

Terahertz spectroscopy study of the confining potential for methane in the endofullerene $\text{CH}_4@C_{60}$

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(Dated: 31 July 2025)

We used terahertz spectroscopy to study the non-covalent interaction between CH_4 and the confining fullerene cage in endofullerene $\text{CH}_4@C_{60}$. The temperature dependence of the THz absorption spectra of powdered $\text{CH}_4@C_{60}$ was measured between 5 and 300 K. At temperatures below 50 K, the THz spectrum of CH_4 shows a single line centered at 214 cm^{-1} , which broadens and shifts to higher energy as the temperature increases. These effects are explained by the anharmonicity of the $\text{CH}_4\text{--}C_{60}$ interaction potential function. The model involves the center-of-mass motion of CH_4 in a spherically symmetric potential well. Line intensities are modeled by invoking an electric dipole moment induced by the translational displacement of CH_4 from the center of the cage C_{60} . The potential function and the dipole moment parameters were derived from the temperature dependence of the THz absorption spectra and compared with the parameters of previously studied endofullerenes. The quantum chemistry calculations reproduce the CH_4 translation motion frequency and the potential function remarkably well.

I. INTRODUCTION

After the discovery of fullerene C_{60} by Kroto et al.¹ in 1985, this highly symmetric molecule gained immediate attention due to its potential to encapsulate atoms and molecules in its hollow cavity. Soon the same group of scientists reported the encapsulation of lanthanum atom by laser ablation method to form $\text{La}@C_{60}$ ², known as endofullerene and denoted as $A@C_{60}$. Since then, the field of studies of endofullerenes has shown significant growth. The advent of the “molecular surgery” method³ has allowed for the synthesis of a variety of endohedral fullerenes in relatively large amount⁴. These includes noble gas atoms^{5–8} and molecular species such as $\text{H}_2@C_{60}$ ⁹, $\text{H}_2@C_{70}$ ¹⁰, $\text{HF}@C_{60}$ ¹¹, $\text{H}_2\text{O}@C_{60}$ ¹², $\text{CH}_4@C_{60}$ ¹³, and $\text{CH}_2\text{O}@C_{60}$ ¹⁴. One salient feature of the confinement is the quantization of the center-of-mass translational degrees of freedom of the guest species. This phenomenon, thanks to “molecular surgery” is accessible to various spectroscopic techniques and has been studied in detail for endofullerenes hosting noble gas atoms and small molecules by terahertz (THz) and infrared spectroscopy^{10,14–24} and inelastic neutron scattering spectroscopy^{18,20,22,25–30}.

The confining potential energy function of atoms and small molecules inside the C_{60} molecular cage is the result of non-bonding interactions between the guest and C_{60} . This function has been a frequent target of theoretical calculations^{31–46}. The noble gas atoms are spherically symmetric and only have translational degrees of freedom, which makes them a relatively simple system for quantum chemistry calculations. The calculation of more complicated endohedral species in which the guest is a polar molecule, such as H_2O and $\text{HF}@C_{60}$, has been widely regarded as a challenge. Endofullerenes like $\text{CH}_4@C_{60}$, in which the molecule fits tightly inside the cage, also presents computational difficulties. The quantum chemistry calculation often requires a careful selection of compu-

tational techniques and the basis set to precisely determine the weak non-bonding interactions. Therefore, experimental findings which guide the selection of computational model and the basis set, are highly valuable. Over the years, reliable potential energy functions have been determined for $\text{H}_2@C_{60}$ ^{15–17,29} and noble gas atoms^{21,22}. The translational excitation frequencies from the ground to the first excited state have been determined for $\text{HF}@C_{60}$ ¹⁸, $\text{H}_2\text{O}@C_{60}$ ¹⁹, and $\text{CH}_2\text{O}@C_{60}$ ¹⁴. However, to the best of our knowledge, no potential energy function nor translational excitation frequency has so far been determined experimentally for a larger molecule such as $\text{CH}_4@C_{60}$. $\text{CH}_4@C_{60}$ has been the subject of several theoretical studies, including the prediction of terahertz and infrared spectra^{47–49}.

Here we report a THz study of translational dynamics of CH_4 in the molecular cavity of C_{60} . To determine the anharmonicity of the confining potential, we studied the temperature dependence of the THz absorption spectra. CH_4 is classified as a spherical top molecule, for which the translation-rotation coupling is expected to be negligible compared to less symmetric molecules such as $\text{H}_2@C_{60}$ ¹⁶, $\text{HF}@C_{60}$ ¹⁸, $\text{H}_2\text{O}@C_{60}$ ¹⁹ and $\text{CH}_2\text{O}@C_{60}$ ¹⁴. Hence, the translation motion of $\text{CH}_4@C_{60}$ can be treated independently of its rotations, and the Hamiltonian model is similar to that of a confined noble gas atom²⁰.

II. MATERIALS AND METHODS

A. Sample preparation

$\text{CH}_4@C_{60}$ sample was prepared using the multiroute “molecular surgery” method¹³. The procedure involves a series of controlled chemical reactions to create a hole in the fullerene molecule cage, then incorporating the guest species

through the hole, and finally closing the hole with another series of chemical reactions while keeping the guest inside the fullerene.

Following the synthesis, the CH₄@C₆₀ sample was subjected to high-performance liquid chromatography (HPLC) to remove the traces of empty C₆₀. Eventually, CH₄@C₆₀ was obtained with filling factor $f_0 = 100.0 \pm 0.3\%$. The sample was sublimed under a vacuum before THz measurements.

B. Measurement technique

The CH₄@C₆₀ powdered sample (12.7 mg) was put into the 3 mm brass frame and pressed into a $d = 1.1$ mm thick pellet.

To achieve cryogenic temperatures a cold-finger continuous flow cryostat was used, equipped with a sample cell. The brass frame containing the pressed pellet was placed into the vacuum-tight sample cell with two thin polypropylene windows. The sample cell was filled with 100 mbar of He gas at room temperature to facilitate good thermal contact between the cold finger and the pellet. The cryostat was inserted into the sample compartment of the interferometer. The transmission spectra of CH₄@C₆₀ were measured up to 300 cm⁻¹ using a FTIR Bruker Vertex 80v spectrometer equipped with SiC (globar) radiation source, a 6 μm thick Mylar beamsplitter, and a 4 K bolometer detector. The spectral resolution was 0.3 cm⁻¹, which was less than the line width of CH₄@C₆₀ absorption lines.

To record the transmission spectra, the cold finger was moved up and down relative to the beam, allowing the light to pass through the sample or a 3 mm reference hole attached to the cold finger. The transmission spectra, $T(\omega)$, were measured as the ratio of the intensity of light transmitted through sample, $I_s(\omega)$ at frequency ω , to the intensity transmitted by the reference hole, $I_r(\omega)$, $T(\omega) = I_s(\omega)/I_r(\omega)$. The absorption spectra $\alpha(\omega)$ were calculated from the transmission spectra, $\alpha(\omega) = -d^{-1} \ln [T(\omega)R(\omega)^{-1}]$, where d is the sample thickness. $R(\omega)$ is the amount of radiation lost in reflections from the surfaces of the pellet and sample chamber windows. Since R is featureless in the spectral range of CH₄ absorption lines it was subtracted as a background absorption without affecting the CH₄ absorption line intensities and shape.

C. Confined CH₄ translational motion: Anharmonic spherical oscillator model

To describe the quantized translational motion of CH₄ trapped inside the C₆₀ we use the spherical anharmonic oscillator model. The detailed formulation of the model has been discussed in Ref.20 and Ref.21. Here, we summarize the key features. We treat C₆₀ as a rigid body with a fixed center of mass. Within this approximation, we ignore the effects of C₆₀ rotations and librations on the motion of the confined CH₄. We also ignore the coupling of CH₄ to the vibrations of C₆₀ and to the crystal lattice modes. We assume the confining potential stays constant over the 5 to 300 K temperature range.

Fullerene has icosahedral symmetry, but for simplicity, we approximate it with spherical symmetry. This approximation excludes any angular dependence and as a result, the potential function of CH₄ depends only on the radial displacement r from the C₆₀ center of mass.

The Hamiltonian $\hat{H}$ for CH₄ in the spherically symmetric potential is

$$\hat{H} = \frac{\hat{p}^2}{2m} + V_2 r^2 + V_4 r^4, \quad (1)$$

where $V_4 r^4$ is the anharmonic correction. The first two terms are the kinetic and potential energy of the harmonic oscillator with the energy eigenvalues

$$E_n = \hbar\omega_0 \left(n + \frac{3}{2} \right), \quad (2)$$

where the frequency of the harmonic spherical oscillator is $\omega_0 = \sqrt{2V_2/m}$ and m is the mass of CH₄. The eigenstates of the harmonic spherical oscillator are well known^{21,50}. They are characterized by translational quantum number, $n \in \{1, 2, 3, \dots\}$ and angular momentum quantum number ℓ , where $\ell \in \{2, 4, 6, \dots\}$ for even n and $\ell \in \{1, 3, 5, \dots\}$ for odd n . The anharmonic spherically symmetric Hamiltonian of CH₄ is solved by diagonalizing Eq. (1) numerically using a finite basis set of harmonic spherical oscillator eigenstates, using all the states up to and including $n_{max} = 18$. Since the potential is spherically symmetric, there is no mixing of eigenstates with different ℓ and the energy levels are $(2\ell + 1)$ -fold degenerate.

The translational motion of CH₄ is decoupled from electromagnetic radiation since the molecule is neutral. We assume that the electric field of THz radiation couples to the dipole moment induced by the displacement of CH₄ from the center of the C₆₀ cage, $\mathbf{r} = (r, \phi, \theta)$, given in spherical coordinates. A similar analysis was used to treat the THz spectrum of He@C₆₀²¹. The dipole moment operator, as discussed in Ref.21, is expressed as a function of spherical harmonic of rank one,

$$d_{1q} = \sqrt{\frac{4\pi}{3}} A_{1q} r Y_{1q}(\theta, \phi), \quad (3)$$

where A_{1q} is the real-valued dipole amplitude coefficient and $q \in \{-1, 0, +1\}$. For spherical symmetry, A_{1q} does not depend on q , so $A_{1q} \equiv A_1$. In case of CH₄@C₆₀, we found that it was not necessary to include higher order odd powers of r in the expansion Eq. (3). The selection rules for the electric dipole transition of harmonic oscillator are $\Delta\ell = \pm 1$ and $\Delta n = \pm 1$ ²¹.

The fitting parameters $\kappa = \{V_2, V_4, A_1\}$ are determined by minimizing the difference-squared between the baseline-corrected experimental spectrum and the spectrum calculated with the fitting parameters. At each step the Hamiltonian was diagonalized numerically and the dipole moment matrix transformed into the Hamiltonian eigenbasis. The line intensities were calculated by taking into account the thermal populations of the energy levels as described in Ref. 21. The linewidth of the CH₄@C₆₀ experimental spectra changes with temperature. Up to 80 K the full width at half maximum

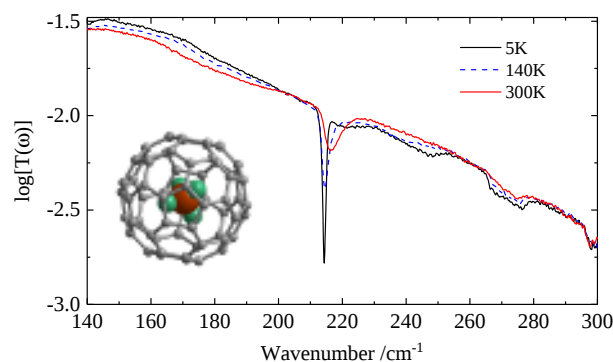


FIG. 1. Temperature dependence of THz transmission spectra of $\text{CH}_4@C_{60}$ at 5 K (black solid line), 140 K (dashed blue line) and 300 K (red solid line). Plotted is the $\log_{10}[T(\omega)]$ where $T(\omega) = I_s(\omega)/I_r(\omega)$ and I_s and I_r are the intensities transmitted through the sample and through the reference hole, respectively.

was determined from the experimental spectra. Above 80 K it was not possible to resolve individual lines and therefore the linewidth was assumed to be equal to 2 cm^{-1} and independent of temperature. The confidence limits of the fit parameters were calculated with the method described in Ref.¹⁹.

D. Quantum chemistry calculations

The structure of $\text{CH}_4@C_{60}$ was minimised with Gaussian 09 revision D1.01⁵¹ using Density Functional Theory (DFT) with pure PB86^{52,53} functional, and the harmonic frequencies calculated for the translational modes. The basis set was cc-pVDZ⁵⁴ with a superfine (175,974 points for H, 250,974 points for C) integration grid. Tight criteria were used for convergence.

III. RESULTS AND DISCUSSIONS

The temperature dependence of THz transmission spectra of $\text{CH}_4@C_{60}$ is shown in Fig. 1. At the lowest temperature of 5 K, the THz spectrum displays one prominent absorption line at 214 cm^{-1} . As the temperature increases the absorption line broadens and shifts to higher frequency. The peak is exclusive to $\text{CH}_4@C_{60}$ because such a peak is present in the THz spectra of neither C_{60} nor $A@C_{60}$. The peak does not belong to the vibrational mode of free CH_4 because all of the vibrational modes frequencies are above 1200 cm^{-1} . Also, it is not the rotational transition of $\text{CH}_4@C_{60}$ because the rotational constant is small, $B = 5.2 \text{ cm}^{-1}$ ⁵⁵, which correspond to 10.4 cm^{-1} energy difference between the ground and the first excited rotational state.

A more detailed temperature dependence of the absorption spectra with the baseline subtracted is shown in Fig. 2. We attribute the 214 cm^{-1} peak in the THz absorption spectrum to the quantized center-of-mass translational motion of CH_4 inside C_{60} . The peak broadening and the shifts of its maximum to higher frequency is due to the increased population of

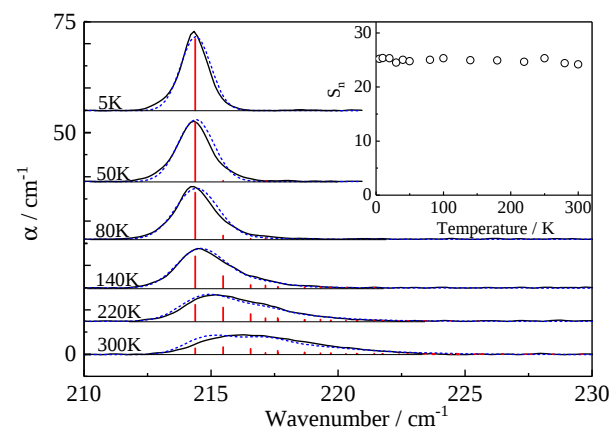


FIG. 2. Temperature dependence of THz absorption spectra of $\text{CH}_4@C_{60}$. Experimental spectra (black) and the calculated spectra (blue dashed) using best fit parameters given in Table I. Calculated spectra are plotted using Gaussian line shape and T -dependent line width, see text. Sticks represent positions of individual lines from the model fit with stick height proportional to the line area. The inset shows the integrated line area across measured temperatures.

excited translational states at higher temperature; transitions starting from excited translational states have an increased energy due to the anharmonicity of the potential function. The inset to Fig. 2 shows that the total line area does not change with temperature. This confirms that all electric-dipole-active transitions of CH_4 translational motion are contained within the same peak.

To validate our experimental findings, we fitted the experimental spectra with the spherical anharmonic oscillator model, Sec. II C. This model only includes calculations of the frequencies and intensities, and does not take into account line width effects. To obtain the experimental line widths the low temperature spectra were fitted with a single Gaussian line from where the temperature-dependent line widths followed: (T/K , FWHM / cm^{-1}): (5, 1.4), (10, 1.4), (20, 1.52), (30, 1.55), (40, 1.6), (50, 1.68), (60, 1.77), (80, 1.93). Since the individual lines could not be resolved in the experimental spectra above 80 K, the line width was assumed constant, 2 cm^{-1} , in the spectra measured at 100, 140, 180, 220, 250, 280 and 300 K. When fitting the spectra with the anharmonic oscillator model these line widths were used to calculate the model spectra. The model spectra, calculated using the best fit potential and dipole moment parameters listed in Table I are plotted in Fig. 2 for selected temperatures. In Table II we list the energy levels up to $n = 5$ calculated with the best fit potential parameters.

The anharmonic spherical oscillator parameters that give the best fit to the experimental THz spectra are given in Table I. The anharmonic V_4 term is positive, which means that the distance between the energy levels increases with increasing energy. This behaviour is found for all $A@C_{60}$ species, as shown in Table I. The effect of positive V_4 term is visible in Fig. 2: the additional absorption lines in the high temperature

TABLE I. The best fit polynomial coefficients and their confidence limits for the spherically symmetric potential function $V(r) = V_2 r^2 + V_4 r^4 + V_6 r^6$ and induced dipole function $d = (4\pi/3)^{1/2}(A_1 r + A_3 r^3)Y_{10}(\theta, \phi)$ of $A@C_{60}$. $d_{01} = \langle 1|d|0 \rangle$ is the expectation value of the dipole moment between the ground state and the first excited state. ω_{01} is the peak frequency of the absorption line at 5 K in the measured THz spectrum which corresponds to the energy separation of the ground state and the first excited state. $\nu_{\text{anh}} = (\omega_{01} - \omega_0)/\omega_{01}$ is the fractional contribution of the anharmonic potential to ω_{01} where $\omega_0 = (2\pi c)^{-1} \sqrt{2V_2/m}$ is the frequency of the harmonic oscillator, Eq. (2), in wavenumber units and c is the speed of light in vacuum. R_W is the van der Waals radius of A . The data for atoms is from Ref. 21 and Ref. 22.

Parameter	^4He	^{20}Ne	^{40}Ar	^{84}Kr	CH_4
$V_2 / \text{J m}^{-2}$	0.39 ± 0.006	1.58 ± 0.04	9.56 ± 0.03	17.81 ± 0.12	21.10 ± 0.04
$V_4 / \text{J m}^{-4} / 10^{20}$	(0.60 ± 0.01)	(2.28 ± 0.22)	(8.19 ± 0.16)	(13.2 ± 1.60)	(11.6 ± 0.56)
$V_6 / \text{J m}^{-6} / 10^{39}$	(3.94 ± 0.09)	0	0	0	0
$A_1 / \text{C} / 10^{-21}$	(0.68 ± 0.04)	(1.84 ± 0.13)	(3.31 ± 0.01)	(3.30 ± 0.21)	(2.73 ± 0.03)
$A_3 / \text{C m}^{-2}$	0.04 ± 0.01	0	0	0	0
d_{01} / Debye	0.017	0.019	0.020	0.014	0.017
$\omega_{01} / \text{cm}^{-1}$	81.4	56.6	91.8	85.4	214.1
ν_{anh}	0.29	0.085	0.018	0.007	0.014
R_W / pm	140 ⁵⁶	154 ⁵⁶	188 ⁵⁶	202 ⁵⁶	206 ⁵⁷

spectra appear on the higher frequency side of the low temperature absorption line. However, the transitions from thermally excited energy levels merge because of the small energy separation of individual lines relative to the line width, resulting in a single broad unresolved line. Similar behaviour is observed for endofullerenes containing the noble gas atoms Ne, Ar, and Kr²². This contrasts to the case of $\text{He}@C_{60}$, which shows a comb of well-resolved peaks as the excited levels become thermally populated at high temperatures²⁰.

TABLE II. Translational energy levels of $\text{CH}_4@C_{60}$ obtained from the fits of THz absorption spectra. $|\xi|^2$ is the amplitude-squared of the dominant component of the eigenstate with the quantum numbers (n, ℓ) . The zero point energy, 319.47 cm^{-1} , has been subtracted.

E / cm^{-1}	n	ℓ	$ \xi ^2$
0	0	0	1
214.4	1	1	1
429.9	2	2	1
431.5	2	0	0.999
646.4	3	3	0.999
649.2	3	1	0.998
864.0	4	4	0.998
867.8	4	2	0.997
869.5	4	0	0.996
1082.7	5	5	0.998
1087.6	5	3	0.995
1090.2	5	1	0.994

Anharmonicity in the confining potential induces mixing between the harmonic oscillator eigenstates. Hence, a good indicator of the degree of anharmonicity is the largest coefficient of a harmonic oscillator state in each eigenstate of the anharmonic oscillator. This coefficient is equal to 1 for a harmonic oscillator but takes a smaller value for an anharmonic oscillator. Table II lists the computed coefficients for the anharmonic oscillator eigenstates used to match the experimental THz spectrum of $\text{CH}_4@C_{60}$, as shown in Figure 2. In case of CH_4 , $|\xi|^2$ falls off slowly with increasing n indicating the weak anharmonicity of the potential function. For example,

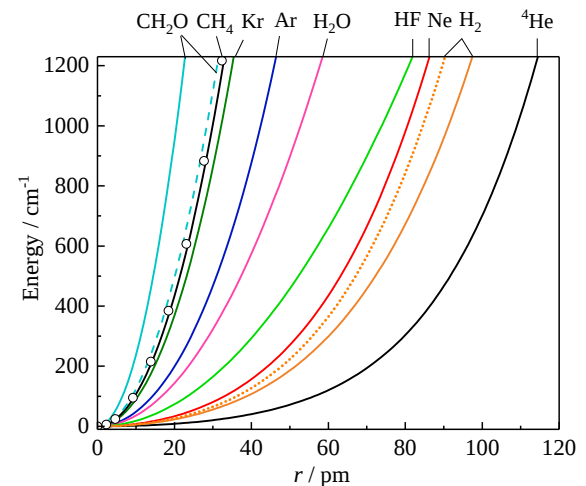


FIG. 3. The experimentally determined potential energy curve $V(r)$ of several endohedral complexes of C_{60} . The potential energy curves of ^4He , ^{20}Ne , ^{40}Ar , ^{84}Kr and CH_4 are calculated with parameters from Table I. The open symbols are the result of quantum chemistry calculation for $\text{CH}_4@C_{60}$, see Section II D. The potential curves of H_2 are calculated from best fit parameters given in Ref. 16, where the H_2 molecule axis is parallel to the displacement $\mathbf{r}$ (dotted orange) and perpendicular to it (solid orange). The degree of anharmonicity of HF, H_2O and $\text{CH}_2\text{O}@C_{60}$ is not known experimentally. Here the potential curve is plotted in harmonic approximation where $V_2 = m\omega_0^2/2$ and $\omega_0 (2\pi c)^{-1}$ is the observed translational frequency in wavenumber units: 78.6 cm^{-1} for $\text{HF}@C_{60}$ ¹⁸, 110 cm^{-1} for $\text{H}_2\text{O}@C_{60}$ ¹⁹ and 166.8 (dashed) and 231.1 cm^{-1} (solid) for $\text{CH}_2\text{O}@C_{60}$ ¹⁴; c is the speed of light in vacuum.

the $|\xi|^2$ in the state which is predominantly $(n, \ell) = (3, 3)$, is 0.69 in $^4\text{He}@C_{60}$ ²¹ while it is 0.999 in $\text{CH}_4@C_{60}$.

Just like other $A@C_{60}$ in Table I, CH_4 is neutral and lacks permanent dipole moment. The guest molecule gains the dipole moment through its interaction with the inner surface of C_{60} when it moves away from the cage center. The induced

dipole moment, $\langle 0|d|1\rangle$, of CH₄ and atoms for the transition from the ground ($n = 0$) to the first excited state ($n = 1$) is listed in Table I. It can be seen that the induced dipole moments are about 100 times smaller than the permanent dipole moment of free H₂O (1.85D), for example.

Previous DFT studies on CH₄@C₆₀ using the Becke–Perdew BP86 exchange-correlation functional^{52,53} gave the translational mode frequencies of 209, 217, and 220 cm⁻¹⁴⁷. Although the mean (215.3 cm⁻¹) is in exceptionally good agreement with the experimental value (214 cm⁻¹) the wide spread of values does not reflect the high symmetry of the CH₄@C₆₀ system. Repeating the calculation using a large integration grid gave translational mode frequencies of 207.3, 207.5 and 208.1 cm⁻¹. Although the mean (207.6 cm⁻¹) is further from that observed the narrow spread of three calculated mode frequencies is an improvement. A potential energy curve for the 207.5 cm⁻¹ translational mode was constructed using single point energy calculations on structures generated along the mode using GaussView and is shown in Fig. 3. The calculated potential provides an overall good description of the confining potential of the encapsulated CH₄ molecule.

In Fig. 3, we also compare the experimentally derived potential energy function curves of several endohedral complexes of C₆₀. The comparison of CH₄@C₆₀ and Noble gas atoms shows that there is a correlation with the van der Waals radius (listed in Table I): the potential steepens with the increase of the van der Waals radius. This conforms to the intuitive picture that large species fit more snugly into the C₆₀ cavity and have less room to “rattle around”. The comparison to other four molecules is not so straightforward. *Firstly*, H₂, HF, H₂O and CH₂O are asymmetric; this asymmetry, manifested as translation-rotation coupling in the Hamiltonian^{15,36}, is demonstrated for H₂ where two potential curves are shown, for the H₂ molecule axis parallel and perpendicular to the displacement vector **r**; although the anisotropic experimental potential curves have not been derived for CH₂O@C₆₀, the translation-rotation coupling must be strong in comparison to H₂ as the two well-separated lines are seen at 166.8 and 231.1 cm⁻¹ in the CH₂O@C₆₀ THz absorption spectrum¹⁴. *Secondly*, there is no experimental data about the anharmonicity for H₂O@C₆₀, HF@C₆₀ and CH₂O@C₆₀.

To summarize, the translational mode of CH₄ was observed at 214 cm⁻¹ at 5 K in the molecular cavity of C₆₀. The potential energy curve, including the anharmonic correction, was determined from the temperature dependence of the THz absorption spectra which shift to higher energy and broaden as the temperature increases. The THz spectra are well described by a spherical anharmonic oscillator for the CH₄ center-of-mass motion despite the internal vibrational and rotational degrees of freedom of CH₄. The experimentally determined potential function is in good agreement with quantum chemistry calculations. The lighter mass of CH₄ combined with the steep confining potential sets the CH₄@C₆₀ mode frequency to be higher than that of C₆₀ endofullerenes containing noble gas atoms in C₆₀.

AUTHOR CONTRIBUTIONS

E.S.M., M.C.W., G.H., S.B., and R.J.W. carried out synthesis and purification of endofullerenes. T.J., A.S., U.N., and T.R. performed the THz experiments and processed the THz data. T.J., and T.R. derived the potential parameters by fitting the THz spectra. R.J.W. performed the quantum chemistry calculation. T.J. wrote an initial draft of the paper. T.R. developed the concept of the paper. All authors reviewed and developed the manuscript.

ACKNOWLEDGMENTS

This research was supported by the Estonian Ministry of Education, personal research funding PRG736, and the European Regional Development Fund project TK134, and by EPSRC grants EP/T004320/1, EP/P009980/1 and EP/Y010515/1 of UK. RJW acknowledges the use of the IRIDIS High Performance Computing Facility at the University of Southampton.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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