

Electronic Transitions Responsible for C₆₀⁺ Diffuse Interstellar Bands

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Supporting Information

ABSTRACT: Diffuse interstellar bands (DIBs) are puzzling absorption features believed to contain critical information about molecular evolution in space. Despite the fact that C_{60}^{+} recently became the first confirmed carrier of several DIBs, the nature of the corresponding transitions is not understood. Using electronic structure methods, we show that the two strong C_{60}^{+} DIBs cannot be explained by electronic transitions to the two different excited ${}^{2}E_{1g}$ states or the two spin-orbit components of the lowest ${}^{2}E_{1g}$ state, as suggested before. We argue that the strong DIBs at 9632 and 9577 Å correspond to the cold excitations from the non-Franck-Condon region of the ground electronic state to the two components of the lowest ${}^{2}E_{1g}$ state split by Jahn-Teller distortion. The weak DIBs at 9428 and 9365 Å are assigned to the first vibronic transitions involving the low-energy vibrational modes and components of the lowest ${}^{2}E_{1g}$ electronic state.



iffuse interstellar bands (DIBs) are spectroscopic features caused by the absorption of light passing through the interstellar medium (ISM).¹ About 500 DIBs mostly in the visible and infrared regions have been observed, but the origin of these bands is not clear.²⁻⁶ DIBs are substructured and therefore most likely caused by the molecules in the gas phase rather than by interstellar dust and grains.^{7,8} Polycyclic aromatic hydrocarbons (PAHs) and fullerenes are considered to be the main candidates for the origin of DIBs as these molecules can survive under extreme interstellar conditions^{9–11} and because of the abundance of interstellar spectral features attributed to carbon-rich polyatomic molecules.^{12–19} Despite significant efforts, no specific PAHs have been identified as the origin of DIBs.²⁰ Soon after the discovery of the fullerene C_{60}^{21} the C_{60}^{+} ion was suggested to be a DIB carrier.²² However, only recently, the unprecedented agreement between the wavelengths of two strong DIBs in the nearinfrared (NIR) region and two peaks in the photodesorption spectrum of the C_{60}^+ -He complex has confirmed C_{60}^+ as the first accepted carrier of DIBs.²³ The closely spaced absorption peaks at 9632 and 9577 Å have similar intensities, with 84:100 ratio obtained at 4.9 K.²⁴ The intensity ratio extracted from astronomical data is still a matter of debate.^{25,26} In addition to the two strong bands, there are two notable weak bands in the C_{60}^{+} -He NIR spectrum. However, the assignment of these weak bands at 9428 and 9365 Å to specific DIBs^{27,28} is still disputed.^{29,30} The initial assignment of two absorption peaks of C_{60}^+ in a neon matrix³¹ to the two strong DIBs³² was complicated by the irregular matrix-caused frequency shift. Recently, using the helium tagging infrared photodissociation spectroscopy,^{33–37} the strong absorption bands of the C_{60}^+ -He complex at 10 382 cm⁻¹ (9632 Å) and 10 442 cm⁻¹ (9577 Å) were measured within 1 cm^{-1} of the two DIBs.²³ The weak effect from He tagging on the absorption wavelengths was supported by the small perturbation (less than 0.5 cm⁻¹ redshift) from the second helium atom attached to $C_{60}^{+.27}$ Furthermore, it was shown that the red-shift is linearly dependent on the number of He atoms;³⁸ this was used to extrapolate the absorption wavelengths to the bare C_{60}^{+} ion (Table 1).^{24,39} However, the absence of actual data for the bare C_{60}^{+} ion still leaves a concern about the perturbative effect of the first He on the absorption wavelengths.

Table 1. Experimental Absorption Wavelengths in Air (λ) , Frequencies in Air (ν) , Spectroscopic Gaps Relative to the First Band (Δ), and Relative Intensities (I) of Electronic Transitions in C₆₀⁺-He²⁴

band	type	$\nu ({\rm cm}^{-1})$	$\Delta (cm^{-1})$	λ (Å)	I
I	strong	10 382	0	9 632	0.84
II	strong	10 442	60	9 577	1.00
III	weak	10 607	225	9 428	0.17
IV	weak	10 678	296	9 365	0.26

The nature of the electronic and vibrational transitions responsible for the strong (I and II) and weak (III and IV) DIBs is not currently understood. Multiple hypotheses concerning the origin of the two strong closely spaced absorption bands include (i) transitions from the ground to excited electronic states in two C_{60}^{+} isomers of different symmetry,³¹ (ii) transitions from two low-lying thermally populated electronic states to the same excited state,^{23,40} (iii) transitions from the ground state to two different excited states, $^{24,41-43}$ (iv) transitions to two components of a doubly degenerate excited state, with degeneracy lifted because of spin-orbit coupling (SOC),^{42,44} pseudo-Jahn-Teller distor-

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tion, or distortion caused by the helium atom. In this Letter, we investigate the likelihood of different absorption mechanisms and the origin of two strong and two weak absorption bands in C_{60}^+ and C_{60}^+ -He.

An electron ejection from the h_u molecular orbital in icosahedral C_{60} is followed by the Jahn–Teller distortion to the D_{5d} isomer of C_{60}^+ (Figure 1).^{45–49} The other possible



Figure 1. Left: Orbital diagrams for C_{60} (I_h) and C_{60}^+ (D_{5d}). The blue dashed rectangle contains the active space. Right: Electronic energy levels (cm⁻¹) in C_{60}^+ (D_{5d}) obtained at the TD-B3LYP/def2-TZVP level of theory. Black and gray lines indicate the bright and dark states, respectively.

distortions to D_{2h} and D_{3d} geometries⁵⁰ lead to energetically unfavorable transition states and higher-order stationary points, respectively. In good agreement with previous studies,^{47,51} our calculations indicate that the D_{5d} isomer has no imaginary frequencies and stabilized by 976 cm⁻¹ with respect to the icosahedral C_{60}^+ .

According to the selection rules, electronic transitions are allowed between the states whose direct symmetry product contains an irreducible representation of the transition dipole moment, $\Gamma(\hat{\mu})$:

$$\Gamma(\Psi_{i}) \otimes \Gamma(\Psi_{f}) \in \Gamma(\hat{\mu}) \tag{1}$$

In the D_{5d} symmetry group, $\Gamma(\hat{\mu})$ transforms as $A_{2u} \oplus E_{1w}$ making excitations from the ${}^{2}A_{1u}$ ground state to the first and second ${}^{2}E_{1g}$ excited states the only symmetry-allowed transitions within the 12 lowest excited states (6 doubly degenerate states shown in Figure 1). These two transitions were suggested to be the origin of two strong DIBs.^{42,43} Indeed, given the typical accuracy of the Franck–Condon approximation,⁵² the predicted vertical excitation energies are in reasonable agreement with the experimental absorption maxima of two strong DIBs (Table 2). However, the predicted

energy gap between the two bright ${}^{2}E_{1g}$ states is more than an order of magnitude larger than the experimental value, indicating that the two ${}^{2}\check{A}_{1u} \rightarrow {}^{2}E_{1g}$ (D_{5d}) transitions cannot be responsible for the two closely spaced DIBs. This conclusion is also supported by the 25:1 ratio of oscillator strengths for these two transitions, which contradicts the experimental bands having similar intensities. Interestingly, the second ${}^{2}A_{1u} \rightarrow {}^{2}E_{1g}$ transition matches well the energy and relative intensity of the dim broad band at $\sim 12\,000$ cm⁻¹ observed in C₆₀⁺ trapped in a Ne matrix.³¹ Because of the low intensity of this second transition, it would be challenging to detect the corresponding DIBs in astronomical spectra. To account for the two strong bands originating from the nondegenerate ground state,^{23,39} the degeneracy of the first ${}^{2}E_{1g}$ excited state must be lifted. Alternatively, the small (60 ¹) splitting between these two bands, observed in the cm⁻ laboratory spectrum, can be explained by excitations from the thermally populated ${}^{2}E_{1u}$ and ${}^{2}E_{2u}$ excited states (Figure 1). However, the latter is very unlikely, as the population of these states, lying about 1700 cm⁻¹ above the ground state, would be negligible at the low experimental and ISM temperatures.⁵³

The degeneracy of a doublet electronic state can be lifted by SOC.^{42,44} However, SOC does not split the ${}^{2}A_{1u}$ ground state because of the symmetry selection rules (Figure 2).⁵⁴ The



Figure 2. Schematic representation of ${}^{2}E_{1g}$ splitting mediated by spin–orbit coupling.

splitting is expected to be negligible because the direct product of $\Gamma(\Psi_i)$ with itself does not contain the irreducible representation of the SOC operator. In D_{5d} , this operator transforms as $A_{2g} \oplus E_{1g}$, resulting in the two degenerate spin components of the ground state ${}^2A_{1u}{}^+$ and ${}^2A_{1u}{}^-$. In contrast, the ${}^2E_{1g}$ excited state splits into two doubly degenerate spin components giving rise to two electronic transitions and potentially explaining the two strong bands. However, our calculations predict the spin–orbit splitting of only 1 cm⁻¹, which is almost 2 orders of magnitude smaller than the experimental energy gap of 60 cm⁻¹. This is in good agreement

Table 2. Theoretical and Experimental Excitation Energies and Intensity Ratios for Different Isomers of C₆₀^{+a}

	JT stabilization energy relative to C_{60} (I_h)	relative energy	imaginary modes	strong ban	ds I and II	gap	intensity ratio
exptl ²⁴				10 382	10 442	60	84:100
D_{5d}	976	0	no	$11\ 376\ (^2A_{1u} \rightarrow {}^2E_{1g})$	$12744~(^{2}A_{1u} \rightarrow {}^{2}E_{1g})$	1 368	25:1
D_{2h}	641	335	i400 (b _g)	$11\ 059\ (^2A_u \to {}^2B_g)$	$11\ 356\ (^2A_u \rightarrow {}^2A_g)$	297	14:10

^aAll energies and frequencies are in cm⁻¹. TD-B3LYP/def2-TZVP level of theory.

	B3LYP		B3LYP-D3		CAM-B3LYP-D3			
	hexagon C _s	pentagon C ₅	hexagon C _s	pentagon C ₅	hexagon C _s	pentagon C _s	exptl ²³	
C ₆₀ ⁺ -He distance (Å)	3.31	3.38	3.13	3.18	2.66	2.76		
binding energy (cm ⁻¹)	327	193	172	81	-117	-228	binding below 6 K	
first excitation $(A'' \rightarrow A')$ (cm^{-1})	11 378	11 384	11 374	11 375	9 538	9 538	10 382	
second excitation $(A'' \rightarrow A'')$ (cm^{-1})	11 390	11 385	11 390	11 376	9 544	9 547	10 442	
splitting (cm ⁻¹)	12	1	16	1	6	9	60	
^a The negative binding energies indicate thermodynamically stable complexes.								

Table 3. Properties of the C_{60}^{+} -He Isomers^{*a*}

with the previous theoretical studies reporting a very small SOC for the fullerenes and their anions. $^{55-57}$

The importance of the Jahn–Teller effect (JTE) in C₆₀ and its ions has been reported in previous theoretical and experimental studies.^{48,58-61} While the first-order JTE stabilizes C_{60}^{+} by removing the degeneracy of the ground state and reducing the symmetry from I_h to D_{5d} , the symmetry could be lowered further by a pseudo-JTE through the interaction with the low-lying excited states.⁶² These excited states soften the ground state with respect to e_{1g} and e_{2g} distortions, leading to a potentially more stable C_{2h} isomer. The distortions also lift the degeneracy of the first bright excited state giving rise to the two symmetry-allowed transitions ${}^{2}A_{u} \rightarrow {}^{2}A_{g}$ and ${}^{2}A_{u} \rightarrow {}^{2}B_{g}$. However, we could not locate a C_{2h} isomer that is lower in energy than the D_{5d} isomer. A simple distortion of the D_{5d} isomer along the lowest e_{1g} vibrational mode (250 cm⁻¹) leads to the D_{2h} saddle point, which is 335 cm⁻¹ above the D_{5d} geometry (Table 2). At this saddle point, the energy gap between the lowest two symmetry-allowed transitions $({}^{2}A_{u} \rightarrow {}^{2}A_{g} \text{ and } {}^{2}A_{u} \rightarrow {}^{2}B_{g})$ is about six times larger than the experimental value. The minimum energy path calculations showed that the D_{2h} saddle point links two identical D_{5d} minima, which is consistent with the previous studies.^{47,48} However, the absence of a low-lying C_{2h} isomer is difficult to prove. In addition, the large number of closely spaced excited states makes it very challenging to estimate the vibronic coupling constant.⁶² Thus, the pseudo-JTE hypothesis cannot be completely ruled out.

The helium binding to C_{60}^+ can also break the symmetry and split the ${}^{2}E_{1g}$ state into two components. The B3LYP/ def2-TZVP level of theory predicts a metastable C_{60}^+ -He complex even with the D3 dispersion correction (Table 3). An earlier B97/6-31++G(d,p) study also predicted a metastable coordination of He to hexagonal and pentagonal facets with binding energies of 83 and 72 cm⁻¹, respectively.⁶³ In contrast, the CAM-B3LYP-D3 functional predicts two thermodynamically stable Cs isomers with He bound to hexagonal or pentagonal sites. The most stable C_{60}^{+} -He complex has the binding energy of -228 cm^{-1} with He positioned 2.76 Å from the center of a pentagon. The predicted energy gap between the two components of ${}^{2}E_{1g}$ state (with A' and A'' symmetries in C_{s}) is only 9 cm⁻¹, which is almost an order of magnitude smaller than the experimental value. Therefore, the ${}^{2}E_{1g}$ splitting due to the He binding is not sufficient to explain the origin of the two strong bands. In a recent experimental study, it has been shown that the presence of multiple C_{60}^{+} -He isomers results in about 2 cm⁻¹ broadening of the strong bands,²⁴ which is consistent with our CAM-B3LYP-D3 estimates (Table 3). The light He atom does not change the spin–orbit splitting of the ${}^{2}E_{1g}$ state significantly, yielding 0.9 cm⁻¹ for C₆₀⁺–He. Interestingly, in the experimental studies, replacing He with the heavier noble atoms increases the gap

between the strong bands and splits one of them in two components.⁶⁴ This effect can be attributed to SOC growing with the atomic charge and/or to larger distortion of the fullerene cage.

The origin of the experimental absorption bands (Table 1) can be explained by accounting for the Jahn–Teller distortion of the ${}^{2}E_{1g}$ excited state and the non-Franck–Condon effect. The ${}^{2}A_{1u} \rightarrow {}^{2}E_{1g}$ vertical excitation is expected to have small Franck–Condon factors because of the vanishing vibrational wave functions at the intersection point of the two components of the ${}^{2}E_{1g}$ state (Figure 3). According to the epikernel principle, 65,66 the JTE lifts the degeneracy of the ${}^{2}E_{1g}$ excited state and distorts the D_{5d} fullerene cage toward the C_{2h} minima. The strong-intensity electronic transitions to the ${}^{2}A_{g}$ and ${}^{2}B_{g}$ components of the ${}^{2}E_{1g}$ excited state can occur from



Figure 3. Energy diagram of vibronic transitions in C_{60}^+ . The lower potential represents the ground state; the upper one represents the E_{1g} excited state split into A_g and B_g states by the Jahn–Teller distortion. The global minimum and turning points on the ground state have D_{5d} and C_{2h} symmetries, respectively. The cold (I and II) and hot (III and IV) band transitions are color-coded with black and dark red arrows, respectively.

outside the Franck-Condon region of the ground state. The strong bands at 10 382 cm⁻¹ (I) and 10 442 cm⁻¹ (II) are the lowest-energy features in the absorption spectrum and therefore can be assigned to the $0-0 \ {}^{2}A_{u} \rightarrow {}^{2}B_{g}$ and ${}^{2}A_{u} \rightarrow$ ${}^{2}A_{g}$ transitions. The C_{2h} -symmetrical ${}^{2}A_{g}$ and ${}^{2}B_{g}^{g}$ minima are very similar to the D_{5d} geometry, with the root-mean-square deviations of only 0.012 and 0.015 Å, respectively. The energy difference between the ${}^{2}A_{g}$ and ${}^{2}B_{g}$ minima was found to be 41 cm⁻¹, which is in good agreement with the spectroscopic splitting of 60 cm⁻¹. The computed oscillator strength ratio of 87:100 matches well the 84:100 intensity ratio of the two strong bands observed in the C_{60}^+ -He spectrum. The weak bands of similar intensities at 10 607 cm⁻¹ (III) and 10 678 cm⁻¹ (IV), which are shifted by 225 and 236 cm⁻¹ with respect to the strong bands (Table 1), can be assigned to the first vibronic transitions. This assignment is supported by the magnitudes of the lowest vibrational frequency of the D_{5d} isomer (250 cm⁻¹ for e_{1g} mode). When corrected for anharmonicity, these vibrational levels are expected to be slightly lower in energy, matching the position of the two weak bands.

In conclusion, we have tested multiple hypotheses about the origin of absorption bands in the C_{60}^+ -He spectrum. We showed that the nature of two strong bands coinciding with DIBs cannot be explained by transitions from the ground electronic state to the first excited E_{1g} state that is split by either spin-orbit coupling or He-induced distortion because both these effects appear to be too weak. Transitions to the two $E_{1\sigma}$ excited states, transitions from different C_{60}^{+} isomers, and transitions from thermally populated low-lying excited states can also be eliminated from the list of reasonable explanations. We claim that the Jahn-Teller distortion in the excited state and the non-Franck-Condon excitations in the vicinity of the D5d-symmetrical minimum naturally explain both the strong and weak C_{60}^{+} absorption features in the NIR region. We assign the strong bands at 10 382 cm⁻¹ (I) and 10 442 cm⁻¹ (II) to cold ${}^{2}A_{u} \rightarrow {}^{2}B_{g}$ and ${}^{2}A_{u} \rightarrow {}^{2}A_{g}$ electronic transitions based on the predicted energy gap between the two excited states (41 cm⁻¹), which is in good agreement with the experimental splitting of 60 cm⁻¹. This assignment is also supported by the predicted intensity ratio of 87:100 being in excellent agreement with the 84:100 ratio in the C_{60}^{+} -He spectrum. We assign the weak bands at 10 607 cm^{-1} (III) and 10 678 cm^{-1} (IV) to the first vibronic transitions based on the vibrational analysis of C_{60}^{+} . The other reported low-intensity bands lying 315–630 cm⁻¹ above the first strong band³⁹ are associated with transitions to the higher-lying vibronic states. This range covers the fifth DIB at 10 697 cm⁻¹ (9348 Å) recently assigned to $C_{60}^{+,39}$ Electronic excitations to the two components of the second ${}^{2}E_{1g}$ state are predicted to be about 25 times less intense with respect to the strong bands and are unlikely to be detected in the ISM. We speculate that the rovibrational coupling can affect the Franck-Condon factors and therefore the intensities of the bands. Therefore, the intensity ratio of the two strong DIBs observed in different ISM regions can vary because of the different thermal population of the rotational levels. Thus, this intensity ratio can be potentially used to determine the temperature of the ISM regions containing C_{60}^+ .

THEORETICAL METHODS

The optimized geometries and harmonic vibrational frequencies of the C_{60}^{+} and C_{60}^{+} -He isomers were obtained with

density functional theory (DFT) using the $B3LYP^{67,68}$ and CAM-B3LYP-D3^{69,70} functionals. The def2-TZVP basis set was used in all electronic structure calculations, except for the SOC computations, where it was replaced with def2-SVP.7 Time-dependent density functional theory (TD-DFT)⁷² was used to determine the excitation energies and oscillator strengths for up to 12 electronic excited states. The stateaveraged complete active space self-consistent field (SA-CASSCF) method⁷³ was used to obtain the wave functions for the SOC calculations.⁷⁴ The active space comprised 17 electrons in 9 orbitals, and state-averaging was performed over two components of the lowest bright ${}^{2}E_{1g}$ excited state (Figure 1). SOC was calculated using the complete active space configuration interaction (CASČI) method⁷⁵ with the full twoelectron Breit-Pauli spin-orbit Hamiltonian.^{76,77} In the C_{60}^{+} -He complexes, the He atom was placed above the pentagonal and hexagonal faces and excitation energies were obtained with TD-CAM-B3LYP/def2-TZVP. The above calculations were carried out using the GAMESS suite of programs.^{78,79} The equilibrium geometries of ${}^{2}A_{g}$ and ${}^{2}B_{g}$ excited states (components of the Jahn-Teller-split E_{1g} state) were found by imposing the spatial symmetry constraints on the nuclear geometries and electronic wave functions at the B3LYP/def2-TZVP level of theory in the Molpro program package.⁸⁰

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jp-clett.8b03534.

Excitation energies and oscillator strengths for the isomers of C_{60}^+ and C_{60}^+ -He, vibrational frequencies of the C_{60}^+ isomers, Cartesian atomic coordinates of optimized geometries, and symmetry rules for electronic and vibronic transitions (PDF)

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The authors declare no competing financial interest.

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