Infrared spectroscopy of endohedral H$_2$O in C$_{60}$.

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(Dated: 15 February 2021)

Infrared absorption spectroscopy study of endohedral water molecule in a solid mixture of H$_2$O@C$_{60}$ and C$_{60}$ was carried out at liquid helium temperature. From the evolution of the spectra during the ortho-para conversion process, the spectral lines were identified as para- and ortho-H$_2$O transitions. Eight vibrational transitions with rotational side peaks were observed in the mid-infrared: $\omega_1$, $\omega_2$, $\omega_3$, $2\omega_1$, $2\omega_2$, $\omega_1 + \omega_2$, $\omega_2 + \omega_3$, and $2\omega_2 + \omega_3$. The vibrational frequencies $\omega_2$ and $2\omega_2$ are lower by 1.6% and the rest by 2.4%, as compared to free H$_2$O. A model consisting of a rovibrational Hamiltonian with the dipole and quadrupole moments of H$_2$O interacting with the crystal field was used to fit the infrared absorption spectra. The electric quadrupole interaction with the crystal field lifts the degeneracy of the rotational levels. The finite amplitudes of the pure $v_1$ and $v_2$ vibrational transitions are consistent with the interaction of the water molecule dipole moment with a lattice-induced electric field. The permanent dipole moment of encapsulated H$_2$O is found to be 0.5 ± 0.1 D as determined from the far-infrared rotational line intensities. The translational mode of the quantized center of mass motion of H$_2$O in the molecular cage of C$_{60}$ was observed at 110 cm$^{-1}$ (13.6 meV).

I. INTRODUCTION

Endohedral fullerenes consist of atoms or molecules fully encapsulated in closed carbon cages. The remarkable synthetic route known as “molecular surgery” has led to the synthesis of atomic endofullerenes He@C$_{60}$ and Ar@C$_{60}$ and several molecular endofullerene species, including H$_2$@C$_{60}$, H$_2$O@C$_{60}$, HF@C$_{60}$, CH$_4$@C$_{60}$, and their isotopologues. It is well established that these endohedral molecules do not form chemical bonds with the carbon cage and rotate freely. The rotation is further facilitated by the nearly spherical symmetry of the C$_{60}$ cage. The thermal and chemical stability of A@C$_{60}$ opens up the unique possibility of studying the dynamics and the interactions of a small molecule with carbon nano-surfaces. The trapping potential of dihydrogen H$_2$ has been described with high accuracy using infrared (IR) spectroscopy, inelastic neutron scattering (INS), and theoretical calculations. The non-spherical shape of the small molecule and the quantized translational motion of its center of mass leads to coupled rotational and translational dynamics.

The water-endofullerene H$_2$O@C$_{60}$ is of particular interest. The encapsulated water molecule possesses rich spatial quantum dynamics. It is an asymmetric-top rotor, supports three vibrational modes, displays nuclear spin isomerism (para- and ortho-water) and has an electric dipole and quadrupole moment.

Low-temperature dielectric measurements on solid H$_2$O@C$_{60}$ show that the electric dipole moment of the encapsulated water is reduced to 0.51 ± 0.05 D from the free water value 1.85 D. The C$_{60}$ carbon cage responds to the endohedral water molecule with a counteracting induced dipole, resulting in the lower total dipole moment.

The dynamics of isolated or encapsulated single water molecules have been studied before in other environments, such as noble gas matrices, solid hydrogen and liquid helium droplets. Although the trapping sites in these matrices have high symmetry and allow water rotation, these systems exist only at low temperatures. Water has also been studied in crystalline environments with nano-size cavities. However, in this case, the interactions with the trapping sites inhibit the free rotation of the water molecule.

Several spectroscopic techniques have been used to study H$_2$O@C$_{60}$, including nuclear magnetic resonance (NMR), INS and IR, and time-domain THz spectroscopy. The low-lying rotational states of the encapsulated molecule are found to be very similar to those of an isolated water molecule, with the notable exception of a 0.6 meV splitting in the J = 1 rotational state. This indicates that the local environment of the water molecule in H$_2$O@C$_{60}$ has a lower symmetry than theicosahedral point group of the encapsulating C$_{60}$ cage. The splitting has been attributed to the interaction between the electric quadrupole moment of H$_2$O and the electric field gradients generated by the electronic charge distribution of neighbouring C$_{60}$ molecules. The merohedral disorder present in solid C$_{60}$ leads to two C$_{60}$ sites with different quadrupolar interactions. This merohedral disorder also leads to splittings of the IR phonons in solid C$_{60}$. There is also evidence from dielectric measurements that merohedral disorder leads to electric dipolar activity in solid C$_{60}$.

Confined molecules exhibit quantization of their translational motion (“particle in a box”), in addition to their quantized rotational and vibrational modes. Quantized translational modes have been observed at 60 to 70 cm$^{-1}$ for water in noble gas matrices. However, comparatively lit-
tle is known about the centre-of-mass translational mode of H$_2$O@C$_{60}$. The fundamental frequency of the water translation mode in H$_2$O@C$_{60}$ has been predicted to occur at $\sim$160 cm$^{-1}$\[9\]. This relatively high frequency reflects the rather tight confinement of the water molecule in the C$_{60}$ cage.

The energy level separation between the ground para rotational state and the lowest ortho rotational state in H$_2$O@C$_{60}$ has been determined to be 2.6 meV (21 cm$^{-1}$) by IN$^{[9]}$. This energy level separation corresponds to a temperature of 28 K. The full thermal equilibration of H$_2$O@C$_{60}$ at temperatures below 30 K therefore requires the conversion of ortho into para water. This conversion process takes between tens of minutes to several hours below 20 K in H$_2$O@C$_{60}$\[9\].

The spin-isomer conversion is much faster at ambient temperature, with a time constant of about 30 s reported for H$_2$O@C$_{60}$ dissolved in toluene\[12\].

In this paper, we report on a detailed low-temperature far- and mid-IR spectroscopic study of H$_2$O@C$_{60}$ and C$_{60}$ solid mixtures. The IR technique allows us to measure the frequencies of rotational, vibrational and translational modes and from the line intensities to determine the dipole moment of encapsulated water. In addition, the IR spectra reveal the interaction of endohedral water with the electrostatic fields present in solid C$_{60}$.

The rest of this paper is organized as follows. Section II discusses the sample preparation, the recording procedures of the IR spectra, and the determination of the IR absorption cross-sections for different filling factors, temperatures and ortho-para ratios. The quantum mechanical vibrating rotor model for the encapsulated water molecules is introduced in Section III A. We include in this model the interactions between the H$_2$O electric dipole and quadrupole moments with the electrostatic fields present in solid C$_{60}$. The theory of the IR line intensities is presented in Section III B. Section IV presents the measured IR spectra and the fitting of this data by the quantum-mechanical model. The results are discussed in Section V, followed by a summary in Section VI. The Appendix contains more detailed theory for the interaction of the water molecules with the electrostatic fields and the infrared radiation, and more details on the fitting of the experimental data by the quantum-mechanical model.

II. METHODS

A. Sample preparation

H$_2$O@C$_{60}$ was prepared by multi-step synthetic route known as “molecular surgery”\[12\]. The H$_2$O-filled (number density $N_2$) and empty (number density $N_0$) C$_{60}$ were mixed and co-sublimed to produce small solvent-free crystals with a filling factor $f = N_2/(N_2 + N_0)$. Five samples with filling factors $f = 0.014, 0.052, 0.10, 0.18$, and 0.80 were studied. The powdered samples were pressed into pellets under vacuum. The diameter of sample pellets was 3 mm and the thickness $d$ varied from 0.2 mm to 2 mm. The thinner samples were used in the mid-IR because of light scattering in the powder sample. Samples were thicker for lower filling factors and thinner for higher filling factors to avoid the saturation of absorption lines in the far-IR.

B. Measurement techniques

The far-IR measurements were done with a Martin-Puplett type interferometer and $^3$He cooled bolometer from 5 to 200 cm$^{-1}$ as described in Ref. [11]. The IR measurements between 600 cm$^{-1}$ and 12000 cm$^{-1}$ were performed with an interferometer Vertex 80v (Bruker Optics) as described in Ref. [12].

Two methods were used to record the H$_2$O@C$_{60}$ absorption spectra.

Method 1. The intensity through the sample, $I_s$, was referenced to the intensity through a 3 mm diameter hole, $I_0$. The sample was allowed to reach ortho-para thermal equilibrium at a temperature of 30 or 45 K, and the temperature was rapidly reduced to 10 or to 5 K. The sample spectrum $I_s(t = 0)$ was recorded immediately after the temperature jump. Since the ortho-para conversion process is slow, the ortho fraction was assumed to be preserved during the T jump, corresponding to the high temperature ortho fraction $n_o \approx 0.74$. The absorption coefficient $\alpha$ was calculated from the ratio $Tr = I_s(t = 0)/I_0$ as $\alpha(t = 0) = −d^{-1}\ln[(1 − R)^{-2} Tr]$ where factor $(1 − R)^2$ with $R = (\eta − 1)^2(\eta + 1)^{-2}$ corrects for the losses of radiation, one reflection from the sample front and one from the back face. The refraction index of solid C$_{60}$ was assumed to be given by $\eta = 2.35$. To identify para- and ortho-water absorption peaks the difference of two spectra was calculated, $\Delta\alpha = \alpha(t = 0) − \alpha(\Delta t)$, where $\alpha(\Delta t)$ is the absorption spectrum measured after the waiting time $\Delta t$. Only the para- and ortho-H$_2$O@C$_{60}$ peaks show up in the differential absorption spectra, with the para- and ortho-H$_2$O@C$_{60}$ peak amplitudes having different signs, ortho positive and para negative. This method was used for the far- and mid-IR part of the spectrum.

Method 2. The sample was allowed to reach ortho-para thermal equilibrium at a temperature of 30 or 45 K, leading to an ortho-rich state, as in the first method. The temperature was rapidly reduced to 10 or to 5 K and a series of spectra recorded at intervals of a few minutes starting immediately after the $T$ jump, and continued until the ortho-para equilibrium was reached. The differential absorption $\Delta\alpha = −d^{-1}\ln[I_s(0)/I_s]$ was calculated, where $I_s(0)$ is the spectrum recorded immediately after the $T$ jump and $I_s$ is the spectrum recorded when the low temperature equilibrium was reached. The equilibrium ortho fraction is approximately 0.01 at 5 K. Method 2 was used for the far-IR part of the spectrum.

C. Line areas and absorption cross-sections

The absorption line area $A_j^{(k)}$ was determined by fitting the measured absorption $\alpha_j^{(k)}(\omega)$ with Gaussian line shape. $|i⟩$ and $|j⟩$ are the initial and final states of the transition and $k$ denotes para ($k = p$) or ortho ($k = o$) species. From these
experimental line areas, $A_{ji}^{(k)}$, a temperature and para (ortho) fraction independent line area $A_{ji}^{(k)}$ was calculated,

$$
\overline{A_{ji}^{(k)}}(f) = \frac{A_{ji}^{(k)}(f)}{n_k(p_{j}^{(k)} - p_{j}^{(k)})}. \tag{1}
$$

The population difference of initial and final states, $p_j^{(k)} - p_{j}^{(k)}$, is given by the sample temperature $T$, while the para (ortho) fraction $n_k$ depends on the history of the sample because of the ortho-para conversion process. The normalized absorption line area $\langle A_{ji}^{(k)} \rangle$ was determined from the linear fit of $\overline{A_{ji}^{(k)}}(f)$ for each absorption line,

$$
\overline{A_{ji}^{(k)}}(f) = f'(A_{ji}^{(k)}). \tag{2}
$$

Thus, the normalized absorption line area $\langle A_{ji}^{(k)} \rangle$ is the absorption line area of a sample with a filling factor $f = 1$ and spin isomer fraction $n_k = 1$ where all the population is in the initial state, $p_{ji}^{(k)} = 1$. We used $\langle A_{ji}^{(k)} \rangle$ to calculate a synthetic experimental spectrum for the spectral fit with the quantum mechanical model, Section IV B.

Furthermore, to compare the absorption cross-sections of $\text{H}_2\text{O} @ \text{C}_{60}$ in solid $\text{C}_{60}$ and free H$_2$O, a normalized absorption cross-section $\langle \sigma_{ji}^{(k)} \rangle$ was obtained as

$$
\langle \sigma_{ji}^{(k)} \rangle = \left( \frac{3\sqrt{\eta}}{\eta^2 + 2} \right)^2 \frac{\sigma_{ji}^{(k)}}{n_k(p_{j}^{(k)} - p_{j}^{(k)})} = \left( \frac{3\sqrt{\eta}}{\eta^2 + 2} \right)^2 \langle A_{ji}^{(k)} \rangle \frac{n_k(T)}{N_{\text{C}_{60}}}, \tag{3}
$$

where $\eta$ is the index of refraction of solid $\text{C}_{60}$ and $\sigma_{ji}^{(k)}$ is the absorption cross-section of an endohedral water molecule, Eq. (20) in Section III B. This $\text{H}_2\text{O} @ \text{C}_{60}$ absorption cross-section can be compared to the free water normalized cross-section $\langle \sigma_{ji}^{(k)} \rangle = \sigma_{ji}^{(k)}n_k^{-1}(p_{j}^{(k)} - p_{j}^{(k)})^{-1}$, where $p_{j}^{(k)} - p_{j}^{(k)}$ and $n_k(T)$ are given by the temperature of the water vapour in the experiment reporting $\sigma_{ji}^{(k)}$.

III. THEORY

A. Quantum mechanical model of $\text{H}_2\text{O} @ \text{C}_{60}$: Confined vibrating rotor in an electrostatic field

We use the following Hamiltonian to model endohedral water molecule in solid $\text{C}_{60}$:

$$
\mathcal{H} = \mathcal{H}_{\text{M}} + \mathcal{H}_{\text{ES}} + \mathcal{H}_{\text{F}}, \tag{4}
$$

where $\mathcal{H}_{\text{M}} = \mathcal{H}_o + \mathcal{H}_{\text{rot}}$ is the free-molecule rovibrational Hamiltonian and $\mathcal{H}_{\text{ES}}$ is the electrostatic interaction of H$_2$O with the surrounding electric charges. The translational Hamiltonian $\mathcal{H}_{\text{F}}$ consists of water center of mass kinetic and potential energy in the molecular cavity of $\text{C}_{60}$ molecule.

We neglect couplings between vibrational modes and between vibrational and rotational modes. Also, the coupling between translational motion and rotations is neglected. In $\mathcal{H}_{\text{ES}}$, terms describing the coupling of the solid $\text{C}_{60}$ crystal field to the electric dipole and quadrupole moment of H$_2$O are included.

The fitting of IR absorption spectra, Section IV B, is done with the Hamiltonian where the translational part is excluded:

$$
\mathcal{H} = \mathcal{H}_{\text{M}} + \mathcal{H}_{\text{ES}}, \tag{5}
$$

We employ three coordinate frames. The space-fixed coordinate frame is denoted $A. M = \{x, y, z\}$ is the molecule-fixed coordinate frame. Fig. 1. The Euler angles $\Omega_{A \rightarrow M}$ transform $A$ to $M$. The crystal coordinate frame is $C = \{x', y', z'\}$ with the $z'$ axis along the three-fold symmetry axis of the $S_6$ point group, the symmetry group of $\text{C}_{60}$ site in solid $\text{C}_{60}$. The Euler angles $\Omega_{A \rightarrow C}$ transform $A$ to $C$ and $\Omega_{C \rightarrow M}$ transform $C$ to $M$. The coordinate systems $A$ and $C$ are used because the radiation interacting with the molecule is defined in the space-fixed coordinate frame $A$ while the local electrostatic fields are defined by the crystal coordinate frame $C$, which in a powder sample has a uniform distribution of orientations relative to the space-fixed frame $A$.

![FIG. 1. (a) Molecule-fixed coordinate frame $M = \{x, y, z\}$ and the axes of principal moments of inertia, $\{a, b, c\}$. (b) Vibrations: $v_1$ - symmetric stretch, $v_2$ - symmetric bend and $v_3$ - asymmetric stretch. (c) para- and ortho-water rotational energy levels in the ground and excited vibrational states, see Section IV A and the rovibrational IR transitions (arrows) between the levels. The rotational states are labeled by $J_{K_e}$, and $p$ (para) and $o$ (ortho). The IR transitions are between the para or between the ortho states. 1, 3, and 5 are ortho-H$_2$O transitions and 2, and 4 are para-H$_2$O transitions. Transitions 1 and 2 are forbidden for a free water molecule. The transitions where the one-quantum excitation of the asymmetric stretch vibration $v_3$ is involved, are numbered 6 (para-H$_2$O), and 7 and 8 (ortho-H$_2$O transitions). The rotational and translational far-IR transitions in the ground vibrational states are shown in the inset to Fig. 2.](image)
1. Vibrations

H$_2$O has three normal vibrations: the symmetric stretch of O–H bonds, quantum number $v_1$, the bending motion of the H–O–H bond angle, $v_2$, and the asymmetric stretch of O–H bonds, $v_3$, as sketched in Fig. 1(b). The vibrational state is denoted $|\psi\rangle$ where the symbol $\psi$ denotes the three vibrational quantum numbers, $\nu \equiv v_1v_2v_3$, each of which takes values $v_i \in \{0, 1, 2, \ldots\}$. The vibrational energy for a harmonic vibrational potential is

$$E_\nu = \sum_{i=1}^{3} \omega_i(v_i + \frac{1}{2}), \quad v_i = 0, 1, 2, \ldots ,$$

where $\omega_i$ is the vibrational frequency of the $i$th vibration mode, $i \in \{1, 2, 3\}$ and $|\omega_i| = \text{cm}^{-1}$.

2. Rotations

H$_2$O has the rotational properties of an asymmetric top with principal moments of inertia $I_a < I_b < I_c$. The rotational states are indexed by three quantum numbers $|JK\rangle$, where $J = 0, 1, 2, \ldots$ is the rotational angular momentum quantum number. $K_a$ and $K_c$ are the absolute values of the projection of $J$ onto the $a$ and $c$ axes, in the limits of a prolate ($I_b = I_c$) and an oblate ($I_b = I_a$) top respectively: $K_a, K_c \leq J$. Each rotational state $|JK_{K_aK_c}m\rangle$ is the $(2J+1)$-fold degenerate, where $m \in \{-J, -J+1, \ldots, J\}$ is the projection of $J$ onto the $z$' axis of the crystal coordinate frame $C$.

The energies and the wavefunctions, $|JK_{K_aK_c}m\rangle$, of the free rotor Hamiltonian $\mathcal{H}_\text{rot}$ depend on the rotational constants of an asymmetric top, $A_v > B_v > C_v$,

$$\mathcal{H}_\text{rot} = A_\nu J_a^2 + B_\nu J_b^2 + C_\nu J_c^2,$$

where $J_a$ are the components of the angular momentum operator $J^2$ along the principal directions $a, b,$ and $c$. The index $\nu$ labels the rotational constants in vibrational state $|\nu\rangle$.

A molecule-fixed coordinate system $M$ (axes $x, y, z$, Fig. 1) with its origin at the nuclear centre of mass is defined with the following orientations relative to the principal axes of the inertia tensor: $x \parallel b, y \parallel c,$ and $z \parallel a$ where $y$ is perpendicular to the H–O–H plane and $x$ points towards the oxygen atom. The rotational wavefunctions of an asymmetric top in that basis are [16-19]:

$$|J, K, m, \pm\rangle = (|J, K, m\rangle \pm |J, -K, m\rangle) / \sqrt{2},$$

$$|J, 0, m, \pm\rangle \equiv |J, 0, m\rangle \quad \text{if} \quad k = 0,$$

where $k$ is the projection of $J$ on the $a$ axis, axis $z$ of $M$; for $k > 0$, $k \in \{1, 2, \ldots, J\}$ and each state is doubly degenerate. Here, $|J, K, m\rangle$ denotes a normalized rotational function

$$|J, K, m\rangle = \sqrt{\frac{2J+1}{8\pi^2}} |D_{mk}^{J} (\Omega_c \rightarrow M)| \ast,$$

where the Euler angles $\Omega_c \rightarrow M$ transform the crystal-fixed coordinate frame $C$ into the molecule-fixed coordinate frame $M$ and $D_{mk}^{J} (\Omega)$ is the Wigner rotation matrix element or the Wigner $D$-function.

The correspondence between the asymmetric top wavefunctions $|J, K, m, \pm\rangle$, Eq. (8), and asymmetric top wavefunctions $|JK_{K_aK_c}m\rangle$, is given in [19]. The latter notation of wavefunctions is useful for the symmetry analysis and can be used to relate the wavefunction to para and ortho states of the water molecule, see Section III A 5.

3. Electrostatic interactions

We assume two contributions to the electrostatic interaction:

$$\mathcal{H}_\text{ES} = \mathcal{H}_\text{Q} + \mathcal{H}_\text{ed},$$

denoting the coupling of the quadrupole and dipole moments of H$_2$O to the corresponding multipole fields created by the surrounding charges.

Quadrupolar interaction. It was shown by Felker et al.[32] that C$_{60}$ molecules in neighbouring lattice sites generate an electric field gradient at the centre of a given C$_{60}$ molecule. In H$_2$O@C$_{60}$, the electric field gradient couples to the electric quadrupole moment of the water molecule, lifting the three-fold degeneracy of the $J = 1$ ortho-H$_2$O rotational ground state [33].

The quadrupolar Hamiltonian may be expanded in rank-2 spherical tensors as follows [38,39,42]:

$$\mathcal{H}_\text{Q} = \sum_{m=-2}^{2} (-1)^m V_{m}^{(2)} Q_{m}^{C},$$

where $\{V_{m}^{(2)}\}$ are the spherical components of the electric field gradient tensor and $\{Q_{m}^{C}\}$ is the quadrupole moment of the water molecule, both expressed in the crystal-fixed coordinate frame $C$.

The experimental value of the H$_2$O quadrupole moment in the molecule-fixed coordinate frame $M$ is given by $\{Q_{xx}, Q_{yy}, Q_{zz}\} = \{-0.13, -2.50, 2.63\}$ e.s.u.$ \times \text{cm}^2$. Since $|Q_{xx}| << |Q_{yy}|, |Q_{zz}|$, it holds that $Q_{xx} \approx -Q_{yy}$, and we may approximate the water quadrupole moment in spherical coordinates as follows:

$$\{Q_{m}^{(2)}\} = \{\frac{1}{2} (Q_{xx} - Q_{yy}), 0, 0, \frac{1}{2} (Q_{xx} - Q_{yy})\}$$

$$\approx Q_{xx} \{\frac{1}{2}, 0, 0, \sqrt{\frac{3}{2}}\}, \quad m = -2, -1, \ldots +2.$$ (12)

The site symmetry of the C$_{60}$ molecule in solid C$_{60}$ is $S_h$, with the three-fold symmetry axis along the cubic [111] axis, which is chosen here to be the $z$’ axis of the crystal coordinate frame $C$. The spherical tensor component in the frame $C$ is

$$\{V_{m}^{(2)C}\} = V_{Q} \{0, 0, 1, 0\},$$ (13)

where $m \in \{-2, -1, 0, 1, 2\}$, transforms like the fully symmetric $A_g$ irreducible representation of the point group $S_h$ [43]. After the transformation of the quadrupole moment $\{V^{(2)}\}$ from
the H$_2$O-fixed molecular frame $M$ to the crystal frame $C$ (see Eq. A5), the quadrupolar Hamiltonian [11] is given by:

$$\mathcal{H}_Q = V_0 Q_{zz} \left[ \sqrt{\frac{3}{2}} D^2_{00} (\Omega_{C\rightarrow M})^* + \frac{1}{2} [D^2_{00} (\Omega_{C\rightarrow M}) + D^2_{02} (\Omega_{C\rightarrow M})]^* \right].$$

### Dipolar interaction

Dielectric measurements of solid C$_{60}$ have provided evidence for the existence of electric dipoles in solid C$_{60}$[13]. We assume these electric dipoles can be source of an electric field in the C$_{60}$ cage center.

Consider a crystal electric field $\mathcal{E}$ with spherical coordinates $\{r, \phi, \theta\}$ in the crystal-fixed frame $C$, see Appendix A. For simplicity, we assume a homogeneous crystal field with uniform orientation in the crystal-fixed frame. The interaction of the electric dipole moment with the electric field is given by

$$\mathcal{H}_{ed} = -\sum_{m} (-1)^m \mathcal{E}_m \mu^E_m$$

where $\mu^E_m$ is the dipole moment in the molecule-fixed frame $M$, Fig. 1(a). Since there are no other anisotropies than the axially symmetric electric field gradient tensor, the angle $\phi$ is arbitrary and we choose $\phi = 0$.

The Hamiltonian [5] is diagonalized using the basis [8] up to $J \leq 4$ for the ground vibrational state $|000\rangle$ and for the three excited vibrational states $|100\rangle$, $|010\rangle$, and $|001\rangle$. The ground state and the three excited vibrational states are assumed to have independent rotational constants $A$, $B$, and $C$, where $v = 000, 100, 010$ or 001.

After separation of coordinates, see Appendix B, the quadrupole and dipole moments in equations (14) and (15) are replaced by their expectation values, $\langle \mathcal{E}_m \rangle Q_{zz}$ and $\langle \mathcal{E}_m \rangle \mu^E_m$, in the ground and in the three excited vibrational states. We assume for simplicity that the dipole and quadrupole moments of H$_2$O are independent of the vibrational state $|\mathcal{E}\rangle$.

### 4. Confined water translations: spherical oscillator

The translational motion is the center of mass motion and is quantized for a confined molecule. The high icosahedral symmetry of the C$_{60}$ cavity is close to spherical symmetry and therefore the translational motion of trapped molecule can be described by the three-dimensional isotropic molecule [5]. For simplicity we write the potential in the harmonic approximation [23] as

$$V(R) = V_{2} R^2,$$

where $R$ is the displacement of H$_2$O center of mass from the C$_{60}$ cage center. The C$_{60}$ cage is assumed rigid and its center of mass is fixed.

The frequency of the spherical harmonic oscillator is:

$$\omega_N^0 = \sqrt{2 V_{2}/m},$$

where $m$ is the mass of a molecule moving in the potential and $[\omega^0_N] = \text{rad s}^{-1}$. The energy of spherical harmonic oscillator is quantized,

$$E_N = \hbar \omega_N^0 (N + \frac{3}{2}),$$

where $N$ is the translational quantum number, $N \in \{0, 1, 2, \ldots\}$. The orbital quantum number $L$ takes values $L = N, N - 2, \ldots 1(0)$ for $N$ odd (even). Energy of the harmonic spherical oscillator does not depend on $L$ and in isotropic approximation there is an additional degeneracy of each $E_N$ level in quantum number $M_L$, taking $2L + 1$ values, $M_L \in \{-L, -L + 1, \ldots L\}$.

### 5. Nuclear spin isomers: para and ortho water

The Pauli principle requires that the total quantum state is antisymmetric with respect to exchange of the two protons in water, which as spin-1/2 particles are fermions. This constraint leads to the existence of two nuclear spin isomers, with total nuclear spin $I = 1$ (para-H$_2$O) and $I = 1$ (ortho-H$_2$O), and different sets of rovibrational states. The antisymmetric nature of the quantum state has consequences on the IR spectra: only para to para and ortho to ortho transitions are allowed.

The ortho-H$_2$O states have odd values of $K_a + K_c$ while the para-H$_2$O states have even values of $K_a + K_c$ in the ground vibrational state $|000\rangle$, see Fig. 1(c). The allowed rotational transitions are depicted in the inset to Fig. 2(a). The same rule applies to the excited vibrational states $|001\rangle$ and $|010\rangle$, left part. However, the rules are inverted for the states $|001\rangle$, $|010\rangle$ and $|011\rangle$, which involve one-quantum excitation of the asymmetric stretch mode $\nu_3$. In these cases[59] para-H$_2$O has odd values of $K_a + K_c$, while ortho-H$_2$O has even values of $K_a + K_c$, Fig. 1(c), upper right part.

The energy difference between the lowest para rotational state $|000\rangle$ and the lowest ortho rotational state $|101\rangle$ is 2.6 meV (28 K[11]). Above 30 K the ratio of ortho and para molecules is $n_o/n_p \approx 3$. Hence, if the sample is cooled rapidly to 4 K, the number of para molecules slowly grows in the subsequent time interval, while the number of the ortho molecules slowly decreases to the thermal equilibrium value $n_o \approx 0$. The full conversion takes several hours[11].
B. Absorption cross-section of H$_2$O@C$_{60}$

The strengths of the transitions between the rotational states of a polar molecule are determined by the permanent electric dipole moment of the molecule and by the electric field of the infrared radiation, corrected by the polarizability of the medium. In principle, the polarizability $\chi$ of the solid depends on the fraction $f$ of C$_{60}$ cages which contain a water molecule, $\chi(\Omega) = \chi_{\text{vacuum}} + f\chi_{\text{H}_2\text{O}@C_{60}}$. However, we found that within the studied range of filling factors, $f = 0.1$ to 0.8, the absorption cross-section of H$_2$O@C$_{60}$ was independent of $f$. Hence, only the polarizability of solid C$_{60}$ is relevant, $\chi \approx \chi_{\text{C}_{60}}$, and the problem is similar to the optical absorption of an isolated impurity atom in a crystal [46].

Following Ref. [46], the electric field at the molecule embedded into medium with an index of refraction $\eta$ is $\mathcal{E}_{\text{eff}} = \mathcal{E}(\eta^2 + 2)/3$, where $\mathcal{E}$ is the electric field of radiation in the vacuum. The refractive index of solid C$_{60}$ is $\eta = 2.33$, and hence $\mathcal{E}_{\text{eff}} = 2\mathcal{E}$.

In the following discussion, we use the index $k \in \{0, p\}$ to indicate the ortho or para nuclear spin isomers. The absorption cross-section $\sigma_{ji}^{(k)}$ for a given nuclear spin isomer $k$, including the effective field correction, is given by

$$\sigma_{ji}^{(k)} = N_k^{-1} \int_{\text{line}} \alpha_{ji}^{(k)}(\omega) d\omega,$$

where $c_0$ is the speed of light in vacuum and $\varepsilon_0$ the permittivity of vacuum; SI units are used and the frequency $\omega$ is in number of waves per meter, $[\omega] = \text{m}^{-1}$. The integral in (20) is the area of the absorption line of the transition from the state $|i\rangle$ to $|j\rangle$.

The square of the electric dipole matrix element is given by

$$S_{ji}^{(k)} = \frac{1}{3} \sum_{\sigma} \langle j| \mu_\sigma \ |i\rangle_\sigma^2,$$

where $|i\rangle$ and $|j\rangle$ are the eigenstates with corresponding energies $E_i^{(k)}$ and $E_j^{(k)}$. The symbol $\mu_\sigma$ denotes the dipole moment components of a water molecule in the crystal-fixed frame $C$.

This form of $S_{ji}^{(k)}$ is valid for random orientation of crystals in the powder sample and does not depend on the polarization of light, see Appendix B.

The absorption cross-section $\sigma_{ji}^{(k)}$ was evaluated separately for para and ortho water. The concentration of molecules is $N_k = fN_{\text{C}_{60}}n_k$, where $n_k$ is the ortho (or para) fraction and $n_p + n_o = 1$. The filling factor is denoted by $f$ and the number density of C$_{60}$ molecules in solid C$_{60}$ is given by $N_{\text{C}_{60}} = 1.419 \times 10^{21}$ cm$^{-3}$ [42].

$p_i^{(k)}$ and $p_f^{(k)}$ are the probabilities that the initial and final states are thermally populated,

$$p_i^{(k)} = (Z^{(k)})^{-1} \exp\left(-\frac{E_i^{(k)} - E_0^{(k)}}{k_b T}\right),$$

where the statistical sum is

$$Z^{(k)} = \sum_n \exp\left(-\frac{E_n^{(k)} - E_0^{(k)}}{k_b T}\right),$$

and $E_0^{(k)}$ is the ground state energy of para (ortho) molecules. At the low temperatures considered in this work, only the vibrational ground state is significantly populated. Thus, the significantly thermally populated states are rotational states in the ground vibrational states, which can be written as linear combinations of basis states in Eq. (3). Since we expect that the water molecule is not in a spherically symmetric environment in H$_2$O@C$_{60}$, the degeneracy in quantum number $m$ is lifted, in general. Therefore, $p_n^{(k)}$ is the thermal population of a non-degenerate rotational state and the eigenstates $|i\rangle$ and $|j\rangle$ in Eq. (21) include all possible $m$ values for a given $J$.

When thermal equilibrium is reached between the para and ortho water, the fraction of nuclear spin isomer $k$ is

$$n_k(T) = \frac{g_k^{(k)}Z_k^{(k)}}{g_p^{(p)}Z_p^{(p)} + g_o^{(o)}Z_o^{(o)}},$$

For spin isomer $k$, the nuclear spin degeneracy $g_k = 2I + 1$, with $I = 0$ for para and $I = 1$ for ortho.

The absorption line area are calculated from Eq. (20), where the matrix elements in Eq. (21) are between the eigenstates $|\Phi^{(\sigma)}_{\text{rot}}\rangle$ of the Hamiltonian given by Eq. (5). After separation of coordinates (see Appendix B 2), the matrix elements in the crystal-fixed coordinate frame $C$ are

$$\langle j| \mu_\sigma |i\rangle =$$

$$= \sum_{\sigma = -1}^1 \langle \Phi^{(\sigma)}_{\text{rot}} | D_{\alpha \sigma}^i (\Omega_{C\rightarrow M}) | \Phi^{(00)}_{\text{rot}}\rangle \langle \psi'| \mu_\sigma^M |000\rangle,$$

where the initial state is $|i\rangle = |000\rangle |\Phi^{(00)}_{\text{rot}}\rangle$ and $|\Phi^{(00)}_{\text{rot}}\rangle$ are the linear combinations of states $|\Phi^{(00)}_{\text{rot}}\rangle$. The dipole moments $\langle \psi'| \mu_\sigma^M |000\rangle$ are given by Eq. (B13) and (B14) in Cartesian coordinates.

IV. RESULTS AND INTERPRETATION OF SPECTRA

A. Spectra

The water IR absorption lines were identified unambiguously by taking advantage of the slow ortho-para conversion at low temperature. After rapid cooling from 30 K to 5 K, the slow ortho-para conversion causes the intensity of the para lines to slowly increase, while the intensity of the ortho lines decreases. The water absorption lines are readily identified, and assigned to one of the two spin isomers, by taking the difference between spectra acquired shortly after cooling and spectra acquired after an equilibration time at the lower temperature.

A group of H$_2$O lines, numbered 3, 4, and 5, is seen below 60 cm$^{-1}$, Fig. 2(a). These far-IR absorption lines have been reported earlier and correspond to the rotational transitions of...
**H₂O in the C₆₀ cage** [11]. The rotational energy levels involved are shown in the inset to Fig. 2(a). Lines 3 and 5 are ortho water rotational transitions starting from the ortho water ground state |00⟩. Line 4 is the para water transition from the ground rotational state |00⟩. No other rotational transitions were observed at 5 K which is consistent with the selection rules for the electric dipole allowed rotational transitions from states |00⟩ and |01⟩ [39].

Further H₂O lines are observed around 110 cm⁻¹, Fig. 2(b), and in six spectral regions above 600 cm⁻¹ as shown in Figures 3 to 6. Below, we address each wavenumber range separately and assign the spectral lines to the transitions shown in the energy schemes of Fig. 1(c) and Fig. 2(a). The absorption lines associated with transitions of free water, labelled 1 to 8, are listed in Table I. Line assignments are supported by the results of the spectral fitting using the model of a vibrating rotor in a crystal field.

**1. Translational transitions**

A group of absorption lines around 110 cm⁻¹ is shown in Fig. 2(b). These lines do not correspond to any known water rotational transitions. We assign these peaks to the translational transitions (N = 0 → N = 1) of para- and ortho-H₂O, corresponding to the quantized centre-of-mass vibrational motions of the water molecules in the encapsulating C₆₀ cages. Here N denotes the quantum number of a spherical harmonic oscillator [32].

The assignment of these peaks to water centre-of-mass translational oscillations is supported by the presence of lines at 1680 cm⁻¹, visible in the difference spectrum shown in the right-hand inset to Fig. 3. These lines are 110 cm⁻¹ higher than the vibrational transitions 1 and 2 of the v₂ mode and correspond to the simultaneous excitation of the v₂ vibration and the translational modes. A similar combination has been observed in H₂@C₆₀ where a group of lines between 4240 and 4270 cm⁻¹ is the translational sideband to H₂ stretching vibration [10].

The translational side peak of the v₁ vibrational mode is expected at about 3683 cm⁻¹. However, this frequency coincides with a strong rovibrational absorption line 6 of the v₃ mode (Fig. 4), which probably obscures the 3683 cm⁻¹ translational side peak of the v₁ vibration.

The translational ortho transitions display a splitting of 2.9 cm⁻¹ in the ground vibrational state, see Fig. 2(b), and 2.7 cm⁻¹ in the excited vibrational state |01⟩, see Fig. 2. These splittings may be attributed to the coupling between the water translation and rotation, associated with the interaction of the non-spherical rotating water molecule with the interior of the C₆₀ cage. Spectral structure of this type has been analysed in detail for the case of H₂@C₆₀ [30,39]. The simplified theoretical model used here does not include translation-rotation coupling and cannot explain these splittings. A theoretical analysis of the translational peaks will be given in a later paper.

**2. Vibrational and rovibrational transitions**

The vibrational and rovibrational transitions are shown in Fig. 3. The three major features that distinguish the spectrum of H₂O@C₆₀ from the spectrum of free water are as follows:

1. **Pure vibrational transitions.** Absorptions corresponding to pure vibrational transitions, i.e. without simultaneous rotational excitation, are present around ω₁ = 3573 cm⁻¹ and ω₂ = 1570 cm⁻¹. Both features are split into two components, labeled 1 and 2, identified from the difference spectra, Fig. 3 and 4, as para (1) and ortho (2) transitions.

The transition 1 is a transition from the ground vibrational state to the excited vibrational state without a change of rotational state |00⟩. Transition 2 is a vibrational excitation without change in the rotational state |10⟩. The corresponding transitions are forbidden for an isolated water molecule since the corresponding matrix element is zero [30]. As discussed below, the presence of pure vibrational transitions 1 and 2 is consistent with the presence of an electric field in solid H₂O@C₆₀.

The ortho-para splitting, i.e. the separation of lines 1 and 2, is 0.5 cm⁻¹ for the v₁ vibrational mode, and 1.8 cm⁻¹ for the v₂ vibrational mode.

2. **Spectral splittings.** The rovibrational transitions 3 to 8 are split into two or more components (see Figs. 3 and 4). These splittings, as in the case of the rotational transitions, are absent for a water molecule in the gas phase. Moreover, transitions 3, 4, and 5 have the same splitting pattern as the
rotational transitions in the ground vibrational state, also labeled 3, 4, and 5, see Fig. 2. Transitions 6 and 7 are special since they are between the \( |000\rangle \) and \( |101\rangle \) rotational states and thus reflect directly the splitting of the triply degenerate \( |101\rangle \) state either in the ground vibrational state, transition 7, or in the excited vibrational state, transition 6, Fig. 4.

We assign a weak ortho line at 3654 cm\(^{-1}\), marked by * in Fig. 2, to the v\(_1\) vibrational transition from the thermally excited rovibrational state \( |000\rangle |101\rangle \) to \( |001\rangle |111\rangle \). This assignment is further confirmed by calculating the transition frequency with the parameters from Table III, \( \omega_3 + E_{111} - E_{101} = \omega_3 + A_{001} + C_{001} - (A_{000} + B_{000}) = 3655 \text{ cm}^{-1} \).

3. Red shifts. The frequencies of vibrations are red-shifted relative to free H\(_2\)O. The stretching mode frequencies are red-shifted by about 2.4%, while the bending mode frequencies are red-shifted by about 1.6%, see Table I.

### Table I: The Rotational and Rovibrational Transition Frequencies \( \omega_{ji} \) and the Normalized Absorption Cross-sections \( \sigma_{ji}^{(k)} \), Eq. (3), from the ground para, \( |000\rangle \), and ground ortho, \( |101\rangle \), rotational state of H\(_2\)O@C\(_{60}\) and of free H\(_2\)O. The initial vibrational state is \( |000\rangle \) for all transitions. The spectral lines are labelled by # from 1 to 8, each number associated with the same pair of initial and final rotational states. The frequency \( \omega_{ji} \) of lines 3 to 8 in H\(_2\)O@C\(_{60}\) is the intensity-weighted average of line sub-component frequencies. Gas phase \( \omega_{ji} \) are from Ref. [48].

| \(|v_1v_2v_3\rangle\) \# | \(|J_{K_iK_j}\rangle \# | \(\omega_{ji}/\text{cm}^{-1}\) | \(\sigma_{ji}^{(k)}/(\text{cm/molecule})\) | \(\sigma_{ji}^{(k)}/(\text{gas})/(\sigma_{ji}^{(k)})_{(C_{60})}\) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| 000 3 101 110 | 18.6 16.8 | (4.003 ± 0.020) \(\times 10^{-17}\) | (3.24 ± 0.26) \(\times 10^{-18}\) | 12.4 |
| 000 000 111 | 37.1 33.6 | (5.34 ± 0.03) \(\times 10^{-17}\) | (3.02 ± 0.19) \(\times 10^{-18}\) | 17.4 |
| 000 101 212 | 55.7 51.1 | (1.203 ± 0.006) \(\times 10^{-16}\) | (7.5 ± 0.4) \(\times 10^{-18}\) | 16.1 |
| 100 1 000 000 | 3657.1 3573.2 | (3.4 ± 0.6) \(\times 10^{-20}\) |
| 100 101 101 | 3674.7 3589.1 | (4.39 ± 0.17) \(\times 10^{-19}\) | 1.52 |
| 010 1 000 000 | 1594.8 1569.3 | (2.3 ± 0.6) \(\times 10^{-19}\) |

are sketched in Fig. 4(c). Again, the splitting pattern of each higher order rovibrational transition is similar to the splitting of rotational transition with \( \Delta V = 0 \) (Fig. 2) and rovibrational transitions with \( \Delta V = +1 \) (Fig. 3 and 4).

We assign a line marked by “*” at 7059 cm\(^{-1}\) to \( 2\omega_1 + para\)-H\(_2\)O rotational transition, \( |000\rangle \to |111\rangle \), Fig. 6(b). Another two rotational side peaks of \( 2\omega_0 \) are ortho transitions 3 and 5 expected at \( 2\omega_0 + E_{111} - E_{011} = 7042 \text{ cm}^{-1} \) and at \( 2\omega_0 + E_{212} - E_{101} = 7076 \text{ cm}^{-1} \), where \( E_{111} = A - C \) and \( E_{212} = E_{101} = A + 3B \), with the approximation \( A = A_{200} \approx A_{100} \), \( C = C_{200} \approx C_{100} \). The numerical values of \( A_{100} \) and \( C_{100} \) are taken from Table III. The first line overlaps with line 7, rovibrational transition of \( \omega_0 + \omega_2 \). The second line is not observed but this could be due to the low intensity of ortho line 5 relative to the para line 4, see for example Fig. 5(a).

All two- and three-quantum vibrational transitions are red-shifted approximately by 2.4% except the \( 2\omega_2 \) where the red shift is 1.5%, see Table II.

3. Overtone and combination rovibrational transitions

Overtone and combination vibrational transitions where two vibrational quanta are excited are presented for the \( 2\omega_2 \) transition in Fig. 5(a) and for the \( \omega_0 + \omega_3 \) and \( \omega_0 + \omega_1 \) transitions in Fig. 6(a) and (b). A three-quantum transition, \( 2\omega_2 + \omega_1 \), is shown in Fig. 5(b). Rotational levels involved are sketched in Fig. 4(c). Again, the splitting of each higher order rovibrational transition is similar to the splitting of rotational transition with \( \Delta V = 0 \) (Fig. 2) and rovibrational transitions with \( \Delta V = +1 \) (Fig. 3 and 4).

We assign a line marked by “*” at 7059 cm\(^{-1}\) to \( 2\omega_1 + para\)-H\(_2\)O rotational transition, \( |000\rangle \to |111\rangle \), Fig. 6(b). Another two rotational side peaks of \( 2\omega_0 \) are ortho transitions 3 and 5 expected at \( 2\omega_0 + E_{111} - E_{011} = 7042 \text{ cm}^{-1} \) and at \( 2\omega_0 + E_{212} - E_{101} = 7076 \text{ cm}^{-1} \), where \( E_{111} = A - C \) and \( E_{212} = E_{101} = A + 3B \), with the approximation \( A = A_{200} \approx A_{100} \), \( C = C_{200} \approx C_{100} \). The numerical values of \( A_{100} \) and \( C_{100} \) are taken from Table III. The first line overlaps with line 7, rovibrational transition of \( \omega_0 + \omega_2 \). The second line is not observed but this could be due to the low intensity of ortho line 5 relative to the para line 4, see for example Fig. 5(a).

All two- and three-quantum vibrational transitions are red-shifted approximately by 2.4% except the \( 2\omega_2 \) where the red shift is 1.5%, see Table II.

B. Spectral fitting with a quantum mechanical model

A synthetic spectrum consisting of Gaussian lines with full width at half maximum 1.5 cm\(^{-1}\) was calculated from the experimental normalized line areas \( \langle A_{ji}^{(k)} \rangle \), Eq. (2), using \( f = 1 \),
FIG. 3. Absorption spectra of H$_2$O@C$_{60}$ vibrational, rovibrational and vibration-translational transitions of bending vibration $v_2$ at 5 K. Spectrum $\alpha(0)$ was measured after the temperature jump from 30 K to 5 K (black) and the difference $\Delta\alpha = \alpha(0) - \alpha(\Delta t)$ was measured $\Delta t = 3$ h later (blue). Sample filling factor $f = 0.1$. Lines numbered 1 and 2 are pure vibrational transitions and 3, 4, and 5 are rovibrational transitions, Fig. 1(c). Left inset shows the para, line 1, and ortho, line 2, components of the pure vibrational transitions difference spectrum with time delay 1 h of the $f = 0.8$ sample. The differential spectrum of $v_2$ vibration-translational transitions $T_p$, $T_{p_3}$, and $T_{p_2}$, at 110 cm$^{-1}$ higher frequency from 1 and 2, is in the right inset.

FIG. 4. Absorption spectra of H$_2$O@C$_{60}$ vibrational, rovibrational and vibration-translational transitions of symmetric stretching, $v_1$, and anti-symmetric stretching vibration $v_3$ at 5 K. Spectrum $\alpha(0)$ was measured after the temperature jump from 30 K to 5 K (black) and the difference $\Delta\alpha = \alpha(0) - \alpha(\Delta t)$ was measured $\Delta t = 3$ h later (blue dashed line multiplied by 4 and blue line). Sample filling factor $f = 0.1$. Lines numbered 1 and 2 are pure vibrational transitions and 3, 4, and 5 are rovibrational transitions of mode $v_1$ and lines 6, 7, 8 are rovibrational transitions of $v_3$, Fig. 1(c). (*) marks the $v_3$ rovibrational transition at 3654 cm$^{-1}$ from the thermally excited rotational state $|000\rangle |101\rangle$ to rovibrational state $|001\rangle |111\rangle$. Inset shows the para, line 1, and the ortho, line 2, components of the pure vibrational transition of mode $v_1$ of the $f = 0.8$ sample as the difference spectrum with time delay 1 h.

FIG. 5. Absorption spectra of H$_2$O@C$_{60}$ at 10 K. (a) Overtone, 2$\omega_2$, and (b) combination, 2$\omega_2 + \omega_3$, rovibrational transitions. Spectrum $\alpha(0)$ was measured after the temperature jump from 45 K to 10 K (black) and the difference $\Delta\alpha = \alpha(0) - \alpha(\Delta t)$ was measured $\Delta t = 2.75$ h later (blue). The numbers 3 – 8 label the transitions shown in Fig. 1(c). Sample filling factor $f = 0.8$.

TABLE II. Frequencies of symmetric stretching ($\omega_1$), symmetric bending ($\omega_2$), and asymmetric stretching ($\omega_3$) modes and of their combinations 2$\omega_2$, $\omega_2 + \omega_3$, 2$\omega_2 + \omega_1$, 2$\omega_1$, and $\omega_1 + \omega_3$ measured from the ground vibrational state $|000\rangle$ for H$_2$O@C$_{60}$ (this work) and for free H$_2$O [13]. ortho and para components of pure vibrational transitions $v_1$ and $v_2$ are indicated by superscripts o and p. The frequencies of transitions involving $v_3$ in H$_2$O@C$_{60}$ are the average of frequencies of transition 6 and 7, see Fig. 4(b) and 6. The overtone $2\omega_2$ is estimated from the frequency of line 4, Fig. 5(a), 2$\omega_2 + E_{111} = 3141$ cm$^{-1}$, where $E_{111} = A + C$ is the energy of rotational state $|111\rangle$, and $A = A_{010}$, $C = C_{010}$ from Table III. The 2$\omega_1$ overtone frequency is estimated from the frequency of para line 2$\omega_1 + E_{111} = 7059$ cm$^{-1}$, Fig. 6(b), where $E_{111} = A_{100} + C_{100}$. Shift $\Delta\omega = \omega_{111} - \omega_{\text{gas}}$.

| $v_0v_1v_2$ | H$_2$O@C$_{60}$ free H$_2$O $\Delta\omega$ $\Delta\omega/\omega_{\text{gas}}$ |
|-------------|-----------------|----------|----------------|
| (001)       | 1569.2$^p$      | 1594.8  | -25.6          | -0.016          |
|             | 1571.0$^p$      |          |                |                 |
| (010)       | 3573.2$^p$      | 3657.1  | -83.9          | -0.023          |
|             | 3573.7$^p$      |          |                |                 |
| (001)       | 3569.6          | 3755.3  | -95.7          | -0.025          |
| (020)       | 3105.5          | 3151.6  | -46.1          | -0.015          |
| (011)       | 5205.2          | 5331.3  | -126.1         | -0.024          |
| (021)       | 6716.6          | 6871.5  | -154.9         | -0.023          |
| (200)       | 7027.0          | 7201.5  | -173.5         | -0.024          |
| (101)       | 7065.8          | 7249.8  | -184.0         | -0.025          |

TABLE III. Frequencies of symmetric stretching and vibration-translational transitions (for free H$_2$O).

| $j\omega_1$ | $j\omega_2$ | $j\omega_3$ | $j\omega_2 + \omega_3$ | $j\omega_2 + \omega_1$ | $j\omega_1 + \omega_3$ |
|-------------|-------------|-------------|----------------------|----------------------|----------------------|
| (000)       | 3408.9      | 3438.9      | 3468.9               | 3498.9               | 3528.9               |
| (010)       | 3440.3      | 3470.3      | 3499.3               | 3528.3               | 3558.3               |
| (100)       | 3472.3      | 3502.3      | 3532.3               | 3561.3               | 3591.3               |
| (111)       | 3503.8      | 3533.8      | 3563.8               | 3593.8               | 3623.8               |

Note: $\omega_1$, $\omega_2$, and $\omega_3$ are the frequencies of symmetric stretching, symmetric bending, and asymmetric stretching, respectively.
nα = 0.7, nβ = 0.3 and T = 5 K. The parameters of the model Hamiltonian (from Section III A) and the transition dipole moments (from Section III B) were determined with a non-linear least squares method by minimizing the difference of synthetic and modeled spectrum squared, Appendix C. The reported parameter error is the average of errors calculated with +δαv and −δαv in Eq. (C9), where the parameter variation of νv at its best value αv is |δαv| = 0.005 αv. The fit was applied to the rotational transitions in the ground vibrational state (000) and to the rovibrational transitions from the ground state to the vibrational states |010⟩, |100⟩, and |001⟩. In total, 45 absorption lines were fitted.

The synthetic experimental spectra and the best fit spectra are shown in Fig. 7 with the best fit parameters given in Table III. The result of the fit overlaps well with the synthetic spectrum, except for the transition 5 as seen in the first three panels of Fig. 7. While for other transitions one or two Gaussian components were sufficient, the experimental transition lineshape required three components to get a reliable fit of its line area. Also, transitions 6 and 7 were represented by two components in the synthetic spectrum, although four peaks are seen in the experimental spectrum, Fig. 4. The additional structure of experimental peaks may originate from the merohedral disorder as discussed in Section V E.

Tables IV and V list energies and the main components of rotational states in the ground vibrational state. The rotational energies are in qualitative agreement with recent computational estimates. The 2J + 1 degeneracy of rotational states is fully removed by the electrostatic field interacting with dipole and quadrupole moment of H₂O.

From our fit the permanent dipole moment μx of the encapsulated water is given by the absorption cross-section of the IR rotational transitions 3, 4, and 5 in the ground vibrational state. With the value of μx in hand and by using the intensities of transitions 1 and 2 we were able to determine the internal static electric field in solid C₆₀. The interaction of μx with the crystal electric field mixes rotational states within ground and excited vibrational states. For example, in case of ortho water the components of state |100⟩ are mixed into the ground state |101⟩, Table V. This mixing gives the oscillator strength to the pure vibrational transitions 1 and 2. As shown in table III, the fitted value of the electric field at the C₆₀ cage centres is (110 ± 5)×10⁶ V/m⁻¹.

A splitting of 4 cm⁻¹ is observed for transition 7 and is due to the splitting of the ortho ground state |101⟩, Fig. 1(c). In principle, a splitting could be caused by the interaction of the water electric dipole with an electric field, or by the interaction of the water electric quadrupole moment with an electric field gradient. The electric field 110×10⁶ V/m⁻¹ is too small to cause splitting of this magnitude. This electric field lifts the degeneracy of m = ±1 levels of |101⟩, but the gap between m = 0 and m = ±1 levels is due to the quadrupolar interaction. As the splitting is determined by the product of Vq and Qzz, it is not possible to have an estimate of how much is the water

| Parameter | Value | Error |
|-----------|-------|-------|
| nα       | 0.7   | 0     |
| f        | 1     | 0     |
| ω₁       | 3574.1| 0.3   |
| ω₂       | 1569.2| 0.3   |
| ω₃       | 3659.9| 0.9   |
| A₀₀₀     | 24.15 | 0.17  |
| B₀₀₀     | 15.3  | 0.8   |
| C₀₀₀     | 8.48  | 0.07  |
| A₁₁₀     | 23.1  | 0.3   |
| B₁₁₀     | 14.3  | 0.8   |
| C₁₁₀     | 8.50  | 0.09  |
| A₂₀₁     | 26.7  | 0.3   |
| B₂₀₁     | 14.6  | 0.9   |
| C₂₀₁     | 8.81  | 0.07  |
| A₃₀₁     | 26    | 6     |
| B₃₀₁     | 15    | 3     |
| C₃₀₁     | 8.2   | 1.8   |
| μ²       | 0.474 | 0.008 |
| μ₀₁      | 1.031×10⁻²| 0.021×10⁻²|
| μ₀₂      | 3.40×10⁻²| 0.05×10⁻²|
| μ₀₃      | 2.83×10⁻²| 0.07×10⁻²|
| δ        | 110   | 5     |
| θq       | 1.4   | 1.0   |
| VqQzz    | −5.0  | 0.5   |

| Parameter | Value | Error |
|-----------|-------|-------|
| nα       | 0.7   | 0     |
| f        | 1     | 0     |
| ω₁       | 3574.1| 0.3   |
| ω₂       | 1569.2| 0.3   |
| ω₃       | 3659.9| 0.9   |
| A₀₀₀     | 24.15 | 0.17  |
| B₀₀₀     | 15.3  | 0.8   |
| C₀₀₀     | 8.48  | 0.07  |
| A₁₁₀     | 23.1  | 0.3   |
| B₁₁₀     | 14.3  | 0.8   |
| C₁₁₀     | 8.50  | 0.09  |
| A₂₀₁     | 26.7  | 0.3   |
| B₂₀₁     | 14.6  | 0.9   |
| C₂₀₁     | 8.81  | 0.07  |
| A₃₀₁     | 26    | 6     |
| B₃₀₁     | 15    | 3     |
| C₃₀₁     | 8.2   | 1.8   |
| μ²       | 0.474 | 0.008 |
| μ₀₁      | 1.031×10⁻²| 0.021×10⁻²|
| μ₀₂      | 3.40×10⁻²| 0.05×10⁻²|
| μ₀₃      | 2.83×10⁻²| 0.07×10⁻²|
| δ        | 110   | 5     |
| θq       | 1.4   | 1.0   |
| VqQzz    | −5.0  | 0.5   |
quadrupole moment \( Q_{zz} \) screened in \( C_{60} \).

V. DISCUSSION

A. Vibrations of confined \( H_2O \)

All eight frequencies of the encapsulated \( H_2O \) vibrations found in this work are red-shifted relative to those of free water, see Table II. The red-shift of the vibrational frequency has been observed for other endofullerenes, \( H_2@C_{60} \)[10,12], HD and \( D_2@C_{60} \)[6] and \( HF@C_{60} \)[6]. Six water modes have a relative shift between \(-2.3\%\) and \(-2.5\%\). Two frequencies, namely the bond-bending mode frequency \( \omega_1 \) and its overtone frequency \( 2\omega_1 \) are shifted by \(-1.6\%\) and \(-1.5\%\), respectively.

The observed red shifts of the stretching mode frequencies \( \omega_1 \) and \( \omega_2 \) is partially consistent with previous DFT calculations. The DFT-based calculations published by Varadwaj et al. predict vibrational redshifts, while some of the calculations reported by Farimani et al. predict blue shifts rather than red shifts.

The calculation predicts a blue shift of the bending mode \( \omega_2 \), although ten times less in absolute value than the predicted shift of stretching modes[55]. The experimental shift of \( \omega_2 \) is less than that of stretching modes but it is still red-shifted. The other method, fully coupled nine-dimensional calculation, predicts blue-shifts for all three vibrational modes[55].

B. Translations of \( H_2O \)

Table VI lists the measured translational energies from the ground to the first excited state, \( \omega_i \), of small-molecule endofullerenes. It is known that the potential of di-hydrogen in \( C_{60} \) is anharmonic[51] while the degree of anharmonicity of \( HF@C_{60} \) and \( H_2O@C_{60} \) potentials is not known. For simplicity, we assume that the potential is harmonic for the current case of endohedral molecules, \( \omega_i \approx \omega_i^0 \), and show its scaling relative to \( H_2 \) in Table VI. In this approximation the harmonic potential parameter is similar among the hydrogen isotopologs but for \( HF \) and \( H_2O \) \( V_2 \) is larger by a factor of 1.9 and 3.4, respectively. The steeper translational potential for \( HF \) and \( H_2O \), relative to dihydrogen, is consistent with the larger size of these molecules, and hence their tighter confinement.

The last line of Table VI is the frequency and the harmonic potential of \( H_2O@C_{60} \) derived by Bacic and co-workers[6,55] using Lennard-Jones potentials. The calculated potential is more steep than the experimentally determined potential.

As seen in Fig. 2b, the absorption line of the ortho-\( H_2O \) translational mode is split by \( 2.9\ cm^{-1} \). This splitting may be attributed to the coupling between the endohedral molecule translation and rotation, associated with the interaction of the non-spherical rotating molecule with the interior of the \( C_{60} \) cage, as seen in \( H_2@C_{60} \)[10,12]. For the particular transition, shown in Fig. 2b, it is the coupling between translational state with \( N = 1, L = 1 \) and rotational state \( |_{01} \) of ortho water. Within spherical symmetry a good quantum number is \( \Lambda = J + L \). Thus, the translation-rotation coupled translational state \( L = 1 \) and rotational state \( J = 1 \) form three states with \( \Lambda \)-values \( 0, 1, \) and \( 2 \). The calculated energy difference of ortho-water \( \Lambda = 0 \) and \( \Lambda = 1 \) states is \( 8\ cm^{-1} \) as compared to the experimental value \( 2.9\ cm^{-1} \).

C. Rotations of \( H_2O \)

There are two possibilities why the rotational constants of water change when it is encapsulated. First is that the bond length and angles of \( H_2O \) change. The second is that \( H_2O \), because of confinement and being non-centrosymmetric, is forced to rotate about the “center of interaction” which does not coincide with its nuclear center of mass[53].

The rotational constant relates to the moment of inertia \( I_{\alpha\alpha} \) as \( A = h^2/(8\pi^2c_0I_{\alpha\alpha})^{-1} \) where \( c_0 \) is the speed of light. Similarly, \( B = h^2/(8\pi^2c_0I_{bb})^{-1} \) for the \( b \)-axis and \( C = h^2/(8\pi^2c_0I_{cc})^{-1} \) for the \( c \)-axis rotation \( (|A| = m^{-1} \) in SI units and 0.01 \( |A| \) = cm\(^{-1} \). The moments of inertia are \( I_{\alpha\alpha} = \sum m_i(\beta_i^2 + \gamma_i^2) \), where \( \{ \alpha_i, \beta_i, \gamma_i \} \) are the Cartesian coordinates of the \( i \)-th nucleus with mass \( m_i \) with the origin at the nuclear center of mass.

For non-centrosymmetric molecules, the translation-rotation coupling shifts the rotational energy levels. In quantum mechanical terms, the shift of rotational states is caused by the mixing of rotational and translational states by translation-rotation coupling, example is \( HD@C_{60} \)[59].

Translation-rotation coupling was not included in our quantum mechanical model of \( H_2O@C_{60} \). The rotational constants of the model were free parameters to capture the effect of translation-rotation coupling and the change of the \( H_2O \) molecule geometry caused by the \( C_{60} \) cage. The rotational constants of the free water are \( A_0 = 27.88\ cm^{-1} \), \( B_0 = 14.52\ cm^{-1} \) and \( C_0 = 9.28\ cm^{-1} \) in the ground vibrational state[51]. The rotational constants of endohedral water have relative shifts \(-13\%, 5.5\%, -8.7\% \) for \( A_0, B_0 \) and \( C_0 \), in the ground vibrational state, Table III. In the following discussion, we use classical arguments to assess whether the shift of rotational levels is caused by the change of water molecule geometry or by the translation-rotation coupling.

From the symmetry of the \( H_2O \) molecule, the nuclear center of mass is on the \( b \) axis, Fig. 1. The shift of \( H_2O \) center of rotation in the negative direction of \( b \) axis decreases \( A \) and \( C \) while it does not affect \( B \). If \( B \) changes it must be due to the change of \( H-O-H \) bond angle and \( O-H \) bond length. The calculation predicts the shortening of the \( H-O \) bond by 0.0026Å and decrease of the \( H-O-H \) bond angle by 0.65%, -0.46%, an order of magnitude smaller than derived from the IR spectra of \( H_2O@C_{60} \). However, by shifting the rotation center by -0.07Å in the \( b \) direction (further away from the oxygen) gives relative changes \(-14\%, 0.65\% \) and \(-5.2\% \). This relative change of \( A_{000} \) and \( C_{000} \) is not very different from the values derived from the IR spectra while the relative change of \( B_{000} \) is within the error limits, Table III. Thus, it is likely that the dominant contribution to the observed changes of rotational constants in the ground translational state comes not from the change of \( H_2O \) molecule bond lengths and bond
angle but from the shifting its center of rotation away from the nuclear center of mass of H$_2$O molecule.

D. Permanent and transition dipole moments

A comparison of the normalized absorption cross-sections $\langle \sigma_{ji} \rangle$, Eq. 15, for H$_2$O@C$_{60}$ and for free water is given in the last column of Table 4. In general, for all observed transitions the absorption cross-section of endohedral water is smaller than that of free water. The $v_1$ mode has the smallest relative change while the largest relative change is for the combination mode $\omega_1 + \omega_2$.

The comparison of H$_2$O@C$_{60}$ and free H$_2$O absorption cross-sections, Table 4 enables us to estimate independently from the spectral fit the permanent and the transition dipole
Theory

The cross-section-error weighted averages of the three transition, 3, 4 and 5 or 6, 7 and 8 in Table VI. The cross-section-derivative dipole moments are the cross-section-error weighted averages of the three transition, 3, 4 and 5 or 6, 7 and 8 in Table VI.

TABLE VII. Absolute values of the dipole moment, unit D, determined by the capacitance method, 0.0153 ± 0.0031, 0.0126 ± 0.008, 0.0684 ± 0.0021. The reduction of fullerene-encapsulated water dipole moment has been predicted by several theoretical calculations [18, 186, 189, 203].

The results are collected together with the dipole moments obtained from the fit of IR spectra in Table VII. The permanent dipole moment of encapsulated water is nearly four times smaller than that of a free H$_2$O. The results of the IR spectroscopy study are consistent with the dipole moment determined by the capacitance method, 0.51 ± 0.05 [2]. The reduction of fullerene-encapsulated water dipole moment has been predicted by several theoretical calculations [18, 186, 189, 203].

E. Effect of solid C$_{60}$ crystal field

The electric dipolar and quadrupolar interactions of the H$_2$O@C$_{60}$ molecule with the electrostatic field in solid C$_{60}$ explains the oscillator strength of the pure v$_1$ and v$_2$ vibrational transitions and the splitting of the rotational states with J > 0.

Theoretical work of Felker et al. [33] shows that the source of the quadrupole crystal field is the orientation of electron-rich double bonds of 12 nearest-neighbour C$_{60}$ relative to the central H$_2$O@C$_{60}$. When the solid C$_{60}$ is cooled below 90 K a merohedral disorder is frozen in where approximately 85% of C$_{60}$ have electron-rich 6:6 bond (bond between the two hexagonal rings) facing pentagonal ring of a neighbouring cage, the P-orientation [34]. The rest are H-oriented where the 6:6 bond faces neighbouring cages hexagonal ring. The calculated quadrupolar interaction for the P-oriented molecules is ten times bigger than for the H-oriented molecules [32].

Further splitting is possible if the symmetry is lower than S$_6$, but the maximum number of components for J = 1 remains three. However, we see that line 7 consists of four components instead of three, Fig. 4. This suggests that there are two sites with different local electrostatic fields. Anomalous splitting of triply degenerate phonons into quartets has been seen in solid C$_{60}$ by IR spectroscopy [33] and was attributed to the merohedral disorder. Thus, our work and IR study of phonon [34] clearly show that there are two different quadrupolar interactions in solid C$_{60}$. As was proposed by Felker et al. [33], the crystal field has a different magnitude for P-oriented sites and for H-oriented sites. The small population of H-oriented sites (about 15%) justifies our spectral fitting with a single quadrupolar interaction.

We assumed that there is an internal electric field in C$_{60}$ and this field is a possible reason why the pure vibrational transitions 1 and 2, see Fig. 1(c), become visible in the IR spectrum. It is also plausible that 1 and 2 gain intensity through the translation-rotation coupling from the induced dipole moment of translational motion. However, there is evidence that local electric fields exist in solid C$_{60}$ as a result of merohedral disorder C$_{60}$ [33]. The estimate of un-balanced charge by Alers et al. [35] was $q = 6 \times 10^{-3}e$ assuming a dipole moment $\mu = qd_0$, where $e$ is the electron charge and $d_0 = 0.7$ nm is the diameter of a C$_{60}$ molecule. Our estimate is that the electric field $E = 1.1 \times 10^8$ Vm$^{-1}$ at the center of C$_{60}$ cage is created by the dipole moment with charge $q = 4.7 \times 10^{-3}e$. These two estimates are very close.

C$_{60}$ has six nearest-neighbor equatorial cages and three axial cages above and three axial cages below the equatorial plane, following the notation of Ref. [32]. The $z'$ axis of the crystal field coordinate frame is normal to the equatorial plane. As our fit shows, the electric field is rotated away from the $z'$ axis by $\theta_z \approx 80^\circ$, Table III, almost into the equatorial plane. It is possible that one of the 6 nearest-neighbours in the equatorial plane does not have P-orientation and this mis-oriented cage is the source of the electric field. $\theta_z$ has a large relative error consistent with the probability to have the mis-oriented cage in the equatorial or in the axial position.
FIG. 7. The synthetic experimental spectra (black solid line) and the spectra calculated with the best fit parameters from Table III (blue dashed line) with filling factor $f = 1$, ortho fraction $n_o = 0.7$ and at temperature of 5 K. (a) Rotational transitions in the ground vibrational state, (b) vibrational (1 and 2) and rovibrational (3, 4, 5) transitions of $v_2$ and (c) $v_1$. (d) Rovibrational transitions (6, 7, 8) of $v_3$.

VI. SUMMARY

The infrared absorption spectra of solid H$_2$O@C$_{60}$ samples were measured close to liquid He temperature and rotational, vibrational, rovibrational, overtone, and combination rovibrational transitions of H$_2$O were seen. The spectral lines were identified as para and ortho water transitions by following the para-ortho conversion process over the timescale of hours. The vibrational frequencies are shifted by -2.4% relative to free water, except bending mode frequency $\omega_2$ and its overtone $2\omega_2$, where the shift is -1.6%. An absorption mode due to the quantized center of mass motion of H$_2$O in the molecular cage of C$_{60}$, was observed at 110 cm$^{-1}$. The dipole moment of encapsulated water is 0.50 ± 0.05 D, approximately 4 times less than for free water and agrees with previous estimates.

The rotational and rovibrational spectra were fitted with a quantum mechanical model of a vibrating rotor in electrostatic field with dipolar and quadrupolar interactions. The quadrupolar interaction splits the $J \geq 1$ rotational states of H$_2$O. The source of quadrupolar interaction is the relative orientation of electron-rich chemical bonds relative to pentagonal and hexagonal motifs of C$_{60}$ and its 12 nearest neighbours. Further IR study by using pressure to change the ratio of P- and H-oriented motifs would provide more information on the quadrupolar crystal fields of these motifs. The finite oscillator strength of the fundamental vibrational transitions is attributed to a finite electric field at the centres of the C$_{60}$ cages due to merohedral disorder, as has been postulated in different contexts. Our results are consistent with an internal electric field of $10^8$ Vm$^{-1}$. However, it is also plausible that the fundamental vibrational transitions gain intensity through the translation-rotation coupling from the dipole moment induced by the translational motion, something that can be addressed in further theoretical studies.

To conclude, H$_2$O in the molecular cavity of C$_{60}$ behaves as a vibrating asymmetric top, its dipole moment is reduced, and the translational motion is quantized. The splitting of rotational levels is caused by the quadrupolar interaction with the crystal field of solid C$_{60}$. Evidence is found for the existence of a finite electric field at the centres of the C$_{60}$ cages in the water-endofullerene, due to merohedral disorder.

Two out of three components necessary for a rigorous, comprehensive description of the water translations, rotations and vibrations inside C$_{60}$ molecular cage are now in place: firstly, the infrared spectroscopy data reported here and secondly, the 9-dimensional quantum bound-state methodology plus the theory of symmetry breaking in solid C$_{60}$. What is missing is a high-quality ab initio 9-dimensional potential energy surface for this system.
ACKNOWLEDGMENTS

We thank Prof. Zlatko Bačić for useful discussions. This research was supported by the Estonian Ministry of Education and Research institutional research funding IUT23-3, personal research funding PRG736, and the European Regional Development Fund project TK134. We thank EPSRC (UK), grant numbers EP/P009980/1 and EP/T004320/1, for support.

Appendix A: Interaction of dipole moment with local electric field

The dipole moment in spherical components is

\[ \mu_{\pm 1} = \pm \frac{1}{\sqrt{2}}(\mu_x + i \mu_y), \]
\[ \mu_{0} = \mu_z. \]  

(A1)

The dipole moment of water in the Cartesian molecule coordinate frame, as shown in Fig. 1 is \( \mu^M = \{-\mu_x, 0, 0\} \), where we use a convention that the dipole moment is directed from the negative charge to the positive charge. Then, from Eq. (A1) the dipole moment in spherical components is

\[ \{ \mu^M_m \} = \frac{\mu_z}{\sqrt{2}} \{-1, 0, 1\}, \quad m = -1, 0, +1. \]  

(A2)

We consider the coupling of H2O dipole moment to the local electric field, \( \mathcal{E} \), with spherical coordinates \( \{ \mathcal{E}, \phi_E, \theta_E \} \) in the crystal frame \( C \) (frame where the electric field gradient tensor is defined) and in the coordinate frame \( E \) of electric field \( \{ E^E_x, E^E_y, E^E_z \} = \mathcal{E}(0,0,0) \), i.e. along \( z_E \) axis. Corresponding Euler angles are \( \Omega_{C \rightarrow E} = \{ \phi_E, \theta_E, 0 \} \) and \( \Omega_{E \rightarrow C} = \{ \pi, \theta_E, -\pi - \phi_E \} \). The dipole moment of the molecule in the frame \( E \) is

\[ \mu^E_m = \sum_{m' = -1}^1 \left[ D^E_{mm'}(\Omega_{E \rightarrow C}) \right]^* \mu^C_{m'}. \]  

(A3)

Here we used Wigner D-functions relating the components of a spherical rank \( j \) irreducible tensor \( T_{jm} \) in coordinate frames \( A \) and \( B \):

\[ T^B_{jm} = \sum_{m' = -j}^j D^j_{jm'}(\Omega_{A \rightarrow B}) T^A_{jm'}, \]

(A4)

and

\[ T^A_{jm} = \sum_{m' = -j}^j \left[ D^j_{mm'}(\Omega_{A \rightarrow B}) \right]^* T^B_{jm'}, \]  

(A5)

where \( \Omega_{A \rightarrow B} = \{ \phi, \theta, \chi \} \) are Euler angles transforming coordinate frame \( A \) into frame \( B \). The angles for the inverse transformation are \( \Omega_{B \rightarrow A} = \{ \pi - \chi, \theta, -\pi - \phi \} \).

The interaction of molecular dipole moment \( \mu^M_m \) with electric field is

\[ \mathcal{H}_{ed} = - \sum_{m = -1}^1 (-1)^m e^E_m \mu^E_m \]
\[ = - \sum_{m = -1}^1 (-1)^m e^E_m \left[ \sum_{m' = -1}^1 \left[ D^1_{mm'}(\Omega_{E \rightarrow C}) \right]^* \mu^C_{m'} \right] \]
\[ = - \sum_{m, m' = -1}^1 (-1)^m e^E_m \left[ D^1_{mm'}(\Omega_{E \rightarrow C}) \right]^* \mu^C_{m'}, \]

\[ \times \left[ \sum_{m'' = -1}^1 \left[ D^1_{m''m}(\Omega_{C \rightarrow M}) \right]^* \mu^M_{m''} \right]. \]

The minus sign in front of sum in the formula above is consistent with \( \mathcal{H}_{ed} = - \mathbf{e} \cdot \mathbf{\mu} \) if the spherical components of vectors \( \mathbf{e} \) and \( \mathbf{\mu} \) are defined as in (A1).

Appendix B: Interaction of dipole moment with electric field of radiation

Here we derive the electric dipole transition matrix elements of a molecule, part (21) of absorption cross section (20). The derivation of (21) starts from

\[ S_{fi} = \frac{1}{e^2} \left| \langle f | \mathcal{H}_{ed} | i \rangle \right|^2, \]  

(B1)

and

\[ \mathcal{H}_{ed} = - \sum_{m = -1}^1 (-1)^m e^A_m \mu^A_m, \]  

(B2)

where the electric field of radiation, \( e = \{ e^A_m \} \) and the dipole moment of a molecule, \( \mu^A_m \), are in the space-fixed frame \( A \); \( e^2 = \sum_{m = -1}^1 (e^A_m)^2 \).

The Euler angles of transformation of crystal frame \( C \) to space-fixed frame \( A \) and vice versa are \( \Omega_{C \rightarrow A} = \{ \phi_R, \theta_R, 0 \} \) and \( \Omega_{A \rightarrow C} = \{ \pi, \theta_E, -\pi - \phi_E \} \).

The dipole moment in frame \( A \) is

\[ \mu^A_m = \sum_{m' = -1}^1 \left[ D^1_{mm'}(\Omega_{A \rightarrow C}) \right]^* \mu^C_{m'}, \]  

(B3)

where \( \mu^C_m \) is the dipole moment in the crystal frame \( C \).
The absolute value of matrix element squared is

$$S_{ji} =
= e^{-2} \left| \langle j | \sum_{m=-1}^{1} (-1)^m e^{-m} \mu_A^m | i \rangle \right|^2
= e^{-2} \left| \sum_{m,m'=1}^{1} (-1)^m \mu^C_{m'} | j \rangle \langle i \rangle \right|^2
= e^{-2} \sum_{m,m'=1}^{1} (-1)^m \mu^C_{m'} \left[ D^A_{m-m} \right]^{*} \langle j | \mu_C^m | i \rangle}
\times \left[ D^A_{m'-m} \right] \Omega_{A-C}
\times \langle j | \mu_C^{m'} | i \rangle \langle j | \mu_C^m | i \rangle.
$$

(B4)

1. Random orientation of crystals

We assume all the crystals are identical and there are no other static fields outside the crystal what could brake the directional isotropy. We average over the random orientation of crystal coordinate frames with respect to the space-fixed frame, $\Omega_{A-C}$, and get:

$$\langle S_{ji} \rangle_{\Omega_{A-C}} =
\frac{1}{3} e^{-2} \sum_{m,m'=1}^{1} \left| \langle j | \mu_C^m | i \rangle \right|^2
= \frac{1}{3} e^{-2} \sum_{m=1}^{1} \left| \langle j | \mu_C^m | i \rangle \right|^2
= \frac{1}{3} \sum_{m=1}^{1} \left| \langle j | \mu_C^m | i \rangle \right|^2.
$$

(B5)

where we used a property of rotation matrices,

$$\int \left[ D^A_{m m} \right]^* D^A_{m' m'} \Omega_{A-C} \, d\Omega =
8\pi^2 \frac{1}{2j_1 + 1} \delta_{j_1 j_2} \delta_{m_1 m_2} \delta_{m'_1 m'_2},
$$

and

$$\int_{0}^{\pi} \sin \theta d\theta \int_{0}^{2\pi} d\phi_R \int_{0}^{2\pi} d\chi_R = 8\pi^2.
$$

(B6)

(B7)

If the sample is in the powder form then it follows from Eq. (B5) that the absorption is independent of light polarization.

2. Transition matrix element and separation of coordinates

The absorption of radiation by a molecule, Eq. (20), depends on the matrix elements of an electric dipole moment between the initial and final states,

$$\sum_{\sigma=-1}^{1} \left| \langle \Phi' | \mu_A^\sigma | \Phi \rangle \right|^2.
$$

(B8)

where $\mu_A^\sigma$ is the molecule dipole moment in the space-fixed coordinate frame. Molecule wavefunction consists of nuclear spin wavefunction $|I_m\rangle$, electron $|\Phi^e\rangle$ and electron spin wavefunction $|S_m\rangle$, vibration wavefunction $|\Phi^v\rangle$, and rotation wavefunction $|\Phi^r\rangle$.

$$|\Phi\rangle = |I_m\rangle |S_m\rangle |\Phi^e\rangle |\Phi^v\rangle |\Phi^r\rangle.
$$

(B9)

Using these separable wavefunctions the matrix element

$$\langle \Phi' | \mu_A^\sigma | \Phi \rangle = \langle \Phi' | I_{m'} \langle I_m | S'_{m'} \rangle S_m \rangle \langle S'_{m'} | \Phi^v \rangle \langle \Phi^v | \mu^M_{\sigma} | \Phi^e \rangle,
$$

(B10)

where

$$\mu^M_{\sigma} = \langle \Phi^v | \mu^M_{\sigma} | \Phi^v \rangle
$$

and we have taken into account that the electric dipole moment does not depend on nuclear and electron spin coordinates. Furthermore, if the energies of initial and final states of the transition are independent of spin projections $m$ and $m'$, the summation over initial and final states in the transition probability leads to degeneracy factors $g_I = 2I + 1$ and $g_S = 2S + 1$ in (20). The electron spin is zero in the ground electronic state of H$_2$O, thus $g_S = 1$. Degeneracy of $para$ molecules ($I = 0$) is $g_I^{(p)} = 1$ and $ortho$ molecules ($I = 1$) is $g_I^{(o)} = 3$.

If the electronic orbital does not change in the transition then (B8) is the molecule electric dipole moment in the ground electronic state $|\Phi^e\rangle$.

$$\mu^M_{\sigma} \equiv \langle \Phi^v | \mu^M_{\sigma} | \Phi^v \rangle.
$$

(B12)

For the rest of the discussion we use a shorthand notation $\mu^M_{\sigma}$ for the molecule dipole moment in the ground electronic state, $\mu^M_{\sigma}^{(eg)}$.

Using Cartesian coordinates the dipole moment in the ground vibrational state is

$$\mu^x = (000) |\mu^M_x | 000 \rangle.
$$

(B13)

In the quantum mechanical model of H$_2$O@C$_{60}$ what we used to fit the IR spectra we set the dipole moment equal to $\mu^x$ in three excited vibrational states $|100\rangle$, $|010\rangle$, and $|001\rangle$.

The vibrational transition dipole moments are

$$\mu^{(1)}_{01} = (100) |\mu^M_x | 000 \rangle,
$$

$$\mu^{(2)}_{02} = (010) |\mu^M_x | 000 \rangle,
$$

$$\mu^{(3)}_{03} = (001) |\mu^M_x | 000 \rangle.
$$

(B14)

The relation between spherical and Cartesian dipole moment components is given by Eq. (A1).
Appendix C: Fitting of synthetic spectra with quantum mechanical model and model parameter error estimation

We determined the Hamiltonian parameters and the dipole moments, parameter set \( a = \{a_1, \ldots, a_v, \ldots, a_M\} \), by finding the parameter set \( a_{\min} \) what gives the minimum value, \( \chi^2_{\min} \), of function

\[
\chi^2 = \sum_{i=1}^{N} [S(v_i) - f(v_i; a)]^2
\]

where \( S(v_i) \) is the synthetic spectrum, argument frequency \( v_i \), generated from the fit of the experimental spectra, and \( f(v_i; a) \) is the spectrum calculated from the model with \( M \) parameters \( a = \{a_1, \ldots, a_v, \ldots, a_M\} \); \( N \) is the number of points in the spectrum. The goal is to minimize \( \chi^2 \) over parameters \( a \). The result is \( \chi^2_{\min} \) and \( a_{\min} \).

Let’s define matrix

\[
F_{iv} = \frac{\partial f(v_i; a)}{\partial a_v}
\]

and dispersion matrix \( \bar{V} \), Eq. 12 in \( \text{(5)} \),

\[
V_{\mu \nu} = \sum_{i=1}^{N} F_{ii} F_{i\mu} \bar{V}_{\nu v}
\]

where \( \sigma^2 = \chi^2_{\min}/(N-M) \) and \( \bar{V}^{-1} \) is inverse matrix of \( \bar{V} \), \( \bar{V}^{-1} \bar{V} = 1 \).

The estimated variance of parameter \( a_v \) is

\[
\Delta a_v = \sqrt{\Theta_{VV}} = \sqrt{\chi^2_{\min}/(N-M)}.
\]

The correlation matrix \( \bar{C} \) is

\[
C_{\mu \nu} = \frac{\Theta_{\mu \nu}}{\sqrt{\Theta_{\nu \nu} \Theta_{\mu \mu}}}
\]

The element of \( \bar{F} \), Eq. \( \text{(2)} \), is

\[
F_{iv} = \frac{f(v_i; a_{\min} + \delta a_v) - f(v_i; a_{\min})}{\delta a_v}
\]

where \( a_{\min} \) minimizes \( \chi^2 \) and \( \delta a_v \) is a small variation of parameter \( a_v \).

We change the sum for an integral over \( v \) in \( \text{(1)} \),

\[
\chi^2 = \int_{v_{k1}}^{v_{k2}} A_k^2 [S(v) - f(v; a)]^2 dv
\]

where the experimental spectrum is available in several spectral ranges \( \{v_{k1}, v_{k2}\} \) indexed by \( k \). \( A_k \) is the weight factor for each spectral range \( k \). \( A_k \) is chosen so that the strongest lines for each range \( k \) are equal. The spectrum \( S(v) \) is calculated with constant linewidth using line areas and frequencies from the fits of the experimental spectra.

By inserting \( \text{(C7)} \) into \( \text{(C3)} \) and using continuum limit we get matrix \( \bar{V} \),

\[
V_{\mu \nu} = \frac{1}{\delta a_v} \int_{v_{k1}}^{v_{k2}} A_k^2 f(v; a_{\min}) dv
\]

We define the number of experimental points \( N \) as the number of lines fitted in the experimental spectra multiplied by two as each line has two parameters, area and frequency. We estimate the parameter error with Eq. \( \text{(C5)} \) using \( \text{(8)} \) and \( \text{(9)} \).

1. Y. Morinaka, F. Tanabe, M. Murata, Y. Murata, and K. Komatsu, “Rational synthesis, enrichment, and \(^{13}\)C NMR spectra of endohedral C\(_{60}\) and C\(_{70}\) encapsulating a helium atom,” Chem. Commun. 46, 4532–4534 (2010).
2. S. Bloodworth, G. Hoffman, M. C. Walkey, G. R. Bacanu, J. M. Herniman, M. H. Levitt, and R. J. Whitby, “Synthesis of Ar@C\(_{60}\) using molecular surgery,” Chem. Commun. 56, 10521–10524 (2020).
3. K. Komatsu, M. Murata, and Y. Murata, “Encapsulation of molecular hydrogen in fullerene C\(_{60}\) by organic synthesis,” Science 307, 238–240 (2005).
4. K. Kurotobi and Y. Murata, “A single molecule of water encapsulated in fullerene C\(_{60}\),” Science 333, 613–616 (2011).
5. A. Krachmalnicoff, R. Bounds, S. Mamone, S. Alom, M. Concistrè, B. Meier, K. Kouril, M. E. Light, M. R. Johnson, S. Rols, A. J. Horsewill, A. Shugai, U. Nagel, T. Rööm, M. Carravetta, M. H. Levitt, and R. J. Whitby, “The dipolar endofullerene H\(_2\)@C\(_{60}\),” Nat. Chem. 8, 953–957 (2016).
6. S. Bloodworth, G. Sitinova, S. Alom, S. Vidal, G. R. Bacanu, S. L. Elliott, M. E. Light, J. M. Herniman, G. J. Langley, M. H. Levitt, and R. J. Whitby, “First synthesis and characterization of ch\(_{13}\)@C\(_{60}\),” Angew. Chem. Int. Ed. 58, 1–7 (2019).
7. A. J. Horsewill, S. Rols, M. R. Johnson, Y. Murata, M. Murata, K. Komatsu, M. Carravetta, S. Mamone, M. H. Levitt, J. Y.-C. Chen, J. A. Johnson, X. Lei, and N. J. Turro, “Inelastic neutron scattering of a quantum translator-rotator encapsulated in a closed fullerene cage: Isotope effects and translation-rotation coupling in H\(_2\)@C\(_{60}\) and HD@C\(_{60}\),” Phys. Rev. B 82, 081410 (2010).
8. M. Ge, U. Nagel, D. Hüvonen, T. Rööm, S. Mamone, M. H. Levitt, M. Carravetta, Y. Murata, K. Komatsu, X. Lei, and N. J. Turro, “Infrared spectroscopy of endohedral HD and D\(_2\) in C\(_{60}\),” J. Chem. Phys. 135, 114511 (2011).
9. A. Krachmalnicoff, M. H. Levitt, and R. J. Whitby, “An optimised scalable synthesis of h\(_2\)@C\(_{60}\) and a new synthesis of h\(_2\)@C\(_{60}\),” Chem. Commun. 50, 13037–13040 (2014).
10. M. Mamone, M. Ge, D. Hüvonen, U. Nagel, A. Daquigny, F. Cuda, M. C. Grossel, Y. Murata, K. Komatsu, M. H. Levitt, T. Rööm, and M. Carravetta, “Rotor in a cage: Infrared spectroscopy of an endohedral hydrogen-fullerene complex,” J. Chem. Phys. 130, 081103 (2009).
11. C. Beduz, M. Carravetta, J. Y.-C. Chen, M. Concistrè, M. Denning, M. Frunzi, A. J. Horsewill, O. G. Johannessen, R. Lawler, X. Lei, M. H. Levitt, Y. Li, S. Mamone, Y. Murata, U. Nagel, T. Nishida, J. Ollivier, S. Rols, T. Rööm, R. Sarkar, N. J. Turro, and Y. Yang, “Quantum rotation of ortho and para-water encapsulated in a fullerene cage,” Proc. Nat. Acad. Sci. U. S. A. 109, 12894–12898 (2012).
12. M. Ge, U. Nagel, D. Hüvonen, T. Rööm, S. Mamone, M. H. Levitt, M. Carravetta, Y. Murata, K. Komatsu, J. Y.-C. Chen, and N. J. Turro, “Interaction potential and infrared absorption of endohedral H\(_2\) in C\(_{60}\),” J. Chem. Phys. 134, 054507 (2011).
13. A. J. Horsewill, K. S. Panesar, S. Rols, J. Ollivier, M. R. Johnson, M. Carravetta, S. Mamone, M. H. Levitt, Y. Murata, K. Komatsu, J. Y.-C. Chen,
"Inelastic neutron scattering investigations of the quantum molecular dynamics of a H_2 molecule entrapped inside a fullerene cage," Phys. Rev. B 85, 205440 (2012)

M. Xu, F. Sebastianelli, B. R. Gibbons, Z. Baicic, R. Lawler, and N. J. Turro, "Coupled translation-rotation eigenstates of H_2 in C_{60} and C_{70} on the spectroscopically optimized interaction potential: Effects of cage anisotropy on the energy level structure and assignments," J. Phys. Chem. A, 130, 224306 (2009)

M. Xu, F. Sebastianelli, Z. Baicic, R. Lawler, and N. J. Turro, "Quantum dynamics of coupled translational and rotational motions of H_2 inside C_{60}," J. Chem. Phys. 128, 011101 (2008)

P. M. Felker and Z. Baicic, "Communication: Quantum six-dimensional calculations of the coupled translation-rotation eigenstates of H_2O@C_{60}," J. Chem. Phys. 144, 201101 (2016), http://dx.doi.org/10.1063/1.4935180

B. Meier, B. Mamone, M. Conciestré, J. Alonso-Valdesueiro, A. Krachmalnicoff, R. J. Whitby, and M. H. Levitt, "Electrical detection of ortho-para conversion in fullerene-encapsulated water," Nat. Commun. 6, 8112 (2015)

B. Ensing, F. Costanzo, and P. L. Silvestrelli, "On the polarity of buckminsterfullerene with a water molecule inside," J. Phys. Chem. A 116, 12184–12188 (2012), http://pubs.acs.org/doi/10.1021/jp311161q

J. Ceponkus, P. Uvdal, and B. Nelandter, "The coupling between translation and rotation for monomeric water in noble gas matrices," J. Chem. Phys. 136, 244309 (2012)

M. E. Fajardo, S. Tam, and M. E. DeRose, "Matrix isolation spectroscopy of an incarcerated quantum rotor: The infrared spectroscopy, inelastic neutron scattering, and their nitroxide derivatives," J. Phys. Chem. Lett. 5, 224317 (2014), http://dx.doi.org/10.1021/jz4020697

A. I. Kolesnikov, G. F. Reiter, N. Choudhury, T. R. Prisk, E. Mannont, A. Poldesnyak, G. Ehlers, A. G. Scel, D. J. Wesolowski, and L. M. Anovitz, "Quantum tunneling of water in beryl: A new state of the water molecule," Phys. Rev. Lett. 116, 168702 (2016)

M. A. Belyanchikov, M. Savinov, Z. V. Bedran, P. Bednyakov, P. Proskotch, J. Proksela, V. A. Abalamov, J. Petzet, E. S. Zhukova, V. G. Thomas, A. Dudka, A. Zhugayevych, A. S. Prokhvorov, V. B. Anzin, R. K. Kremer, I. K. H. Fischer, P. Lunkenheimer, A. Loidl, E. Uykur, M. Dressel, and B. Gorshunov, "Dielectric ordering of water molecules arranged in a dipolar lattice," Nature Communications 11, 3927 (2020)

M. A. Belyanchikov, M. Savinov, Z. V. Bedran, P. Bednyakov, P. Proskotch, J. Proksela, V. A. Abalamov, J. Petzet, E. S. Zhukova, V. G. Thomas, A. Dudka, A. Zhugayevych, A. S. Prokhvorov, V. B. Anzin, R. K. Kremer, I. K. H. Fischer, P. Lunkenheimer, A. Loidl, E. Uykur, M. Dressel, and B. Gorshunov, "Dielectric ordering of water molecules arranged in a dipolar lattice," Nature Communications 11, 3927 (2020)

J. K. H. Fischer, P. Lunkenheimer, A. Loidl, E. Uykur, M. Dressel, and B. Meier, K. Kouřil, C. Bengs, H. Kouřilová, T. C. Barker, S. J. Elliott, A. Podlesnyak, G. Ehlers, A. G. Seel, D. J. Wesolowski, and L. M. Anovitz, "Anomalous splitting of the F_{1g}→3E_g vibrations in single-crystal C_{60} below the orientational-ordering transition," Phys. Rev. B 49, 7052–7055 (1994)

G. B. Alers, B. Goldberg, A. R. Kortan, R. C. Haddon, and F. A. Theil, "Existence of an orientational electric dipole response in C_{60} single crystals," Science 257, 511 (1992)

L. Abouaif-Marguin, A.-M. Vasserot, C. Pardanau, and X. Michaut, "Nuclear spin conversion of H_2O@C_{60} trapped in solid xenon at 4.2 K: A new assignment of ν1 vibrational lines," Chem. Phys. Lett. 480, 82–85 (2009)

S. Aoyagi, N. Hoshino, T. Akutagawa, Y. Sado, R. Kitaura, H. Shinohara, F. A. Theil, G. S. Shakurov, R. K. Kremer, E. V. Pestriakov, V. G. Thomas, D. A. Fursenko, O. G. Johannessen, X. Lei, Y. I, M. Denning, M. Carravetta, K. Goh, A. J. Horwill, R. J. Whitby, and M. H. Levitt, "Nuclear spin conversion of water inside fullerene cages detected by low-temperature nuclear magnetic resonance," J. Chem. Phys. 140, 194306 (2014)

R. N. Zare, Angular Momentum, Baker lecture series (John Wiley & Sons, Inc., 1988).

P. P. Bunker and P. Jensen, Molecular Symmetry and Spectroscopy, 2nd ed. (NRC of Canada, 1998) p. 747.

D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, Quantum Theory of Angular Momentum (World Scientific, 1988).

E. W. Weissstein, "Wigner D-Function," MathWorld–A Wolfram Resource.

C. Cohen-Tannoudji, B. Diu, and F. Laloe, Quantum Mechanics (John Wiley & Sons, 2005).

J. Verhoeven and A. Dymanus, "Magnetic properties and molecular quadrupole tensor of the water molecule by beam-maser Zeeman spectroscopy," J. Chem. Phys. 52, 3222–3233 (1970) https://doi.org/10.1063/1.1673462

S. L. Altman and P. Herzig, Point-Group Theory Tables, 2nd ed. (Wien, 2011).

W. H. Shaffer, "Degenerate modes of vibration and perturbations in polyatomic molecules," Rev. Mod. Phys. 16, 245–259 (1944).

D. L. Dexter, "Absorption of light by atoms in solids," Phys. Rev. 101, 48–55 (1956)

S. Aoyagi, N. Hoshino, A. Katakagawa, Y. Sado, R. Kitaura, H. Shinohara, K. Sugimoto, R. Zhang, and Y. Murata, "A cubic dipole lattice of water molecules trapped inside carbon cages," Chem. Commun. 50, 524–526 (2014)

J. Tennyson, N. F. Zobov, R. Williamson, O. L. Polanskyf, and P. F. Bernath, "Experimental energy levels of the water molecule," J. Phys. Chem. Ref. Data 30, 735 (2001).

L. Rothman, R. G. Palumbo, R. Tipping, C. Rinsland, M. Smith, D. Benner, V. Devi, J.-M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S. Massie, L. Brown, and R. Toth, "The HITRAN molecular database: Editions of 1991 and 1992," J. Quant. Spectrosc. Radiat. Transfer 48, 469 – 507 (1992) special Issue Conference on Molecular Spectroscopic Databases.

A. S. Aoyagi, N. Hoshino, A. Katakagawa, Y. Sado, R. Kitaura, H. Shinohara, K. Sugimoto, R. Zhang, and Y. Murata, "A cubic dipole lattice of water molecules trapped inside carbon cages," Chem. Commun. 50, 524–526 (2014)
54. R. A. Toth, “Strengths and air-broadened widths of H$_2$O lines in the 2950–3400 cm$^{-1}$ region,” J. Quant. Spectrosc. Radiat. Transfer 13, 1127–1142 (1973).
55. P. M. Felker and Z. Bačić, “Flexible water molecule in C$_{60}$: Intramolecular vibrational frequencies and translation-rotation eigenstates from fully coupled nine-dimensional quantum calculations with small basis sets,” J. Chem. Phys. 152, 014108 (2020), https://doi.org/10.1063/1.5138992.
56. A. Varadwaj and P. R. Varadwaj, “Can a single molecule of water be completely isolated within the subnano-space inside the fullerene C$_{60}$ cage: a quantum chemical prospective,” Chem. Eur. J. 18, 15345–15360 (2012).
57. A. B. Farimani, Y. Wu, and N. R. Aluru, “Rotational motion of a single water molecule in a buckyball,” Phys. Chem. Chem. Phys. 15, 17993–18000 (2013).
58. H. Friedmann and S. Kimel, “Theory of shifts of vibration—rotation lines of diatomic molecules in noble-gas matrices. intermolecular forces in crystals,” J. Chem. Phys. 43, 3925–3939 (1965).
59. M. Xu, F. Sebastianelli, Z. Bačić, R. Lawler, and N. J. Turro, “H$_2$, HD, and D$_2$ inside C$_{60}$: Coupled translation-rotation eigenstates of the endohedral molecules from quantum five-dimensional calculations,” J. Chem. Phys. 129, 064313 (2008).
60. S. A. Clough, Y. Beers, G. P. Klein, and L. S. Rothman, “Dipole moment of water from stark measurements of H$_2$O, HDO, and D$_2$O,” J. Chem. Phys. 59, 2254–2259 (1973).
61. C. Camy-Peyret and J.-M. Flaud, “Line positions and intensities in the $\nu_2$ band of H$_{16}^{17}$O,” Mol. Phys. 32, 523–537 (1976).
62. C. Ramachandran and N. Sathyamurthy, “Water clusters in a confined non-polar environment,” Chem. Phys. Lett. 410, 348 – 351 (2005).
63. K. Yagi and D. Watanabe, “Infrared spectra of water molecule encapsulated inside fullerene studied by instantaneous vibrational analysis,” Int. J. Quantum Chem. 109, 2080 (2009).
64. P. A. Heiney, “Structure, dynamics and ordering transition of solid C$_{60}$,” J. Phys. Chem. Solids 53, 1333–1352 (1992).
65. B. Sundqvist, “Fullerenes under high pressures,” Adv. Phys. 48, 1–134 (1999).
66. D. L. Albritton, A. L. Schmeltekopf, and R. N. Zare, “Molecular spectroscopy: modern research,” (Academic Press, Inc., New York, 1976) Chap. An introduction to the least-square fitting of spectroscopic data, pp. 1–67.