

Encapsulation-induced alignment in endofullerenes

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Methods for creating endofullerenes have been steadily improving since their discovery, allowing for new types of endofullerenes to be created in larger numbers. When a molecule is trapped in a fullerene, the fullerene creates a harmonic trapping potential that leaves most of the fundamental properties of the internal molecule intact. The fullerene cage does create a preferred axis for the internal molecule, which we refer to as the encapsulation-induced alignment of the molecule. We explore the alignment of AlF and N₂ inside of C₆₀ by first computing the interaction between the internal molecule and the fullerene cage using *ab initio* electronic structure methods. Our results show that the internal molecules are found to be strongly aligned despite finding that all the calculated spectroscopic constants are relatively unaffected by the fullerene cage.

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I. INTRODUCTION

When first discovered, Buckminster fullerene (C₆₀) was thought to be of niche interest to astrophysics. Methods for producing C₆₀ in a laboratory were rapidly developed and fullerenes were discovered to have many applications in physics, chemistry, astronomy, and material science [1]. Rapidly expanding studies of fullerenes quickly discovered that atoms and molecules could be trapped inside the hollow carbon cage [2–4], these complexes were named endohedral fullerenes or just endofullerenes. When the internal atom or molecule is light enough, the rotation and vibration of the internal molecule becomes quantized and cannot be treated classically [5]. When the internal atom or molecule of an endofullerene is sufficiently heavy, it maintains many of its individual properties [2], similar to a molecule or atom inside a carbon nanotube. The internal molecule or atom is therefore protected from outside collisions while effectively remaining unperturbed. These properties have drawn attention from researchers due to possible applications in medical science, photovoltaics, quantum computing, and electronics [2,3,6].

Thanks to experimental developments over the last 40 years, a wide range of molecules have been trapped inside fullerene cages [3,5]. Of particular interest is the development of molecular surgery, a process in which a fullerene cage is chemically pried open allowing an atom or small molecule to be placed inside before the fullerene is sealed again [7]. Modern experimental methods allow much greater control over what type of molecule or atom is trapped inside the fullerene and allow more diverse sets of endofullerenes to be produced. With molecular endofullerenes more available than ever, more and more studies are focusing on the properties

of these endofullerenes rather than their production. Specifically, many of these studies focused on the translational and rotational energy of the trapped atom or molecule [8–13]. Some of these studies use the sum of pairwise Lennard-Jones type interactions to predict the interaction between the internal molecule with the outer fullerene wall. We instead employ a grid of single point energy calculations to obtain our potential energy surfaces. Studies of vibration are limited.

This study focuses on the alignment of molecules inside of C₆₀, which we refer to as the encapsulation-induced alignment. The fullerene creates a preferred axis for the internal molecule, similar to the preferred axis created by an external electric field in alignment studies of free molecules. Our study focuses on two endofullerenes: N₂@C₆₀ and AlF@C₆₀. We demonstrate how the fullerene cage shifts the spectroscopic constants of these internal molecules. We also briefly study the effects of the fullerene on the dipole moment of AlF. N₂ represents a molecule with a highly covalent bond and a short equilibrium distance. AlF has a much higher ionic character and a much longer equilibrium distance. The contrast between these two internal molecules helps to provide insight on how a wider variety of molecules might behave while trapped inside a fullerene cage.

II. COMPUTATIONAL METHODS

The optimized geometries and the energies of various configurations were calculated using density functional theory (DFT) as implemented in GAUSSIAN 16 [14]. First, we performed a comparative study for the encapsulation energy of N₂@C₆₀ using different functionals and basis sets, and the results are shown in Table I.

We note that the B3LYP [15] and PBEH1PBE [16] functionals, which are well suited to describe covalent interactions, predict positive binding energies. However, functionals that are better suited for unbonded interactions, such as MN15 [17], PW6B95 [18], APFD [19], and wB97XD [20], show negative binding energies. These findings agree with previously published results on the same system [21], al-

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TABLE I. Comparison of the encapsulation energy of $N_2@C_{60}$ calculated using various different methods. None of these calculations accounted for basis superposition error (BSSE).

Method	Def2TZV basis (kcal/mol)	6-31G** basis (kcal/mol)
B3LYP-D3	-15.87	-14.63
B3LYP	6.70	8.07
CAM-B3LYP	0.29	1.76
MN15	-23.68	-19.36
PW6B95	-11.85	-12.12
PW6B95D3	-20.63	-20.85
PBEh1PBE	0.42	1.24
wB97XD	-12.12	-12.04
APFD	-18.79	-18.04

though these results used fixed geometries for C_{60} . Moreover, functionals including dispersion corrections or empirical dispersion corrections predict negative encapsulation energies with the exception of CAM-B3LYP [22], although the encapsulation energy for CAM-B3LYP is very small. Based on the nature of the two systems under consideration, $AlF@C_{60}$ and $N_2@C_{60}$, we conclude that it is appropriate to use a functional with dispersion correction to accommodate weak interactions beyond the covalent interactions common in C_{60} . This conclusion agrees with other studies that emphasize the requirement of functionals that include dispersion corrections to accurately describe observed spectra in endofullerenes [23].

From studies comparing experimental spectroscopic data on $He@C_{60}$ [23], it has been shown that the wB97XV functional leads to the most accurate results, followed by B3LYP-D3. Fueled by the results displayed in Table I and following that recommendation, we tested the computational cost of the wB97XV [20] functional, the B3LYP functional with GD3BJ empirical dispersion (B3LYP-D3), and the APFD functional. These results are displayed in Fig. 1. The computational cost of the wB97XV method is comparable to

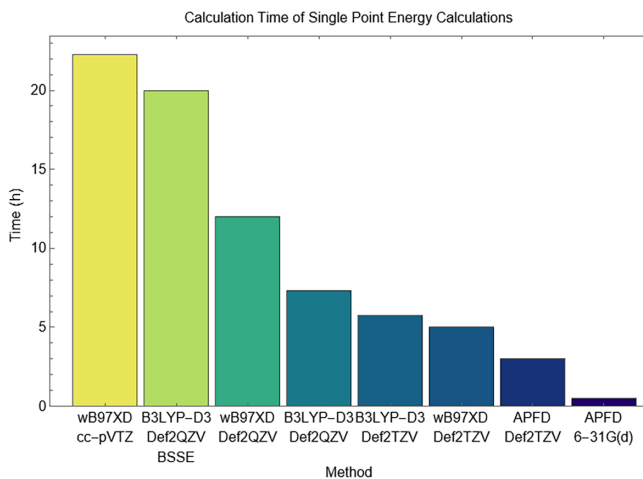


FIG. 1. Comparison of the calculation times for single point calculations using various methods. Only the second method (shown in green) accounts for the basis set superposition error using the counterpoise method [24,25].

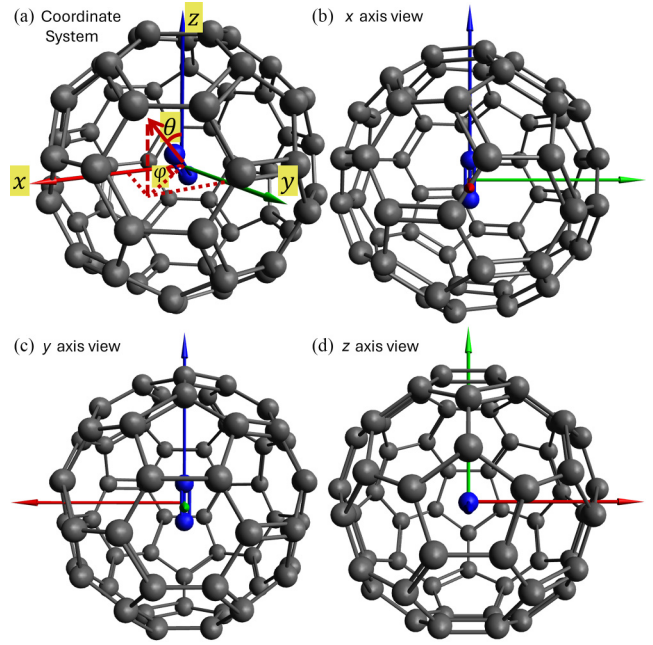


FIG. 2. The optimized geometry of $N_2@C_{60}$. Panel (a) shows the coordinate system used throughout this paper. Panels (b–d) show the optimized geometry of $N_2@C_{60}$ as viewed from the x, y, and z axes, respectively [39].

the cost of the B3LYP-D3 method when using the Def2TZV basis set. When using the Def2QZV basis set, the cost of the wB97XV functional surpassed the cost of the B3LYP-D3 method significantly. For this reason, we used the B3LYP-D3 method as a compromise between precision and computational cost. This is the method that we used for all the DFT calculations reported in this study, unless otherwise stated. All our calculations account for the basis set superposition error (BSSE) using the counterpoise method [24,25] unless otherwise stated.

For the choice of basis set we ran calculations with the cc-pVnZ (n being D, T, Q, 5, etc.) class of basis sets, the 6-31G** basis set, and the Def2nZV class of basis sets. The Def2nZV class of basis sets are optimized for DFT calculations and significantly smaller than their cc-pVnZ counterparts. The 6-31G** basis set is small and likely inaccurate. The cc-pVnZ basis sets proved to be impractical. For $N_2@C_{60}$ we used the Def2QZV basis set, particularly because it was the largest basis set that was still practical in terms of computation times. For $AlF@C_{60}$ the computation times were roughly double. To reduce computational cost, we used the Def2QZV basis for the optimization and the Def2TZV basis for calculations of the energy as a function of stretching and rotation. The energies for $AlF@C_{60}$ as a function of rotation were also found to be a factor of 10 larger than for $N_2@C_{60}$. Due to this, the difference between the Def2QZV basis set and the Def2TZV basis set was significant for $N_2@C_{60}$ but not for $AlF@C_{60}$, justifying the use of the smaller basis.

The optimized geometry calculated for $N_2@C_{60}$ at the B3LYP level of theory with the Def2QZV basis set with counterpoise correction and GD3BJ dispersion included is shown in Fig. 2. The optimized geometry for $AlF@C_{60}$ calculated

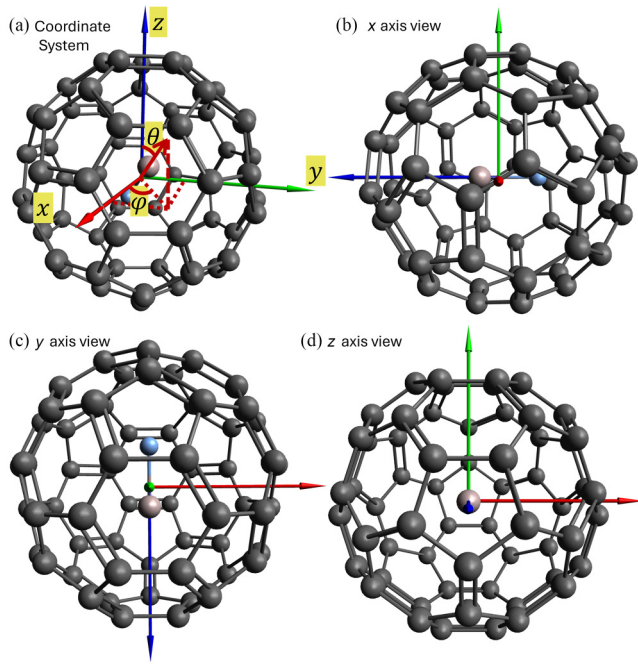


FIG. 3. The optimized geometry of AlF@C₆₀. Panel (a) shows the coordinate system used throughout this paper. Panels (b–d) show the optimized geometry of AlF@C₆₀ as viewed from the *x*, *y*, and *z* axes, respectively [39].

using the same method is shown in Fig. 3. N₂ is found to be in the exact center of the fullerene, while AlF is slightly shifted off center. The outer C₆₀ cage changes slightly due to the introduction of the internal molecule. These changes are small, but they are enough to break the icosahedral symmetry of the fullerene. The optimized N₂@C₆₀ geometry exhibits perfect *D*_{5d} symmetry as previously predicted [21,26,27]. However, the optimized AlF@C₆₀ geometry is slightly shifted from the perfect *D*_{5d} symmetry. The bond length of the equilateral pentagon centered around the *z* axis closest to the aluminum atom [the nearest pentagon in Fig. 3(d)] is predicted to be 1.467 06 Å. For the pentagon centered around the *z* axis closest to the fluorine atom [the furthest pentagon in Fig. 3(d)], the bond length is predicted to be 1.466 10 Å. Symmetry breaking in endofullerenes has been reported in HF@C₆₀ [28,29], H₂O@C₆₀ [30–32], and in H₂@C₆₀ [33,34]. However, it has been shown that this symmetry breaking is due to the nearby molecules in the solid state [35]. Symmetry breaking has also been found in C₆₀ ions [36,37]. As we will discuss later, the deviation from the icosahedral symmetry, despite being small, prevents both N₂ and AlF from aligning equally with all 12 pentagon faces of C₆₀. The optimized geometries can be found in Ref. [38].

The equilibrium bond length of AlF inside the C₆₀ cage was found to be about 1.69 Å as compared to the 1.65 Å equilibrium bond length expected for free AlF [40,41]. For N₂, the equilibrium bond length inside of the C₆₀ cage was found to be 1.11 Å compared to 1.10 Å for the free molecule [40,41]. The AlF molecule is predicted to stretch slightly more due to the cage when compared to N₂. This might be expected because of the larger bond length, making the nuclei closer to the cage, and due to the dipole moment causing stronger

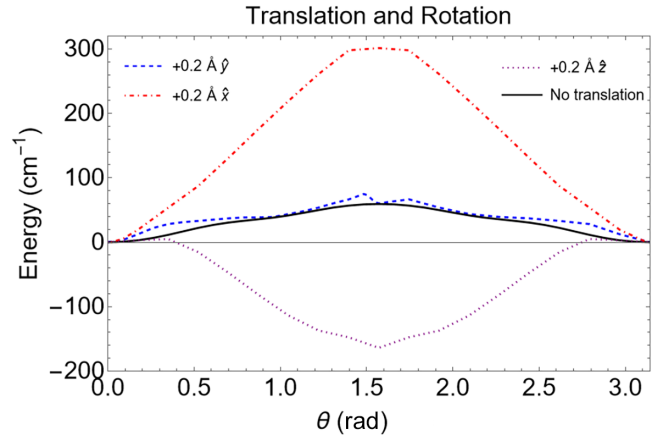


FIG. 4. The energy of N₂@C₆₀ as a function of the angle θ when the internal N₂ molecule is slightly shifted by 0.2 Å along the three cardinal axes.

long-range interactions. However, using the same methods, the equilibrium distance of free AlF is calculated to be 1.74 Å. Since this is larger than the experimentally determined bond length of free AlF (1.65 Å) [40] and larger than the bond length predicted for AlF inside of a fullerene (1.69 Å), these disagreements are likely the result of uncertainties in our calculations. The change in bond length for N₂ is even smaller and therefore is even more likely to be insignificant.

III. ALIGNMENT AND ORIENTATION

When a molecule is placed inside a fullerene, assuming that its center of mass does not move (neglecting translational degrees of freedom), the interaction energy could depend on the orientation of the molecule. If that is the case, the anisotropy of the interaction will mix up the rotational states, causing alignment and orientation effects.

Strong coupling between rotational and translational degrees of freedom has been observed in systems of other fullerenes [8–12]. Using the DFT methods discussed, we calculated the energy as a function of rotation angle θ when the N₂ molecule is slightly shifted from the center of the fullerene. Translating the N₂ molecule along the *y* axis (the axis perpendicular to the plane of rotation) has only a small effect on the energy as a function of the rotation angle. When translating the N₂ molecule along the *x* axis the molecule becomes even more strongly aligned with the *z* axis. However, when the N₂ molecule is translated along the *z* axis (the internuclear axis of the N₂ molecule in the optimized geometry), we see the preferred axis of the internal molecule change. This indicates that the rotational and translational degrees of freedom are significantly dependent. Including translational degrees of freedom into our methods is not computationally practical at this time; this will be addressed in future work.

Using the results from the DFT calculations, we can calculate various spectroscopic properties of the internal molecule and calculate the degree of alignment and orientation of the molecule (see Fig. 4). Couplings between rotational states can be calculated given a specific bond length *R* for the internal

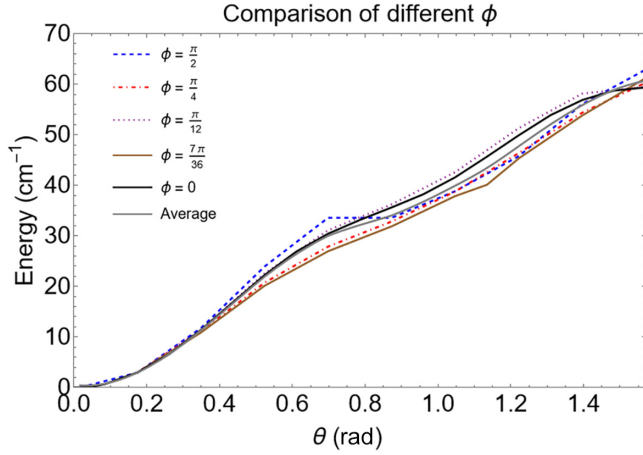


FIG. 5. The energy of $N_2@C_{60}$ as the internal N_2 molecule rotates along the angle θ . This energy is shown for various angles ϕ . The gray lines represents the average of all the angles ϕ .

molecule by expanding in the unperturbed rotational basis:

$$\Psi(\theta, \phi) = \sum_{m=-l}^l \sum_l c_{lm} Y_l^m(\theta, \phi), \quad (1)$$

where θ is the angle from the z axis and ϕ is the angle from the x axis [the typical definitions for spherical coordinates; see Figs. 3(a) and 2(a)].

The Hamiltonian of the molecule is given by $\hat{H} = \hat{H}_{\text{rot}} + \hat{H}_c$, where $\hat{H}_{\text{rot}}$ represents the rigid rotor Hamiltonian, which is diagonal in the basis given by Eq. (1), $H_{\text{rot},l,m,l',m'} = B_e l(l+1) \delta_{ll'} \delta_{mm'}$. Here, B_e is the rotational constant of the ground state of the free molecule. It is worth noticing that the rotational constant of the free molecule is roughly equal to the rotational constant predicted for the internal molecule. $\hat{H}_c$ represents the interaction energy between the molecule and the cage, and its matrix elements are given by

$$H_{c,l,m,l',m'} = \langle Y_l^{*m}(\theta, \phi) | V(R, \theta, \phi) | Y_{l'}^{m'}(\theta, \phi) \rangle, \quad (2)$$

which is nondiagonal. The potential $V(R, \theta, \phi)$, is produced by interpolating a grid of single point energy calculations. As previously stated, these calculations were done at the B3LYP level of theory with the Def2TZV basis set for $N_2@C_{60}$ and with the Def2TZV basis set for $AlF@C_{60}$. The calculations for both molecules include counterpoise corrections and GD3BJ dispersion. The energy as the molecule stretches is significantly greater than the energy as the molecule rotates for both AlF and N_2 . This allows these two degrees of freedom to be treated separately and for the internal molecule to be treated as a rigid rotor.

Figure 5 shows a comparison of the energy as a function of the angle θ for various angles ϕ . At $\phi = 7\pi/36$, $\theta = 13\pi/36$ the N_2 molecule is aligned with the center of a different pentagon of the C_{60} . Because of the broken icosahedral symmetry of the fullerene cage, these angles do not correspond to a second energy minimum. The difference between the curves shown in Fig. 5 never exceeds 12.2%, so it is accurate to treat the potential as independent of ϕ . This result implies that $V(R, \theta)$ is enough to describe the interaction of the molecule

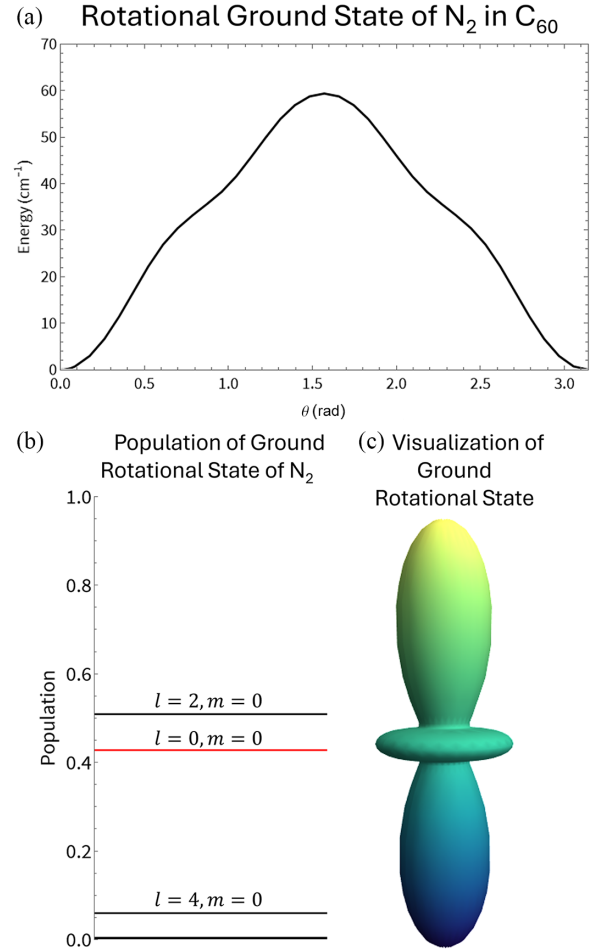


FIG. 6. Mixing of the rotational states of N_2 due to the interaction with the C_{60} cage. Panel (a) shows the populations of the rotational states of a free N_2 molecule in the new ground rotational state. Panel (b) shows the new ground state as a spherical plot. Panel (c) shows the energy as a function of rotation of the N_2 molecule inside the C_{60} cage.

with the fullerene, and hence

$$H_{l,l'} = B_e l(l+1) \delta_{ll'} + \langle Y_l^0(\theta, \phi) | V(R, \theta, 0) | Y_{l'}^0(\theta, \phi) \rangle. \quad (3)$$

In other words, states with different values of m will not mix and only rotational states with $m = 0$ contribute to the rotational ground state.

Assuming that the internal molecules are rigid rotors, the diagonalization of Eq. (3) reveals the rotational states of the molecule inside the fullerene, which can be used to analyze the changes to the rotational states caused by the interaction with the fullerene cage. The results for $N_2@C_{60}$ are shown in Fig. 6. Due to the symmetry of N_2 , the potential is symmetric around $\theta = 90^\circ$. This results in the molecule being strongly aligned but not very strongly oriented. A strong alignment corresponds to high populations in states with even values of l since alignment is calculated as $\langle \cos^2(\theta) \rangle$. Because the potential is relatively weak, the ground state is mainly composed of the lowest-lying even l state, which is the $l = 2$ state. Therefore, the ground state appears as a slightly altered version of the $l = 2$ spherical harmonic, shown in panel (b)

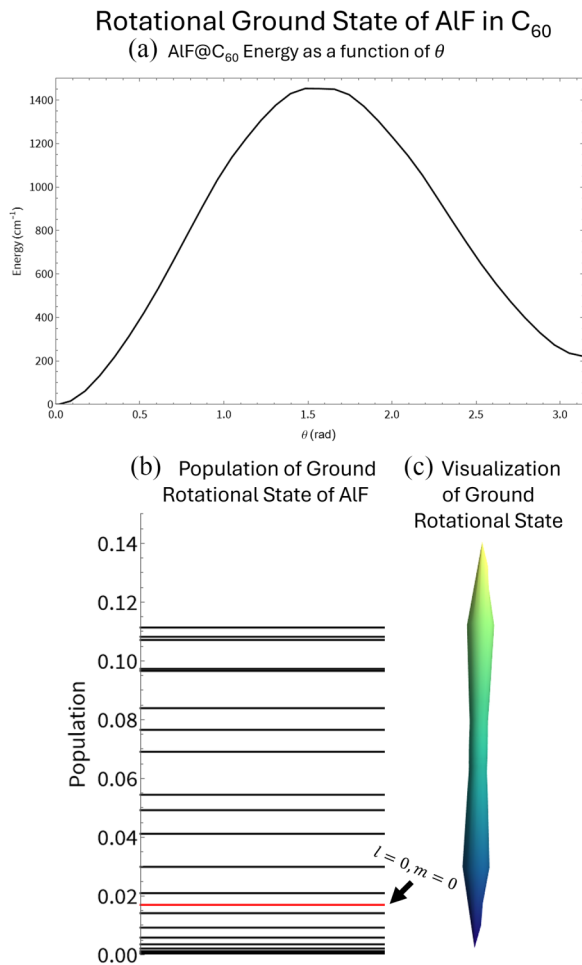


FIG. 7. Mixing of the rotational states of AlF due to the interaction with the C₆₀ cage. Panel (a) shows the populations of the rotational states of a free AlF molecule in the new ground rotational state. The new ground state is thoroughly mixed with no clear preference for even or odd values of l . Panel (b) shows the new ground state as a spherical plot. Panel (c) shows the energy as a function of rotation of the AlF molecule inside the C₆₀ cage.

of Fig. 6. This weak mixing means that the new ground state can be described accurately by only accounting for a few unperturbed rotational states. Our calculations of the perturbed rotational ground state accounted for eleven unperturbed rotational states. However, sufficient convergence was found by accounting for as little as five states, as the populations of the higher l values were found to rapidly approach zero. The alignment of the new ground state was calculated to be 0.82 as opposed to the orientation ($\langle \cos(\theta) \rangle$) of the new ground state which was calculated to be 0.0053. The small orientation should not come as a surprise, as the N₂ molecule is homonuclear.

The potential of AlF as it rotates inside the C₆₀ molecule, shown in panel (c) of Fig. 7, has a few important differences from N₂. The potential for AlF is symmetric around a 180° rotation. The energy at $\theta = 180^\circ$ is higher than the energy at the optimal geometry, due to the optimized geometry's slight deviation from perfect D_{5d} symmetry. This forces the AlF molecule to be strongly oriented and strongly aligned. The

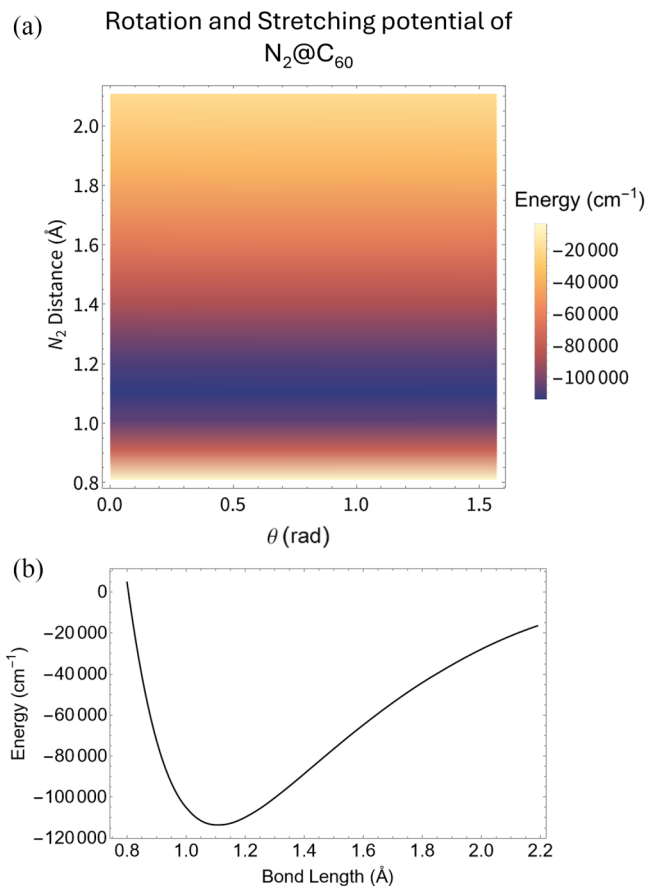


FIG. 8. The potential for the N₂ molecule within a fullerene. Panel (a) shows the potential energy as a function of both rotation and stretching calculated using DFT. Panel (b) shows the rotational average of the potential shown in panel (a).

alignment of the new ground state was calculated to be 0.98 and the orientation of the new ground state was calculated to be 0.99. The increased alignment is due to the increased strength of the potential. Compared to N₂@C₆₀, the energy as a function of rotation is approximately 10 times stronger for AlF@C₆₀. This results in the perturbed rotational ground state becoming a heavy mix of a wide variety of unperturbed rotational states. To calculate the new rotational ground state, we needed to account for approximately 27 unperturbed states in order to find sufficient convergence, compared to the five needed for N₂. Since the molecule is aligned and oriented, there is no strong preference for states with an even value of l like what we predicted for N₂. The strong alignment causes the visualization of the new ground state, shown in panel (b) of Fig. 7, to be very long and thin. The many unperturbed states represented within the new ground state cause the visualization to not closely resemble any one spherical harmonic.

We find that the change in energy as the internal molecules stretch is significantly greater than the change in energy as the internal molecule rotates for both endofullerenes studied. Panel (c) of Fig. 7 shows that the energy as a function of rotation for AlF inside of C₆₀ is on the order of 10³ cm⁻¹, compared to the energy as a function of stretching, shown in panel (b) of Fig. 9, which is on the order of 10⁴ cm⁻¹. This energy difference is even greater in the case of N₂@C₆₀ due to

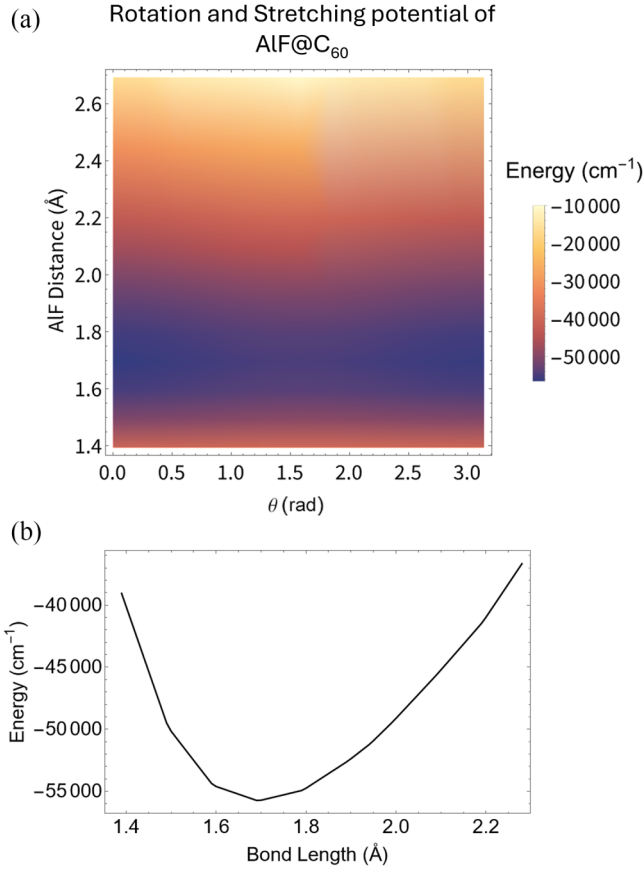


FIG. 9. The potential for the AIF molecule within a fullerene. Panel (a) shows the potential energy as a function of both rotation and stretching calculated using DFT. Panel (b) shows the rotational average of the potential shown in panel (a).

the tight bond between the two nitrogen atoms. This difference in energy allows for the rotational and vibrational degrees of freedom to be treated separately, as we have done, without significant loss in accuracy.

IV. SPECTROSCOPIC CONSTANTS

The potential, $V(r, \theta, \phi)$, as a function of both rotation and stretching is shown in panel (a) of Figs. 8 and 9 for $N_2@C_{60}$ and $AIF@C_{60}$, respectively. On both of these plots the energy appears to change little as the rotation angle changes. This difference in energy allows for the rotational and vibrational degrees of freedom to be treated separately without a significant loss in accuracy. Therefore, it is possible to introduce the rotationally averaged potential as

$$\widetilde{V}(r) = \langle V(r, \theta, \phi) \rangle = \int_0^{2\pi} d\phi \int_0^\pi d\theta Y_l^{m*}(\theta, \phi) \times V(r, \theta, \phi) Y_l^m(\theta, \phi) \sin \theta, \quad (4)$$

where r is the internuclear separation of the internal molecule. Panel (b) of Figs. 8 and 9 shows the rotationally averaged potential, $\widetilde{V}(r)$, for $N_2@C_{60}$ and $AIF@C_{60}$, respectively. We notice that for both systems the interaction potential resembles a Morse potential, characteristic of covalent systems, especially $N_2@C_{60}$.

Assuming that the energy as a function of nuclear separation is described by a Morse potential, we find

$$\widetilde{V}(r) = D_e(1 - e^{a(R_e - r)})^2 - D_e, \quad (5)$$

where D_e is the dissociation energy, R_e is the equilibrium distance given by the DFT calculations, and a is a fit parameter related with anharmonicity of the potential. To obtain a , we adjusted D_e until the R -squared value of the fit was maximized. This technique introduces a source of error, but this error should be smaller than the errors already introduced through the use of DFT. This technique has the benefit of allowing us to use existing methods developed to describe diatomic molecules using Morse potentials [42].

In a Morse potential, the spectroscopic constants of the molecule depend uniquely on the reduced mass of the molecule, μ , and the three parameters of the Morse potential: R_e , D_e , and a . For instance, the vibrational harmonic frequency is given by [43]

$$\omega_e = \frac{a}{2\pi c} \sqrt{\frac{2D_e}{\mu}}, \quad (6)$$

where c is the speed of light. The first anharmonic correction $\omega_e \chi_e$ is then given as

$$\omega_e \chi_e = \frac{\hbar a^2}{4\pi \mu c}, \quad (7)$$

where $\hbar$ is the reduced Planck's constant. The rotational constant B_e is calculated directly from the equilibrium distance as

$$B_e = \frac{\hbar}{4\pi c \mu R_e^2}. \quad (8)$$

Finally, the first correction to the rotational constant is

$$\alpha_e = \frac{3\hbar^2 \omega_e}{4\mu R_e^2 D_e} \left(\frac{1}{a R_e} - \frac{1}{a^2 R_e^2} \right). \quad (9)$$

The resulting spectroscopic constants are shown in Table II for $N_2@C_{60}$ and $AIF@C_{60}$. The errors shown in Table II come from errors in D_e and a resulting from the fit. These errors are then propagated through the equations above. Overall, the spectroscopic constants of a free molecule and the molecule in a fullerene are very similar. In other words, the intrinsic properties of a molecule in the gas phase and a molecule inside a fullerene are roughly the same. However, there are general trends worth discussing. For instance, molecules appear stretched inside the fullerene with respect to their free case. As a result, the rotational constant of a molecule inside a fullerene is smaller than the rotational constant when the molecule is in free space. In a similar vein, ω_e is slightly larger for molecules in fullerenes than it is for the same molecules in free space.

V. DIPOLE MOMENT

Heteronuclear molecules show a permanent dipole moment, which can be viewed as another spectroscopic constant and, as such, may be affected by the presence of the cage when the molecule is placed in a fullerene. Studies of $HF@C_{60}$ have

TABLE II. Constants calculated for AlF and N₂ inside of C₆₀ using our methods compared to known values for the ground states of free AlF and N₂ [40]. All errors shown below come from the fitting of the potential to a Morse potential. The only error accounted for is the error due to the fit of the potential to a Morse potential. This error is small, since the rotationally averaged potential $\bar{V}(r)$ fits very well to a Morse potential (both *R*-squared values are over 0.99). Errors due to the level of theory used or the limited size of the basis set used are not accounted for and are likely the most significant sources of error.

Species	Re (Å)	ω_e (cm ⁻¹)	$\omega_e\chi_e$ (cm ⁻¹)	<i>Be</i> (cm ⁻¹)	α_e (cm ⁻¹)
N ₂ @C ₆₀	1.11	2376 ± 4	12.30 ± 0.03	1.95	0.01455 ± 5 × 10 ⁻⁵
N ₂	1.097685	2358.57	14.324	1.998241	0.017318
AlF@C ₆₀	1.69	843 ± 3	3.18 ± 0.02	0.53	0.00288 ± 10 ⁻⁵
AlF	1.654369	802.26	4.77	0.55248	0.00498

shown that the fullerene cage can shield the dipole moment of the internal molecule [28].

Here, we focus on AlF@C₆₀. To calculate its dipole moment, we use the B3LYP-D3 functional and the Def2TZpp basis set including the counterpoise correction. Using this approach, we obtained a dipole moment for free AlF of 1.51 D, which agrees with the experimentally determined value of 1.530 D [44]. For AlF@C₆₀, we find a dipole moment of 1.63 D. Therefore, it seems that the cage slightly enhances the dipole moment of the internal molecule.

Our results are the opposite of the measured results for HF@C₆₀ [28], where the fullerene cage has been measured to suppress the dipole moment of the internal HF molecule by as much as 75%. However, as noted above, the molecule is stretched when placed inside the fullerene, so if the Pauling ionic character is similar, then the dipole moment of the molecule inside the cage should be larger than in the free case. In addition, it could be possible that the influence of the fullerene on the dipole moment of the internal molecule changes dramatically depending on the type of internal molecule. Polarizabilities of endofullerenes have been shown to be different for different types of internal molecules [45], so it is reasonable for the effects on the dipole moment to depend on the internal molecule as well. There is also the possibility that the discrepancy between our findings and the results for HF@C₆₀ is a failure of the quantum chemistry methods implemented. This could also be a result of temperature which is not accounted for in our study but is accounted for in the study of HF@C₆₀. In any case, this contradiction warrants future study.

VI. CONCLUSIONS

After exploring the interaction energy landscape of AlF@C₆₀ and N₂@C₆₀, we predict that the icosahedral symmetry of the outer fullerene is broken by the internal molecule creating only one preferred axis of alignment. We also predict that the spectroscopic constants of an internal molecule of an endofullerene are not significantly altered by the interaction with the carbon cage. We report no significant changes to the equilibrium distance, the rotational constant, the first correction to the rotational constant, the harmonic frequency, and the first anharmonic correction. This agreement does provide some evidence that our approach is accurate. While the properties of the internal molecule are predicted to remain mostly unchanged, the molecule-cage interaction is highly

anisotropic, inducing strong interactions between the rotational states of the molecule. This strong interaction causes the molecule to have a high degree of alignment with the C₆₀ cage. In the case of an internal heteronuclear molecule, the molecule is predicted to have both strong alignment and strong orientation with the fullerene.

Our results show a slight enhancement of the dipole moment of AlF when placed inside a C₆₀ molecule. Measurements with HF@C₆₀ [28] reveal the opposite result. In HF@C₆₀, a strong suppression of the dipole moment of HF is observed. Studies of endofullerenes with heteronuclear diatomic molecules are scarce. A better understanding of this disagreement is a topic for future work along with calculations of a full potential surface for N₂ or AlF inside of a fullerene.

Studies of HF@C₆₀ [28] and H₂@C₆₀ [46] have found that the gaps between vibrational levels are redshifted due to the interaction with the fullerene. When comparing the harmonic frequency calculated using our methods with the accepted values for the free molecules (see Table II) we find a slight blueshift. Blueshifts have been found in other computational studies of endofullerenes [47], as well as redshifts [48]. However, these shifts are found by comparing to frequencies calculated using the same computational methods applied to the free molecule and not by comparing to experimentally determined values of the free molecule. When calculating the values of the harmonic frequency of the free molecules using our methods we find a redshift of 28 cm⁻¹ for N₂ and a redshift of 166 cm⁻¹ for AlF. For N₂, our results are about three times smaller than what was found using the MP2 level of theory [48]. The 166 cm⁻¹ redshift predicted for AlF is reasonably close to the currently accepted value of 171 cm⁻¹ for HF [28,32].

Based on these results, we propose using off-resonant light, with respect to the fullerene transitions, to create laser-induced alignment of the internal molecule of an endofullerene. For instance, using a short laser pulse (pulse durations much shorter than the rotational period of the internal molecule) will lead to the typical time revivals on the alignment of the molecule [49–52]. In this scenario, the revival times should be very similar between a free molecule and one inside a fullerene cage, since these revival times only depend on the rotational constant of the molecule. Therefore, any deviation between a free molecule and a molecule in a fullerene cage can be used to establish the properties of the endofullerene. Perhaps more importantly, this proposed experiment could be used to study the internal molecule's interaction with the fullerene.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [38].

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