

# Circumstellar and interstellar fullerenes and their analogues

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**Abstract.** C<sub>60</sub>, Buckminsterfullerene and/or its complexed exohedral and endohedral analogues, most likely in ionized form, may be ubiquitously distributed in space and stars. The complexes involving abundant elements (Na, K, H, O, etc.) should exhibit strong charge transfer bands with characteristics similar to those of certain unidentified astrophysical spectroscopic features.

**Key words:** fullerenes – C<sub>60</sub>M<sup>+</sup> – exohedral ion complexes – diffuse bands – charge transfer spectra

## 1. Introduction

The characteristics of the diffuse interstellar bands (DIBs), a set of optical absorption bands seen in the spectra of starlight which has passed through dusty regions of the Galaxy, have been extensively discussed by Herbig (1975, 1988). The most curious aspect of the DIBs is the fact that the carriers, though clearly present in copious quantities in space, presumably because they are readily formed and/or stable in this harsh chaotic environment, have so far defied characterization in the laboratory. There are interesting analogies between the properties of the DIB carriers and those of the recently discovered fullerenes, C<sub>60</sub> (fullerene-60) in particular (Kroto 1988). They both form spontaneously (and perhaps symbiotically) together with carbon dust, they are both stable under intense radiation (in isolated situations), and both have eluded detection (until now in the case of the fullerenes). These unusual coincidences, together with ancillary evidence, suggest that fullerene analogues should be considered seriously as possible carriers of the interstellar features (Kroto et al. 1985; Kroto 1986–1990; Léger et al. 1988; Ballester et al. 1990). The proposal has recently gained further weight from the discovery that fullerenes can be produced in significant amounts during the random nucleation processes which occur in a carbon arc (Krätschmer et al. 1990; Taylor et al. 1990). In addition Gerhardt et al. (1987) and Howard et al. (1991) have shown that fullerenes also form during combustion (i.e. in the presence of hydrogen and oxygen!).

Fullerene stability is also an interesting question. It has been found that fullerene-60 can decompose in condensed media in the presence of oxygen and light (Taylor et al. 1991) – almost certainly one reason why C<sub>60</sub> was not detected long ago. Cluster beam experiments, on the other hand, indicate that isolated fullerenes are stable even in intense radiation fields, conditions analogous to

those which obtain in regions of space where the DIB carrier resides. There is thus a further curious parallel which can be drawn between the ambivalent “stability” which C<sub>60</sub> shows and the apparent “stability” of the DIB carrier in space and its perplexing elusiveness on earth.

Some of the similarities discussed above pertain also to the polyynes and the conditions for their formation, particularly in relation to the outflows from carbon-rich stars (Kroto 1981, 82). Furthermore, it should be noted that the DIBs have been studied over many years and there now appears to be very good evidence for the existence of more than one carrier (Krelowski & Walker 1987; Westerlund & Krelowski 1988a, b) although the number does appear to be limited. An important advance has recently been made by Sarre (1991), who has shown that several specific emission features detected in the bi-conical stellar outflow, known as the “Red Rectangle”, are *emission* analogues of a set of DIB features which Krelowski & Walker (1987) had assigned to a single carrier. Fossey (1991) has also drawn attention to this. Our newly acquired knowledge of the fascinating chemical interrelationships which occur in a condensing carbon-rich gas indicates that fullerene analogues may well be formed in carbon-rich objects e.g. RCorBor stars and cool N-type red giants, such as IRC + 10216, as well as in the bipolar outflow nebulae such as the “Red Rectangle” and AFRL 2688.

The possibility that a C<sub>60</sub> analogue might be a DIB carrier was suggested when the molecule was first discovered (Kroto et al. 1985). As far as neutral fullerene-60 is concerned, the electronic transitions in solution (Krätschmer et al. 1990; Hare et al. 1990; Ajie et al. 1990; Cossart-Magos & Leach 1991) are not obviously consistent with any prominent astrophysical features. It should however be noted that solvent effects have yet to be evaluated. As the IE of C<sub>60</sub> is 7.61 eV (Zimmerman et al. 1991; Lichtenberger et al. 1991) it is clear that if fullerene-60 is formed in the ISM, it will most likely ionize (Kroto 1987–1990; Léger et al. 1988). Furthermore, fullerenes may yield *exohedral* complexes in which an atom or molecule may be attached to the outside surface (Huang & Freiser 1991) or *endohedral* complexes (carcerands) where the atom is trapped inside the cage (Heath et al. 1985; Heymann 1986; Ballester et al. 1990; Huang & Freiser 1991).

This study argues that various fullerene analogues, in particular complexes, may exist in significant amounts in the ISM and certain of them may be responsible for certain unidentified interstellar features. Particular attention is drawn to the fact that charge transfer (CT) transitions of the ionized exohedral complexes, could account for the DIBs. The symbols (M) and ( ) · M will be used to denote endohedral and exohedral fullerene-60 cage complexes, respectively. The adsorbed or trapped species, M, are

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likely to be cosmically abundant metal atoms (Na, K, Ca, etc.) as well as hydrogen and oxygen. Furthermore, the abundance of protonated species such as  $\text{HCO}^+$  indicates that the protonated  $\text{C}_{60}$  is likely to be the most abundant fullerene analogue. This conjecture is supported by the recent observation of McElvaney et al. (1992) that fullerene-60 has a high proton affinity. How important oxygen analogues are is still an open question; species such as  $\text{C}_{60}\text{O}$  have been detected, however their spectroscopic properties have yet to be determined experimentally (see below).

A key aspect of the arguments presented here is that the analogues must be a restricted set. For instance they should not be intermediates which lead to the destruction of the cage. This means that adducts which significantly disrupt the basic integrity of the pi orbital system and/or link directly with the carbon atoms causing parts of the  $\text{sp}^2$  cage framework to change to  $\text{sp}^3$  – ultimately causing cage destruction – must not occur if fullerenes are important in the ISM. Interstellar hydrogenated fullerene-60 analogues have been discussed by Webster (1991); however there are circular arguments which appear to preclude their importance in an interstellar context. Once the bonding integrity of fullerene-60 has been breached and “true” hydrogenation initiated, chemical intuition suggests that numerous semi-fullerene/and  $\text{C}_{60}\text{H}_n$  compounds and isomers should form, ultimately resulting in cage rupture and more standard non-cage PAH products. Line dilution is clearly important and, as far as the electronic transitions are concerned, each hydrogenated species will have a totally different electronic structure and associated spectrum. Thus the very properties which make fullerene-60 unique and the crucial (albeit circumstantial) arguments supporting the proposal that fullerenes are important in the ISM, appear to be lost if highly hydrogenated fullerene derivatives form readily in the ISM. If, on the other hand, a *very* small restricted set of stable hydrogen-containing derivatives form (of which the protonated species might be one) their presence in the ISM should be detectable.

## 2. Transitions of fullerene complex analogues

Evidence for endohedral metallofullerene cage complexes was presented soon after fullerene-60 was identified (Heath et al. 1985; Weiss et al. 1988) and these early observations have recently been nicely confirmed by Huang & Freiser (1991), who have also detected exohedral complexes. Alkali and alkaline earth metals show significant propensities for encapsulation during fullerene creation, presumably related to their capability to intercalate in graphite. Ballester et al. (1990) first considered the spectra of neutral endo-complexes theoretically and showed that they may have large absorption coefficients. Further recent studies have been made by Cioslowski (1991), Cioslowski & Fleischmann (1991) and Chang et al. (1991).

Exohedral or endohedral fullerene complex analogues should exhibit several types of electronic transition; for example, intrinsic fullerene transitions perturbed by the complexed atom and intrinsic atomic transitions perturbed by the fullerene cage. The most interesting features in the context of this paper are charge transfer (CT) bands of ionic (and neutral) fullerene complexes.

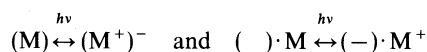
### 2.1. Charge transfer bands of neutral fullerene analogues

For neutral complexes of highly electropositive metals in the ground state, intuition suggests that the positive charge is likely to reside on M and the negative charge on the cage. This has been

discussed by Chang et al. (1991). The charge transfer energy is given, very roughly, by

$$\text{IE}(\text{M}) - \text{EA}(\text{C}_{60}) - \text{CE}(\text{e}^-),$$

where IE is the ionization energy, EA is the electron affinity and CE is the Coulombic energy of the displaced electron (Murrell 1963). The IE of  $\text{C}_{60}$  is now known to be 7.61 eV (Zimmerman et al. 1991; Lichtenberger 1991). The EA of  $\text{C}_{60}$  has also been measured as  $2.7 \pm 0.1$  eV (Yang et al. 1987). Thus the ground state will be either neutral or a charge transfer (salt) configuration depending the size of the Coulombic term CE. This term is difficult to estimate but is crudely approximated by  $e^2/r = 14.4/r(\text{\AA})$ , in eV. This value is of course also the photon energy absorbed on excitation of the associated charge transfer band from neutral to charge transfer state or vice versa. The transitions can be written as

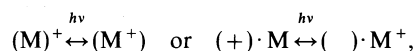


for the endo- and exo-complexes, respectively. Charge transfer transitions are well known in chemistry (Murrell 1963), and may give rise to strong absorptions associated with the electron jump involved. The carbon-to-carbon diameter of fullerene-60 is 7 Å and the effective pi-electron cloud layer thickness is ca. 1.5 Å. For exo-complexes the loss of symmetry and the fact that the ion is embedded in the pi cloud surrounding the cage should ensure a very large overlap integral. If in addition it is recognized that on excitation charge displacements of 6 Å or more are feasible, absorption coefficients 1–2 orders of magnitude larger than those for normal strong transitions should result.

In endohedral complexes, M (e.g. Na or  $\text{Na}^+$ , etc.) need not lie at the center of the cage; in fact the atom or ion is likely to be displaced (Cioslowski 1991; Cioslowski & Fleischmann 1991), breaking  $I_h$  symmetry selection rules. On excitation the equilibrium configuration should also change. Even if the atom lies at the center, for alkali or alkaline earth metals the transition should be strongly allowed because the LUMO of  $\text{C}_{60}$  possesses  $t_u$  symmetry and the donating atomic orbitals have s symmetry. In the calculations made by Ballester et al. (1990) the atom was assumed to be at the center of the cage.

### 2.2. Charge transfer bands of ions

For cationic alkali or alkaline earth metal complexes the positive charge almost certainly resides on the metal nucleus in the ground state. In this situation the transitions are



which are best described in terms of an electron hopping between the cage and M. To a first order of approximation the transition energy of the associated charge transfer band is given by

$$h\nu = \text{IE}(\text{C}_{60}) - \text{IE}(\text{M}).$$

This relation is not likely to be very accurate, however the IEs of the most cosmically abundant elements which are likely to adsorb or encapsulate and the resulting (approximate) transition energies and associated wavelengths are given in Table 1. The Coulomb term makes estimates of the neutral CT transitions even less reliable and thus we have not estimated the transition energies. In

**Table 1.** Ionization potential, electron affinity, abundance and estimated transition data for various fullerene complex ions

Element	Cosmic number abundance	IE (eV)	$h\nu$ (eV)	Wavelength (nm)
Na	1.7 (-6)	5.14	2.46	504
K	1.1 (-7)	4.34	3.26	380
Mg	3.5 (-5)	7.64	(0)	—
Ca	2.0 (-6)	6.11	1.49	832
Al	2.5 (-6)	5.98	1.62	765
Fe	2.5 (-5)	7.90	0.29	4334
H	1.0	13.6	6.0	207
O	6.8 (-4)	13.6	6.0	207
C	3.7 (-4)	11.3	3.7	335
N	1.2 (-4)	14.6	7.0	177

addition it is almost certain (on the basis of foregoing arguments) that ionized analogues are expected to predominate.

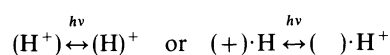
### 2.3. Intrinsic transitions of atoms in complexes

Intrinsic transitions of the adsorbed or caged species, perturbed by the environment of the surrounding cage, are also important. The shift in frequency and “line” intensity relative to those of the bare atom or ion will depend upon several factors including how far the atom or ion is from the center of the cage (equilibrium position) or how deeply it is embedded in the surface electron sea of the fullerene. The transitions may be strong (Ballester et al. 1990) but they are unlikely to be as strong as the charge transfer bands of exohedral complexes discussed above, because the net electron displacements involved are smaller.

### 3. Fullerene analogues in the ISM

From the foregoing arguments we see that exohedral metallofullerene cation complexes such as  $(\cdot)M^+$  ( $M = \text{Na}, \text{K}, \text{Ca}, \text{etc.}$ ) are expected to give rise to exceptionally strong CT transitions in the optical range. All the arguments which support the proposal that they may be responsible for the DIBs are presented in detail in the next section. Charge transfer processes in species such as  $(\text{Mg}^+)$  and  $(\cdot)\text{Mg}^+$  present a fascinating case in that the ionization potentials of the cage and Mg are almost identical – within the error of the simple first-order energy relation. As a consequence a strong resonance near zero frequency might be expected and indeed a prominent IR feature, thought to be associated with Mg, has been observed (Goebel & Moseley 1985). The electrical conductivity of condensed magnesium fullerene may be unusual as it should have a very small band gap.

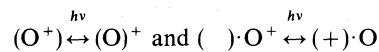
The interstellar abundance of  $\text{HCO}^+$  suggests that the most likely fullerene analogue in the ISM will be the exohedrally protonated species  $(+)\cdot\text{H}$  (except in highly hydrogen-depleted regions (e.g. RCorBor stars). Indeed McElvany & Callahan (1991) have shown, by an elegant bracketing technique, that the proton affinity of  $\text{C}_{60}$  is close to that of ammonia (between 204 and 207 kcal mol<sup>-1</sup>, i.e. ca. 8.9 eV). Cox et al. (1991) have also observed protonation. According to Table 1 the transitions



should also lie near 207 nm, i.e. very close to the well-known feature which appears to be associated with carbon at 217 nm. Day & Huffman (1973) and Hecht et al. (1984) have discussed the correspondence between this feature and the optical scattering from small carbon particles. In this context it is interesting to note that Day and Huffman observe scattering near 240–260 nm, which is rather close to the scattering observed in RCorBor stars – which are H-deficient objects. In all other cases, the scattering is at 217 nm and is unusually stable except for a few observations in which it appears to have shifted to 213 nm. This suggests that the carrier is a rather well-defined aggregate (molecule?) which is very weakly perturbed in the 213 nm interstellar regions. According to Fitzpatrick & Massa (1986) the area under the 217 nm feature for  $E(B-V)=1$  mag is 1500 Å. For an oscillator strength of 1 the carrier column density must be ca.  $4 \cdot 10^{16}$  cm<sup>-2</sup> and  $N(\text{carrier})/N(\text{H})=10^{-5}$ . As 60 carbons are tied up in fullerene-60 such a set of assumptions would require the entire interstellar carbon abundance be in the form of a  $\text{C}_{60}$  analogue. We have however argued (above) that exohedral charge transfer absorption coefficient are likely to be 30–100 times greater than standard absorption coefficients; so this suggests that only 3–1% of the interstellar carbon need be in the form of a  $\text{C}_{60}$  analogue. This seems to be a reasonable amount in view of the fact that when fullerenes form some 10% of the carbon ends up as  $\text{C}_{60}$  (Krätschmer et al. 1990; Taylor et al. 1990).

We note that if M has an IE greater than that of  $\text{C}_{60}$  (as is the case for hydrogen) then the positive charge will reside on the cage and CT-type absorption involves an electron jump from the adsorbed atom to the cage. Importantly, a very high steady-state concentration for the exo-protonated complex should build up, even if the photo-desorption (i.e. photodissociation) rate is high because complex re-formation is likely to occur efficiently, even by simple two-body radiative association.

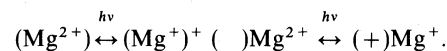
Evidence for the carbon oxide  $\text{C}_{60}\text{O}$  has been obtained (Heath et al. 1985) and the associated transitions



should lie at roughly 6.0 eV (207 nm). However oxygen may be an agent for fullerene destruction (Taylor et al. 1991), though whether this is the case in isolated situations has yet to be determined.

### 4. Multiply-ionized complexes

Doubly charged species are very important in beam experiments as has been shown by Limbach et al. (1991). Thus higher-energy transitions associated with doubly charged ions must be considered. For instance species involving ions such as  $\text{Ca}^{2+}$  constitute fascinating possibilities. McElvany and co-workers (1991, 1992) have shown that the second IP of fullerene-60 is less than 10 eV so as 13.6 eV radiation is essentially ubiquitous in the visible regions of ISM such systems must be considered as very likely to be important.



Leach (1988) has also argued that doubly charged ions are likely to be very important in the ISM.

### 5. Broadening processes

Broadening effects are most likely to arise from rotations and the resulting band structure will depend on various factors such as

structural distortions on excitation and various standard molecular vibronic interactions. For hydrogen, tunneling between potential wells on the fullerene surface is also likely to be very important even at very low temperatures. For the exo-complex, intra-cage oscillations should be the main source of broadening (Ballester et al. 1990) and these should be very similar in character to matrix isolated bands.

As far as  $(\text{H}^+)$  is concerned, small shifts may be caused by further adsorbed species, such as a second H atom, which is likely to cause little disruption of the electronic structure of the molecular complex. As far as the linewidth is concerned it is likely to be dominated by surface tunnelling which in the case of such a novel round surface is a totally new, fascinating and as yet to be investigated phenomenon.

Tunneling will not occur for heavier atoms where the spectra are likely to be dominated by rotational band structure. Scarrot et al. (1992) have discussed this problem and shown that  $\text{C}_{60}$  analogues would have line shapes consistent with those observed, contrary to the conclusion of Fossey (1991).

## 6. Summary

Having determined which fullerene analogues are likely to be abundant in space and having discussed the strongest electronic transitions, it is possible to draw a number of conclusions of astrophysical significance:

(1) As has already been pointed out (Introduction), the most important argument (albeit circumstantial) implicating  $\text{C}_{60}$  in the DIB puzzle is the finding that from a chaotic chemical mix, a small set of specific stable molecules remains, when all others have been removed from the gas phase by nucleation and/or destroyed by photofragmentation – ultimately into atoms. This property appears to be unique to the fullerene family. The cage is not only unreactive as far as further up-clustering is concerned but is highly resistant to fragmentation. The most likely “reaction” which  $\text{C}_{60}$  or its ion should undergo is complex formation. This process does not seriously disrupt the highly stable electronic structure of  $\text{C}_{60}$  and may, due to the size of  $\text{C}_{60}$ , occur by simple bimolecular radiative association on almost every collision.

(2) According to Table 1, no abundant ionic CT bands lie between those of the K complexes (calculated to lie at ca. 380 nm) and those of the H and O complexes (at ca. 210 nm). (Note that C atoms do not form complexes, they are incorporated into the fullerene cage network.) It is difficult to estimate the accuracy of the above simple formulae for the transition energies, however we note that no interstellar diffuse features have so far been detected between 217 and 443 nm. Of course this might be because spectroscopic observations are very difficult in this region.

(3) The DIB linewidths and line shapes are important parameters and have been much studied. It is probably fair to say that there is no clear consensus at present as to whether they are consistent with (a) molecular rovibronic envelopes, (b) matrix broadening effects or (c) predissociation processes. We propose that the larger of (a) or (b) will tend to dominate the observed pattern and if (b) is important the fullerene proposal explains why the DIBs exhibit characteristics similar to matrix spectra but without the wavelength variability expected due to variations in the trapping environment.

The spectra of the complexes will be broadened by the motion of the adsorbed species on the surface of the carbon cage or intra-cage oscillations if trapped. The degree of broadening will depend

on the potential and decrease rapidly with the mass of the trapped or adsorbed species. For protonated fullerenes, the reduced mass associated with the H motion will be an order of magnitude less than that of other atoms and tunneling on the surface should give rise to a very broad resonance. In general complicated oscillations are likely to be excited as the equilibrium position of the adsorbed or encapsulated atom may change significantly on charge transfer excitation. For endohedral complexes Ballester et al. (1990) have estimated the broadening anticipated, with certain rather gross assumptions about the potential, and they find it to be roughly in line with observation. Photodissociation will only be important for exo-complexes and radiative association may be an efficient two-body process which should maintain a high steady-state abundance.

Fossey (1991) suggests that fullerene analogues are too large and cannot account for the diffuse bands. This argument is however based on the assumption that the “doublet” features seen in emission from the Red Rectangle are associated with the P and R branches. The (absorption) DIB features however do not appear to exhibit this “doublet” pattern suggesting the satellites seen in emission are due to vibrationally excited sequence or progression components.

(4) Fullerene-60 may be chemically and photochemically unstable under condensed phase conditions (Taylor et al. 1991). This behaviour might explain why this molecule, though apparently involved to varying degrees in combustion processes, does not appear to build up in the terrestrial environment and thus was not discovered much earlier. On the other hand cluster beam studies suggest that fullerene-60 is very stable when isolated and is able to withstand intense radiation fields. These dual properties are curiously consistent with those which the DIB carrier or carriers appear to possess – ubiquitous in space and still (?) undiscovered in the terrestrial environment. Indeed there are also interesting parallels between the physicochemical scenarios in cluster beam experiments and circumstellar shell processes – in both cases the particle formation which occurs at high temperatures and pressures is followed by “freeze-out” and apparent “stability” as expansion occurs.

(5) Fullerene-60 forms whenever carbon nucleates to generate carbon particles in the gas phase. Indeed we now know that under some conditions some 10–20% of arc-processed carbon ends up as  $\text{C}_{60}$  Buckminsterfullerene. It remains to be determined how this percentage varies as a function of physicochemical conditions, however it is important to note that fullerene-60 forms in significant quantities even in the presence of relatively high concentrations of other elements such as hydrogen and oxygen (Hallet et al. 1992; Doverstal et al. 1991).

(6) For exohedral complexes the CT bands discussed here arise as a result of charge transfer between the adsorbed species M and the 10 Å diameter cage. Very large absorption cross-sections are likely to be associated with this process as effective electron displacements are ca. 6 Å or more – nearly an order of magnitude larger than in normal molecular electronic transitions. The recent discovery that alkali-metal-doped fullerene-60 is a high-temperature superconductor may be taken as experimental confirmation of the extreme facility with which electron transfer can occur in alkali metal exohedral complexes. Transition moments associated with endohedral complexes will also be large with effective electron displacements of 2–4 Å.

(7) Many atoms show significant interstellar depletions, by factors of the order of 90% or more, and in the case of metals such

as Ca, Mg, etc., the intensities of the transitions should correlate with regional elemental abundances. Alkali and alkaline earth metals are not only abundant in the interstellar medium but also exhibit a clear propensity for adsorption and entrapment in the  $C_{60}$  cage. Evidence for the production of such complexes from carbonaceous microparticles containing entrapped atoms under the influence of ionizing radiation may also exist.

## 7. Discussion

Various arguments support the conjecture that ionized fullerene complexes are abundant in space and may be the carriers of certain well-known unidentified interstellar features. The present proposal has the merit that it should be possible, in due course, to confirm or falsify it by experiment. Recent advances in fullerene chemistry imply that spectra of the cage complex ions may soon be obtainable either directly or perhaps by photoelectron spectroscopy. As far as assignment is concerned, the accuracy with which theory can predict the energies of electronic transitions is very poor and arguments should not rest heavily on the accuracy of the fit between experiment and theory in general.

We conclude that the ion complex  $(C_{60})^+ \cdot H$  should be the most abundant fullerene analogue and if a simple CT transition occurs it should absorb near 217 nm. For a  $C_{60}$  complex to be responsible for the 217 nm feature an extremely high absorption coefficient is required. We have discussed the likelihood that the associated absorption coefficient might be ca. 25–36 times stronger than for a typical strong fully allowed transition. Such transitions usually occur within a chromophore of atomic (0.1 nm) dimensions. In this case the transition occurs between the adduct and the substrate. Estimates vary but on the basis of an absorption coefficient of this order only 0.3–0.4% of the available carbon budget needs to be locked up in the  $C_{60}$  complex. Recent studies show that in the absence of H, the  $C_{60}$ /carbon ratio may be as high as 40%. Several other unexplained optical features in addition to the DIBs and the 217 nm feature also exist – such as Sellgren's (1981) observations – which the unusual electrical properties of these novel complexes might help to explain.

Absorbed energy needs to be dissipated. When a CT transition occurs, the main geometry change on excitation will involve the relative position of the adduct, M, to the substrate  $C_{60}$ . The motion excited will involve oscillations of M in a potential well on the surface rather than vibrations of the cage and the two motions need not be particularly strongly coupled. Even though energy is equilibrated quickly, relation to the IR fluorescence lifetime, the symmetry breaking modes associated with the motion of M offer the most available avenue of energy release. Consequently vibrational emission characteristics of  $C_{60}$  itself may not be observed strongly. The characteristic oscillations of the complex are novel and yet to be studied so the resulting structure is something of an unknown quantity at this time. However the motion is unlikely to give rise to recognizable harmonically related sequences or progressions and we note that no sequences or progressions have ever been identified among the DIBs.

As far as linewidths are concerned there are two possible sources of broadening; one is lattice vibrations and the other is rotational structure. For the endohedral metal complexes the lattice vibrations have been discussed by Ballester et al. (1990), who have shown that these are of the correct order of magnitude. The oscillations of exohedral species should possess similar line shapes. However our model suggests that rotational contours

may be the main contributor to the linewidth for the DIB features. Scarrott et al. (1992) Fitzpatrick E.L. and Massa D have recently carried out line shape calculations for an electronic excitation of a fullerene analogue and find that with a 3% change in rotational constant on excitation the observed line shapes and widths of certain of the features can be reproduced. Certainly these studies lend great weight to the argument that the DIB carrier is a molecule.

Here we have discussed only the simplest fullerene analogues and then only in minimal semiquantitative detail. The present capability of theory to obtain frequency/wavelength estimates for a meaningful quantitative prediction or comparison is severely limited for such multi-atom systems. Thus no attempt has been made to assign the observed DIB features to specific species. We should also note that the facility with which fullerene-60 can accommodate multiple charges, both positive and negative, suggests that a range of intra-complex ion variants may also be present in the ISM.

Finally we note that it would be a truly bizarre turn of events if the species ( $C_{60}$  and/or analogues) which have been visible in space for much of the century turn out to have been virtually under our noses on earth since time immemorial and invisible until now. Furthermore it seems, at this moment, that it would be even more bizarre if these species were not in some way involved because it would mean that yet another family of carbon containing molecules, with similarly surprising properties (of interstellar ubiquity, stability and elusiveness) is still at large in the Universe.

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