POLYCYCLIC AROMATIC HYDROCARBONS

Infrared spectra of protonated and deuteronated C\textsubscript{60} in interstellar environments

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Abstract. With the credible detection of C\textsubscript{60}, C\textsubscript{70} and C\textsubscript{70}\textsuperscript{+} in the interstellar medium (ISM), new prospects have opened up for the search of other fullerenes and their derivatives. Since fullerenes show high proton affinities, their protonated forms should predominate in the ISM, which can easily go through deuterium enrichment. Here, we present the infrared (IR) spectra and standard enthalpy of formation of C\textsubscript{60}H\textsuperscript{+}, C\textsubscript{60}D\textsuperscript{+}, C\textsubscript{60}H\textsubscript{18} and C\textsubscript{60}D\textsubscript{18} using Density Functional Theory (DFT) in singly ionized forms. The obtained computed IR spectra are compared with the observations. The results show that the four mid-infrared bands of neutral C\textsubscript{60} are still visible in C\textsubscript{60}H\textsuperscript{+} and C\textsubscript{60}D\textsuperscript{+}, but their strength diminishes in C\textsubscript{60}H\textsubscript{18} and C\textsubscript{60}D\textsubscript{18}. As a conclusion, it is possible that the IR bands ascribed to C\textsubscript{60} are a mixture of pure and slightly protonated and deuteronated fullerenes. In this way, the observed scattering of the C\textsubscript{60} band ratios could be explained.

Keywords. Molecular spectroscopy—interstellar medium—astrochemistry.

1. Introduction

Large organic compounds like fullerenes and polycyclic aromatic hydrocarbons (PAHs) are expected to make up around 10% of the elemental carbon in the Universe (Tielens 2008). Fullerenes, carbon-based cage-like molecules, have been the subject of speculation since the discovery of Buckminsterfullerene (C\textsubscript{60}) in laboratory during an experiment trying to recreate the chemistry of carbon-rich evolved stars (Kroto et al. 1985). The formation of caged molecular structures, suggests significant amounts of fullerenes in space.

The first discovery of C\textsubscript{60} and C\textsubscript{70} in planetary nebula Tc1, based on their IR emission features (Cami et al. 2010), has been followed by observations in numerous other astronomical sources. These are HII regions, evolved stars, young stellar objects, diffuse interstellar medium (ISM) and reflection nebulae (García-Hernández et al. 2010, 2012; Sellgren et al. 2010; Boersma et al. 2012; Peeters et al. 2012; Roberts et al. 2012; Berné et al. 2017). C\textsubscript{60}\textsuperscript{+} has also been confirmed with diffuse interstellar bands (DIBs) (Campbell et al. 2015, 2016). Other than C\textsubscript{60}\textsuperscript{+}, C\textsubscript{70}\textsuperscript{+} is also suggested as carrier of weaker DIBs (Campbell et al. 2016).

The dominant form of fullerene in the ISM is not known. However, their significant reactivity with atomic H, relatively high proton affinities and also that their features have been seen in H-rich astronomical sources (García-Hernández et al. 2010) indicate that their hydrogenated/protonated (fullerane) forms may be dominated in interstellar environments. Since fullerane can easily be photolyzed and go through deuterium enrichment by losing a hydrogen (Cataldo et al. 2009), their deuterated/deuteronated forms might also be significant.

Based on this, we report theoretical IR emission spectra and standard enthalpy of formation of protonated and deuteronated C\textsubscript{60}. The IR absorption spectra of C\textsubscript{60}H\textsuperscript{+} has been reported previously both experimentally and theoretically (Palotás et al. 2020). Here, we present C\textsubscript{60}D\textsuperscript{+}, C\textsubscript{60}H\textsubscript{18} and C\textsubscript{60}D\textsubscript{18} for the first time in singly ionized forms. Since fullerenes features are observed in emission, the present work also includes C\textsubscript{60}H\textsuperscript{+} for a direct comparison with observations. The obtained computed IR spectra are compared with the observed spectra of planetary nebula SMP LMC56. The intrinsic band ratios

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of fundamentals bands of neutral C$_{60}$ are also calculated for the considered species to compare them with the observed band ratios.

2. Model and methods

With Gaussian 09 suite of program, density functional theory (DFT) calculations are carried out for the chosen fullerene molecules. Owing to its success in computing the IR spectra of fullerenes, the B3LYP functional is used (Zhang et al. 2017; Candian et al. 2019; Palotás et al. 2020, 2021). To fully optimize the considered structures, the B3LYP/6-31G* combination has been employed. These structures are then used to compute the IR spectra using the harmonic oscillator approximation, convoluted with a Gaussian profile with an FWHM of 10 cm$^{-1}$. Then, a scaling factor of 0.978 is used to scale the calculated harmonic frequencies. A closer agreement with experimental data is produced by the aforementioned combination with this scaling factor (Palotás et al. 2020, 2021).

The theoretical absorption spectra of the considered fullerenes were converted into emission spectra using a UV photon excitation model, assuming a blackbody emission with a high temperature ($T = 40,000$ K), allowing direct comparison with the observed emissions. The model is developed by Cook & Saykally (1998), Pech et al. (2002) and Pathak & Rastogi (2008). The relative standard enthalpy of formation ($\Delta_f H^\circ$) of the considered fullerene molecules ($M$) is calculated using the following relation:

$$\Delta_f H^\circ(M) = E_0(M) - \sum nE_0(X) + \sum n\Delta_f H^\circ(X).$$

The above relation has been used effectively in numerous studies, e.g., Candian et al. (2019) and references therein. Here, $E_0(M)$ are the sum of the total electronic and zero point energies (ZPE) for the $M$, $E_0(X)$ represents the ground state electronic energy of C, H and D. $\Delta_f H^\circ(X)$ is the standard enthalpy of formation at 0 K, which are 171.29, 51.63 and 52.53 kcal mol$^{-1}$ for gas-phase C, H and D atoms, respectively. Here, $E_0(M)$ and $E_0(X)$ are computed using DFT.

3. Results and astronomical implications

3.1 Relative stability of protonated and deuterated C$_{60}$

The chosen fullerene molecules are given in Table 1 with corresponding optimized energies ($E_0$) and enthalpy of formation ($\Delta_f H^\circ$) to assess their stabilities. The data regarding stabilities implies that partial protonated/deuterated fullerenes are more stable compared to the fullerenes with higher degree of hydrogenation or deuteration. This is due to the fact that additional hydrogens in fullerenes cause the change in orbital hybridization from sp$^2$ to sp$^3$ that result in the destabilization of the carbon cage (Van Lier et al. 2002). However, the single attachment of H or D does not affect the cage stability (Palotás et al. 2020, 2021).

3.2 IR spectroscopy

The computed IR emission spectra of the considered protonated and deuterated fullerenes are given in Figure 1 together with the observed emission spectrum of a planetary nebula SMP LMC56. In Figure 1, the band positions of neutral C$_{60}$ at 7.0, 8.5, 17.3 and 18.9 m (1428.5, 1176.4, 578 and 529.1 cm$^{-1}$) are also shown. The IR spectra of C$_{60}$H$^+$ and C$_{60}$D$^+$ show closer resemblance with C$_{60}$ and the fundamentals bands of neutral C$_{60}$ are still present (Figure 1). The 7.0 and 8.5 m (1428.5 and 1176.4 cm$^{-1}$) bands in both C$_{60}$H$^+$ and C$_{60}$D$^+$ are present at 6.94 and 8.43 m (1440.9 and 1186.2 cm$^{-1}$). However, the interstellar neutral C$_{60}$ bands present at longer wavelengths at 17.3 and 18.9 m (578 and 529.1 cm$^{-1}$) in C$_{60}$D$^+$ are little redshifted compared to C$_{60}$H$^+$. The 17.3 (578 cm$^{-1}$) m band is present at 17.47 (572.4 cm$^{-1}$) and 17.44 m (573.3 cm$^{-1}$) in C$_{60}$D$^+$ and C$_{60}$H$^+$, respectively. On the other hand, the 18.9 (529.1 cm$^{-1}$) m band in C$_{60}$D$^+$ and C$_{60}$H$^+$ is present at 19.005 (526.1 cm$^{-1}$) and 19.076 (524.2 cm$^{-1}$), respectively.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$E_0$ ($E_h$)</th>
<th>$\Delta_f H^\circ$ (kcal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$</td>
<td>−2285.8</td>
<td>850.7</td>
</tr>
<tr>
<td>C$_{60}^+$</td>
<td>−2285.5</td>
<td>1014.1</td>
</tr>
<tr>
<td>C$_{60}$H$^+$</td>
<td>−2286.4</td>
<td>1027.1</td>
</tr>
<tr>
<td>C$_{60}$D$^+$</td>
<td>−2286.7</td>
<td>1028.1</td>
</tr>
<tr>
<td>C$<em>{60}$H$</em>{18}^+$</td>
<td>−2296.3</td>
<td>1011.5</td>
</tr>
<tr>
<td>C$<em>{60}$D$</em>{18}^+$</td>
<td>−2296.4</td>
<td>1012.2</td>
</tr>
</tbody>
</table>

$E_0$ = ground state electronic energy.

$\Delta_f H^\circ$ = standard enthalpy of formation.
Figure 1. Comparison of the computed IR emission spectra of the considered fullerene species with the Spitzer IR emission spectra from SMP LMC56 planetary nebula. The vertical dotted lines show band positions of neutral C$_{60}$ at 7.0, 8.5, 17.3 and 18.9 μm (1428.5, 1176.4, 578 and 529.1 cm$^{-1}$).

With the increasing protonation and deuteration in C$_{60}$, the fundamentals bands at 8.5, 17.3 and 18.9 μm (1176.4, 578 and 529.1 cm$^{-1}$) starts diminishing and new features arise around 13–16 μm (769.2–625 cm$^{-1}$; Figure 1). In C$_{60}$H$_{18}^{-}$ and C$_{60}$D$_{18}^{-}$, only the 7.0 (1428.5 cm$^{-1}$) μm band is visible, which is present at 6.93 and 6.96 μm (1443 and 1436.7 cm$^{-1}$), respectively (Figure 1).

To further investigate the presence of the considered fullerene species in the ISM, the present work calculates the intrinsic strength ratios of fundamental bands of neutral C$_{60}$ for each protonated and deuteronated fullerene computed here, to compare them with the observed band ratios. The intrinsic strengths of 17.4/18.9 and 7.0/8.5 μm are given in Figure 2 for both the observations and computations. It is clear from Figure 2 that the observed band ratios are scattered and confirms the presence of other fullerene derivatives in space. Although the observed data is limited in Figure 2, the results derived for C$_{60}$H$^{+}$ and C$_{60}$D$^{+}$ seem better compared to C$_{60}$H$_{18}^{+}$ and C$_{60}$D$_{18}^{+}$. This hints the significance of partially protonated and deuteronated fullerene species in space.

Based on the above, the emission spectra of C$_{60}$H$^{+}$ and C$_{60}$D$^{+}$ show excellent agreement with the observations, as reported earlier for C$_{60}$H$^{+}$ (Palotás et al. 2020). Here, we found that C$_{60}$D$^{+}$ might also contribute to the observed fullerenes features, and confirm the importance of C$_{60}$H$^{+}$ with its emission spectra as well.

4. Conclusion

The present work reports theoretical IR emission spectra and standard enthalpy of formation of C$_{60}$H$^{+}$, C$_{60}$D$^{+}$, C$_{60}$H$_{18}^{+}$ and C$_{60}$D$_{18}^{+}$ in interstellar environments. The computed emission spectra is compared with the Spitzer IRS emission spectra of a planetary nebula SMP LMC56. The intrinsic band ratios of fundamentals bands of neutral C$_{60}$ are also calculated for the considered species to compare them with the observed band ratios. The conclusions are summarized as follows:

1. The data regarding enthalpy of formation indicates that C$_{60}$H$^{+}$ and C$_{60}$D$^{+}$ are more stable than C$_{60}$H$_{18}^{+}$ and C$_{60}$D$_{18}^{+}$, which further implies that partial protonated or deuteronated fullerenes species might be more stable compared to the fullerenes with higher degree of hydrogenation (Table 1).

2. The spectral behavior of C$_{60}$H$^{+}$ and C$_{60}$D$^{+}$ strongly resemble the IR spectra of C$_{60}$, while new feature arises around 13–16 μm (769.2–625 cm$^{-1}$) for C$_{60}$D$^{+}$ and C$_{60}$H$_{18}^{+}$ (Figure 1).

3. The fundamentals bands of neutral C$_{60}$ at 7.0, 8.5, 17.3 and 18.9 μm (1428.5, 1176.4, 578 and 529.1 cm$^{-1}$) are still visible in C$_{60}$H$^{+}$ and C$_{60}$D$^{+}$, however, their strength diminishes as hydrogenation or deuteration increases (Figure 1).
4. The observed fullerene emission shows scattering in the band ratios, which might be explained by partially protonated and deuteronated fullerene species (Figure 2).

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