Infrared spectroscopy of small-molecule endofullerenes

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Hydrogen is one of the few molecules which has been incarcerated in the molecular cage of C₆₀ and forms endohedral supramolecular complex H₂@C₆₀. In this confinement hydrogen acquires new properties. Its translational motion becomes quantized and is correlated with its rotations. We applied infrared spectroscopy to study the dynamics of hydrogen isotopologs H₂, D₂ and HD incarcerated in C₆₀. The translational and rotational modes appear as side bands to the hydrogen vibrational mode in the mid infrared part of the absorption spectrum. Because of the large mass difference of hydrogen and C₆₀ and the high symmetry of C₆₀ the problem is identical to a problem of a vibrating rotor moving in a three-dimensional spherical potential. The translational motion within the C₆₀ cavity breaks the inversion symmetry and induces optical activity of H₂. We derive potential, rotational, vibrational and dipole moment parameters from the analysis of the infrared absorption spectra. Our results were used to derive the parameters of a pairwise additive five-dimensional potential energy surface for H₂@C₆₀. The same parameters were used to predict H₂ energies inside C₇₀[Xu et al., J. Chem. Phys., 130, 224306 (2009)]. We compare the predicted energies and the low temperature infrared absorption spectra of H₂@C₇₀.

INTRODUCTION

A small cavity inside the fullerene cage is a potential trapping site of atoms and has attracted attention of scientists from the moment of discovery of C₆₀.¹ The demonstration of formation of La@C₆₀ after laser bombardment of La-impregnated graphite was immediate.² Since then the field of studies of endohedral fullerenes has expanded. Endohedral fullerenes with noble gas (He and Ne in ³, Ar, Kr, Xe ⁴), nitrogen ⁵ or phosphorus ⁶ atoms and with metal clusters ⁷ are made under extreme conditions using arc discharge, ion bombardment or high pressure and high temperature treatment.

Extreme methods are not suitable for encapsulation of small molecules. A different approach, “chemical surgery”, was applied by Rubin when he made first open-cage fullerene ⁸ with a orifice large enough to load it with ³He or H₂ using less extreme temperature and pressure ⁹. Soon Y. Murata, M. Murata and K. Komatsu synthesized another opened-cage derivative of C₆₀ and achieved 100% yield in filling with H₂ ¹⁰. There a generation of closed-cage H₂@C₆₀ was observed in the process of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry analysis of this opened-cage complex. Chemical methods were developed to close opened-cage fullerenes and H₂@C₆₀ was produced in milligram quantities ¹¹, ¹². To accommodate two hydrogen molecules a cavity larger than C₆₀ is needed. Two H₂ were trapped in opened-cage C₇₀ with the yield 3:97 in the favour of species with one H₂ per cage ¹³. The restoration of closed cage retains approximately the same ratio of (H₂)₂@C₇₀ to H₂@C₇₀ ¹⁴. Molecules other than hydrogen trapped in opened-cage fullerenes are carbon monoxide ¹⁵, water ¹⁶, ¹⁷, ammonia ¹⁸ and methane ¹⁹.
Recently Kurotobi and Murata succeeded in closing one of them and making the first closed-cage endohedral complex with a trapped polar molecule, $\text{H}_2\text{O}\@\text{C}_{60}$ [20]. The rotational modes of endohedral water were observed by inelastic neutron scattering (INS), far infrared (far-IR) and nuclear magnetic resonance (NMR) at cryogenic temperatures [21].

Up to date $\text{H}_2\@\text{C}_{60}$ has been the most studied small molecule endofullerene. The local environment of a hydrogen molecule in the fullerene cage has a negligible inhomogeneous distribution of interaction parameters. All the trapping sites are similar in $\text{H}_2\@\text{C}_{60}$, except the isotopic distribution of carbon atoms and crystal field effects in solid $\text{H}_2\@\text{C}_{60}$. The $\text{H}_2\@\text{C}_{60}$ is a stable complex and can survive a short period of heating up to 500 °C under vacuum [12]. These properties make $\text{H}_2\@\text{C}_{60}$ appealing for spectroscopic and theoretical investigations of interactions between the molecular hydrogen and carbon nanosurfaces.

Three spectroscopic techniques NMR, INS and infrared (IR), have been used to study endohedral hydrogen. NMR studies cover spin lattice relaxation rates of $\text{H}_2\@\text{C}_{60}$ in organic solvents [22, 23], and in the presence of paramagnetic relaxants [24, 25]. NMR was used to follow the ortho-para conversion in $\text{H}_2\@\text{C}_{60}$ in the presence of molecular oxygen at 77 K [26] or upon photoexcitation of a $\text{C}_{70}$ triplet state [27]. NMR study of micro-crystalline $\text{H}_2\@\text{C}_{60}$ samples at cryogenic temperatures shows splitting of the $J = 1$ rotational state [28, 21], a sign of the symmetry reduction from the icosahedral symmetry in the solid phase. Similarly, splitting of the ground ortho state was deduced from the heat capacity measurements [30].

The overview of the low temperature NMR, INS and IR work on $\text{H}_2\@\text{C}_{60}$ is given by Mamone et al. [31]. The first IR study of $\text{H}_2\@\text{C}_{60}$ was limited to 6 K [32]. The translational and rotational transitions appeared as sidebands to the hydrogen molecule bond-stretching vibrational transition, $v = 0 \rightarrow 1$, in the mid-IR spectral range. The direct translational and rotational transitions were not observed in the far-IR below 200 cm$^{-1}$ [33]. The extension of IR studies to higher temperature made possible to probe the hydrogen-C$_{60}$ interaction potential in the ground $v = 0$ and first excited $v = 1$ vibrational states and a whole range of hydrogen isotopologs $\text{H}_2$, $\text{D}_2$ and $\text{HD}$ was studied [33, 34]. The isotope effects and translation-rotation coupling were also studied by INS in $\text{H}_2\@\text{C}_{60}$ and $\text{HD}\@\text{C}_{60}$ [35]. The translational and rotational energies of $\text{H}_2\@\text{C}_{60}$ and $\text{HD}\@\text{C}_{60}$ in the $v = 0$ state determined by IR spectroscopy are consistent with the low temperature INS results [35]. There is no Raman data on $\text{H}_2\@\text{C}_{60}$, except a report on $\text{H}_2$ inside an opened-cage fullerene [36].

In this paper we will review the IR studies of hydrogen isotopologs in C$_{60}$ and present the analysis of IR low temperature spectra of $\text{H}_2\@\text{C}_{70}$. The far-IR properties of $\text{H}_2\text{O}\@\text{C}_{60}$ will not be reviewed here [21].

**THEORY**

Quantum statistics plays an important role in the dihydrogen wavefunction symmetry and has a pronounced effect on the rotation of the hydrogen molecule [37]. The symmetry relative to the interchange of two protons dictates that there are two forms of molecular hydrogen, called para- and ortho-$\text{H}_2$. The two proton spins ($I_p = 1/2$) are in the anti-symmetric $I = 0$ total nuclear spin state in para-$\text{H}_2$ and in the symmetric $I = 1$ state in ortho-$\text{H}_2$. Even rotational quantum numbers $J$ are allowed for para-$\text{H}_2$ and odd $J$ for ortho-$\text{H}_2$. The nucleus of $\text{D}$ is a boson, nuclear spin $I_d = 1$. Thus the rotational state with an even quantum number $J$ has $D_2$ in the state where the total nuclear spin of $\text{D}_2$ is either zero or two, $I = 0, 2$. This is called ortho-D$_2$, while para-D$_2$ has the total nuclear spin $I = 1$ and odd $J$ values.

A homonuclear diatomic molecule with the total nuclear spin $I = 1$ that is rotating in its ground state. This $J = 1$ rotational state is 118 cm$^{-1}$ for H$_2$, and 58 cm$^{-1}$ for D$_2$, above the rotational ground state $J = 0$ of even-$I$ species. A thermal transition $J = 1 \rightarrow 0$ must be accompanied by
the change of the total nuclear spin of the molecule, a process of very low probability. The time constant of thermal relaxation between the ortho and the para manifolds is very long and the room $T_{ortho-para}$ ratio is maintained even at cryogenic temperatures. The equilibrium distribution of $H_2$ nuclear spin isomers is $n_o/n_p = 3$ and of $D_2$ is $n_o/n_p = 2$ at room temperature. To change the total nuclear spin of a molecule the two nuclei must experience different magnetic field. The ortho-para conversion can be activated by using a paramagnetic center as a source of the magnetic field gradient. The equilibrium $n_o/n_p = 1$ is reached at 77 K by dispersing $H_2@C_{60}$ on a zeolite surface and exposing it to molecular oxygen which acts like a spin catalyst [38]. There are no ortho and para species for HD. All rotational levels of HD are in thermal equilibrium and there is one rotational ground state, $J = 0$.

Quantum chemistry calculations are challenging for a hydrogen molecule in a weak van der Waals interaction with a large fullerene molecule. The availability of experimental data on endohedral $H_2$ has stimulated theoretical work in this direction. Theoretical investigations currently cover the calculations of rotation-translation energies of hydrogen isotopologs in $C_{60}$ [39, 40] and $H_2$ in $C_{70}$ [41], and the stability of $C_{60}$ or $C_{70}$ with one or more incarcerated $H_2$ [42, 43]. Empirical parameters of the Morse potential between H-H and contact Dirac interaction between H-C were adjusted [44] and density-fitting local Möller-Plesset theory tested [45] using the experimental $H_2$ vibrational frequency inside $C_{60}$. Classical molecular dynamics and density-functional theory have been combined to reproduce accurately the NMR chemical shift of $^1H$ in $H_2@C_{60}$ [46].

Both the hydrogen molecule and fullerene have closed shell electronic structures and therefore the interaction between them is the van der Waals interaction. The simplicity makes $H_2@C_{60}$ ideal for the studies of non-covalent bondings between $H_2$ and carbon nano-surfaces, the knowledge needed for the design of carbon-based hydrogen storage materials. The high icosahedral symmetry of the $C_{60}$ cavity is close to spherical and therefore $H_2@C_{60}$ represents a textbook example of a body moving in a spherical potential well [47, 48]. In addition, $H_2$ rotates around its center of mass. $H_2$ is not spherical and therefore its interaction with the walls of the cavity depends on its orientation what leads to the coupling between translational and rotational motion [49]. If the translational and the rotational motions are coupled then in the spherical potential the conserved angular momentum is the sum of translational and rotational angular momenta [39, 50]. $H_2@C_{60}$ is a rare example where the quantum dynamics of a diatomic rotor in a confined environment can be studied. Another, but with limited degrees of freedom, interesting example related to the fullerenes is the quantum rotor $C_2$ in a metallofullerene $C_2@Sc_2C_{84}$ [51, 52]. The two scandium atoms limit the translational motion and fix the rotational axis of $C_2$ relative to the fullerene cage. At low temperature the rotation of $C_2$ is hindered because it has a small rotational constant and is therefore more susceptible to the corrugations of the carbon surface. $H_2$ provides examples of two-dimensional rotors, like $H_2$ on a Cu surface [53] or $H_2$ in intercalated graphite [54].

High pressure loading of solid $C_{60}$ creates interstitial $H_2$. Exohedral $H_2$ has been studied by IR [55, 56], INS [57, 58], NMR [59, 60] and Raman [61] spectroscopies. Hydrogen is trapped in an interstitial site of octahedral symmetry and theory predicts translation-rotation coupling [50, 62]. However, broadening of experimental lines has prohibited accurate determination of the $H_2$-$C_{60}$ interaction potential.

The observed IR spectra of hydrogen encapsulated in $C_{60}$ consist of several absorption lines. We construct a model Hamiltonian and a dipole moment operator with few adjustable parameters to describe accurately the position and intensity of such multi-line spectrum.
FIG. 1. Coordinates of a diatomic rotor inside the C_{60} cage are the relative position \( s \) of two nuclei in the diatomic molecule and the diatomic center of mass displacement \( \mathbf{R} \) from the C_{60} cage center. In case of heteronuclear diatomic molecule (HD) the center of mass is not in the middle of the chemical bond between the two nuclei. Two polar spherical coordinates, \( \Theta \) and \( \theta \), are shown. (Online version in Colour)

Diatomic molecule in a spherical potential well

To describe the motion of a hydrogen molecule inside C_{60} we use the following model. The C_{60} is considered to be rigid, its center of mass is not moving and it does not rotate. We treat H_{2}@C_{60} as an isolated molecular complex and approximate the true icosahedral symmetry of an isolated C_{60} with spherical symmetry. It means that in this approximation H_{2} moves in a rigid spherically symmetric bounding potential provided by the cavity of C_{60}. Beside the translational movement inside C_{60} the hydrogen molecule has its internal degrees of freedom, vibration and rotation of two nuclei relative to its center of mass. There are no coupling terms between ortho- and para-states in our model Hamiltonian.

The theoretical work of Olthof et al. \[63\] is a comprehensive description of the dynamics of a loosely bound molecule inside C_{60}. Olthof et al. model the intermolecular potential as a sum of atom-atom potentials and expand it in spherical harmonics. They determined the radial part of the wavefunction with discrete variable representation method. The radial part of the wavefunction in our approach is given by algebraic functions, solution of the three-dimensional spherical oscillator \[47, 48, 64\]. The advantage is that matrix elements are calculated in algebraic form avoiding time-consuming numerical integration.

The position and orientation of the H_{2} molecule is given by spherical coordinates \( \mathbf{R} = \{ R, \Omega \} \), \( \Omega = \{ \Theta, \Phi \} \) and \( \mathbf{s} = \{ s, \Omega_s \} \), \( \Omega_s = \{ \theta, \phi \} \) where \( \mathbf{R} \) is the vector from the center of the C_{60} cage to the center of mass of H_{2} and \( \mathbf{s} \) is the internuclear H-H vector, as shown in Fig. 1. The center of mass translational motion of H_{2} is given by eigenfunctions of the isotropic three-dimensional harmonic oscillator \[47, 48, 64\]

\[
\Psi^v_{NLML}(R, \Omega) = \psi^v_{NL}(R) Y_{LM}(\Omega),
\]  

(1)

where \( \psi^v_{NL} \) is the radial wave function and \( Y_{LM} \) is the spherical harmonic. The size of the H_{2} molecule depends on its vibrational state \( |v\rangle \). Therefore both, the bounding potential and \( \psi^v_{NL}(R) \), depend on the vibrational quantum number \( v \). The translational quantum numbers are \( N = 0, 1, 2, \ldots \) The orbital angular momentum quantum number takes values \( L = N, N-2, \ldots, 1 \) or 0, depending on the parity of \( N \), and the azimuthal quantum number is \( M_L = -L, -L+1, \ldots, L \). The rotational wavefunctions, defined by the rotational quantum numbers \( J = 0, 1, \ldots \) and \( M_J = -J, -J+1, \ldots, +J \), are given by the spherical harmonics \( Y_{JM}(\theta, \phi) \).

We use bipolar spherical harmonics with overall spherical rank \( \Lambda \) and component \( M_\Lambda \)

\[
F^J_{\Lambda M_\Lambda}(\Omega, \Omega_s) = \sum_{M_L, M_J} C^{\Lambda M_\Lambda}_{LM_L J M_J} Y_{LM_L}(\Omega) Y_{JM_J}(\Omega_s),
\]  

(2)
where $C$ are the Clebsch-Gordan coefficients $[64]$. Then the full wavefunction describing the motion of the $H_2$ molecule is

$$|vJNL\Lambda M\Lambda\rangle = \psi_v^{\text{vib}}(s)\psi_{NL}^{v}(R)F_{\Lambda M\Lambda}(\Omega, \Omega_s)$$  \hspace{1cm} (3)$$

where $\psi_v^{\text{vib}}(s) \equiv |v\rangle$ is the vibrational wavefunction with the quantum number $v$.

The Hamiltonian $\mathcal{H}$ for the trapped molecule includes coupling terms between vibrational, translational, and rotational motion. For simplicity, we neglect all matrix elements non-diagonal in $v$ and introduce a parametric dependence on $v$,

$$\mathcal{H} = \psi_v^{\text{vib-rot}} + \frac{p^2}{2m} + vV(R, \Omega, \Omega_s),$$  \hspace{1cm} (4)$$

where $\psi_v^{\text{vib-rot}}$ is the vibration-rotation Hamiltonian, $p$ is the molecular momentum operator and $m$ is the molecular mass of the diatomic molecule. $vV = \langle v|V(R, s, \Omega, \Omega_s)|v\rangle$ is the potential energy of the hydrogen molecule in the vibrational state $\psi_v^{\text{vib}}(s)$. The vibration-rotation Hamiltonian $\psi_v^{\text{vib-rot}}$ is diagonal in the basis set $|vJNL\Lambda M\Lambda\rangle$ with eigenvalues given by

$$\psi_v^{\text{vib-rot}}|\Omega\rangle = \hbar\omega_0(v + 1/2) + B_rJ(J + 1),$$  \hspace{1cm} (5)$$

$B_r = B_c - \alpha_e(v + 1/2) - D_eJ(J + 1)$, where $\omega_0$ is the fundamental vibrational frequency, $\alpha_e$ is the anharmonic correction and $D_e$ is the centrifugal correction to the rotational constant $B_\Theta$ $[65, 66]$.

We start from the general expansion of the potential in multipoles

$$\psi_v^{\text{vib}}(s) = \sum_{l, j, \lambda, m_\lambda} \psi_{l j}^{\lambda m_\lambda}(R)F_{\lambda m_\lambda}(\Omega, \Omega_s).$$  \hspace{1cm} (6)$$

and expand the radial part of potential $\psi_{l j}^{\lambda m_\lambda}(R)$ in powers of $R$

$$\psi_{l j}^{\lambda m_\lambda}(R) = \sum_n \psi_{l j n}^{\lambda m_\lambda} R^n,$$  \hspace{1cm} (7)$$

where $n \geq l$ and the parity of $l$ and $n$ is the same.

$V(R,s)$ is a scalar and transforms under fully symmetric representation $A_g$ of the symmetry group $I_h$. The spherical harmonics $\lambda = 0, 6, 10, \ldots$ transform like $A_g$ of the symmetry group $I_h$ $[67]$. We use fully spherical approximation of the potential, $\lambda = 0$. Because $\lambda = 0$ and $\lambda = |l - j|, |l - j| + 1, \ldots, l + j$ it must be that $l = j$.

The total potential is

$$\psi_v^{\text{vib}} = \psi_{00}^{00} F_{00}^{00} + \psi_{00}^{02} R^2 \psi_{00}^{04} R^4 F_{00}^{00} + \psi_{11}^{11} R + \psi_{13}^{11} R^3 F_{00}^{11} + \psi_{22}^{22} R^2 + \psi_{24}^{22} R^4 F_{00}^{22},$$  \hspace{1cm} (8)$$

if we limit our expansion to $j = l = 2$ and $n = 4$. The odd-$j$ terms are not allowed by symmetry for $H_2$ and $D_2$ and thus the coefficients $\psi_{l j}^{11}$ and $\psi_{00}^{11}$ are zero for homonuclear diatomic molecules.

If we set the constant off-set $\psi_{00}^{00} F_{00}^{00}$ to zero and write the perturbation part as

$$\psi_v' = \psi_{00}^{04} R^4 F_{00}^{00} + \psi_{00}^{11} R + \psi_{00}^{13} R^3 F_{00}^{11} + \psi_{00}^{22} R^2 + \psi_{00}^{24} R^4 F_{00}^{22},$$  \hspace{1cm} (9)$$

and the isotropic harmonic term as $\psi_v^0 = \psi_{00}^{02} R^2 F_{00}^{00}$, then the total Hamiltonian reads

$$\mathcal{H} = \psi_v^{\text{vib-rot}} + \frac{p^2}{2m} + \psi_v^0 + \psi_v'. $$  \hspace{1cm} (10)$$
The unperturbed Hamiltonian eigenvalues in the basis $|\nu JNL\Lambda \rangle$ are

$$E^{0}_{\nu JNL \Lambda \Lambda} = \nu E_{J}^{\text{rot}} + \hbar \omega^{T}_{0} (N + 3/2),$$

(11)

where $\nu \omega^{T}_{0} = (\nu V_{00}^{002}/(2\pi m))^{1/2}$ is the frequency for translational oscillations within the cavity.

The meaning of different parts of the perturbation is explained by their influence on the energy levels of a harmonic 3D spherical oscillator. Table I. Translation-rotation energies of a 3D spherical oscillator $\langle \nu JNL\Lambda | \mathcal{H} - \nu \mathcal{H}^{\text{vib-rot}} | \nu JNL\Lambda \rangle$ for a perturbation given by Eq. 9 and $\mathcal{H}$ by Eq. 10 for few lower states. Here $\nu \Delta^{004} = V_{00}^{004}/V_{00}^{0004}$, $\nu \Delta^{222} = V_{00}^{222}/V_{00}^{0000}$, $\nu \Delta^{224} = 1/2 \sqrt{\nu} \nu^{224}/V_{00}^{0000}$, and for $\nu \beta$ see Eq. 12.

| $JNL\Lambda$ | $\langle \nu JNL\Lambda | \mathcal{H} - \nu \mathcal{H}^{\text{vib-rot}} | \nu JNL\Lambda \rangle$ |
|---------------|---------------------------------------------------------|
| 0000          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004}$            |
| 0001          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004}$            |
| 0002          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004}$            |
| 0110          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004} + 10(\nu \Delta^{222} + \nu \Delta^{224})$ |
| 0111          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004} - 5(\nu \Delta^{222} + \nu \Delta^{224})$ |
| 0112          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004} + 1(\nu \Delta^{222} + \nu \Delta^{224})$ |
| 2111          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004} + 5(\nu \Delta^{222} + \nu \Delta^{224})$ |
| 2112          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004} - 5(\nu \Delta^{222} + \nu \Delta^{224})$ |
| 2113          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004} + \frac{10}{7}(\nu \Delta^{222} + \nu \Delta^{224})$ |
| 0200          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004}$            |
| 0202          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004}$            |
| 1201          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004}$            |
| 1221          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004} + 7(\nu \Delta^{222} + \nu \Delta^{224})$ |
| 1222          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004} - 7(\nu \Delta^{222} + \nu \Delta^{224})$ |
| 1223          | $\hbar \omega_{0}^{T}/2 + \nu \Delta^{004} + 2(\nu \Delta^{222} + \nu \Delta^{224})$ |

The length scale $\nu \beta = m \omega^{T}_{0}/\hbar$ (dimension $m^{-2}$) of the radial part of a 3D spherical oscillator wavefunction is related to the expectation value of the center of mass amplitude in state $|N\rangle$ as

$$\langle N | R^{2} | N \rangle = \nu \beta^{-2} (N + 3/2) = \hbar \sqrt{2\pi m \nu^{002}_{00}} (N + 3/2).$$

(12)

Terms described by the translation-rotation coupling coefficients $V_{00}^{111}$ and $V_{00}^{113}$ do not appear in Table I because the first order correction to energies vanishes as the matrix element of $F_{00}^{11}$ is zero if diagonal in $L$ or $J$. These terms mix states with different $N$ and $J$. For example, the first excited rotational state $J = 1$, $N = 0$ (expectation value of HD center of mass is on the cage center) has the state $J = 0$, $N = 1$ (expectation value of HD center of mass is off the cage center) mixed in $|34\rangle$. The effect is that HD is forced to rotate about its geometric center instead of center of mass.
It was found by the 5D quantum mechanical calculation that the rotational quantum number \( J \) is almost a good quantum number for the homonuclear \( \text{H}_2@\text{C}_{60} \) and \( \text{D}_2@\text{C}_{60} \) and not for the heteronuclear \( \text{HD}@\text{C}_{60} \) \([40]\). Indeed, \( V_{00}^{22n} \) mixes states with different \( J \) for homonuclear species as well but the effect is reduced compared to the effect of \( V_{00}^{11n} \). In the former case \( J \pm 2 \) and \( L \pm 2 \) are mixed while in the latter case the \( J \pm 1 \) and \( L \pm 1 \) states that have a smaller energy separation are mixed.

The states with different \( \Lambda \) are not mixed in the spherical approximation, i.e. the total angular momentum \( \Lambda = L + J \) is conserved and \( \Lambda \) is a good quantum number. The other consequence of the spherical symmetry is that the energy does not depend on \( M_{\Lambda} \). Therefore it is practical to use a reduced basis and reduced matrix elements \([68]\) which are independent of \( M_{\Lambda} \). This reduces the number of states by factor \( 2\Lambda + 1 \) for each \( \Lambda \).

**Model Hamiltonian of \( \text{H}_2@\text{C}_{70} \)**

A spherical approximation of the potential of a molecule trapped in \( \text{C}_{70} \) would be an oversimplification because of the elongated shape of \( \text{C}_{70} \). The symmetry of \( \text{C}_{70} \) is \( D_{5h} \), the distance between the centers of two capping pentagons (\( z \) direction) is 7.906 Å. The diameter of the equatorial \( xy \) plane is 7.180 Å \([69]\), similar to the diameter of the icosahedral sphere of \( \text{C}_{60} \), 7.113 Å \([70]\). The anisotropy of the potential of \( \text{H}_2 \) inside \( \text{C}_{70} \) is supported by the 5D quantum mechanical calculation \([41]\) what shows that the lowest translational excitation in the \( z \) direction is 54 cm\(^{-1} \) and in the \( xy \) plane is 132 cm\(^{-1} \) while in \( \text{C}_{60} \) it is 180 cm\(^{-1} \) and isotropic \([33]\). We derive from the IR spectra (see below) that the \( xy \) plane excitation energy is 151 cm\(^{-1} \), somewhat larger than theoretically predicted.

Although the \( z \) axis translational energy in \( \text{C}_{70} \) is three times less than in the icosahedral \( \text{C}_{60} \), the effect of the \( \text{C}_{70} \) potential on the rotational motion is moderate. The splitting of the \( J = 1 \) state is 7 cm\(^{-1} \) what is relatively small compared to the rotational energy 120 cm\(^{-1} \) in this state \([41]\).

To analyze the IR spectra of \( \text{H}_2@\text{C}_{70} \) we use a simplified Hamiltonian where the translational energy is represented in the form of the sum of two oscillators, 1D linear and 2D circular oscillator, and we do not consider anharmonic corrections and the translation-rotation coupling.

The vibration-rotation energy

\[
\nu E_{J,J_z}^{\text{vib}-\text{rot}} = \hbar \omega_0 (v + \frac{1}{2}) + B_v^{(J)} J(J + 1) + \nu \kappa (3J_z^2 - 2),
\]

is the same as for \( \text{H}_2@\text{C}_{60} \) except the last term which accounts for the axial symmetry of the \( \text{C}_{70} \) potential with the rotational anisotropy parameter \( \kappa \) \([71]\). For example, the three-fold degenerate \( J = 1 \) rotational state in \( I_h \) symmetry is split in \( D_{5h} \) symmetry and if \( \kappa > 0 \) the \( J_z = 0 \) state is \( 3\kappa \) below the twice degenerate \( J_z = \pm 1 \) rotational state.

The translational part is added to the vibration-rotation Hamiltonian, Eq.\([13]\) and the total energy reads

\[
E_{v,J,J_z;n,n_z}^{0} = \nu E_{J,J_z}^{\text{vib}-\text{rot}} + \hbar \nu \omega_{xy}^T (n + 1) + \hbar \nu \omega_z^T (n_z + \frac{1}{2}).
\]

Here the translational energy is written as a sum of two oscillators, a linear oscillator along the \( z \) axis with translational quantum \( \hbar \nu \omega_z^T \) and a 2D (circular) oscillator \([48, 64]\) in the \( xy \) plane with translational quantum \( \hbar \nu \omega_{xy}^T \). Quantum numbers \( n_z \) and \( n \) are positive integers including zero and \( l = n, n - 2, \ldots, -n + 2, -n \).

We will show below that the frequencies of \( z \) and \( xy \) translational modes, \( \nu \omega_z^T \) and \( \nu \omega_{xy}^T \), can be determined from the experimental data even though the translation-rotation coupling is not
known. We take the advantage of translation-rotation coupling being zero in the $J=0$ rotational state. The complication arises from the fact that the potential is different in the initial and final states of the IR transitions, $v=0$ and 1. However, this complication could be resolved if the energy of the fundamental vibrational transition $v=0 \rightarrow 1$ (without change of $n$ and $n_z$) is known.

The $\Delta J = 0$ transition from the para-$H_2$ ground state leads to two excitation energies in the IR spectrum, one for the $z$ mode and second for the $xy$ mode

$$
E_{100;001}^0 - E_{000;000}^0 = h[\omega_0 + \frac{1}{2} \omega_z^T + (\frac{1}{2} \omega_{xy}^T - \omega_{xy}^T) + \frac{1}{2} (\frac{1}{2} \omega_z^T - \omega_z^T)],
$$

$$
E_{100;110}^0 - E_{000;000}^0 = h[\omega_0 + \frac{1}{2} \omega_{xy}^T + (\frac{1}{2} \omega_{xy}^T - \omega_{xy}^T) + \frac{1}{2} (\frac{1}{2} \omega_z^T - \omega_z^T)].
$$

Defining the fundamental para transition energy as $E_{100;000}^0 - E_{000;000}^0 = h[\omega_0 + (\frac{1}{2} \omega_{xy}^T - \omega_{xy}^T) + \frac{1}{2} (\frac{1}{2} \omega_z^T - \omega_z^T)]$ we may rewrite Eq.(15) and (16) as

$$
E_{100;001}^0 - E_{000;000}^0 = h\omega_z^T + E_{100;000}^0 - E_{000;000}^0. \tag{17}
$$

From these equations translational frequencies in the excited $v=1$ state, $\frac{1}{2} \omega_z^T$ and $\frac{1}{2} \omega_{xy}^T$, can be determined without knowing the translation-rotation coupling.

The classification of energy levels up to $J=1$ and $n = n_z = 1$ by irreducible representations $\Gamma_i$ of the symmetry group $D_{5h}$ is given in Table II. We get the irreducible representations $\Gamma_j$: $L = 0 \rightarrow A_1'$ and $L = 1 \rightarrow A_2'$ by subducting the translational states represented by spherical harmonics $Y_{LM}$ from the full rotational group $O(3)$ to the symmetry group $D_{5h}$. $A_1'$ is the para-$H_2$ ground state, $n = l = n_z = 0$. The first excited state of the $z$ mode is $n_z = 1$ and $A_2'$. The first excited state of the $xy$ mode $n = l = 1$ is doubly degenerate $E_1'$. The full symmetry when translations and rotations are taken into account is $\Gamma_i = \Gamma_j \otimes \Gamma^{(J)}$. For example, the ortho-$H_2$ ground state, $J = 1$ and $(nlnz) = (000)$, is split into $J_z = 0$ ($A_2'$) and $J_z = \pm 1$ ($E_1'$), see Table II.

### Induced dipole moment of hydrogen in spherical environment

IR light is not absorbed by vibrations and rotations of homonuclear diatomic molecules. IR activity of $H_2$ is induced in the presence of intermolecular interactions, such as in the solid and liquid phases, in constrained environments, and in pressurized gases. IR spectra of such systems are usually broad due to inhomogeneities in the system or due to random molecular collisions. As an exception, narrow lines are observed in semiconductor crystals and solid hydrogen. An overview of collision-induced dipoles in gases and gas mixtures is given in the book by L. Frommhold. The confinement of the endohedral $H_2$ introduces two differences as compared to $H_2$ in the gas. First, the translational energy of $H_2$ is quantized. In the gas phase it is a continuum.
starting from zero energy. Second, the variation of the distance between $H_2$ and the carbon atom is limited to the translational amplitude of $H_2$ in the confining potential. In the gas phase the distance varies from infinity to the minimal distance given by the collision radius. The selection rule $\Delta N = \pm 1$ for the endohedral $H_2$ follows from these two conditions, as shown below.

Quantum mechanical calculations of induced dipoles are available for simple binary systems like $H_2$-He, $H_2$-Ar, and $H_2$-$H_2$. An extensive set of theoretical results for the $H_2$-He system associated with the roto-translation electric dipole transitions, both in the vibrational ground state $v = 0$ and accompanying the $v = 0 \rightarrow 1$ transition of the $H_2$ molecule, can be found in [80–84]. Related to the fullerene studies are calculations of the dipole moment of $CO@C_{60}$ [63] and exohedral $H_2$ in solid $C_{60}$ [62].

We express the induced part of the dipole moment as an interaction between hydrogen molecule and $C_{60}$. Another approach was used in [33] where the summation over 60 pair-wise induced dipole moments between $H_2$ and carbon atoms was done. The relation between two sets of parameters was given [34].

We write the expansion of the dipole moment from the vibrational state $v$ to $v'$ in bipolar spherical harmonics and in power series of $R$ as

$$d_{v'v}(\mathbf{R}, \Omega_s) = \frac{4\pi}{\sqrt{3}} \sum_{l,j,n} v'v A^{ijn}_{\lambda m \lambda} R^n F^{ij}_{\lambda m \lambda}(\Omega, \Omega_s).$$  \hspace{1cm} \text{(18)}$$

This is similar to the expansion of the potential discussed above, except the dipole moment is a polar vector while the potential is a scalar. The dipole moment transforms according to the irreducible representation $T_{1u}$ of the symmetry group $I_h$. The spherical harmonics of the order $\lambda = 1, 5, 7, \ldots$ transform according to $T_{1u}$ of the symmetry group $I_h$ [67]. We use $\lambda = 1$ and are interested in $v = 0 \rightarrow 1$ transitions. In spherical symmetry it is sufficient to calculate one component of the dipole moment vector, $m_\lambda = 0$, and if we drop the explicit dependence of $d_{v'v}$ on $v$, $v'$ and of $v'v A^{ijn}_{\lambda m \lambda}$ on $\lambda, m_\lambda$, the $m_\lambda = 0$ component of the dipole moment reads

$$d_0(\mathbf{R}, \Omega_s) = \frac{4\pi}{\sqrt{3}} \sum_{l,j,n} A^{ijn} R^n F^{ij}_{10}(\Omega, \Omega_s).$$  \hspace{1cm} \text{(19)}$$

As $\lambda = |l-j|, |l-j| + 1, \ldots, l+j$ and $\lambda = 1$ it must be that $l = |j \pm 1|$. The possible combinations are $(l,j) \in \{(01), (10), (12), (21), (23), \ldots\}$. If we restrict the expansion up to $n = l = 1$, we get

$$d_0(\mathbf{R}, \Omega_s) = \frac{4\pi}{\sqrt{3}} A^{010} F^{01}_{10} + \frac{4\pi}{\sqrt{3}} (A^{101} F^{10}_{10} + A^{121} F^{12}_{10}) R.$$

$A^{010}$ is zero for homonuclear diatomic molecules $H_2$ and $D_2$. It is the sum of the HD permanent rotational dipole moment in the gas phase and the induced rotational dipole moment inside $C_{60}$. The selection rule is $\Delta N = 0, \Delta J = 0, \pm 1$, but $J = 0 \rightarrow 0$ is forbidden.

The expansion coefficients $A^{101}$ and $A^{121}$ are allowed by symmetry for both, homo- and heteronuclear diatomic molecules. The expansion coefficient $A^{101}$ describes the induced dipole moment that is independent of the orientation of the diatomic molecular axis $s$, selection rule $\Delta N = 0, \pm 1, \Delta J = 0$, but $N = 0 \rightarrow 0$ is forbidden. $A^{121}$ describes the induced dipole moment that depends on the orientation of $s$, $\Delta N = 0, \pm 1, \Delta J = 0, \pm 2$, but $N = 0 \rightarrow 0$ and $J = 0 \rightarrow 0$ are both forbidden. All terms in Eq. (20) satisfy the selection rule $\Delta \Lambda = 0, \pm 1$, but $\Lambda = 0 \rightarrow 0$ is forbidden.

Although HD has a permanent rotational dipole moment, the induced dipole moment dominates inside $C_{60}$ [34].

IR absorption line intensity [33] is proportional to the thermal population of the initial state. If the thermal relaxation between para-$H_2$ and ortho-$H_2$ is very slow we can define a temperature
independent fractional ortho and para populations $n_k$ of the total number of molecules $N$, where $k = o, p$ selects ortho or para-H$_2$. Then the probability that the initial state $|v_iJ_iN_iL_i\Lambda_iM_{\Lambda_i}\rangle$ is populated is

$$p_i = n_k \frac{e^{-E_i/k_BT}}{\sum_j g_j e^{-E_j/k_BT}}.$$  \hspace{1cm} (20)$$

where $E_i$ is the energy of the initial state measured from the ground state $v = N = 0$ and $j$ runs over all para- (or ortho-) H$_2$ states in the basis used. $g_j = 2\Lambda_j + 1$ is the degeneracy of the energy level $E_j$. Please note that $g_i$ does not appear in the numerator because $p_i$ is the population of a individual state $|v_iJ_iN_iL_i\Lambda_iM_{\Lambda_i}\rangle$ although the reduced basis $|vJNL\rangle$ is used. Hetero-nuclear HD has no para and ortho species and the coefficient $n_k$ in Eq.(20) must be set to one, $n_k = 1$.

**Infrared absorption by H$_2@C_{70}$**

The infrared absorption in H$_2@C_{70}$ is given by electric dipole operators $d_0$ and $d_{\pm 1}$, which transform like $A''_2$ and $E'_1$ irreducible representations of $D_{5h}$. At low $T$ the symmetry-allowed transitions from the ground para state are $A'_1 \stackrel{d_0}{\rightarrow} A''_2$ and $A'_1 \stackrel{d_{\pm 1}}{\rightarrow} E'_1$. Two ortho states, $A''_2$ and $E'_1$, are populated at low $T$, Fig.2. The transitions are $A''_2 \rightarrow A'_1$ and $A''_2 \rightarrow E'_1$. The symmetry-allowed transitions from the $E'_1$ state are $E'_1 \rightarrow E''_1$ and $E'_1 \rightarrow A'_1, A'_2, E''_2$.

The IR absorption line area is proportional to the Boltzmann population of the initial state, Eq.(20). The degeneracy $g_j$ of the energy level $E_j$ is one or two in case of H$_2@C_{70}$. Fig.2 shows the Boltzmann population of the few first para and ortho levels in the $v = 0$ vibrational state. The para state (000) population (solid line) starts to drop above 20 K as the first excited state (001) (black dashed line) at 54 cm$^{-1}$ above the ground state becomes populated and drains the population from

FIG. 2. Boltzmann population of the H$_2@C_{70}$ para ground translational state (000)(solid line) and first thermally excited (dotted line) state (001) and of the two ortho states, A''$_2$ (dashed line) and E'$_1$ (dash-dot line), in the ground translational state (000), calculated using energy levels of the 5D quantum mechanical calculation [41]. Here the para states have $J = 0$ and the ortho states have $J = 1$; irreducible representations are from Table II. (Online version in Colour)
FIG. 3. Infrared absorption spectra of $\text{H}_2@\text{C}_{60}$ at 6 K are shown with the black line. The green line in panel (a) is the Gaussian fit of fundamental *para* and *ortho* transitions, $\Delta N = \Delta J = 0$. The red line in panels (b), (c), (d) is the simulated spectrum with parameters taken from the model fit of 200 K spectra [33]. The $S(1)^3$ labeled green line in panel (c) is the Gaussian fit of the $\Delta N = 0, \Delta J = 2$ forbidden *ortho* transition, experimentally observed at 4612.5 cm$^{-1}$ and predicted to be at 4613.1 cm$^{-1}$ by our model [33]. Line labels are the same as in Fig. 4a; the superscript to line label shows the final state $\Lambda$.

the (000) state. The abrupt change of the population of *ortho* ground states above 2 K is because of the transfer of population from the non-degenerate $A''_2$ ground level (dotted line) to the doubly degenerate $E'_1$ (dash-dot line) 7 cm$^{-1}$ higher. The populations of $A''_2$ and $E'_1$ states decrease above 30 K as the first excited translational (001) *ortho* state get more populated.

**EXPERIMENT**

The endohedral complexes were prepared by “molecular surgery” as described in [11, 12]: $\text{H}_2@\text{C}_{60}$, $\text{D}_2@\text{C}_{60}$ and $\text{H}_2@\text{C}_{70}$ at Kyoto University, and $\text{HD}@\text{C}_{60}$ at Kyoto University and Columbia University. The $\text{HD}@\text{C}_{60}$ sample was a mixture of the hydrogen isotopomers $\text{H}_2$:HD:$\text{D}_2$ with the ratio 45:45:10. Since all $\text{C}_{60}$ cages are filled, the filling factor for HD is $\rho = 0.45$. The content of $\text{C}_{70}$ sample was empty: $\text{H}_2:(\text{H}_2)_2$ = 28:70:2 and the filling factor $\rho = 0.7$. Experimental absorption spectra were corrected for the filling factor.

The *para* enriched sample was made at Columbia University using molecular oxygen as a spin catalyst for *ortho-para* conversion [26]. Briefly, the $\text{H}_2@\text{C}_{60}$ adsorbed on the external surface of NaY zeolite was immersed in liquid oxygen at 77 K for 30 minutes, thereby converting the incarcerated $\text{H}_2$ spin isomers to the equilibrium distribution at 77 K, $n_o/n_p = 1$. The liquid oxygen was pumped away and the endofullerene-NaY complex was brought back rapidly to room temperature. The *para* enriched $\text{H}_2@\text{C}_{60}$ was extracted from the zeolite with CS$_2$ and the solvent was evaporated by argon. The powder sample in argon atmosphere and on dry ice arrived in Tallinn four days after the preparation.

Powdered samples were pressed under vacuum into 3 mm diameter pellets for IR transmission measurements. Typical sample thickness was 0.3 mm. Two identical vacuum tight chambers with Mylar windows were employed in the IR measurements. The chambers were put inside an optical cold finger type cryostat with KBr windows. In the measurements, the chamber containing the pellet for analysis was filled with He exchange gas while the empty chamber served as a reference. Transmission spectra were obtained using a Bruker interferometer Vertex 80v with a halogen lamp and a HgCdTe or an InSb detector. The apodized resolution was typically 0.3 cm$^{-1}$ or better.

Transmission $T_s(\omega)$ was measured as the light intensity transmitted by the sample divided by the
light intensity transmitted by the reference. The absorption coefficient $\alpha(\omega)$ was calculated from the transmission $T_r(\omega)$ through $\alpha(\omega) = -d^{-1} \ln \left[ T_r(\omega)(1-R)^{-2} \right]$, with the reflection coefficient $R = [\eta - 1]/(\eta + 1)^2$ calculated assuming a frequency-independent index of refraction $\eta = 2$. Absorption spectra were cut into shorter pieces around groups of H$_2$ lines and a baseline correction was performed before fitting the H$_2$ lines with Gaussians.

RESULTS AND DISCUSSION

C$_{60}$

The IR absorption spectra of H$_2$@C$_{60}$ at 6 K together with the simulated spectra are shown in Fig. 3 and the diagram of energy levels involved in Fig. 4a. The simulated spectra are calculated using Hamiltonian, dipole moment and the ortho-para ratio parameters (see Table IV) obtained from the fit of 200 K spectra [33]. Temperature does not affect these parameters and the line intensities follow the Boltzmann population of initial states [33]. Intensity of three lines, Q(0)$^0$ and Q(1)$^1$ in Fig. 3a) and S(1)$^3$ in c) can not be simulated because the induced dipole moment theory does not describe $\Delta N = 0$ transitions. However, the position of these three lines was used to fit the Hamiltonian parameters [33]. The splitting of the ortho state $N = J = 1$ into $\Lambda = 0, 1$ and 2 by translation-rotation coupling is seen in Fig. 3b). The para $N = 1, J = 2$ and ortho $N = 1, J = 3$ states are split into three sublevels as well. However, because of the selection rule $\Delta \Lambda = \pm 1$ only one para and one ortho $S$-transition is IR active.

FIG. 4. Diagrams of the observed low temperature IR transitions in hydrogen isotopologs (a) H$_2$, D$_2$ and (b) HD incarcerated in C$_{60}$. The initial states surrounded by a dashed box have the vibrational quantum number $v = 0$; all the final states are in the excited vibrational state $v = 1$. Dashed lines in (a) are forbidden transitions ($\Delta N = 0$) that are observed in H$_2$@C$_{60}$ but not in D$_2$@C$_{60}$. The S(1) line (dotted) with $\Delta J = 1$ is not observed in D$_2$@C$_{60}$. The line label $Q(J_i)$ is used for $\Delta J = 0$, $R(J_i)$ is used for $\Delta J = +1$ and $S(J_i)$ for $\Delta J = +2$ transitions where $J_i$ is the initial state $J$. 

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are minority for D\(^2\) of the splitting, states of the optical transitions under discussion have only \(\Lambda = 0\) value for the state which is split by the icosahedral symmetry is three while the initial and final relaxed but initially para symmetry. Even not by considering the true icosahedral symmetry of C\(^60\) responsible for the part of this splitting. Note that the \(Q\) value three, Table IV. We confirmed the assignment of spectral lines to para- and ortho-H\(^2\) by measuring the spectrum of a para enriched H\(^2\)@C\(^60\) sample [33]. Low \(T\) spectra in the region of \(Q\) lines are shown in Fig.5. The time delay between para enrichment and first IR measurement was 4 days. The 4255 cm\(^{-1}\) para line is stronger and other three ortho lines are weaker in the para-enriched sample, as compared to the non-enriched sample.

The Fig.5 deserves some attention. Lines \(Q(0)^1\) and \(Q(1)^0\) have a clear multicomponent structure and it is different for the two samples. This is not possible in the approximation of spherical symmetry. Even not by considering the true icosahedral symmetry of C\(^60\) because the lowest \(\Lambda\) value for the state which is split by the icosahedral symmetry is three while the initial and final states of the optical transitions under discussion have only \(\Lambda = 0, 1\). Later measurements on the relaxed but initially para converted sample showed that the difference between the line shapes of the normal and para converted sample is not due to the different ortho-para ratio. Thus it is likely that the difference in the line splitting is due to a different impurity content of the two samples. However, it is not completely excluded that the crystal field or the distortion of the C\(^60\) cage is responsible for the part of this splitting. Note that the \(Q(1)^0\) line of D\(_2\)@C\(^60\), Fig.6, bears similar splitting pattern as in H\(_2\)@C\(^60\).

The D\(_2\)@C\(^60\) spectrum, Fig.6, is shifted to lower frequency compared to H\(_2\)@C\(^60\) because of the heavier mass of D\(_2\). The spectrum has less lines than the H\(_2\)@C\(^60\) spectrum. The missing transitions in D\(_2\)@C\(^60\) are shown in red color in Fig.6b, and they belong to \(J\)-odd species which are minority for D\(_2\).

The splitting of \(N = J = 1\) into \(\Lambda = 0, 1\) and 2 states is similar in D\(_2\) and H\(_2\). The magnitude of the splitting, \(h\omega_0^T\sqrt{\frac{V_{000}}{20} + \frac{V_{222}}{V_{020}}}\), see Table IV is less in D\(_2\) because \(\frac{1}{2}\omega_0^T\) is smaller although \(V_{000}^D\) and \(V_{222}^D\) are similar for two isotopologs, Table IV. Line \(Q(1)^2\) overlaps partially with \(Q(0)^1\) line, Fig.6. However, this is not because the translation-rotation splitting is different for two isotopologs but because of a smaller anharmonic correction \(\alpha_e\) of the rotational constant for D\(_2\), Table IV.

The spectrum of HD@C\(^60\) is more simple, Fig.7; because there are no para and ortho species and therefore only one state is populated at low \(T\). There is one spectral line, not present in homonuclear dihydrogen, labeled \(R(0)\) in Fig.7b and Fig.7. HD has no inversion symmetry and the ban on \(\Delta J = 1\) transitions is lifted. The classification of this transition as \(\Delta J = 1\) is arbitrary.
FIG. 6. Infrared absorption spectra of D$_2$@C$_{60}$ at 5 K. The simulated spectrum is shown by red line (para), blue line (ortho) and black thin line (sum of para and ortho spectra). The parameters for the simulated spectrum are taken from the model fit of the 90 K spectrum [34]. Line labels are the same as in Fig. 4a; superscript to line label shows the final state $\Lambda$.

first, because the weight of $JNL\Lambda = 1201$ is only 0.5 in this state [34] and secondly, the change of translational state is $\Delta N = 2$, not allowed by any of the dipole operator components in our model. The next component in weight 0.29 in the final state is $J = 1, N = 0 \rightarrow 1, J = 0 \rightarrow 2$ and therefore it would be more appropriate to classify it as an $S$ line. Another interesting feature of the HD spectrum is the absence of $\Delta N = 0, \Delta J = 1$ (0000 $\rightarrow$ 1001) transition although the induced dipole moment coefficient $A^{101}$ gives a two orders of magnitude larger dipole moment than the permanent dipole moment of free HD, as was discussed in [34]. This $\Delta J = 1$ transition in HD@C$_{60}$ is suppressed because there is an interference of two dipole terms, $A^{010}$ and $A^{101}$ which have opposite signs. The final state consists of 80% of the pure rotational state $J = 1, N = 0$ and 18% of the the pure translational state $N = 1, J = 0$. This mixed final state has matrix elements from the ground state for both $A$ coefficients, $A^{010}$ and $A^{101}$, which nearly cancel each other.

The observed low $T$ IR transitions of H$_2$, D$_2$ and HD@C$_{60}$ are collected in Table III. The content of the unperturbed $|JNL\Lambda\rangle$ state in the final state is above $|\xi^1|^2 = 0.9$ in homonuclear species in most cases while for HD it varies and could by as low as 0.5. The mixing of states $\xi^v$ is proportional to the energy separation of mixed states, $E_j - E_i$ in the first order perturbation theory. $F_{00}^{00}$ couples states where $L_i = L_j$ and $J_i = J_j$. These states are far from each other as $L_i = L_j$ only if $N_j = N_i \pm 2$. The other term $F_{02}^{22}$ mixes $L_j = L_i \pm 2$ and $J_j = J_i \pm 2$ which are even further from each other for small $N$. It was found by Xu et al. [41] that $J$ is almost a good quantum number in H$_2$ and D$_2$@C$_{60}$ but not in HD@C$_{60}$. Indeed, the distance between states mixed decreases for HD as $F_{10}^{10}$ mixes $L_j = L_i \pm 1$ and $J_j = J_i \pm 1$ and for this $N_j = N_i \pm 1$.

The vibrational frequency $\omega_0$ is redshifted from its gas phase value for H$_2$ and D$_2$, Table IV. The relative change of the frequency $[\omega_0(\text{gas}) - \omega_0(\text{C}_{60})]/\omega_0(\text{gas})$ depends on the cage and is independent of the hydrogen isotopomer [87]. Based on our fit results, Table IV we get that for the H$_2$ $\omega_0(\text{C}_{60})/\omega_0(\text{gas}) = 0.9763$ and for the HD $\omega_0(\text{C}_{60})/\omega_0(\text{gas}) = 0.9773$. We used the average of these two ratios to calculate the D$_2$@C$_{60}$ fundamental vibrational frequency, $\omega_0 = 2924$ cm$^{-1}$ what was necessary to fit the IR spectra to a model Hamiltonian [34]. At this point we cannot say how much of the redshift is caused by change in the zero-point vibrational energy and how much is
The rotational constant $B_e$ is the transition frequency in wavenumber units, $\text{cm}^{-1}$, for HD. The integrated line area for HD is 0.95 of 0000, and for HD is 0.99 of 0000. Integrated absorption cross-section $\sigma$ is used by some authors. The integrated line area $S$ is transformed into $\sigma$ (unit cm/molecule) using $\sigma = SV/N$ where $N$ is the number of hydrogen molecules in the volume $V$ [87]. Here $N/V = 1.48 \times 10^{21}$ cm$^{-3}$, the number density of molecules in solid C$_{60}$. * It was not possible to separate overlapping $Q(1)^1$ and $Q(1)^2$ lines of D$_2$ and the line area given is the sum of both transitions.

TABLE III. Experimental IR absorption line parameters of endohedral dihydrogen isotopologs in C$_{60}$ at 5 K. $\omega$ is the transition frequency in wavenumber units, cm$^{-1}$ and $S$ is the integrated absorption line area in cm$^{-2}$ units. $JNLA$ are the quantum numbers of the main component with the weight $|\xi^1|^2$ in the final state $v = 1$. The $|\xi^0|^2$ of the main component $JNLA$ in the initial $v = 0$ state for H$_2$ are 0.97 of 0000 and 0.97 of 1001, for D$_2$ are 0.99 of 0000 and 0.99 of 1001, and for HD is 0.95 of 0000. Integrated absorption cross-section $\sigma$ is used by some authors. The integrated line area $S$ is transformed into $\sigma$ (unit cm/molecule) using $\sigma = SV/N$ where $N$ is the number of hydrogen molecules in the volume $V$ [87]. Here $N/V = 1.48 \times 10^{21}$ cm$^{-3}$, the number density of molecules in solid C$_{60}$. * It was not possible to separate overlapping $Q(0)^1$ and $Q(1)^2$ lines of D$_2$ and the line area given is the sum of both transitions.

| Line label | $H_2$ | $D_2$ | HD | Final state, $v = 1$ |
|------------|-------|-------|----|--------------------|
| $Q(1)^1$   | 4065.4| 0.993 | 0.98| 0.99               |
| $Q(0)^0$   | 4071.4| 0.011 | 0.98| 0.99               |
| $Q(0)^1$   | 4244.5| 0.576 | 0.95| 0.98               |
| $Q(1)^1$   | 4250.7| 0.94  | 3045.1| 0.98               |
| $Q(0)^0$   | 4255.2| 10.6  | 3050.2*| 10.8               |
| $Q(0)^1$   | 4261.0| 8.86  | 3056.8| 1.55               |
| $R(0)^1$   | 4371.0| 8.86  | 3056.8| 1.55               |
| $S(0)^0$   | 4592.0| 3.08  | 3224.35| 1.66               |
| $S(1)^1$   | 4612.5| 0.3   | 3224.35| 1.66               |
| $S(0)^1$   | 4802.5| 5.65  | 0.94  | 0.96               |

caused by the change of anharmonic corrections to the vibrational levels in the C$_{60}$ as our data set is limited to energy differences of $v = 0$ and $v = 1$ levels only. Note that the vibrational frequency of H$_2$@C$_{60}$ is $\omega_0 = 4062.4$ cm$^{-1}$, Table IV, while the para vibrational transition is shifted up by 9 cm$^{-1}$, to $\omega_0 = 4071.4$ cm$^{-1}$, Table III. This is because the zero-point translational energies are different in the $v = 0$ and $v = 1$ vibrational states [83].

The rotational constant $B_e$, the vibrational correction $\alpha_e$, and the centrifugal correction $D_e$ of the hydrogen inside C$_{60}$ and in free space are compared in Table IV. The smaller than the gas phase value of $B_e$ may be interpreted as 0.8% (0.9%) stretching of the nucleus-nucleus distance $s$ in H$_2$@C$_{60}$ (D$_2$@C$_{60}$), as $B_e \sim (1/s^2)$. An attractive interaction between hydrogen atoms and the cage causes $s$ to be longer. The elongation of the equilibrium proton-proton distance is consistent with the redshift of $\omega_0$ [83]. However, the anharmonic vibrational correction to rotational constant, $\alpha_e$, is smaller inside the cage than in the gas phase. Here the cage has the opposite, repulsive, effect.

FIG. 7. Infrared absorption spectra of HD@C$_{60}$ at 5 K, black line. The parameters for the simulated spectrum (red line) are taken from the model fit of 90 K spectra [34]. The broad lines indicated by arrows are not due to HD. Line labels are the same as in Fig 4b; superscript to line label shows the final state $\Lambda$. (Online version in Colour)
and reduces the elongation of the proton-proton distance in the excited $v$ states when compared to H$_2$ being in the free space. This is supported by the fact that within the error bars $\alpha_e$ of D$_2@C_{60}$ is equal to $\alpha_e$ of D$_2$. The vibrational amplitude of D$_2$ is less than of the H$_2$ and therefore the repulsive effect of the cage becomes important at $v > 1$ for D$_2$.

Among the rotational and vibrational constants of HD@C$_{60}$ the centrifugal correction $D_e$ to the rotational constant is anomalously different from its gas phase value compared to other two isotopomers, Table IV. Positive $D_e$ means that the faster the molecule rotates, the longer is the bond. We speculate that since the rotation center of HD inside the cage is further away from the deuteron, the centrifugal force on the deuteron increases and the bond is stretched more than in the free HD molecule.

A similar system to the one studied here is exohedral H$_2$ in C$_{60}$. There H$_2$ occupies the octahedral interstitial site in the C$_{60}$ crystal. The prominent features in the exohedral H$_2$ IR spectra [54] are the translational, $\Delta N = \pm 1$, sidebands to the fundamental transitions, $\Delta v = 1$ and $\Delta J = 0, 2$. The redshift of the fundamental vibrational frequency is about 60 cm$^{-1}$, which is less than in H$_2@C_{60}$ where it is 98.8 cm$^{-1}$. Also the separation of translational $N = 0$ and $N = 1$ levels, approximately 120 cm$^{-1}$, is smaller, when compared to 184.4 cm$^{-1}$ in H$_2@C_{60}$. It is likely that the main contribution to the latter difference comes from the larger van der Waals volume available for H$_2$ in the octahedral site than in the C$_{60}$ cage.

**H$_2@C_{70}$**

IR absorption spectra of H$_2@C_{70}$ measured at 5 K are shown in Fig. 8 and the scheme of energy levels with the low $T$ transitions indicated with arrows is shown in Fig. 9. The transitions where $\Delta J = 0$ and the translational state changes by $\Delta n = 1$ or $\Delta n_z = 1$ are labeled as $Q_{xy}(J)$ and $Q_z(J)$ where $J$ is the rotational quantum number of the initial state. The transitions where $\Delta J = 2$ are labeled by $S_{xy}(J)$ and $S_z(J)$. The $z$ and $xy$ translational modes have distinctly different energies. For the $Q$ lines they are shown in different panels, Fig. 8a and 8b. The para and ortho $S$ lines are well separated because of different rotational energies. The para $S$ lines are shown in Fig. 8c.

### Table IV

| $\omega_0$ | H$_2@C_{60}$ | H$_2$ | HD@C$_{60}$ | HD | D$_2@C_{60}$ | D$_2$ |
|------------|--------------|-------|-------------|----|-------------|-------|
| cm$^{-1}$  | cm$^{-1}$    | cm$^{-1}$ | cm$^{-1}$   |
| 16024      | 1616.18      | 349.7 | 3632.20     | 2924 | 2993.69     |
| $B_e$      | 59.87        | 60.853 | 45.4        | 45.655 | 29.89      | 30.444 |
| cm$^{-1}$  | cm$^{-1}$    | cm$^{-1}$ | cm$^{-1}$   |
| 2.97       | 3.062        | 1.70  | 1.986       | 1.09 | 1.079       |
| $D_e$      | 4.83 - 10$^{-2}$ | 4.71 - 10$^{-2}$ | 1.5 - 10$^{-1}$ | 2.605 - 10$^{-2}$ | 8 - 10$^{-3}$ | 1.141 - 10$^{-2}$ | cm$^{-1}$ |

**Notes:**

- $n_0/n_p$ for HD@C$_{60}$.
- $A^{10}$ for HD@C$_{60}$.
- $A^{21}$ for HD@C$_{60}$.
- $\omega_0$ is set to zero when $\Delta J = 2$.
FIG. 8. IR absorption spectra of H$_2$@C$_{70}$ at 5 K. Features shown with arrows in panel (c) are likely caused by impurities, not by endohedral H$_2$.

FIG. 9. Energy levels and observed IR transitions of H$_2$@C$_{70}$ from the ground para and ortho translational states in the $v = 0$ state to the excited vibrational state $v = 1$. The irreducible representations of the symmetry group $D_{5h}$ are given for few lower states and are listed in Table II. The ordering of the states is based on [41]. ortho-H$_2$ transitions marked by a and b are $Q_z(1)^a$ and $Q_z(1)^b$ in Table V and start from the thermally excited state, which is $E'_1(000)$ according to [41]. There are three experimentally observed ortho-H$_2$ transitions from the ground $A''_2(000)$ state: $Q_{xy}(1)^c$, and $Q_{xy}(1)^d$.

and ortho $S$ lines are shown in Fig. 8d. The $Q$ lines cannot be sorted out into para and ortho that easily. An exception is the $Q(1)$ transition, inset to Fig. 8a. This is a pure vibrational transition, $v = 0 \rightarrow 1$, without the change of translational or rotational states. The corresponding (fundamental) para transition $Q(0)$ would be at 4069.3 cm$^{-1}$ according to the model, Table V. We expect it to be much weaker than the ortho $Q(1)$ transition, as in H$_2$@C$_{60}$, and for this reason it is not observed in the experiment.
FIG. 10. Normalized line area and Boltzmann population of \(\text{para}\) and \(\text{ortho}\) transitions of \(\text{H}_2@\text{C}_{70}\) starting from the ground translational state. (a) \(\text{para}\) lines, (b) and (c) \(\text{ortho}\) lines. Solid line in (b) is the normalized intensity when the initial state is the ground state \(A''_2\) \((J_z = 0)\) and in (c) when the initial state is \(E'_1\) \((J_z = \pm 1)\), \(7 \text{ cm}^{-1}\) above \(A''_2\). This corresponds to \(\kappa > 0\), Eq. \(14\). Dashed line in (b) and (c) is the reversed situation when the ground state is doubly degenerate \(E'_1\) and \(A''_2\) is \(7 \text{ cm}^{-1}\) above it, i.e. \(\kappa < 0\). The normalized intensities are calculated using the translational energy levels from the 5D quantum mechanical calculation \(41\) and Eq. \(20\).

In Fig. 10 we plot the normalized line area and normalized Boltzmann population. Fig. 10a shows the \(T\) dependence of \(\text{para}\) lines. The assignment of the 4125.6 cm\(^{-1}\) line to \(Q_{xy}(0)\) and the 4219.9 cm\(^{-1}\) line to \(Q_{xy}(0)\) is supported by our model that is summarized in Table V and will be discussed below.

The uniaxial symmetry of \(\text{C}_{70}\) splits the \(\text{ortho}\) ground state \(J = 1\). This splitting is about \(7 \text{ cm}^{-1}\) i.e. \(10 \text{ K}\) and creates a sharp \(T\) dependence of the \(\text{ortho}\) line intensity at low \(T\) as is shown in Fig. 2. This feature could be used to determine which of the \(Q\) lines belong to the \(\text{ortho}\) species. Two lines, 4110.5 cm\(^{-1}\) and 4124.2 cm\(^{-1}\), have a \(T\) dependence consistent with the \(\text{ortho}\) transitions starting from the ground translational \((000)\) state of \(E'_1\) symmetry, Fig. 10a. However, according to our model there is no transition close to 4124.2 cm\(^{-1}\) from the thermally excited \(\text{ortho} E'_1\) state, Table V. This might be due to our simplified model where the rotational anisotropy parameter \(\kappa\) is assumed equal in \(v = 0\) and \(v = 1\) vibrational states. The rest of the \(\text{ortho}\) lines are shown in Fig. 10b. Several lines follow the same \(T\) dependence, the fundamental transition at 4063.2 cm\(^{-1}\), \(Q_{xy}(1)\) lines 4213.4, 4224.7, and 4226.9 cm\(^{-1}\) and the \(S_x(1)\) line at 4678.8 cm\(^{-1}\). Lines \(Q_x(1)\) at 4116 and \(S_{xy}(1)\) at 4761 cm\(^{-1}\) have distinctly different \(T\) dependence than the rest of the lines. Such deviation could be due to the overlap of transitions starting from \(A''_2\) and \(E'_1\) symmetry states. However, none of the ortho lines behaves like the theoretical prediction, black line, so the possibility that the ground ortho state is doubly degenerate \(E'_1\) and not the \(A''_2\), i.e. \(0\kappa < 0\), is not ruled out by our data. The dashed black line shows the ground state population if the ground state is \(E'_1\) and the \(A''_2\) state is \(7 \text{ cm}^{-1}\) above it. This \(T\) dependence is more close to the experimental situation than the solid black line, where \(0\kappa > 0\). The change of sign of \(0\kappa\) affects intensities only a little if the transitions start from the thermally excited state, Fig. 10c, where the red dashed line is the normalized Boltzmann population of \(A''_2\) state if this state is \(7 \text{ cm}^{-1}\) above the ground state \(E'_1\), i.e. if \(0\kappa < 0\).

It is not unreasonable that \(0\kappa < 0\) and the \(E'_1\) \((J_z = \pm 1)\) state is the ground rotational state of \(\text{ortho-} \text{H}_2\). It requires that there is an attraction instead of repulsion between \(H\) and \(C\) when \(\text{H}_2\) is in the center of the \(\text{C}_{70}\) cage. The attraction is stronger for the \(\text{H}_2\) if its molecular axis is in the \(xy\) plane, \(J_z = \pm 1\), where the distance between \(H\) an \(C\) is less than if the axis is along the \(z\), \(J_z = 0\), where the \(H\)-\(C\) distance is longer. Indeed, the attraction between \(C\) and \(H\) in \(\text{H}_2@\text{C}_{60}\) was deduced from the redshift of vibrational energy and reduced rotational constant compared to \(\text{H}_2\) in the gas phase \(33\). However, it was found by 5D quantum mechanical calculation that \(A''_2\) is the ground state \(41\). More elaborate model with dipole moment parameters that describe the IR line
TABLE V. Low temperature IR transitions of H$_2$@C$_{70}$ observed at 5 K from the ground vibrational state $v = 0$ to the excited vibrational state $v = 1$. $J(nln_z)$ are the quantum numbers for the initial and final states and the labels indicate corresponding transitions in Fig. 8 and 9. The experimental spectra were fitted with Gaussians, $S_{exp}$ is the experimental line area; the experimental line position $\omega_{exp}$ could always be determined with a precision better than 0.1 cm$^{-1}$. The model parameters, $\omega_{mod}$ were determined as described in the text by matching the model frequency $\omega_{mod}$ to the experimental frequency $\omega_{exp}$ for four lines indicated with error $0$. The model parameters are vibrational frequency $\omega_0 = 4069.1$ cm$^{-1}$, 1D oscillator frequency along the $z$ axis $\nu_0 = 56.5$ cm$^{-1}$, 2D circular oscillator frequency $\nu_{xy}^T = 150.9$ cm$^{-1}$, and the rotational anisotropy parameter $\kappa = 3.1$ cm$^{-1}$. The rotational constant $B_e = 59.865$ cm$^{-1}$ and its corrections, $\alpha_e = 2.974$ cm$^{-1}$ and $D_e = 0.04832$ cm$^{-1}$ were assumed to be the same as in H$_2$@C$_{60}$.

| Frequency (cm$^{-1}$) | $S_{exp}$ (cm$^{-2}$) | Initial $v = 0$ | Final $v = 1$ | Label | Error (cm$^{-1}$) |
|----------------------|-----------------------|-----------------|---------------|-------|-----------------|
| $\omega_{exp}$       | $\omega_{mod}$        | $J$ (nln$_z$)   | $J$ (nln$_z$) |       | $\omega_{exp} - \omega_{mod}$ |
| 4063.2               | 4063.2                | 0.146 ± 0.005   | 1 (000)       | (000) | Q(1)            | 0 |
| −                   | 4069.1                | −               | 0 (000)       | 1 (000) | Q(0)            | − |
| 4110.3               | 4110.3                | 0.311 ± 0.014   | 1 (000)       | (000) | Q$_x$(1)$^a$     | 0 |
| 4115.7               | 4119.7                | 0.824 ± 0.009   | 1 (000)       | (000) | Q$_x$(1)        | -4.0 |
| 4124.2               | 4119.7                | 0.045 ± 0.007   | 1 (000)       | (000) | Q$_x$(1)$^b$     | 4.5 |
| 4125.6               | 4125.6                | 0.096 ± 0.007   | 0 (000)       | 0 (000) | Q$_x$(0)        | 0 |
| 4213.3               | 4214.1                | 1.759 ± 0.024   | 1 (000)       | 1 (110) | Q$_{xy}$(1)     | -0.8 |
| 4220.0               | 4220.0                | 7.702 ± 0.027   | 0 (000)       | 0 (110) | Q$_{xy}$(0)     | 0 |
| 4224.2               | 4214.1                | 2.111 ± 0.066   | 1 (000)       | 1 (110) | Q$_{xy}$(1)$^c$ | 10.1 |
| 4227.2               | 4214.1                | 10.143 ± 0.067  | 1 (000)       | 1 (110) | Q$_{xy}$(1)$^d$ | 13.1 |
| 4462.3               | 4456.3                | 0.570 ± 0.023   | 0 (000)       | 2 (001) | S$_x$(0)        | 6.0 |
| 4543.4               | 4550.7                | 0.582 ± 0.012   | 0 (000)       | 2 (110) | S$_{xy}$(0)     | -7.3 |
| 4678.8               | 4667.0                | 0.831 ± 0.012   | 1 (000)       | 3 (001) | S$_x$(1)        | 11.8 |
| 4761.3               | 4761.3                | 1.900 ± 0.019   | 1 (000)       | 3 (110) | S$_{xy}$(1)     | 0.0 |

intensities together with the Boltzmann population could resolve the issue.

Table V summarizes the assignment of transitions observed in the experiment. Since our model described in Theory section did not include translation-rotation coupling we used the transitions where $L$ and $J$ are both zero or one of them is zero in the initial and final states. The fundamental frequency $\omega_0 = 4069.1$ cm$^{-1}$ was chosen to match the experimental fundamental $\text{ortho}$ transition $Q(1)$; the rotational constant $B_e = 59.865$ cm$^{-1}$ and its corrections $\alpha_e = 2.974$ cm$^{-1}$, $D_e = 0.04832$ cm$^{-1}$ of H$_2$@C$_{60}$ were used. Next the two $\text{para}$ transitions were matched, Q$_z$(0) and Q$_{xy}$(0) to obtain $\nu_0^T = 56.5$ cm$^{-1}$, $\nu_{xy}^T = 150.9$ cm$^{-1}$. The 4220 cm$^{-1}$ line was chosen as Q$_{xy}$(0) because its $T$ dependence, Fig.10(a), is similar to S$_z$(0) and S$_{xy}$(0) line $T$ dependence. The $\text{ortho}$ ground state splitting is 9.4 cm$^{-1}$ (7.4 cm$^{-1}$ from the 5D calculation [41]) with $\kappa = 3.1$ cm$^{-1}$ which was obtained by assuming that the $Q_z(1)^{\text{ortho}}$ transition, (000)E'$_1$ $(001)$A'$_1$ in Fig.10(b) is centered at 4110.3 cm$^{-1}$. It was assumed that the anharmonic corrections to translational energy and to $\kappa$ are same for the $v = 0$ and $v = 1$ vibrational states.

The variation of the experimental frequencies compared to the model frequencies is within ±10 cm$^{-1}$, Table V. This is reasonable since our model did not include translation-rotation coupling and the translation-rotation coupling in H$_2$@C$_{60}$ creates splittings of this magnitude. The vibrational frequency $\omega_0$ is larger in H$_2$@C$_{70}$ than in H$_2$@C$_{60}$. This difference must be taken with a reservation because the correction due to the difference of zero point translational energies in two vibrational states is not taken into account for H$_2$@C$_{70}$ as it was done for H$_2$@C$_{60}$ [33]. Again, a more elaborate model is needed for C$_{70}$ than the two oscillator model described in Theory section.
CONCLUSIONS

IR absorption spectra of endohedral hydrogen isotopologs, H$_2$ [32, 33], D$_2$ [34], and HD [34] in C$_{60}$ are informative, involving excitations of vibrations, rotations and translational motion of dihydrogen. The translational motion of the encapsulated molecule is quantized and coupled to its rotations because of the surrounding C$_{60}$ cage. The vibrational frequency of dihydrogen is redshifted compared to the gas phase value. Together with the smaller rotational constant it shows that the hydrogen bond is stretched inside the cage and there is an attraction between H (or D) and C. The heteronuclear HD does not rotate about its center of mass because of the surrounding cage. Different rotational and translational states are mixed and rotational quantum number $J$ is not a good quantum number for HD@C$_{60}$.

Our study shows that the vibrations and rotations of C$_{60}$ and the crystal field effects of solid C$_{60}$ are not important on the energy scale of IR measurements. If these effects are important their contribution to the IR spectra is the order of one wavenumber splitting of few absorption lines. Such small splitting is consistent with the NMR [28, 29] and heat capacity [30] results.

C$_{70}$ has ellipsoidal shape and this splits the translation-rotation states of H$_2$. The translational frequency is about 180 cm$^{-1}$ in H$_2$@C$_{60}$. In C$_{70}$ this three dimensional mode is split into a two dimensional mode at 151 cm$^{-1}$ and a one dimensional mode at 56 cm$^{-1}$. The 5D quantum mechanical calculation [41] is in very good agreement with this experimental result.

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