Hydrogen is one of the few molecules that has been incarcerated in the molecular cage of C\textsubscript{60} to form the endohedral supramolecular complex H\textsubscript{2}@C\textsubscript{60}. In this confinement, hydrogen acquires new properties. Its translation motion, within the C\textsubscript{60} cavity, becomes quantized, is correlated with its rotation and breaks inversion symmetry that induces infrared (IR) activity of H\textsubscript{2}. We apply IR spectroscopy to study the dynamics of hydrogen isotopologues H\textsubscript{2}, D\textsubscript{2} and HD incarcerated in C\textsubscript{60}. The translation and rotation modes appear as side bands to the hydrogen vibration mode in the mid-IR part of the absorption spectrum. Because of the large mass difference of hydrogen and C\textsubscript{60} and the high symmetry of C\textsubscript{60} the problem is almost identical to a vibrating rotor moving in a three-dimensional spherical potential. We derive potential, rotation, vibration and dipole moment parameters from the analysis of the IR 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. We compare the predicted energies and the low-temperature IR absorption spectra of H₂@C₇₀.

1. Introduction

A small cavity inside the fullerene cage is a potential site for trapping atoms and has attracted the 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 been expanding. Endohedral fullerenes with noble gas (He and Ne [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 [8] when he made the first open-cage fullerene with an orifice large enough to load it with ³He or H₂ using less extreme temperature and pressure [9]. Soon Murata et al. [10] synthesized another open-cage derivative of C₆₀ and achieved 100% yield in filling with H₂. Subsequently, the generation of a closed-cage H₂@C₆₀ was observed in the process of matrix-assisted laser desorption/ionization time-of-flight mass spectrometry analysis of this open-cage complex. Chemical methods were developed to close open-cage fullerenes and H₂@C₆₀ was produced in milligram quantities [11,12]. To accommodate two hydrogen molecules a cavity larger than C₆₀ was needed. Two H₂ were trapped in open-cage C₇₀ with a yield of 3:97 in favour of species with one H₂ per cage [13]. The restoration of the closed cage retains approximately the same ratio of (H₂)₂@C₇₀ to H₂@C₇₀ [14]. Molecules other than hydrogen trapped in open-cage fullerenes are carbon monoxide [15], water [16,17], ammonia [18] and methane [19]. Recently, Kurotobi & Murata [20] succeeded in closing one of them and making the first closed-cage endohedral complex with a trapped polar molecule, H₂O@C₆₀. 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].

To date, H₂@C₆₀ has been the most studied small-molecule endofullerene. The inhomogeneous distribution of interaction parameters is expected to be small, mainly because of the crystal field effects in solid H₂@C₆₀. The H₂@C₆₀ is a stable complex and can survive a short period of heating up to 500°C under vacuum [12]. These properties make H₂@C₆₀ 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 H₂@C₆₀ in organic solvents [22,23], and in the presence of paramagnetic relaxants [24,25]. NMR was used to follow the ortho–para conversion in H₂@C₆₀ in the presence of molecular oxygen at 77 K [26] or upon photoexcitation of a C₇₀ triplet state [27]. NMR study of micro-crystalline H₂@C₆₀ samples at cryogenic temperatures shows splitting of the J = 1 rotational state [28,29], 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].

An overview of the low-temperature NMR, INS and IR work on H₂@C₆₀ is given by Mamone et al. [31]. The first IR study of H₂@C₆₀ was limited to 6 K [32]. The translational and rotational transitions appeared as sidebands to the hydrogen molecule bond-stretching vibrational transition, v = 0 → 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 it possible to probe the hydrogen–C₆₀ interaction potential
in the ground $v = 0$ and first excited $v = 1$ vibrational states and a whole range of hydrogen isotopologues $\text{H}_2$, $\text{D}_2$ and HD were 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 are no Raman data on $\text{H}_2@\text{C}_{60}$, except a report on $\text{H}_2$ inside an open-cage fullerene [36].

In this paper, we will review the IR studies of hydrogen isotopologues in $\text{C}_{60}$ 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].

2. Theory

Quantum statistics plays an important role in the dihydrogen wave function 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 $\text{para}$- and $\text{ortho}$-$\text{H}_2$. The two proton spins ($I_p = \frac{1}{2}$) are in the antisymmetric $I = 0$ total nuclear spin state in $\text{para}$-$\text{H}_2$ and in the symmetric $I = 1$ state in $\text{ortho}$-$\text{H}_2$. Even rotational quantum numbers $J$ are allowed for $\text{para}$-$\text{H}_2$ and odd $J$ for $\text{ortho}$-$\text{H}_2$. The nucleus of 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 $D_2$ is either zero or two, $I = 0, 2$. This is called $\text{ortho}$-$\text{D}_2$, while $\text{para}$-$\text{D}_2$ has the total nuclear spin $J = 1$ and odd $J$ values.

The ground rotational state of a homonuclear diatomic molecule with the total nuclear spin $I = 1$ is the $J = 1$ state. This $J = 1$ rotational state is $118\text{ cm}^{-1}$ for $\text{H}_2$, and $58\text{ cm}^{-1}$ for $\text{D}_2$, above the rotational ground state $J = 0$ of even-$I$ species. A thermal transition $J = 1 \rightarrow 0$ must be accompanied by a change in the total nuclear spin of the molecule, a process of very low probability. The time constant of thermal relaxation between the $\text{ortho}$ and the $\text{para}$ manifolds is very long and the room temperature $\text{ortho}$–$\text{para}$ ratio is maintained even at cryogenic temperatures. The equilibrium distribution of $\text{H}_2$ nuclear spin isomers is $n_0/n_p = 3$ and of $\text{D}_2$ is $n_0/n_p = 2$ at room temperature. To change the total nuclear spin of a molecule the two nuclei must experience different magnetic fields. The $\text{ortho}$–$\text{para}$ conversion can be activated by using a paramagnetic centre as a source of the magnetic field gradient. The equilibrium $n_0/n_p = 1.0$ is reached at $77\text{ K}$ by dispersing $\text{H}_2@\text{C}_{60}$ on a zeolite surface and exposing it to molecular oxygen, which acts like a spin catalyst [38]. There are no $\text{ortho}$ and $\text{para}$ 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 $\text{H}_2$ has stimulated theoretical work in this direction. Theoretical investigations currently cover the calculations of rotation–translation energies of hydrogen isotopologues in $\text{C}_{60}$ [39,40] and $\text{H}_2$ in $\text{C}_{70}$ [41], and the stability of $\text{C}_{60}$ or $\text{C}_{70}$ with one or more incarcerated $\text{H}_2$ [42,43]. Empirical parameters of the Morse potential between $\text{H}$–$\text{H}$ and contact Dirac interaction between $\text{H}$–$\text{C}$ were adjusted [44], and the density-fitting local Møller–Plesset theory was tested [45] using the experimental $\text{H}_2$ vibrational frequency inside $\text{C}_{60}$. Classical molecular dynamics and density functional theory have been combined to reproduce accurately the NMR chemical shift of $^1\text{H}$ in $\text{H}_2@\text{C}_{60}$ [46].

Both the hydrogen molecule and fullerene have closed-shell electronic structures and therefore the interaction between them is the van der Waals interaction. This simplicity makes $\text{H}_2@\text{C}_{60}$ ideal for the studies of non-covalent bondings between $\text{H}_2$ and carbon nanosurfaces, the knowledge needed for the design of carbon-based hydrogen storage materials. The high icosahedral symmetry of the $\text{C}_{60}$ cavity is close to spherical; therefore, $\text{H}_2@\text{C}_{60}$ represents a textbook example of a body moving in a spherical potential well [47,48]. In addition, $\text{H}_2$ rotates around its centre of mass. $\text{H}_2$ is not spherical and therefore its interaction with the walls of the cavity depends on its orientation, which 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 in which 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$_2$C$_{84}$ [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, such as 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 a multi-line spectrum.

(a) 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 centre of mass is not moving and also 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$_{60}$. Besides the translational movement inside C$_{60}$ the hydrogen molecule has its internal degrees of freedom, vibration and rotation of two nuclei relative to its centre 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. [63] model the intermolecular potential as a sum of atom–atom potentials and expand it in spherical harmonics. They determined the radial part of the wave function with a discrete variable representation method. The radial part of the wave function in our approach is given by algebraic functions, which are solutions 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 $\mathbf{s} = (s, \Omega_s)$, $\Omega_s = (\theta_s, \phi_s)$, where $\mathbf{R}$ is the vector from the centre of the C$_{60}$ cage to the centre of mass of H$_2$ and $\mathbf{s}$ is the internuclear H–H vector. The centre of mass translational motion of H$_2$ is given by eigenfunctions of the isotropic three-dimensional harmonic oscillator [48, 64]

$$
\psi_{NLM_L}(R, \Omega) = \psi_{NL}^v(R) Y_{LM_L}^{\Omega}(\Omega),
$$

(2.1)

where $\psi_{NL}$ is the radial wave function and $Y_{LM_L}$ is the spherical harmonic. The size of the H$_2$ molecule depends on its vibrational state $|v\rangle$. Therefore both the bounding potential and $\psi_{NL}^v(R)$ 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 $L = N, N - 1, \ldots, 1$ or 0, depending on the parity of $N$, and the azimuthal quantum number is $M_L = -L, -L + 1, \ldots, L$. The rotational wave functions, defined by the rotational quantum numbers $J = 0, 1, \ldots$ and $M_J = -J, -J + 1, \ldots, J$, are given by the spherical harmonics $Y_{JM_J}(\theta, \phi)$.

We use bipolar spherical harmonics with overall spherical rank $\Lambda$ and component $M_A$

$$
F_{\Lambda M_A}^{IJ}(\Omega, \Omega_s) = \sum_{M_L, M_J} C_{LM_LJM_J}^{\Lambda M_A} Y_{LM_L}^{\Omega}(\Omega) Y_{JM_J}(\Omega_s),
$$

(2.2)
where $C$ are the Clebsch–Gordan coefficients [64]. Then the full wave function describing the motion of the H$_2$ molecule is

$$|v⟩_{NLAM} = ψ^v_{vl}(s)|ψ^v_{vNL}(R)|L^j_{AM} (Ω, Ω_v),$$

(2.3)

where $ψ^v_{vNL}(s) ≡ |v⟩$ is the vibrational wave function with the quantum number $v$.

The Hamiltonian $H$ 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 $v$,

$$H = ℏω_0(v + \frac{1}{2}) + BrI(I + 1),$$

(2.5)

$$B_r = B_r - α_v(v + \frac{1}{2}) - D_cJ(J + 1),$$

where $ω_0$ is the fundamental vibrational frequency, $α_v$ is the anharmonic correction and $D_c$ is the centrifugal correction to the rotational constant $B_c$ [65,66].

We start from the general expansion of the potential in multi-poles,

$$V(R, Ω, Ω_v) = \sum_{l, j, λ, m}^∞ v^l_j(λ)_{l, m}^λ(Ω, Ω_v),$$

(2.6)

and expand the radial part of potential $v^l_j(λ)_{l, m}^λ(R)$ in powers of $R$

$$v^l_j(λ)_{l, m}^λ(R) = \sum_n^∞ v^l_j(n)_{l, m}^λ R^n,$$

(2.7)

where $n ≥ l$ and the parities of $l$ and $n$ are the same.

$V(R, s)$ is a scalar and transforms under fully symmetric representation $A_8$ of the symmetry group $I_h$. The spherical harmonics $λ = 0, 6, 10, \ldots$ transform as $A_8$ of the symmetry group $I_h$ [67]. We use fully spherical approximation of the potential, $λ = 0$. Because $λ = 0$ and $λ = |l - j|, |l - j| + 1, \ldots, l + j$ it must be that $l = j$.

The total potential is

$$V = v^{000}_0 + (v^{002}_0 R^2 + v^{002}_0 R^4)F^{00}_0 + (v^{111}_0 R + v^{111}_0 R^3)F^{11}_0 + (v^{222}_0 R^2 + v^{222}_0 R^4)F^{22}_0,$$

(2.8)

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 $v^{111}_0$ and $v^{111}_0$ are zero for homonuclear diatomic molecules.

If we set the constant off-set $v^{000}_0 F^{00}_0$ to zero and write the perturbation part as

$$V' = v^{002}_0 R^2 F^{00}_0 + (v^{111}_0 R + v^{111}_0 R^3)F^{11}_0 + (v^{222}_0 R^2 + v^{222}_0 R^4)F^{22}_0,$$

(2.9)

and the isotropic harmonic term as $v^0 = v^{002}_0 R^2 F^{00}_0$, then the total Hamiltonian reads

$$H = ℏω_0(v + \frac{1}{2}) + ℏω_0^t(N + \frac{3}{2}),$$

(2.10)

The unperturbed Hamiltonian eigenvalues in the basis $|v⟩_{NLAM}$ are

$$E^0_{vNLAM} = ℏω_0^t(N + \frac{3}{2}),$$

(2.11)

where $ω_0^t = (√v^{002}_0 / (2πm))^1/2$ 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 three-dimensional spherical oscillator (table 1). The translation–rotation coupling term $v^{222}_0$ splits the energy of the $|v⟩_{NL}$ state into levels with different
\( \Lambda \), where \( \Lambda = | L - J|, | L - J| + 1, \ldots, L + J \). For example, the \( N = L = J = 1 \) state is split into three levels with different total angular momentum \( \Lambda = 0, 1, 2 \). The ordering of levels depends on the sign of \( \nu V^{222}_{00} \). The anharmonic correction to translation–rotation coupling is \( \nu V^{224}_{00} \). If isotropic anharmonic correction \( \nu V^{004}_{00} \) is positive, the distance between energy levels increases with \( N \) and this correction is different for the levels with same \( N \) but different \( L \). For example, for positive \( \nu V^{004}_{00} \) the \( N = 2, L = 0 \) level has higher energy than the \( N = 2, L = 2 \) level.

The length scale \( \nu = m \nu V^{002}_{00} / \hbar \) (dimension m\(^{-2}\)) of the radial part of a three-dimensional spherical oscillator wave function is related to the expectation value of the centre of mass amplitude in state \( | N \rangle \) as [47]

\[
\langle N | R^2 | N \rangle = \nu^{-2} \left( N + \frac{3}{2} \right) = \hbar \sqrt{\frac{2\pi}{m \nu V^{002}_{00}}} \left( N + \frac{3}{2} \right). \tag{2.12}
\]

Terms described by the translation–rotation coupling coefficients \( \nu V^{111}_{00} \) and \( \nu V^{113}_{00} \) do not appear in table 1 because the first-order correction to energies vanishes as the matrix element of \( F^{11}_{00} \) 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 centre of mass is on the cage centre) has the state \( J = 0, N = 1 \) (expectation value of HD centre of mass is off the cage centre) mixed in [34]. The effect is that HD is forced to rotate about its geometric centre instead of its centre of mass.

It was found by the five-dimensional quantum mechanical calculation that the rotational quantum number \( J \) is almost a good quantum number for the homonuclear H\(_2@C_{60}\) and D\(_2@C_{60}\) and not for the heteronuclear HD@C\(_{60}\) [40]. Indeed, \( \nu V^{22n}_{00} \) mixes states with different \( J \) for homonuclear species as well, but the effect is reduced compared with the effect of \( \nu V^{11n}_{00} \). 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.

| \( \nu N L A \) | \( \langle \nu N L A | \mathcal{H} - \nu \mathcal{H}^{\text{vib}-\text{rot}} | \nu N L A \rangle \) |
|---|---|
| 0000 | \( \hbar \nu \omega_v [\frac{1}{2} + \nu \Delta^{004}_v] \) |
| 1001 | \( \hbar \nu \omega_v [\frac{1}{2} + \nu \Delta^{004}_v] \) |
| 0111 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{7}{3} \nu \Delta^{004}_v] \) |
| 1110 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{7}{3} \nu \Delta^{004}_v + 10(\nu \Delta^{222}_v + \nu \Delta^{224}_v)] \) |
| 1111 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{7}{3} \nu \Delta^{004}_v - 5(\nu \Delta^{222}_v + \nu \Delta^{224}_v)] \) |
| 1112 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{7}{3} \nu \Delta^{004}_v + 1(\nu \Delta^{222}_v + \nu \Delta^{224}_v)] \) |
| 2111 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{7}{3} \nu \Delta^{004}_v + 5(\nu \Delta^{222}_v + \nu \Delta^{224}_v)] \) |
| 2112 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{7}{3} \nu \Delta^{004}_v - 5(\nu \Delta^{222}_v + \nu \Delta^{224}_v)] \) |
| 2113 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{7}{3} \nu \Delta^{004}_v + 10(\nu \Delta^{222}_v + \nu \Delta^{224}_v)] \) |
| 0200 | \( \hbar \nu \omega_v [\frac{1}{2} + 5\nu \Delta^{004}_v] \) |
| 0222 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{21}{5} \nu \Delta^{004}_v] \) |
| 1201 | \( \hbar \nu \omega_v [\frac{1}{2} + 5\nu \Delta^{004}_v] \) |
| 1221 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{21}{5} \nu \Delta^{004}_v + 7(\nu \Delta^{222}_v + \frac{9}{7} \nu \Delta^{224}_v)] \) |
| 1222 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{21}{5} \nu \Delta^{004}_v - 7(\nu \Delta^{222}_v + \frac{9}{7} \nu \Delta^{224}_v)] \) |
| 1223 | \( \hbar \nu \omega_v [\frac{1}{2} + \frac{21}{5} \nu \Delta^{004}_v + 2(\nu \Delta^{222}_v + \frac{9}{7} \nu \Delta^{224}_v)] \) |
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 \( M_A \). Therefore, it is practical to use a reduced basis and reduced matrix elements [68] which are independent of \( M_A \). This reduces the number of states by factor \( 2\Lambda + 1 \) for each \( \Lambda \).

(b) 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 quantum mechanical calculation [41] that shows that the lowest translational excitation in the \( z \)-direction is \( 54 \text{ cm}^{-1} \) and in the \( xy \) plane is \( 132 \text{ cm}^{-1} \), while in \( \text{C}_{60} \) it is \( 180 \text{ cm}^{-1} \) and isotropic [33]. We derive from the IR spectra (see below) that the \( xy \) plane excitation energy is \( 151 \text{ cm}^{-1} \), 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 \( 7 \text{ cm}^{-1} \), which is relatively small compared with the rotational energy \( 120 \text{ cm}^{-1} \) in this state [41].

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

The vibration–rotation energy

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

(2.13)

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 \( \nu \kappa \) [71]. For example, the three-fold degenerate \( J = 1 \) rotational state in \( I_h \) symmetry is split in \( D_{5h} \) symmetry and if \( \nu \kappa > 0 \) the \( J_z = 0 \) state is \( 3\nu \kappa \) below the twice degenerate \( J_z = \pm 1 \) rotational state.

The translational part is added to the vibration–rotation Hamiltonian, equation (2.13), and the total energy becomes

\[
E_{\text{vib-rot}} = \nu E_{\text{vib-rot}} + \hbar \omega_{xy} (n + 1) + \hbar \omega_z (n_z + \frac{1}{2}).
\]

(2.14)

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

We will show below that the frequencies of \( z \) and \( xy \) translational modes, \( \omega_z \) and \( \omega_{xy} \), can be determined from the experimental data even though the translation–rotation coupling is not known. We take 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 \( \Delta \ell = 0 \) transition from the \textit{para}-\( \text{H}_2 \) ground state leads to two excitation energies in the IR spectrum, first for the \( z \) mode and second for the \( xy \) mode

\[
E_{0,000,100}^0 - E_{0,000,000}^0 = \hbar \omega_0 + \omega_z^1 + (\omega_{xy}^1 - \omega_{xy}^0) + \frac{1}{2} (\omega_z^1 - \omega_z^0)
\]

(2.15)

and

\[
E_{0,011,000}^0 - E_{0,000,000}^0 = \hbar \omega_0 + \omega_{xy}^1 + (\omega_{xy}^1 - \omega_{xy}^0) + \frac{1}{2} (\omega_z^1 - \omega_z^0)
\]

(2.16)
The confinement of the endohedral H$_2$ introduces two differences when compared with 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 such as 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 a hydrogen molecule and C_{60}. Another approach was used by Ge et al. [33], who carried out a summation over 60 pair-wise induced dipole moments between H_{2} and carbon atoms. 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

\[
d_{v'v}(\mathbf{R}, \Omega_\lambda) = \frac{4\pi}{\sqrt{3}} \sum_{l,j,m} v' v A_{l,m_1}^{l'n} R_{l,m_2}^n F_{l,m_3}^j(\Omega, \Omega_\lambda) . \tag{2.18}
\]

This is similar to the expansion of the potential discussed above, except the dipole moment is a polar vector whereas 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 \( v' v A_{l,m_1}^{l'n} \) on \( \lambda, m_\lambda \), the \( m_\lambda = 0 \) component of the dipole moment reads

\[
d_{00}(\mathbf{R}, \Omega_\lambda) = \frac{4\pi}{\sqrt{3}} \sum_{l,j} A_{l0}^{n0} R_{l0}^n F_{l0}^j(\Omega, \Omega_\lambda) . \tag{2.19}
\]

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 \((l) \in \{01, 10, 12, 21, 23, \ldots\} \). If we restrict the expansion up to \( n = l = 1 \), we get

\[
d_{00}(\mathbf{R}, \Omega_\lambda) = \frac{4\pi}{\sqrt{3}} A_{01}^{01} R_{01}^0 F_{01}^{01} + \frac{4\pi}{\sqrt{3}} (A_{01}^{10} R_{01}^0 F_{10}^{10} + A_{11}^{12} F_{10}^{10}) R .
\]

\( A_{01}^{01} \) 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 \( A_{01}^{01} \) and \( A_{11}^{12} \) are allowed by symmetry for both homo- and hetero-nuclear diatomic molecules. The expansion coefficient \( A_{01}^{01} \) 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. \( A_{11}^{12} \) 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 equation (2.20) 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 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 \( |v_j n_j L_j \Lambda_j M_{\Lambda_j} \rangle \) is populated is

\[
p_i = n_k \frac{e^{-E_i/k_B T}}{\sum_j g_j e^{-E_j/k_B T}} , \tag{2.20}
\]

where \( E_j \) 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 an individual state \( |v_j n_j L_j \Lambda_j M_{\Lambda_j} \rangle \), although the reduced basis \( |v NL \Lambda \rangle \) is used. Hetero-nuclear HD has no para or ortho species and the coefficient \( n_k \) in equation (2.20) must be set to one, \( n_k = 1 \).
Para- and ortho- states of H$_2$ at C$_{70}$

Figure 1. Boltzmann population of the H$_2@C_{70}$ para ground translational state (000) (solid line) and the first thermally excited (dotted line) state (001) and of the two ortho states A'$_2''$ (dashed line) and E'$_1$ (dashed-dotted line) in the ground translational state (000) calculated using energy levels of the five-dimensional quantum mechanical calculation [41] and equation (2.20) with $n_k = 1$; irreducible representations are from table 2. (Online version in colour.)

(d) 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 as $A''_2$ and $E'_1$ irreducible representations of $D_{5h}$. At low temperature the symmetry-allowed transitions from the ground para state are $A'_1 \xrightarrow{d_0} A''_2$ and $A'_1 \xrightarrow{d_{\pm 1}} E'_1$. Two ortho states, $A''_2$ and $E'_1$, are populated at low temperature (figure 1). The transitions are $A''_2 \xrightarrow{d_0} A'_1$ and $A''_2 \xrightarrow{d_{\pm 1}} E''_1$. The symmetry-allowed transitions from the $E'_1$ state are $E'_1 \xrightarrow{d_0} E''_1$ and $E'_1 \xrightarrow{d_{\pm 1}} A'_1, A''_2, E'_2$.

The IR absorption line area is proportional to the Boltzmann population of the initial state (equation (2.20)). The degeneracy $g_j$ of the energy level $E_j$ is one or two in the case of H$_2@C_{70}$. Figure 1 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) (dotted line) at 54 cm$^{-1}$ above the ground state becomes populated and drains the population from 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 (dashed line) to the doubly degenerate $E'_1$ (dashed-dotted line) 7 cm$^{-1}$ higher. The populations of the $A''_2$ and $E'_1$ states decrease above 30 K as the first excited translational (001) ortho state becomes more populated.

3. Experiment

The endohedral complexes were prepared by ‘molecular surgery’ as described in [11,12]; H$_2@C_{60}$, D$_2@C_{60}$ and H$_2@C_{70}$ at Kyoto University, Kyoto, Japan, and HD@C$_{60}$ at Kyoto University and Columbia University, New York, NY. The HD@C$_{60}$ sample was a mixture of the hydrogen isotopologues H$_2$ : HD : D$_2$ with the ratio 45 : 45 : 10. Since all C$_{60}$ cages are filled, the filling factor
for HD is \( \rho = 0.45 \). The content of the 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 the ortho–para conversion [26]. Briefly, the \( \text{H}_2@C_{60} \) adsorbed on the external surface of NaY zeolite was immersed in liquid oxygen at 77 K for 30 min, thereby converting the incarcerated \( \text{H}_2 \) spin isomers to the equilibrium distribution at 77 K, \( n_o/n_p = 1.0 \). The liquid oxygen was pumped away and the endofullerene–NaY complex was brought back rapidly to room temperature. The para-enriched \( \text{H}_2@C_{60} \) was extracted from the zeolite with CS$_2$ and the solvent was evaporated by argon. The powder sample under an argon atmosphere and on dry ice arrived at the National Institute of Chemical Physics and Biophysics, Tallinn, Estonia, 4 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. During 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 80 v with a halogen lamp and a HgCdTe or an InSb detector. The apodized resolution was typically 0.3 cm$^{-1}$ or better.

Transmission \( T_R(\omega) \) 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 \( \alpha(\omega) = -d^{-1} \ln[T_R(\omega)(1 - R)^{-2}] \), with the reflection coefficient \( R = [(\eta - 1)/(\eta + 1)]^2 \) calculated assuming a frequency-independent index of refraction [85], \( \eta = 2 \). Absorption spectra were cut into shorter pieces around groups of \( \text{H}_2 \) lines and a baseline correction was performed before fitting the \( \text{H}_2 \) lines with Gaussians.

4. Results and discussion

(a) \( \text{H}_2, \text{D}_2 \) and HD in \( \text{C}_{60} \)

The IR absorption spectra of \( \text{H}_2@C_{60} \) at 6 K together with the simulated spectra are shown in figure 2 and the diagram of the energy levels involved is shown in figure 3a. The simulated spectra are calculated using Hamiltonian, dipole moment and the ortho–para ratio parameters (table 3) 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]. The intensity of three lines, \( Q(0)^0 \) and \( Q(1)^1 \) in figure 2a and \( S(1)^3 \) in figure 2c, cannot 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 intensity of the ortho state \( N = J = 1 \) into \( \Lambda = 0, 1 \) and 2 by translation–rotation coupling is seen in figure 2b. 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 \( \Delta \Lambda \leq \pm 1 \) only one para and one ortho \( S \)-transition is IR active.

The intensity of other lines in figure 2b–d is described accurately by two dipole moment parameters, \( A^{101} \) and \( A^{121} \), and the ortho–para ratio \( n_o/n_p = 2.89 \pm 0.045 \), which is very close to the statistical value three (table 3). We confirmed the assignment of spectral lines to para- and ortho-\( \text{H}_2 \) by measuring the spectrum of a para-enriched \( \text{H}_2@C_{60} \) sample [33]. Low-temperature spectra in the region of \( Q \) lines are shown in figure 4. The time delay between para enrichment and the first IR measurement was 4 days. The 4255 cm$^{-1}$ para line is stronger and the other three ortho lines are weaker than the para-enriched sample than in the non-enriched sample.

Figure 4 deserves some attention. Lines \( Q(0)^1 \) and \( Q(1)^0 \) have a clear multi-component structure and it is different for the two samples. This is not possible in the approximation of spherical symmetry—not even by considering the true icosahedral symmetry of \( \text{C}_{60} \) 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 only have \( \Lambda = 0, 1 \). Later measurements
Table 3. Values of the fitted parameters for $\text{H}_2@\text{C}_{60}$ [33] and for HD and $\text{D}_2@\text{C}_{60}$ [34]. The vibrational and rotational constants of a free molecule of the three hydrogen isotopologues are shown for comparison; gas-phase $\omega_0$ is calculated including all terms $(v + \frac{1}{2})^k$ up to $k = 3$ [86]. The parameter $\alpha V^{224}_{00}$ is set to zero for HD@C$_{60}$ and D$_2$@C$_{60}$. Parameter errors are given in [34].

<table>
<thead>
<tr>
<th>$k_i$</th>
<th>$\text{H}<em>2@\text{C}</em>{60}$</th>
<th>HD@C$_{60}$</th>
<th>D$<em>2$@C$</em>{60}$</th>
<th>unit</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$v = 0$</td>
<td>$v = 1$</td>
<td>$v = 0$</td>
<td>$v = 1$</td>
</tr>
<tr>
<td>$V^{002}_{00}$</td>
<td>14.28</td>
<td>15.95</td>
<td>16.36</td>
<td>17.48</td>
</tr>
<tr>
<td>$V^{004}_{00}$</td>
<td>$2.21 \times 10^{21}$</td>
<td>$2.192 \times 10^{21}$</td>
<td>$1.88 \times 10^{21}$</td>
<td>$2.13 \times 10^{21}$</td>
</tr>
<tr>
<td>$V^{222}_{00}$</td>
<td>0.563</td>
<td>1.20</td>
<td>1.31</td>
<td>2.04</td>
</tr>
<tr>
<td>$V^{224}_{00}$</td>
<td>$2.21 \times 10^{20}$</td>
<td>$1.03 \times 10^{20}$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$V^{111}_{00}$</td>
<td>—</td>
<td>—</td>
<td>$3.11 \times 10^{-10}$</td>
<td>$3.25 \times 10^{-10}$</td>
</tr>
<tr>
<td>$V^{115}_{00}$</td>
<td>—</td>
<td>—</td>
<td>$4.3 \times 10^{10}$</td>
<td>$7.1 \times 10^{10}$</td>
</tr>
<tr>
<td>$n_o/n_p$</td>
<td>2.89</td>
<td>—</td>
<td>2</td>
<td>—</td>
</tr>
</tbody>
</table>

on the relaxed but initially para converted sample showed that the difference between the line shapes of the normal and para converted sample are 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 part of this splitting. Note that the Q(1)$^0$ line in D$_2$@C$_{60}$ (figure 5) bears a similar splitting pattern to that in H$_2$@C$_{60}$.

The D$_2$@C$_{60}$ spectrum (figure 5) is shifted to a lower frequency than that of H$_2$@C$_{60}$ because of the heavier mass of D$_2$. The spectrum has fewer lines than the H$_2$@C$_{60}$ spectrum. The missing transitions in D$_2$@C$_{60}$ (table 4) belong to the J-odd species, which are in the 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, $h^2\omega_0(\sqrt{5}/20)(V^{222}_{00}/V^{002}_{00})$ (table 1), is less in D$_2$ because $\omega_0$ is smaller, although $V^{002}_{00}$ and $V^{222}_{00}$ are similar for the two isotopologues (table 3). Line Q(1)$^2$ overlaps partially with the Q(0)$^1$ line (figure 5). However, this is not because the translation–rotation splitting is different for the two isotopologues but because of a smaller anharmonic correction $\alpha_\sigma$ of the rotational constant for D$_2$ (table 3).

The spectrum of HD@C$_{60}$ is more simple (figure 6) because there are no para and ortho species and therefore only one state is populated at low temperature. There is one spectral line, not present in homonuclear dihydrogen, labelled R(0) in figures 3b and 6. 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, first, because the weight of $JNL\Lambda = 1201$ is only 0.5 in this state [34] and, second, the change of translational state is $\Delta N = 2$, which is not allowed by any of the dipole operator components in our model. The next component in the final state is $JNL\Lambda = 2111$ with weight 0.29, which makes this transition $A^{121}$-active, $N = 0 \rightarrow 1, J = 0 \rightarrow 2$, and therefore it would be more appropriate to classify it as an S line.
Figure 2. IR absorption spectra of H$_2$@C$_{60}$ at 6 K are shown by the black line. The green line in (a) is the Gaussian fit of fundamental para and ortho transitions, $\Delta N = \Delta J = 0$. The red line in (b–d) is the simulated spectrum with parameters taken from the model fit of 200 K spectra [33]. The $S(1)^3$ labelled green line in (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 figure 3a; the superscript to the line label shows the final state $\Lambda$.

Another interesting feature of the HD spectrum is the absence of the $\Delta N = 0$, $\Delta J = 1$ (0000 $\rightarrow$ 1001) transition, although the induced dipole moment coefficient $A^{010}$ 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 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-temperature IR transitions of H$_2$, D$_2$ and HD@C$_{60}$ are collected in table 4. The content of the unperturbed $|JNL\Lambda\rangle$ state in the final state is above $|\xi|^2 = 0.9$ in homonuclear species in most cases, while for HD it varies and could be 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 $F^{22}_{00}$ mixes $L_j = L_i \pm 2$ and $J_j = J_i \pm 2$, which are even further
Figure 3. Diagrams of the observed low-temperature IR transitions in hydrogen isotopologues (a) $\text{H}_2$, $\text{D}_2$ and (b) HD incarcerated in $\text{C}_{60}$. 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 $\text{H}_2@\text{C}_{60}$ but not in $\text{D}_2@\text{C}_{60}$. The $S(1)$ line (dotted) with $\Delta N = 1$ is not observed in $\text{D}_2@\text{C}_{60}$. 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 $J$.

Figure 4. IR absorption spectra in the region of $Q$ lines of a $\text{para}$-enriched $\text{H}_2@\text{C}_{60}$ (dashed line) and non-enriched sample (solid line) at low temperature ($T$). The thermal equilibrium $\text{ortho}–\text{para}$ ratio at 77 K where the sample was $\text{para}$ enriched is $n_\text{o}/n_\text{p} = 1.0$. (Online version in colour.)
Figure 5. IR absorption spectra of D\textsubscript{2}@C\textsubscript{60} at 5 K. The simulated spectrum is shown by the red line (\textit{para}), the blue line (\textit{ortho}) and the thin black line (sum of \textit{para} and \textit{ortho} spectra). The parameters for the simulated spectrum are taken from the model fit of the 90 K spectrum \cite{34}. Line labels are the same as in figure 3a; superscript to the line label shows the final state $\Lambda$.

Table 4. Experimental IR absorption line parameters of endohedral dihydrogen isotopologues in C\textsubscript{60} at 5 K. $\omega$ is the transition frequency in wavenumber units, cm\textsuperscript{-1}, and $S$ is the integrated absorption line area in cm\textsuperscript{-2} units. JNL$\Lambda$ are the quantum numbers of the main component with the weight $|\xi|$\textsuperscript{2} in the final state $v = 1$. The $|\xi|$\textsuperscript{2} of the main component JNL$\Lambda$ in the initial $v = 0$ state for H\textsubscript{2} is 0.97 of 0000 and 0.97 of 1001, for D\textsubscript{2} is 0.99 of 0000 and 0.99 of 1001, and for HD is 0.95 of 0000. Integrated absorption cross-section $\sigma$ (unit: cm per molecule) is used by some authors, $\sigma = SV/\mathcal{N}$, where $\mathcal{N}$ is the number of hydrogen molecules in the volume $V$ \cite{87}; $\mathcal{N}/V = 1.48 \times 10^{21}$ cm\textsuperscript{-3} in solid C\textsubscript{60}.

| line label | $\omega$ | $S$ | $|\xi|^2$ | $\omega$ | $S$ | $|\xi|^2$ | $\omega$ | $S$ | $|\xi|^2$ | JNL$\Lambda$ |
|------------|--------|-----|-------|--------|-----|-------|--------|-----|-------|--------|
| Q(1)$^1$   | 4065.4 | 0.093 | 0.98  | —      | —   | —     | —      | —   | —     | 1001   |
| Q(0)$^0$   | 4071.4 | 0.011 | 0.98  | —      | —   | —     | —      | —   | —     | 0000   |
| Q(1)$^2$   | 4244.5 | 5.76  | 0.95  | 3045.1 | 0.98 | 0.97  | —      | —   | —     | 1111   |
| Q(0)$^1$   | 4250.7 | 19.3  | 0.94  | 3050.2 | 10.8 | 0.96  | —      | —   | —     | 1112   |
| Q(1)$^3$   | 4255.2 | 10.6  | 0.94  | 3050.2 | 10.8 | 0.96  | —      | —   | —     | 1111   |
| Q(0)$^0$   | 4261.0 | 8.86  | 0.94  | 3056.8 | 1.55 | 0.96  | —      | —   | —     | 1110   |
| R(0)$^1$   | —      | —     | 0.61  | —      | —   | 0.61  | —      | —   | —     | 1201   |
| S(0)$^1$   | 4592.0 | 3.08  | 0.94  | 3224.35| 1.66 | 0.96  | 3988.9 | 1.6  | 0.54  | 2111   |
| S(1)$^1$   | 4612.5 | 0.3   | 0.97  | —      | —   | 0.96  | —      | —   | 0.58  | 3003   |
| S(1)$^2$   | 4802.5 | 5.65  | 0.94  | —      | —   | 0.86  | —      | —   | 0.64  | 3112   |

\textsuperscript{a}It was not possible to separate overlapping Q(0)$^1$ and Q(1)$^2$ lines of D\textsubscript{2} and the line area given is the sum of both transitions.
Figure 6. IR absorption spectra of HD@C₆₀ at 5 K, black line. The parameters for the simulated spectrum (red dashed 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 figure 3b; superscript to the line label shows the final state Λ. (Online version in colour.)

from each other for small $N$. It was found by Xu et al. [41] that $J$ is almost a good quantum number in H₂ and D₂@C₆₀ but not in HD@C₆₀. Indeed, the distance between mixed states decreases for HD as $F_{10}^{11}$ 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 H₂ and D₂ (table 3). The relative change in 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 isotopologue [88]. Based on our fit results (table 3), for H₂ $\omega_0(\text{C}_60)/\omega_0(\text{gas}) = 0.9763$ and for HD $\omega_0(\text{C}_60)/\omega_0(\text{gas}) = 0.9773$. We used the average of these two ratios to calculate the D₂@C₆₀ fundamental vibrational frequency, $\omega_0 = 2924$ cm⁻¹, that 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 a change in the zero-point vibrational energy and how much is caused by the change of anharmonic corrections to the vibrational levels in the C₆₀ as our dataset is limited to energy differences of $v = 0$ and 1 levels only. Note that the vibrational frequency of H₂@C₆₀ is $\omega_0 = 4062.4$ cm⁻¹ (table 3), while the para vibrational transition is shifted up by 9 cm⁻¹, to $\omega_0 = 4071.4$ cm⁻¹ (table 4). This is because the zero-point translational energies are different in the $v = 0$ and 1 vibrational states [33].

The rotational constant $B_e$, the vibrational correction $\alpha_e$, and the centrifugal correction $D_e$ of the hydrogen inside C₆₀ and in free space are compared in table 3. 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 H₂@C₆₀ (D₂@C₆₀), 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 $\omega_0$ [89]. However, the anharmonic vibrational correction to the rotational constant, $\alpha_e$, is smaller inside the cage than in the gas phase. Here, the cage has the opposite, repulsive, effect and reduces the elongation of the proton–proton distance in the excited $v$ states when compared with H₂ in the free space. This is supported by the fact that within the error bars $\alpha_e$ of D₂@C₆₀ is equal to $\alpha_e$ of D₂. The vibrational amplitude of D₂ is less than that of the H₂ and therefore the repulsive effect of the cage becomes important at $v > 1$ for D₂.

Among the rotational and vibrational constants of HD@C₆₀ the centrifugal correction $D_e$ to the rotational constant is anomalously different from its gas-phase value compared with the other two isotopologues (table 3). Positive $D_e$ means that the faster the molecule rotates, the longer is the
and the 4219.9 cm\(^{-1}\) \(\Delta n_{1}\) spectra are the translational, ortho \(Q\) expect it to be much weaker than the para transition, ortho will be discussed below.

The transitions where \(\Delta n_{1} = 1\), \(\Delta J = 0\) [\(\Delta n_{1} = 1\), \(\Delta J = 0\)] and \(S_{1}(J) [S_{2}(J)]\) is the \(\Delta n_{2} = 1\), \(\Delta J = 2\) [\(\Delta n_{2} = 1\), \(\Delta J = 2\)] transition; \(J\) is the initial state rotational quantum number. Inset to (a) shows the pure vibrational ortho-\(\text{H}_2\) transition without the change of translational or rotational state.

bond. We speculate that, since the rotation centre 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 \(\text{H}_2\) in \(\text{C}_{60}\). There, \(\text{H}_2\) occupies the octahedral interstitial site in the \(\text{C}_{60}\) crystal. The prominent features in the exohedral \(\text{H}_2\) IR spectra [56] are the translational, \(\Delta N = \pm 1\), sidebands to the fundamental transitions, \(\Delta v = 1\) and \(\Delta v = 0, 2\). The redshift of the fundamental vibrational frequency is about 60 cm\(^{-1}\), which is less than in \(\text{H}_2@\text{C}_{60}\), where it is 98.8 cm\(^{-1}\). Also, the separation of the translational \(N = 0\) and 1 levels, approximately 120 cm\(^{-1}\), is less than that in \(\text{H}_2@\text{C}_{60}\), 184.4 cm\(^{-1}\). It is likely that the main contribution to the latter difference comes from the larger van der Waals volume available for \(\text{H}_2\) in the octahedral site than in the \(\text{C}_{60}\) cage.

(b) \(\text{H}_2@\text{C}_{70}\)

IR absorption spectra of \(\text{H}_2@\text{C}_{70}\) measured at 5 K are shown in figure 7, and the scheme of energy levels with the low-temperature transitions indicated with arrows is shown in figure 8.

The transitions where \(\Delta J = 0\) and the translational state changes by \(\Delta n_{1} = 1\) or \(\Delta n_{2} = 1\) are labelled as \(Q_{xy}(f)\) and \(Q_{z}(f)\), where \(f\) is the rotational quantum number of the initial state. The transitions where \(\Delta J = 2\) are labelled by \(S_{xy}(f)\) and \(S_{z}(f)\). The \(z\) and \(xy\) translational modes have distinctly different energies. For the \(Q\) lines they are shown in different panels (figure 7a,b). The \(\text{para}\) and ortho \(S\) lines are well separated because of different rotational energies. The \(\text{para}\) \(S\) lines are shown in figure 7c, whereas ortho \(S\) lines are shown in figure 7d. The \(Q\) lines cannot be sorted out into \(\text{para}\) and ortho that easily. An exception is the \(Q(1)\) transition, inset to figure 7a. This is a pure vibrational transition, \(v = 0 \rightarrow 1\), without the change of translational or rotational states. The corresponding (fundamental) \(\text{para}\) transition \(Q(0)\) would be at 4069.3 cm\(^{-1}\) according to the model (table 5). We expect it to be much weaker than the ortho \(Q(1)\) transition, as in \(\text{H}_2@\text{C}_{60}\), and for this reason it is not observed in the experiment.

In figure 9, we plot the normalized line area and normalized Boltzmann population. Figure 9a shows the temperature dependence of \(\text{para}\) lines. The assignment of the 4125.6 cm\(^{-1}\) line to \(Q_{z}(0)\) and the 4219.9 cm\(^{-1}\) line to \(Q_{xy}(0)\) is supported by our model, which is summarized in table 5 and will be discussed below.

The uniaxial symmetry of \(\text{C}_{70}\) splits the ortho ground state \(J = 1\). This splitting is about 7 cm\(^{-1}\) \(\approx 10\) K and creates a sharp temperature dependence of the ortho line intensity at low temperature as is shown in figure 1. This feature could be used to determine which of the \(Q\)
Figure 8. Energy levels and observed IR transitions of \( \text{H}_2@C_{70} \) from the ground \( \text{para} \) and \( \text{ortho} \) translational states in the \( v = 0 \) state to the excited vibrational state \( v = 1 \). The irreducible representations of the symmetry group \( D_{3h} \) (table 2) are given for a few lower states. The ordering of the states is based on \[41\]. \( \text{Ortho-H}_2 \) transitions marked by \( a \) and \( b \) are \( Q_{xy}(1)^a \) and \( Q_{z}(1)^b \) in table 5 and start from the thermally excited state, which is \( E'_1(000) \) according to Xu et al. \[41\]. There are three experimentally observed \( \text{ortho-H}_2 \) transitions from the ground \( A''_2(000) \) state: \( Q_{xy}(1), Q_{xy}(1)^c \) and \( Q_{xy}(1)^d \). Lines belong to the \( \text{ortho} \) species. Two lines, 4110.3 cm\(^{-1}\) and 4124.2 cm\(^{-1}\), have a temperature dependence consistent with the \( \text{ortho} \) transitions starting from the ground translational (000) state of \( E'_1 \) symmetry (figure 9c). 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 5). This might be due to our simplified model, where the rotational anisotropy parameter \( \nu \kappa \) is assumed equal in the \( v = 0 \) and 1 vibrational states. The rest of the \( \text{ortho} \) lines are shown in figure 9b. Several lines follow the same temperature dependence, the fundamental transition at 4063.2 cm\(^{-1}\), \( Q_{xy}(1) \) lines 4213.4, 4224.2 and 4227.2 cm\(^{-1}\) and the \( S_z(1) \) line at 4678.8 cm\(^{-1}\). Lines \( Q_z(1) \) at 4115.7 and \( S_{xy}(1) \) at 4761.3 cm\(^{-1}\) have distinctly different temperature dependence from 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 \( \text{ortho} \) lines behaves like the theoretical prediction (black line) so the possibility that the ground \( \text{ortho} \) 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 cm\(^{-1}\) above it. This temperature dependence is closer to the experimental situation than the solid black line, where \( 0 \kappa > 0 \). The change of sign of \( 0 \kappa \) affects the temperature dependence of intensities only a little if the transitions start from the thermally excited state, as shown in figure 9c, where the red dashed line is the normalized Boltzmann population of the \( A''_2 \) state if this state is 7 cm\(^{-1}\) above the ground state \( E'_1 \), i.e. if \( 0 \kappa < 0 \).
It is not unreasonable that $0 \kappa < 0$ and the $E_1^1$ ($J_z = \pm 1$) state is the ground rotational state of ortho-$H_2$. It requires that there is an attraction instead of repulsion between H and C when $H_2$ is in the centre of the C$_{70}$ cage. The attraction is stronger for the $H_2$ if its molecular axis is in the $xy$ plane, $J_z = \pm 1$, where the distance between H and C is less than if the axis is along the $z$ plane, $J_z = 0$, where the H–C distance is longer. Indeed, the attraction between C and H in H$_2$@C$_{60}$ was deduced from the redshift of vibrational energy and reduced rotational constant compared with $H_2$ in the gas phase [33]. However, it was found by five-dimensional quantum mechanical calculation that $A^1_2$ is the ground state [41]. A more elaborate model with dipole moment parameters that describe the IR line intensities together with the Boltzmann population could resolve the issue.

Table 5 summarizes the assignment of transitions observed in the experiment. Since our model described in §2b did not include translation–rotation coupling we used the transitions where both $L$ and $J$ are 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 ortho transition $Q(1)$; 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$_{60}$.

Table 5. IR transitions of H$_2$@C$_{60}$ observed at 5 K from the vibrational state $v = 0$ to the state $v = 1$. $\langle n_{l_z} \rangle$ are the quantum numbers for the initial and final states and the labels indicate corresponding transitions in figures 7 and 8. The experimental spectra were fitted with Gaussians, $S_{\text{exp}}$ is the experimental line area; the experimental line position $\omega_{\text{exp}}$ could always be determined with a precision better than 0.1 cm$^{-1}$. The model parameters, equation (2.14), were determined as described in the text by setting the model frequency $\omega_{\text{mod}}$ equal to the experimental frequency $\omega_{\text{exp}}$ for four lines indicated with error 0. The model parameters are vibrational frequency $\omega_0 = 4069.1$ cm$^{-1}$, one-dimensional oscillator frequency along the $z$-axis $\nu \omega_z = 56.5$ cm$^{-1}$, two-dimensional circular oscillator frequency $\nu \omega_{xy} = 150.9$ cm$^{-1}$ and the rotational anisotropy parameter $\nu \kappa = 3.1$ 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$_{60}$.

<table>
<thead>
<tr>
<th>frequency (cm$^{-1}$)</th>
<th>initial $v = 0$</th>
<th>final $v = 1$</th>
<th>error (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega_{\text{exp}}$</td>
<td>$\omega_{\text{mod}}$</td>
<td>$S_{\text{exp}}$ (cm$^{-2}$)</td>
<td>$J$</td>
</tr>
<tr>
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<td>0.146 ± 0.005</td>
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</tr>
<tr>
<td>4069.1</td>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
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<td>4110.3</td>
<td>0.311 ± 0.014</td>
<td>1</td>
</tr>
<tr>
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<td>4119.7</td>
<td>0.824 ± 0.009</td>
<td>1</td>
</tr>
<tr>
<td>4124.2</td>
<td>4119.7</td>
<td>0.045 ± 0.007</td>
<td>1</td>
</tr>
<tr>
<td>4125.6</td>
<td>4125.6</td>
<td>0.096 ± 0.007</td>
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</tr>
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</tr>
<tr>
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<td>4220.0</td>
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<td>0</td>
</tr>
<tr>
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<td>4214.1</td>
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<td>1</td>
</tr>
<tr>
<td>4227.2</td>
<td>4214.1</td>
<td>10.143 ± 0.067</td>
<td>1</td>
</tr>
<tr>
<td>4462.3</td>
<td>4456.3</td>
<td>0.570 ± 0.023</td>
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</tr>
<tr>
<td>4543.4</td>
<td>4550.7</td>
<td>0.582 ± 0.012</td>
<td>0</td>
</tr>
<tr>
<td>4678.8</td>
<td>4667.0</td>
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<tr>
<td>4761.3</td>
<td>4761.3</td>
<td>1.900 ± 0.019</td>
<td>1</td>
</tr>
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</table>

Table 5 summarizes the assignment of transitions observed in the experiment. Since our model described in §2b did not include translation–rotation coupling we used the transitions where both $L$ and $J$ are 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 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$^{-1}$ for H$_2$@C$_{60}$ were used. Next the two para transitions were matched, $Q_e(0)$ and $Q_{xy}(0)$, to obtain $\nu \omega_{xy} = 56.5$ cm$^{-1}$, $\nu \omega_{xy} = 150.9$ cm$^{-1}$. The 4220 cm$^{-1}$ line was chosen as $Q_{xy}(0)$ because its temperature dependence (figure 9a) is similar to the $S_e(0)$ and $S_{xy}(0)$ line temperature dependence. The ortho ground-state splitting is 9.4 cm$^{-1}$ (7.4 cm$^{-1}$ from the five-dimensional calculation [41]) with
Figure 9. Normalized line area and Boltzmann population of para and ortho transitions of H$_2$@C$_{70}$ starting from the ground translational state. (a) para lines; (b) and (c) 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 cm$^{-1}$ above $A''_{2}'$. This corresponds to $\nu \kappa > 0$, equation (2.13). Dashed line in (b) and (c) is the reverse situation when the ground state is doubly degenerate $E'_1$ and $A''_{2}'$ is 7 cm$^{-1}$ above it, i.e. $\nu \kappa < 0$. The normalized intensities are calculated using the translational energy levels from the five-dimensional quantum mechanical calculation [41] and equation (2.20).

$\nu \kappa = 3.1$ cm$^{-1}$, which was obtained by assuming that the $Q_z(1)^a$ transition, $(000)E'_1 \rightarrow (001)A'_1$ in figure 8, is centred at 4110.3 cm$^{-1}$. It was assumed that the anharmonic corrections to translational energy and to $\nu \kappa$ are same for the $v = 0$ and $v = 1$ vibrational states.

The variation in the experimental frequencies compared with the model frequencies is within ±10 cm$^{-1}$ (table 5). 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 should not be overinterpreted, because the correction owing to the difference in zero-point translational energies in two vibrational states was not taken into account for H$_2$@C$_{70}$, as 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 §2b.

5. Conclusions

IR absorption spectra of endohedral hydrogen isotopologues 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 with 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 centre 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 of the order of one wavenumber splitting of a few absorption
lines. Such small splitting is consistent with the NMR [28,29] and heat capacity [30] results.

C\(_{70}\) has an 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
five-dimensional quantum mechanical calculation [41] is in very good agreement with this
experimental result.

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