leq 2$ corresponds to an equilibrium on-center position. Then, due to the large influence of repulsive interactions the frequency raises steeply for lower b values. The frequencies corresponding to the exohedral configurations are always lower than the endohedral ones (Iglesias-Groth et al. 1997).

Note that in $C_{N_1}@C_{N_2}$ the inclusion is neutral. Here the dipole is caused by overlap effects. To our knowledge computations of the induced vibrational dipole are not available. However, Joslin et al. 1993 have estimated the induced vibrational dipole for an endohedral system like $\text{He}@C_{60}$. In that case, their mean square induced dipole moment was $\sim 0.01 \text{ au}$ (~ 0.3 Debye), a small but observable quantity (about one-third of the induced dipole for the CO molecule).

The case of a carbon anion with a large number of concentric spherical shells has been studied by Nagy et al. (1994)

who obtained the equilibrium structure and the low-frequency intershell vibrational modes. Their results are consistent with ours. The vibrational density of states of very large structures was found to approach that of an infinite linear chain with site-independent masses and force constants and the vibration frequencies were always smaller than the corresponding Debye frequency ($\sim 80 \text{ cm}^{-1}$).

3. Production sites and detectability

Astronomical sites with a high carbon content and suitable conditions for the formation of multishell fullerenes are good candidates to achieve the detection of these molecules. In laboratory experiments, closed multilayer graphitic molecules have been created via electric arc discharges (Ijima 1980), high temperature (2300–2800 K) treatments (de Heer & Ugarte 1995), high-fluence carbon ion implantation (Cabioc'h et al. 1997), strong electron irradiation of carbon soot (Ugarte 1992), and more recently, as described by Kuznetsov et al. 1994, via a high temperature (1500–1800 K) treatment of nanodiamonds (3–6 nm). Carbon stars possess very high abundances of carbon in their atmosphere as a result of the transport of carbon nuclei synthesized in the interior to superficial layers. Their atmospheric temperatures are in the range 2000–3000 K, suitably high to activate some of the mechanisms which can lead to the production of multishell fullerenes, particularly that of Kuznetsov et al. for generation from nanodiamonds. These stars suffer large mass losses enriching the interstellar medium with the molecular and atomic products existing in their atmospheres, which would favour a broad distribution of these molecules in interstellar space. Nanodiamonds could form via chemical vapor deposition (Lewis et al. 1989) in the physical conditions of the atmospheres of carbon and post-AGB stars or in the circumstellar envelopes frequently formed around them via mass loss processes. The presence of nanodiamonds in the interstellar medium has been a matter of debate for decades, however their occurrence in chondrites seems well established. Recently, these particles have been advocated as possible explanation for the 21μ feature seen in the protoplanetary nebula IRAS 16594-4656 (García-Lario et al. 1999) which gives additional support to the idea that these nanoparticles can form and act as seeds for the generation of the much more stable multishell fullerenes. The results of Henrard et al. 1993, supporting the association of water coated carbon onions with the ultraviolet band at 217.5 nm encourages us to propose the search for the infrared bands related with the vibrational spectra of multishell fullerenes. Suitable targets are the atmospheres and circumstellar envelopes of carbon and post-AGB stars, and protoplanetary nebulae. The Far InfraRed and Submillimeter Telescope (FIRST) of the European Space Agency (Pilbratt 1998) will offer sensitive instrumentation in the relevant spectral range providing an excellent opportunity to achieve the detection of these bands. In particular, those of the endohedral complexes $C_{60}@C_{240}$, $C_{240}@C_{960}$ could be investigated with the Photoconductor Array Camera and Spectrometer (PACS) (see Poglitsch 1998), an instrument based in two 25×16 Ge:Ga detectors which will perform imag-

ing photometry and imaging line spectroscopy in the $80\text{--}210 \mu$ region (with possible extensions to 60μ and 300μ). The spectrometer will provide a resolving power of 1500–2000 (resolution of $100\text{--}250 \text{ km s}^{-1}$) with an instantaneous coverage of $1300\text{--}3000 \text{ km s}^{-1}$. Similarly, the Fabry-Perot spectrometer of the Spectral and Photometric Imaging REceiver (SPIRE, Griffin et al. 1998), an instrument based in bolometers will allow spectroscopy in the range $200\text{--}600 \mu$. A resolving power up to 10^3 will be available in the $200\text{--}300 \mu$ region relevant for detection of the vibrational bands of the endohedral fullerenes $C_{60}@C_{540}$ and $C_{240}@C_{540}$.

4. Conclusions

Using a simple model to describe the interaction of carbon shells, we have calculated the equilibrium characteristics and the frequencies of the relative vibrational modes of fullerenes in endohedral and exohedral configurations. These frequencies mainly lie in the range $20\text{--}65 \text{ cm}^{-1}$, i.e. in the far infrared and submillimeter region of the electromagnetic spectrum. Evolved giant stars (carbon stars, post-AGBs, proto-planetary nebulae, etc) and their circumstellar envelopes are likely sites for the formation of multishell fullerenes and consequently, targets to search for the spectral bands associated to the vibration of these molecules. The spectroscopic facilities planned for ESA's cornermission FIRST offer a potential way to identify these molecules in space through measurements of their vibration spectrum.

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