TITLE:
Interaction potential and infrared absorption of endohedral H-2 in C-60

AUTHOR(S):

CITATION:

ISSUE DATE:
2011-02

URL:
http://hdl.handle.net/2433/160657

RIGHT:
Copyright 2011 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. The following article appeared in JOURNAL OF CHEMICAL PHYSICS 134, 054507 (2011) and may be found at http://link.aip.org/link/?jcp/134/054507
Interaction potential and infrared absorption of endohedral H2 in C60

Min Ge, U. Nagel, D. Hüvonen, T. Rõõm, S. Mamone et al.

Citation: J. Chem. Phys. 134, 054507 (2011); doi: 10.1063/1.3535598
View online: http://dx.doi.org/10.1063/1.3535598
View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v134/i5
Published by the American Institute of Physics.

Additional information on J. Chem. Phys.
Journal Homepage: http://jcp.aip.org/
Journal Information: http://jcp.aip.org/about/about_the_journal
Top downloads: http://jcp.aip.org/features/most_downloaded
Information for Authors: http://jcp.aip.org/authors

Advertisement

Special Topic Section: PHYSICS OF CANCER
Why cancer? Why physics? View Articles Now
Interaction potential and infrared absorption of endohedral H$_2$ in C$_{60}$

Min Ge,¹ U. Nagel,¹ D. Hüvonen,¹ T. Rõõm,¹,a) S. Mamone,² M. H. Levitt,² M. Carravetta,² Y. Murata,³ K. Komatsu,³ J. Y.-C. Chen,⁴ and N. J. Turro⁴
¹National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia
²School of Chemistry, Southampton University, Southampton SO17 1BJ, United Kingdom
³Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan
⁴Department of Chemistry, Columbia University, New York, New York 10027, USA

We have measured the temperature dependence of the infrared spectra of a hydrogen molecule trapped inside a C$_{60}$ cage, H$_2$@C$_{60}$, in the temperature range from 6 to 300 K and analyzed the excitation spectrum by using a five-dimensional model of a vibrating rotor in a spherical potential. The electric dipole moment is induced by the translational motion of endohedral H$_2$ and gives rise to an infrared absorption process where one translational quantum is created or annihilated, $\Delta N = \pm 1$. Some fundamental transitions, $\Delta N = 0$, are observed as well. The rotation of endohedral H$_2$ is unhindered but coupled to the translational motion. The isotropic and translation–rotation coupling part of the potential are anharmonic and different in the ground and excited vibrational states of H$_2$. The vibrational frequency and the rotational constant of endohedral H$_2$ are smaller than those of H$_2$ in the gas phase. The assignment of lines to para- and ortho-H$_2$ is confirmed by measuring spectra of a para enriched sample of H$_2$@C$_{60}$ and is consistent with the earlier interpretation of the low temperature infrared spectra [Mamone et al., J. Chem. Phys. 130, 081103 (2009)]. © 2011 American Institute of Physics. [doi:10.1063/1.3535598]

I. INTRODUCTION

The advancement of “molecular surgery” has led to the breakthrough in experimental studies of hydrogen molecules trapped inside fullerene cages. This method¹–³ results in sample quantities of the order of 100 mg and has made possible nuclear magnetic resonance (NMR),⁴,⁵ infrared (IR),⁶ and inelastic neutron scattering (INS) (Refs. 7 and 8) spectroscopic investigations of the trapped H$_2$ dynamics and simulated theoretical investigations.⁹–¹² It has been established that H$_2$ inside a C$_{60}$ cage is an unhindered vibrating rotor performing translational motion in a nearly spherical potential well.¹³ Similar properties have been predicted theoretically for CO@C$_{60}$ with an additional strong mixing of translational and rotational motions due to the heteronuclear nature of the endohedral molecule.¹⁴ Another known endohedral diatomic rotor, C$_2$@Sc$_2$C$_{84}$, is two-dimensional and shows hindered rotation.¹⁵,¹⁶

The H$_2$@C$_{60}$ represents a system where the simplest molecule is encapsulated by a molecule with the highest symmetry. The vibrational, rotational, and translational levels of H$_2$ inside the cage are well separated because of the small mass of the hydrogen atom. The high icosahedral symmetry of the C$_{60}$ cavity is close to spherical. The local environment of H$_2$ has a negligible inhomogeneous distribution of parameters, and there is one H$_2$ per trapping site. The H$_2$@C$_{60}$ is a stable complex and can survive a short period of heating up to 500°C under vacuum.³ These properties make H$_2$@C$_{60}$ appealing for spectroscopic and theoretical investigations of interactions between the molecular hydrogen and curved nanosurfaces.

The complications that make the system interesting stem from the hydrogen molecule. First, because H$_2$ is not spherical, its interaction potential with C$_{60}$ depends on the orientation of its molecular axis relative to the inner surface of the C$_{60}$ cage,¹⁷ an interaction called translation–rotation coupling. 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.¹⁸ The translation–rotation coupling is measured as a splitting of absorption lines in the IR spectrum.⁹ Second, vibrational and translational motion amplitudes of H$_2$ are relatively large because of its small mass. This makes the potential for H$_2$ translational motion anharmonic and dependent on the vibrational state. Third, the symmetry relative to the interchange of two protons dictates that there are two forms of molecular hydrogen, called para- and ortho-H$_2$. The two proton spins ($I_p = 1/2$) are in the antisymmetric $I = 0$ total nuclear spin state in para-H$_2$ and in the symmetric $I = 1$ state in ortho-H$_2$. Even rotational quantum numbers $J$ are allowed for para-H$_2$ and odd $J$ for ortho-H$_2$. As a consequence the ortho-H$_2$ ground state is above the para-H$_2$ ground state by about 120 cm$^{-1}$, the energy difference between $J = 0$ and 1 rotational energy levels. At room temperature, the equilibrium distribution of H$_2$ spin isomers is $n_o/n_p = 3$. The time constant of thermal relaxation between the ortho and the para manifolds is very long. The relaxation process can be speeded up by using a spin catalyst. For H$_2$@C$_{60}$ it is feasible to reach the thermal equilibrium at liquid nitrogen temperature (77 K), $n_o/n_p = 1$, using liquid oxygen as a spin catalyst for ortho–para conversion.¹⁹,²⁰

①Electronic mail: toomas.room@kbfi.ee.
The IR spectrum of \( \text{H}_2@\text{C}_{60} \) at 6 K, presented and analyzed in Ref. 6, consists of sharp lines positioned between 4000 and 5000 cm\(^{-1}\). The initial and final states for the transitions are the vibrational ground state \( \nu = 0 \) and the excited state \( \nu = 1 \). The IR activity of \( \text{H}_2 \) is induced by the translational motion of \( \text{H}_2 \) relative to the \( \text{C}_{60} \) cage, giving rise to a selection rule \( \Delta N = \pm 1 \), where \( N \) is the translational quantum number. However, the transitions between \textit{para} and \textit{ortho} states are still forbidden, and from this a selection rule, \( \Delta J = 0, \pm 2 \) follows. The allowed transitions are shown with solid lines in Fig. 1. At low \( T \) only the \( \nu = 0, N = 0 \) state is populated and only transitions to the \( N = 1 \) translational state in the excited vibrational state are allowed by the selection rule \( \Delta N = \pm 1 \), shown with black solid lines in Fig. 1. The fundamental \( \Delta \nu = 1, \Delta N = 0 \) \textit{para} and \textit{ortho} absorption lines were detected too (dashed lines in Fig. 1), although 2 orders of magnitude weaker than \( \Delta N = 1 \) lines. This additional information, the frequencies of the fundamental lines, allowed the determination of the energy separation of \( N = 0 \) and \( N = 1 \) translational levels in the \( \nu = 1 \) state.

Based on the available data it has not been possible to separate the harmonic and the anharmonic parts of the bonding potential, experienced by \( \text{H}_2 \). The information about the potential in the ground \( \nu = 0 \) state is limited, too. The separation of \( N = 0 \) and \( N = 1 \) translational levels is known from the INS experiment.\(^8\) The translation–rotation splitting of the \( N = 1 \) translational state of \textit{ortho-}\( \text{H}_2@\text{C}_{60} \) has not been resolved in the ground vibrational state, likely because of the limited spectral resolution of INS.

In this paper we present and analyze the temperature dependence of IR spectra between 6 and 300 K. At elevated temperatures, levels up to \( N = 2 \) in the \( \nu = 0 \) state are sufficiently populated to give rise to detectable IR transitions to terminal states connected to the initial states by the selection rules \( \Delta \nu = 1, \Delta N = \pm 1, \) and \( \Delta J = 0, 2 \). From this spectral information, we have determined the potential, including translation–rotation coupling and anharmonic corrections, for both vibrational states \( \nu = 0 \) and \( \nu = 1 \). We have confirmed the assignment of spectral lines to \textit{ortho-} and \textit{para-}\( \text{H}_2 \) using an \textit{ortho-para} converted sample.

II. THEORY

The theoretical work of Olthof \textit{et al.}\(^{14}\) is a comprehensive description of the dynamics of a loosely bound \textit{molecule} inside \( \text{C}_{60} \). They calculated the dynamics and the IR spectra of \( \text{CO}@\text{C}_{60} \). The main differences between their approach and ours are the following. First, Olthof \textit{et al.} model the intermolecular potential as a sum of atom–atom potentials and expand it in spherical harmonics. We expand the confining potential in spherical harmonics as well but determine the expansion parameters by fitting the calculated IR spectra to our experimental data. The second difference is in the calculation of IR line intensities. The CO molecule has a permanent dipole moment, while in \( \text{H}_2@\text{C}_{60} \) the dipole moment is induced by the translational motion of \( \text{H}_2 \).

A. Five-dimensional spherically symmetric Hamiltonian of \( \text{H}_2@\text{C}_{60} \)

To describe the motion of \( \text{H}_2 \) inside \( \text{C}_{60} \) we use the following model. The \( \text{C}_{60} \) is considered to be rigid, its center of mass is not moving, and it does not rotate. We treat \( \text{H}_2@\text{C}_{60} \) as an isolated molecular complex and approximate the true icosahedral symmetry of an isolated \( \text{C}_{60} \) with spherical symmetry. It means that in this approximation \( \text{H}_2 \) moves in a rigid spherically symmetric bounding potential provided by the cavity of \( \text{C}_{60} \). Besides the translational movement inside \( \text{C}_{60} \), the \( \text{H}_2 \) molecule has its internal degrees of freedom, vibration and rotation of two protons relative to its center of mass. There are no coupling terms between \textit{ortho-}\( \text{H}_2 \) (\( J \) odd) and \textit{para-}\( \text{H}_2 \) (\( J \) even) states in our model Hamiltonian. Compared to our earlier work\(^6\) the model has been extended in few points. Here we include the centrifugal correction term \( D_h \) to the rotational constant \( B_h \) and add an anharmonic term \( \nu V_{124}^{224} \) to the anisotropic confining potential. The basis has been extended to \( N \leq 7 \) for both vibrational states, \( \nu = 0 \) and \( \nu = 1 \). A more detailed description of the model follows.

The position and orientation of the \( \text{H}_2 \) molecule are given by spherical coordinates \( \mathbf{R} = \{ R, \Omega, \Omega = \{ \Theta, \Phi \} \) and \( \mathbf{s} = \{ s, \Omega \} \), \( \Omega = \{ \Theta, \Phi \} \), where \( \mathbf{R} \) is the vector from the center of the \( \text{C}_{60} \) cage to the center of mass of \( \text{H}_2 \) and \( \mathbf{s} \) is the internuclear \( \text{H–H} \) vector, as shown in Fig. 2.
The Hamiltonian $\mathcal{H}$ for the trapped molecule includes coupling terms between vibrational, translational, and rotational motions. For simplicity, we neglect all matrix elements nondiagonal in $v$ and introduce a parametric dependence on $v$:

$$\mathcal{H} = v\mathcal{H}^{vib - rot} + \frac{p^2}{2m} + vV(R, \Omega, \Omega_s),$$

(4)

where $v\mathcal{H}^{vib - rot}$ is the vibration–rotation Hamiltonian, $p$ is the molecular momentum operator, and $m$ is the molecular mass of $H_2$. Here, $vV$ is the potential energy of the $H_2$ molecule in the vibrational state $\psi_{v}^{vib}(s)$. The vibration–rotation Hamiltonian $v\mathcal{H}^{vib - rot}$ is diagonal in the basis set $|v JNLAM\rangle$, with eigenvalues given by

$$vE_{j}^{vib - rot} = h\omega_0(v + 1/2) + Br(J + 1),$$

(5)

where $Br = B_r - \alpha_c(v + 1/2) - D_J(J + 1)$, $\omega_0$ is the fundamental vibration frequency, $\alpha_c$ is the anharmonic correction, and $D_J$ is the centrifugal correction to the rotational constant $B_r$.\textsuperscript{23,24}

The potential energy expanded in multipoles is

$$vV(R, \Omega, \Omega_s) = \sum_{n,l,j,s,J} v^{nlj} r^n F^{lj}_{n,s,J}(\Omega, \Omega_s),$$

(6)

where the functions $F$ are defined in Eq. (2) and $n$ takes even values. Translation–rotation coupling terms are terms with nonzero $l, j$. All odd-$j$ terms vanish for homonuclear diatomic molecules. For an icosahedral cavity, and assuming that longer-range intermolecular perturbations are negligible, all terms with odd $\lambda$ vanish, as well as the terms with $\lambda = 2$ and 4. We assume that all high-order terms starting from $\lambda = 6$ are small and express the potential energy as

$$vV = vV^0 + vV'.$$

The isotropic harmonic term is given by

$$vV^0 = vV_000^2 R^2 F_00^0,$$

where we have neglected the constant offset $vV_000F_00^0$. The perturbation $vV'$ consists of translation–rotation coupling $vV^{222}$ and anharmonic corrections $vV^{004}$ and $vV^{224}$ to both isotropic and anisotropic couplings,

$$vV' = (vV^{222} + vV^{004} R^4) F^{222} + vV^{004} R^4 F^{000}.$$

(7)

The unperturbed Hamiltonian eigenvalues in the basis $|v JNLAM\rangle$ are given by

$$E_{vJNLAM}^0 = vE_{j}^{vib - rot} + h\omega_0^T(N + 3/2),$$

(8)

where $\omega_0^T$ is the frequency for translational oscillations within the cavity,

$$\omega_0^T = \left(\frac{vV_002}{2\pi m}\right)^{1/2}.$$

(9)

B. Induced dipole moment and line intensities

Here we are interested in the dipole moment of the hydrogen–fullerene complex induced by the motion of the hydrogen molecule inside the fullerene cage. We derive the dependence of the induced dipole moment on translational coordinates $R = \{R, \Omega\}$ and rotational coordinates $\Omega_s = \{\theta, \phi\}$ of $H_2$ and relate the dipole moment to the IR absorption line area. The explicit dependence on $R$ is particularly useful as, first, the radial part of the translational wavefunction $\psi_{v}^{vib}(s)$ is different in vibrational states $v = 0$ and

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Coordinates to describe the H$_2$ dynamics and the induced dipole moment inside the C$_{60}$ cage. $C_i$ is the $i$th carbon atom with coordinates $R_i$ relative to the C$_{60}$ cage center. $r_i$ shows the position of the H$_2$ center of mass relative to $i$th carbon atom. $s$ gives the relative position of two protons and $R$ is the H$_2$ center of mass displacement from the C$_{60}$ cage center.}
\end{figure}
ν = 1, which are the initial and final states of IR transitions. Second, the initial state is not only the N = 0 state as was the case when the low T spectra were analyzed, but other states with N > 0 are thermally populated, too. To derive the induced dipole moment for H₂@C₆₀, we assume that it is the sum of dipole moments induced by pairwise interactions between H₂ and ith carbon atom.

An overview of collision induced dipoles in gases and gas mixtures is given in the book by Fromhold. The confinement of the endohedral H₂ introduces two differences as compared to H₂ in the gas. First, the translational energy of H₂ is quantized. In the gas phase it is a continuum starting from zero energy. Second, the variation of the distance between H₂ and the carbon atom is limited to the translational amplitude of H₂ 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 Δν = ±1 for the endohedral H₂ follows from these two conditions, as shown below. Quantum mechanical calculations of induced dipoles are available for simple binary systems like H₂–He, H₂–Ar, and H₂–H₂. An extensive set of theoretical results for the H₂–He system associated with the roto-translational electric dipole transitions, both in the vibrational ground state ν = 0 and accompanying the ν = 0 → 1 transition of the H₂ molecule, can be found in Refs. 26–30.

The dipole moment operator for H₂ and ith carbon atom can be expanded in spherical harmonics

\[ d_\nu(r_i, s) = \frac{4\pi}{\sqrt{3}} \sum_{l, j=0} B^{ij}_l(r_i, s) F_{lq}^{ij}(\Omega_i, \Omega_s). \]

(10)

where \( q = 0, \pm 1 \) denotes the spherical component of the dipole moment vector d and the spherical functions \( F_{lq}^{ij}(\Omega_i, \Omega_s) \) are described by Eq. (2). The position of ith carbon atom is defined by \( r_i = (r_i, \Omega_i) \), \( \Omega_i = (\theta_i, \phi_i) \), and the position of the center of mass of H₂ relative to the ith carbon atom by vector \( r_i = (r_i, \Omega_i, \Omega_s = \{\theta_s, \phi_s\} \), as shown in Fig. 2. The origin of coordinates of \( \mathbf{R} \), and \( \mathbf{R} \) is chosen in the geometric centroid of C₆₀. We introduce the dependence of dipole moment on the initial and the final vibrational states, \( d_\nu^{(1)}(r_i, s) \approx (\psi_{\nu}^{vb}(s) d_\nu(r_i, s) \psi_{\nu}^{vb}(s)) \). Using Eq. (10) and the vibrational part of wavefunctions (3) we get that the dependence of dipole moment on the proton–proton distance \( s \) is absorbed by the B term:

\[ B^{ij}_l(r_i, s) \approx (\psi_{\nu}^{vb}(s)) B^{ij}_l(r_i, s) \psi_{\nu}^{vb}(s)). \]

Since the dipole moment is a vector, there are restrictions on the allowed \( j \) and \( l \) values of the H₂–C pair: (i) \( j + l \) must be odd, (ii) \( j = \pm 1 \) from the triangle relation, and (iii) for homonuclear molecules only even \( j \) terms are allowed. We discuss here the first three terms, \( B^{10}_0 \), \( B^{12}_0 \), and \( B^{32}_0 \). \( B^{10}_0 \) corresponds to the induced dipole moment which is independent of the orientation of H₂ molecular axis. \( B^{32}_0 \) describes the exchange interaction induced dipole which depends on the H₂ molecular axis orientation. \( B^{32}_0 \) is the term describing the dipole moment induced on the “collision” partner by the quadrupolar moment of H₂ and is called the quadrupolar induction term. In the spherical approximation and in the first order of displacement of H₂ from the C₆₀ cage center, the quadrupolar induction term is zero (see below).

We expand the dipole moment \( d_\nu^{(1)}(r_i, s, \Omega_i) \) between the ith C atom and H₂ into a Taylor series in powers of \( \mathbf{R} \) at the center of C₆₀ and sum over all carbon atoms. The zero order term vanishes because \( \mathbf{R} = 0 \) is the center of inversion for H₂@C₆₀. We keep the first nonzero term which is linear in \( \mathbf{R} \):

\[ d^{(1)}_\nu^{(1)}(r_i, s, \Omega_i) = \frac{4\pi}{\sqrt{3}} \sum_{l, j} B^{ij}_l(r_i, s) F_{lq}^{ij}(\Omega_i, \Omega_s) \mathbf{R}. \]

(11)

where \( \nabla_r \) is the nabla operator in the spherical coordinates of \( r_i \). Instead of summation over carbon atoms, we integrate and assume that the distance from the cage center is the same for all carbon atoms, \( R_i \approx R_0 \). One can relate the result of integration to the expansion of the dipole moment in terms of spherical harmonics of angular coordinates \( \Omega_i, \Omega_s \):

\[ d^{(1)}_\nu^{(1)}(r_i, s, \Omega_i) \approx \frac{4\pi}{\sqrt{3}} \sum_{l, j} A^{ij}_l(r_i, s) F_{lq}^{ij}(\Omega_i, \Omega_s). \]

(12)

The nonzero coefficients are \( A^{10}_v \) and \( A^{12}_v \), where

\[ A^{ij}_v(r) = 20 R B^{ij}_v(R). \]

(13)

and we have used the notation

\[ B^{ij}_v[R] = \frac{\partial B^{ij}_v(r)}{\partial r} \bigg|_{r=R_0} + \frac{2}{R_0} B^{ij}_v(R_0). \]

(14)

The calculation shows that in the spherical approximation of C₆₀ and in the first order of \( \mathbf{R} \) the quadrupolar induction term \( A^{32}_v \) vanishes to zero. The selection rules for IR spectroscopy of H₂@C₆₀ follow from the angular and radial dependence of \( d^{(1)}_\nu^{(1)} \) [Eq. (12)]: \( \Delta \nu = \pm 1 \) and change of the total angular momentum is \( \Delta \lambda = 0 \), \( \pm 1 \) with \( \Delta \lambda = 0 \), \( \pm 2 \) and \( \Delta \lambda = \pm 1 \).

The absorption line area (unit m⁻²) in the limit that the linewidth is much smaller than the transition frequency \( \omega_{ij} \) is

\[ S(\omega_{ij}) = \frac{N \pi}{V \hbar c \epsilon_0} p_i \omega_{ij} \left| \langle f | \mathbf{d} | i \rangle \right|^2, \]

(15)

where \( \mathbf{d} = \mathbf{E}/E \) is the unit vector of light electric field, \( N/V = 1.48 \times 10^{27} \) m⁻³ is number density of molecules in solid C₆₀, \( c \) is the speed of light \( c_0 \) is the permittivity of vacuum, \( n \) is the index of refraction (in C₆₀ \( n = 2 \), Ref. 32), \( h \) is the reduced Planck constant, \( \omega_{ij} = (E_f - E_i)/(2\pi \hbar c) \) is the number of waves in one meter, where \( E_i, E_f \) is the energy of the initial state \( |i \rangle \) the final state \( |f \rangle \), \( p_i \) is the probability that the initial state is populated, and \( \mathbf{d} \) is the dipole moment (unit Cm).

The module of the matrix element for depolarized light and randomly oriented molecules is

\[ \langle |f | \mathbf{d} | i \rangle \rangle = \frac{1}{3} \sum_{\zeta=x', y', z'} \langle |f | \mathbf{d}_\zeta | i \rangle \rangle, \]

(16)

where \( \mathbf{d}_\zeta \) are the components of the dipole moment in the molecular frame \( (x', y', z') \). In the case of spherical symmetry all three terms in Eq. (16) are equal and we may write using the \( q = 0 \) component of the dipole moment (12),

\[ S(\omega_{ij}) = \frac{N \pi}{V \hbar c \epsilon_0} p_i \omega_{ij} \left| \langle f | d^{(1)}_\nu^{(1)}(\mathbf{R}) | i \rangle \right|^2. \]

(17)
C. Fitting of IR spectra

First the experimental IR absorption spectrum was fitted using Gaussian lineshapes to find the line areas, linewidths, and frequencies. A synthetic experimental spectrum \( y_\omega \), the distance between the points in the spectrum \( \omega_n - \omega_{n-1} = \Delta \omega / 4 \), was then generated consisting of lines with equal linewidths, \( \Delta \omega = 1 \) cm\(^{-1}\), while keeping the line areas and frequencies of the original experimental lines. The synthetic spectrum approach was needed as our model did not include any line broadening mechanism. For a given model and basis, matrix elements of the Hamiltonian and the dipole operator were evaluated analytically in a symbolic form. At each step of minimizing \( \chi^2 = \sum [y - f(\omega_n, \{ \kappa \})]^2 \), the numerical values were substituted for symbols and the Hamiltonian diagonalized numerically. Here \( f(\omega_n, \{ \kappa \}) \) is the theoretical spectrum with linewidths and lineshape identical to the synthetic experimental spectrum; \( \{ \kappa \} \) is the set of fit parameters: the ortho–para ratio, Hamiltonian and dipole operator parameters. As first partial derivatives are zero at the best fit, we used second derivatives to calculate the error margins \( \Delta \kappa_i \) of the fit parameters,

\[
\Delta \kappa_i = \sqrt{\chi^2 \left( \frac{\partial^2 \chi^2}{\partial \kappa_i^2} \right)^{-1}}. \tag{18}
\]

After the initial determination of reasonable starting values \( \{ \kappa \} \), we assigned the main absorption lines to ortho and para groups and further refined the starting values for proceeding with this nonlinear fit. Before the final rounds of the fit, we assigned the main absorption lines to transitions between certain eigenstates and verified this by their temperature dependence.

In the spherical approximation the energy does not depend on \( M_\Lambda \). Therefore, it is practical to use a reduced basis and reduced matrix elements\(^{33} \) which are independent of \( M_\Lambda \). This reduces the number of states by a factor of \( 2 \Lambda + 1 \) for each \( \Lambda \). The values of other quantum numbers we used to define the eigenstates \( \ket{\nu JNL \Lambda} \) were \( \nu = 0 \) and 1, \( J \leq 3 \), and \( N \leq 7 \). In such reduced basis there are 192 para-H\(_2\) and 292 ortho-H\(_2\) states.

In the line intensity calculation (17) the sum includes all possible \( M_\Lambda \) allowed by the initial and final state \( \Lambda \). This sum can be reduced to the form of reduced dipole matrix elements, \( \langle f\Lambda_f|M_\Lambda_f|d^{(1)}|\tau_i\Lambda_i \rangle \), of the dipole operator (12) using the relation,

\[
\sum_{M_{\Lambda_f},M_{\Lambda_i}} \begin{vmatrix} \langle f\Lambda_f|M_\Lambda_f|d^{(1)}|\tau_i\Lambda_i \rangle \end{vmatrix}^2 = \frac{1}{3} \langle f\Lambda_f|d^{(1)}|\tau_i\Lambda_i \rangle^2, \tag{19}
\]

where \( \tau \equiv \ket{\nu JNL} \). To calculate the IR absorption line area, the formula,

\[
S(\omega_f) = \frac{N \pi 10^{-2}}{3 V \eta e^2 \hbar} p_i \omega_f \langle f\Lambda_f|d^{(1)}|\tau_i\Lambda_i \rangle^2, \tag{20}
\]

was used, where all units are SI, except \( \omega \) in cm\(^{-1}\) and the absorption line area \( S \) in cm\(^{-2}\) units.

If the thermal relaxation between para-H\(_2\) and ortho-H\(_2\) is very slow we can define a temperature independent fractional ortho and para populations \( n_k \) of the total number of molecules \( N \), where \( k = o, p \) selects ortho- or para-H\(_2\). Then the probability that the initial state is populated is

\[
p_i = n_k \frac{(2\Lambda_i + 1)e^{-E_i/k_BT}}{\sum_j(2\Lambda_j + 1)e^{-E_j/k_BT}}. \tag{21}
\]

where \( E_i \) is the energy of the initial state measured from the ground state \( \nu = N = 0 \) and \( j \) runs over all para- (or ortho-) \( \nu \) states in the basis used.

III. EXPERIMENT

H\(_2@C_{60}\) was prepared at Kyoto University by molecular surgery method as described in Ref. 3. The para enriched sample was made at Columbia University using molecular oxygen as a spin catalyst for ortho–para conversion.\(^{19} \) Briefly, the 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 H\(_2\) spin isomers to the equilibrium distribution at 77 K, \( n_o/n_p = 1 \). The liquid oxygen was pumped away and the endofullerene–NaY complex was brought back rapidly to room temperature. The para enriched H\(_2@C_{60}\) was extracted from the zeolite with CS\(_2\), and the solvent was evaporated by argon. The powder sample in argon atmosphere and on dry ice arrived in Tallinn 4 days after the preparation.

The pellets of H\(_2@C_{60}\) for IR transmission measurements were pressed under vacuum. The diameter of sample pellets was 3 mm and thickness \( d = 0.25 \) mm (H\(_2@C_{60}\)) or \( d = 0.12 \) mm (para enriched H\(_2@C_{60}\)). Two identical vacuum tight chambers with Mylar windows were employed in the IR measurements. The chambers were put inside an optical cold finger type cryostat with KBr windows. In the measurements, the chamber containing the pellet for analysis was filled with He exchange gas, while the empty chamber served as a reference. Transmission spectra were obtained using a Bruker interferometer Vertex 80v with a halogen lamp and a HgCdTe or an InSb detector. The apodized resolution was typically 0.3 cm\(^{-1}\) or better.

Transmission \( T_\nu(\omega) \) was measured as the light intensity transmitted by the sample divided by the light intensity transmitted by the reference. Figure 3 shows the transmission spectra of H\(_2@C_{60}\) at 6 and 300 K between 3800 and 4900 cm\(^{-1}\). The absorption coefficient \( \alpha(\omega) \) was calculated from the transmission \( T_\nu(\omega) \) through \( \alpha(\omega) = -d^{-1} \ln[T_\nu(\omega)(1 - R)^{-2}] \), with the reflection coefficient \( R = [(\eta - 1)/(\eta + 1)]^2 \) calculated assuming a frequency independent index of refraction.\(^{32} \) \( \eta = 2 \). Absorbance spectra were cut into shorter pieces around groups of H\(_2\) lines and a baseline correction was performed before fitting the H\(_2\) lines with Gaussians.

IV. RESULTS

Transmission spectra of H\(_2@C_{60}\) at 6 and 300 K between 3800 and 4900 cm\(^{-1}\) are shown in Fig. 3. Sharp lines close to 3850, 4250, 4600, and 4800 cm\(^{-1}\) are from IR absorption of trapped H\(_2\). The main difference between 6 and 300 K spectra

\[\text{Downloaded 11 Sep 2012 to 130.54.110.73. Redistribution subject to AIP license or copyright; see http://jcp.aip.org/about/rights_and_permissions}\]
FIG. 3. Transmission spectra of H2@C60 at 6 K (lower curve, black) and 300 K (upper curve, red) between 3800 and 4900 cm\(^{-1}\). The inset shows much weaker fundamental ortho-H2 transition \(\Delta J = 2, \Delta N = 0\) (4065.4 cm\(^{-1}\)) and para-H2 transition (4071.4 cm\(^{-1}\)) lines at 6 K. The broad interference fringes with 300 cm\(^{-1}\) spacing are caused by the difference in the optical thickness of the sample and reference cell windows.

is an additional group of lines in the 300 K spectrum at about 3850 cm\(^{-1}\).

We compared the C60 absorption lines in the region from 2400 to 3500 cm\(^{-1}\), calculated from the transmission of the single crystal spectrum\(^{34}\) and from our powder sample transmission spectrum. The C60 absorption lines in the single crystal and powder sample spectrum had similar intensities when the background was subtracted, and we concluded that although the overall transmission level in our polycrystalline sample is lower than that in the single crystal spectrum, the line intensities are not affected by the light scattering.

The temperature dependence of the IR absorption spectrum of H2@C60 is shown in Fig. 4. The spectral lines involving transitions from the \(N = 0\) state are present at 6 K. At 90 K, more lines are visible and they correspond to the transitions starting from the \(N = 1\) state. At 200 K, additional lines are present where the initial state is \(N = 2\). Broad lines that are visible already in the 6 K spectrum below 4000 cm\(^{-1}\) in Fig. 4(a) are not H2 absorption lines and were subtracted from the spectra before the fitting of H2 lines.

FIG. 4. Temperature dependence of the infrared absorption spectra of H2@C60. Four panels show groups of transitions with the same change of the quantum numbers \(J\) and \(N\). An exception is the 4612.5 cm\(^{-1}\) line in (c), the fundamental ortho-H2 transition \(\Delta J = 2, \Delta N = 0\). Spectra are shifted vertically for clarification. Broad lines that are visible already in the 6 K spectrum below 4000 cm\(^{-1}\) in panel (a) are not H2 absorption lines and were subtracted from the spectra before the fitting of H2 lines.

To analyze the spectra, we assigned the lines to para and ortho groups and confirmed this by measuring the spectrum of a para enriched H2@C60 sample (Fig. 5). The 300 K spectra of the para enriched sample were measured at the day when sample arrived to Tallinn and again 19 days later [Fig. 5(b)]. The 20 K spectrum, measured on the day of arrival, is compared to the spectrum of a nonenriched sample. The 4255 cm\(^{-1}\) line is stronger and other three lines are weaker in the para enriched sample, as compared to the nonenriched sample. This proves that the previous assignment\(^6\) of ortho and para lines in the 6 K spectrum was correct. The ortho−para ratio, \(n_o/n_p = 2.890 \pm 0.045\), in the nonenriched sample was determined from the fit of the 6 K spectrum using the model Hamiltonian (Sec. II). Then this \(n_o/n_p\) and the areas of three lines, two ortho lines at 4250.7
Solid lines are calculated thermal population probabilities (Eq. 21) for ortho-$H_2$ (a) and para-$H_2$ (b) of transitions starting from states with $N = 0$ (squares and down triangles), $N = 1$ (circles) and $N = 2$ (up triangles). Solid lines are calculated [Eq. (21)] thermal population probabilities $p_i$ of the corresponding initial states, as obtained from the model. $S$ and $p_i$ have been normalized to unity at their maxima. The error bars of $S$ are from fitting the experimental lines with Gaussians.

and 4261 cm$^{-1}$ and one para line at 4255 cm$^{-1}$, were used as calibration standards to calculate $n_s/n_p$ for the para enriched sample. These lines were chosen because they are strong compared to other lines and at higher temperatures have the smallest overlap of ortho and para lines. We did not use the well-resolved low $T$ ortho line at 4244 cm$^{-1}$ because it overlaps with a para line at high $T$.

With increasing temperature the excited translational states, $N = 1$ and $N = 2$, become populated and the lines from $N = 0$ state become weaker. In Fig. 6 the normalized areas of several $H_2$@C$_{60}$ lines are compared to the temperature dependence of the normalized population probability of different initial states, $N = 0$, $N = 1$, and $N = 2$, using the eigenvalues obtained from fitting the 200 K spectrum with the model Hamiltonian. We see that within the error bars the temperature dependence of the normalized line areas is described very well up to 200 K. Above 200 K, there are deviations from the calculated curve, especially for lines starting from $N = 1$ and $N = 2$. These deviations could be due to the rotational motion of C$_{60}$ at higher temperatures. In solid C$_{60}$ there is a structural phase transition from the orientationally ordered low $T$ phase to the high $T$ phase where the molecules of C$_{60}$ rotate isotropically. In H$_2$@C$_{60}$ the phase transition $T$ is lowered from 260 to 240 K as the NMR study shows.\(^5\)

The 200 K spectra were chosen for extensive study. This temperature was selected for the following reasons. First, at lower temperatures higher energy levels in the $v = 0$ state are insufficiently populated, and we lose information about the transitions involving these levels and terminal levels in the $v = 1$ state, reached by the selection rule $\Delta N = \pm 1$. This is essential in determining the harmonic and anharmonic terms of the potential. Second, the 300 K spectrum does not add more information, as there are no new lines compared to the 200 K spectrum. We see from Fig. 4 and Table I that the change in positions of the H$_2$@C$_{60}$ lines is much less than the linewidth. Thus, the parameters determined at 200 K describe the system in the studied 6 to 300 K range relatively well.

Some of the lines in the 200 K spectrum or at lower $T$ show small splittings. These are the lines at 4255, 4261, and 4267 cm$^{-1}$ [Fig. 4(b)]. This splitting is not described by our model and could be due to the crystal field effects or inhomogeneities in the sample. In the synthetic spectrum, each of these three lines was treated as a single line. The fundamental lines with $\Delta v = 1$, $\Delta N = 0$, $\Delta J = 0$ were used in the fit to determine the fundamental frequency $\hbar \omega_0$. The fundamental para line (4071.4 cm$^{-1}$) is difficult to detect within the noise even below 60 K. However, the 4065.4 cm$^{-1}$ ortho line can be tracked almost up to 200 K without showing any frequency shift. In the 6 K spectrum we see weak lines at 4587.0 and 4612.5 and a shoulder to the 4802.6 cm$^{-1}$ line [Figs. 4(c) and 4(d)]. They originate from H$_2$@C$_{60}$, but are not described by the model Hamiltonian. The line at 4612.5 cm$^{-1}$, Table I, is probably the fundamental ortho transition with $\Delta J = 2$.

The best fit parameters at 200 K are listed in Table II. The ortho–para ratio, $n_o/n_p = 2.890 \pm 0.045$, was determined from the fit of the 6 K spectrum and was used here as a fixed parameter. A detailed result of fitting the absorption spectrum is shown in Fig. 7, where the experimental data are displayed in the form of a synthetic absorption spectrum together with the fit. The majority of absorption lines are reproduced by the model remarkably well with only some exceptions among the weaker lines, which are difficult to detect in the background noise. A spectral region around 4430 cm$^{-1}$, not present in Fig. 4, has been added and corresponds to $\Delta J = 2$, $\Delta N = 0$ ortho transitions [Fig. 7(c)]. The expected line at 4424 cm$^{-1}$, which is stronger than the 4407.4 cm$^{-1}$ line, could not be resolved in the experimental spectrum due to a broad background absorption band between 4420 and 4430 cm$^{-1}$.

The experimental and fitted absorption lines are summarized in Table I, together with the dominant components of the initial and final eigenstates. Eigenstates are listed in Tables III and IV up to the highest states that are involved in the measured infrared transitions. For positive $V_{004}^0$, the distance between translational levels increases with the quantum number $N$. Also, the sign of $V_{004}^0$ determines the order of $L$ levels for given $N$: the lowest energy level has the largest $L$. The ordering of $\Lambda$ levels for given $J$, $N$, $L$ is determined by the sign of $V_{222}^0$, which is positive in H$_2$@C$_{60}$ (Table II).

V. DISCUSSION

A. H$_2$ dynamics

The potential parameters $V_{ij}^{\alpha\beta}$ are listed in Table II. The harmonic part of the potential $V_{002}^{00}$ gives, using Eq. (9), $\omega_0 = 138.4$ cm$^{-1}$ and $\omega_0^t = 146.1$ cm$^{-1}$. Thus, the anharmonic correction accounts for 22\% of the energy difference of $N = 0$ and 1 levels, which are 179.5 and 184.4 cm$^{-1}$ in the ground and excited vibrational states (Table III). The value
TABLE I. Experimental and calculated line positions, $\omega$ (cm$^{-1}$), and absorption line areas, $S_\omega$ (cm$^{-2}$), of IR-active modes at 200 K in H$_2@$C$_{60}$. The quantum numbers $JNL$ and the relative weight $|\xi|^2$ of the main component contributing to the initial and final eigenstates are given. Experimental line positions and areas at 6 K are shown for comparison.

<table>
<thead>
<tr>
<th>Experiment, 6 K</th>
<th>Fitted</th>
<th>Initial state, $v = 0$</th>
<th>Final state, $v = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega$</td>
<td>$S_\omega$</td>
<td>$\omega$</td>
<td>$S_\omega$</td>
</tr>
<tr>
<td><strong>para lines</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3866.0</td>
<td>0.47</td>
<td>3866.0</td>
<td>0.09</td>
</tr>
<tr>
<td>3872.2</td>
<td>1.18</td>
<td>3873.2</td>
<td>0.16</td>
</tr>
<tr>
<td>3878.6</td>
<td>1.22</td>
<td>3878.4</td>
<td>0.35</td>
</tr>
<tr>
<td>3884.9</td>
<td>2.80</td>
<td>3884.7</td>
<td>0.64</td>
</tr>
<tr>
<td>3891.3</td>
<td>1.49</td>
<td>3891.8</td>
<td>0.77</td>
</tr>
<tr>
<td>4071.4</td>
<td>0.011</td>
<td>4071.3</td>
<td>0.00</td>
</tr>
<tr>
<td>4071.4</td>
<td>0.011</td>
<td>4071.3</td>
<td>0.00</td>
</tr>
<tr>
<td>4223.3</td>
<td>0.28</td>
<td>4222.2</td>
<td>0.07</td>
</tr>
<tr>
<td>4223.3</td>
<td>0.28</td>
<td>4222.2</td>
<td>0.07</td>
</tr>
<tr>
<td>4239.8</td>
<td>0.64</td>
<td>4239.6</td>
<td>0.64</td>
</tr>
<tr>
<td>4244.4</td>
<td>2.54</td>
<td>4244.5</td>
<td>0.47</td>
</tr>
<tr>
<td>4250.7</td>
<td>7.83</td>
<td>4252.5</td>
<td>0.20</td>
</tr>
<tr>
<td>4272.1</td>
<td>3.70</td>
<td>4272.1</td>
<td>2.78</td>
</tr>
<tr>
<td>4286.5</td>
<td>0.89</td>
<td>4286.4</td>
<td>1.41</td>
</tr>
<tr>
<td>4290.2</td>
<td>2.72</td>
<td>4289.9</td>
<td>0.49</td>
</tr>
<tr>
<td>4294.8</td>
<td>1.08</td>
<td>4294.8</td>
<td>0.28</td>
</tr>
<tr>
<td>4592.0</td>
<td>3.08</td>
<td>4592.4</td>
<td>0.79</td>
</tr>
<tr>
<td>4608.9</td>
<td>0.37</td>
<td>4608.9</td>
<td>0.31</td>
</tr>
<tr>
<td>4608.9</td>
<td>0.37</td>
<td>4608.9</td>
<td>0.31</td>
</tr>
<tr>
<td><strong>ortho lines</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3855.6</td>
<td>0.77</td>
<td>3855.6</td>
<td>0.41</td>
</tr>
<tr>
<td>3866.0</td>
<td>0.47</td>
<td>3866.1</td>
<td>0.27</td>
</tr>
<tr>
<td>3872.2</td>
<td>1.18</td>
<td>3871.6</td>
<td>0.38</td>
</tr>
<tr>
<td>3876.3</td>
<td>0.85</td>
<td>3876.3</td>
<td>0.85</td>
</tr>
<tr>
<td>3876.0</td>
<td>1.13</td>
<td>3874.9</td>
<td>0.27</td>
</tr>
<tr>
<td>3876.0</td>
<td>1.13</td>
<td>3874.9</td>
<td>0.27</td>
</tr>
<tr>
<td>3878.6</td>
<td>1.22</td>
<td>3878.5</td>
<td>1.25</td>
</tr>
<tr>
<td>3884.9</td>
<td>2.80</td>
<td>3884.9</td>
<td>1.88</td>
</tr>
<tr>
<td>3891.3</td>
<td>1.49</td>
<td>3890.5</td>
<td>0.50</td>
</tr>
<tr>
<td>4065.4</td>
<td>0.093</td>
<td>4065.4</td>
<td>0.093</td>
</tr>
<tr>
<td>4223.3</td>
<td>0.28</td>
<td>4222.7</td>
<td>0.24</td>
</tr>
<tr>
<td>4226.2</td>
<td>0.21</td>
<td>4225.3</td>
<td>0.17</td>
</tr>
<tr>
<td>4244.4</td>
<td>2.54</td>
<td>4244.4</td>
<td>1.95</td>
</tr>
<tr>
<td>4250.7</td>
<td>7.83</td>
<td>4250.9</td>
<td>7.71</td>
</tr>
<tr>
<td>4255.6</td>
<td>4.29</td>
<td>4257.3</td>
<td>0.22</td>
</tr>
<tr>
<td>4255.6</td>
<td>4.29</td>
<td>4257.3</td>
<td>0.22</td>
</tr>
<tr>
<td>4261.3</td>
<td>4.11</td>
<td>4261.4</td>
<td>3.74</td>
</tr>
<tr>
<td>4267.1</td>
<td>4.26</td>
<td>4267.0</td>
<td>5.48</td>
</tr>
<tr>
<td>4272.1</td>
<td>3.70</td>
<td>4272.7</td>
<td>1.77</td>
</tr>
<tr>
<td>4277.1</td>
<td>0.82</td>
<td>4277.2</td>
<td>1.27</td>
</tr>
<tr>
<td>4281.2</td>
<td>4.33</td>
<td>4281.2</td>
<td>4.90</td>
</tr>
<tr>
<td>4290.2</td>
<td>2.72</td>
<td>4289.7</td>
<td>2.13</td>
</tr>
<tr>
<td>4291.3</td>
<td>0.90</td>
<td>4291.3</td>
<td>0.90</td>
</tr>
<tr>
<td>4294.8</td>
<td>1.08</td>
<td>4296.2</td>
<td>0.26</td>
</tr>
<tr>
<td>4300.0</td>
<td>0.30</td>
<td>4298.3</td>
<td>0.001</td>
</tr>
<tr>
<td>4306.7</td>
<td>0.92</td>
<td>4305.2</td>
<td>0.19</td>
</tr>
<tr>
<td>4316.4</td>
<td>1.37</td>
<td>4316.8</td>
<td>0.84</td>
</tr>
<tr>
<td>4407.4</td>
<td>0.05</td>
<td>4407.2</td>
<td>0.07</td>
</tr>
<tr>
<td>4426.8</td>
<td>0.35</td>
<td>4427.4</td>
<td>0.34</td>
</tr>
<tr>
<td>4431.9</td>
<td>0.44</td>
<td>4432.5</td>
<td>0.53</td>
</tr>
<tr>
<td>4612.5</td>
<td>0.30</td>
<td>4613.1</td>
<td>0.01</td>
</tr>
</tbody>
</table>
The translation–rotation splitting is the distance between the potential parameters in Table III and IV shows that starting from the potential parameters, although there is slightly larger in the ground state. The same trend holds for the harmonic and anharmonic parts of the translation–rotation coupling potential parameters, although there are differences between the potential parameters in $v = 0$ and 1 states are even bigger. The translation–rotation coupling $V_{00}^{222}$ in the excited state is two times bigger than $V_{00}^{222}$ in the ground state. This difference is partially eliminated by the reversed magnitudes of anharmonic potential parameters as about two times smaller than $V_{00}^{222}$. The separation of energy levels in the $J = N = 1$ states is $E^{0}_{1110} - E^{0}_{1111} = 14.2$ cm$^{-1}$ and $E^{1}_{1110} - E^{1}_{1111} = 17.0$ cm$^{-1}$ (Table IV). Thus, the translation–rotation splitting remains larger for the $v = 1$ state but not as much as if anharmonic terms $V_{00}^{222}$ were zero.

The translation–rotation splitting is the distance between levels with different $\Lambda$ but same $J, N$, and $L$. Closer inspection of Tables III and IV shows that starting from $E_{J \Lambda A}^{0}$ for all $N > 3$ the translation–rotation splitting is larger in the $v = 0$ state than in the $v = 1$ state. This is because $V_{00}^{222} > V_{00}^{222}$. The result that the strength of the translation–rotation coupling in two different vibrational states shows crossover at $N = 3$ is based on the current interpretation of IR spectra where the largest $N$ value represented in the ground state is $N = 2$ and thus has no direct experimental proof.

<table>
<thead>
<tr>
<th>Experiment, 6 K</th>
<th>Experiment</th>
<th>Fitted</th>
<th>Initial state, $v = 0$</th>
<th>Final state, $v = 1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\omega$</td>
<td>$S_\omega$</td>
<td>$\omega$</td>
<td>$S_\omega$</td>
<td>$\omega$</td>
</tr>
<tr>
<td>4802.5</td>
<td>5.65</td>
<td>4802.6</td>
<td>1.80</td>
<td>4802.5</td>
</tr>
<tr>
<td>4814.8</td>
<td>0.39</td>
<td>4815.5</td>
<td>0.16</td>
<td>4816.2</td>
</tr>
<tr>
<td>4821.6</td>
<td>0.49</td>
<td>4821.0</td>
<td>0.52</td>
<td>1111</td>
</tr>
<tr>
<td>4829.7</td>
<td>0.26</td>
<td>4830.3</td>
<td>0.30</td>
<td>1111</td>
</tr>
<tr>
<td>4836.2</td>
<td>0.55</td>
<td>4835.8</td>
<td>0.66</td>
<td>1112</td>
</tr>
<tr>
<td>4846.4</td>
<td>0.23</td>
<td>4845.2</td>
<td>0.05</td>
<td>1222</td>
</tr>
<tr>
<td>4864.5</td>
<td>0.17</td>
<td>4862.9</td>
<td>0.02</td>
<td>1221</td>
</tr>
<tr>
<td>4864.6</td>
<td>0.03</td>
<td>1333</td>
<td>0.83</td>
<td>3444</td>
</tr>
</tbody>
</table>

179.5 cm$^{-1}$ of the separation of the first two translational levels in the $v = 0$ state is consistent with the result of the INS experiment, where it is 179.9 cm$^{-1}$.

The harmonic part $V_{00}^{222}$ is larger in the excited $v = 1$ state than in the ground state, while the anharmonic part $V_{00}^{222}$ is slightly larger in the ground state. The same trend holds for the harmonic and anharmonic parts of the translation–rotation coupling potential parameters, although there are differences between the potential parameters in $v = 0$ and 1 states are even bigger. The translation–rotation coupling $V_{00}^{222}$ in the excited state is two times bigger than $V_{00}^{222}$ in the ground state. This difference is partially eliminated by the reversed magnitudes of anharmonic potential parameters as about two times smaller than $V_{00}^{222}$. The separation of energy levels in the $J = N = 1$ states is $E^{0}_{1110} - E^{0}_{1111} = 14.2$ cm$^{-1}$ and $E^{1}_{1110} - E^{1}_{1111} = 17.0$ cm$^{-1}$ (Table IV). Thus, the translation–rotation splitting remains larger for the $v = 1$ state but not as much as if anharmonic terms $V_{00}^{222}$ were zero.

We reported that the vibrational frequency $\omega_0$ is equal to the frequency of the fundamental $\text{para}$ transition at $\omega = 4071.4$ cm$^{-1}$. This is true if the zero-point translational energies are equal in $v = 0$ and 1 states. Now when we have determined the ground state potential as well, we see that the vibrational frequency is $\omega_0 = 4062.4$ cm$^{-1}$. The difference of the observed fundamental $\text{para}$ line frequency $\omega = 4071.4$ cm$^{-1}$ from the vibrational frequency $\omega_0$ is determined by the different zero-point

| Table II. Values of the fitted parameters $k_i$. |
|----------------|----------------|
| $k_i$ | $\nu = 0$ | $\nu = 1$ |
| $V_{00}^{222}$ | 14.277 ± 0.034 | 15.952 ± 0.032 |
| $V_{00}^{222}$ | 0.5629 ± 0.0059 | 1.199 ± 0.012 |
| $V_{00}^{222}$ | (2.2105 ± 0.0099)$^{10^{21}}$ | (1.920 ± 0.0005)$^{10^{21}}$ |
| $V_{00}^{222}$ | (2.211 ± 0.023)$^{10^{20}}$ | (1.030 ± 0.011)$^{10^{20}}$ |
| $\delta_0$ | 4062.37 ± 0.28 | cm$^{-1}$ |
| $B_v$ | 59.665 ± 0.074 | cm$^{-1}$ |
| $\alpha_v$ | 2.974 ± 0.025 | cm$^{-1}$ |
| $D_v$ | (4.832 ± 0.051)$^{10^{2}}$ | cm$^{-1}$ |
| $B_{10}[10]$ | (4.53 ± 0.13)$^{10^{23}}$ | C |
| $B_{12}[12]$ | (2.13 ± 0.21)$^{10^{23}}$ | C |
| $\eta_0/\eta_p$ | 2.890 ± 0.045 | |
FIG. 7. Synthetic experimental absorption spectra of H$_2$@C$_{60}$ at 200 K (dots) together with the fit result, FWHM = 1 cm$^{-1}$. The total absorbance $\alpha$ is the sum of $\text{para}$ and $\text{ortho}$ components, shifted in vertical direction for clarity and shown separately in panels (a) and (b), where both components have a significant contribution. Above 4400 cm$^{-1}$ only $\text{para}$, panel (d), or $\text{ortho}$, panels (c) and (e), components of the fit are shown, as the other component does not have any contribution.
translational energies in \( v = 0 \) and 1 states. In the harmonic approximation the difference is \( \frac{1}{2}(\omega_{\|}^0 - \omega_{\perp}^0) = 11.6 \) cm\(^{-1}\), but is reduced to 9.0 cm\(^{-1}\) because of anharmonic corrections \( V^{(0)} \). The vibrational frequency \( \omega_{00} \) is redshifted by 98.8 cm\(^{-1}\) from its gas phase value.\(^{38}\) 4161.2 cm\(^{-1}\). At this point we cannot say how much of this redshift is caused by change in the zero-point vibrational energy and how much is caused by the change of anharmonic corrections to the vibrational levels in the \( C_{60} \) as our data set is limited to energy differences of \( v = 0 \) and 1 levels only.

The rotational constant \( B_{e} \) and the vibrational correction \( \alpha_{e} \) of \( H_{2} \) inside \( C_{60} \), Table II, are smaller than the gas phase values,\(^{38}\) 60.853 and 3.062 cm\(^{-1}\). We found that it is necessary to include a centrifugal correction \( D_{e} \) to the rotational constant, that is quite close to the gas phase value of 0.0471 cm\(^{-1}\).\(^{38}\) Without this correction it is not possible to fit the frequencies of \( S(0) \) and \( S(1) \) lines, as is seen in Fig. I of Ref. 6. The value of \( B_{e} \) smaller than the gas phase value may be interpreted as 0.81% stretching of the proton–proton distance \( s \) in \( H_{2}@C_{60} \), as \( B_{e} \sim \langle 1/s \rangle \). 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 \( \omega_{00} \) (Ref. 39). However, the correction \( \alpha_{e} \) 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 to \( H_{2} \) being in the free space. The repulsive effect of the cage follows from the positive anharmonic corrections to the translational levels as well.

Xu et al.\(^{19}\) introduced a three site Lennard-Jones potential to reproduce the translation–rotation levels observed in low \( T \) IR spectra. They found the best set of potential parameters for the \( N = 0 \) and 1 levels in the \( v = 1 \) state, which reproduced the observed IR frequencies very well, within 0.6%. Comparison with additional data available now shows that differences become bigger as \( N \) increases, and the trend is the same for \( \text{para} \ J = 0 \) and \( \text{ortho} \ J = 1 \) states. When compared to energies listed in Tables III and IV, their energies \( E_{J,100,0}^{(200)} \) and \( E_{J,100,0}^{(133)} \) are higher by 10 cm\(^{-1}\) and 25 cm\(^{-1}\). Xu et al. found that three different parameter sets fitted the 6 K data equally well. Since higher \( T \) data were not available at the time, it was not possible to judge which parameter set is the best to reproduce the anharmonic part of the potential.

The symmetry of \( C_{60} \) is icosahedral. Within this symmetry the degeneracy of a \( \Lambda = 3 \) level is lifted. The possible candidate to study the \( \Lambda = 3 \) level splitting in the IR spectrum is the \text{ortho} line at 4267 cm\(^{-1}\) (Table I). This experimental line is split into two components, about 2 cm\(^{-1}\) apart \( \text{see \[90 and 200 K spectra in Fig. 4(b)\]} \). According to our fit with the spherically symmetric potential, it is the \( \{1112\} \rightarrow \{1223\} \) transition and has no other \text{ortho} or \text{para} lines within 2 cm\(^{-1}\) \( \text{[Fig. 7(b)\]} \). However, it is unlikely that the splitting of the 4267 cm\(^{-1}\) line is caused by the icosahedral symmetry because the calculation of Xu et al.\(^{11}\) shows that the splitting of this \( \Lambda = 3 \) level should be only 0.5 cm\(^{-1}\).

A similar system to the one studied here is exohedral \( H_{2} \) in \( C_{60} \). There \( H_{2} \) occupies the octahedral interstitial site.
in the C₆₀ crystal. The prominent features in the exohedral H₂ IR spectra are the translational, ΔN = ±1, sidebands to the fundamental transitions, Δν = 1 and ΔJ = 0, 2. The redshift of the fundamental vibrational frequency is about 60 cm⁻¹, which is less than that in H₂@C₆₀ where it is 98.8 cm⁻¹. Also the separation of translational N = 0 and 1 levels, approximately 120 cm⁻¹, is smaller, when compared to 184.4 cm⁻¹ in H₂@C₆₀. It is likely that the main contribution to the latter difference comes from the larger van der Waals volume available for H₂ in the octahedral site than in the C₆₀ cage.

### B. Dipole moment

The dipole moment parameters B₁₀[10] and B₁₀[12] are given in Table II. The numerical values are consistent with our previous result, where only the ratio of the two dipole moment parameters, −2.0 ± 0.2, was given. The choice of which is negative is arbitrary as the line intensities are insensitive to the sign change of the two parameters. The listed B₁₀[I] depend on the pairwise H₂–C induced dipole parameter B[I] and its derivative (see Eq. (14)). A theoretical calculation of B[I] for H₂–C is outside the scope of the current study. The general trend is consistent with the theoretical calculations for H₂–He pairs, where the signs of B₁₀ and B₁₂ are opposite and B₁₂ has the smaller absolute value.25

Herman and Lewis calculated the dipole moment of interstitial H₂ at the octahedral site in solid C₆₀ using H₂–He interaction data. They considered the isotropic exchange (overlap) induced dipole (B₁₀) at short range and the quadrupole induced dipole (B₁₂) at short and long ranges. We showed in Sec. II that B₁₂ does not contribute to ΔN = ±1 electric dipole transitions in endohedral H₂.

The dipole moment calculated from the 6 K area S = 10.6 cm⁻² of the 4255 cm⁻¹ ortho line (Table I) using Eq. (20) gives d = 3.28 × 10⁻³² Cm = 9.83 × 10⁻³ D. For example, the permanent dipole moment of a free HD molecule corresponding to ν = 0 → 1, J → J + 1 transitions is only 5 × 10⁻⁵ D. To estimate an effective charge associated with the 4255 cm⁻¹ transition, we use q = 20B₁₀[10] [see Eq. (13)] and get q = 9.1 × 10⁻²² C after substituting the fitted value for B₁₀[10] from Table II. This is about 0.006 electron charges. However, the displacement (R)₁₀ = d/q = 0.36 Å associated with this dipole moment is comparable to the typical atomic scale, the Bohr radius. Thus, the small dipole moment is mainly the consequence of the small induced charge disproportionation of the H₂@C₆₀, when H₂ experiences translational motion in the C₆₀ cage.

The IR transitions reported here are the transitions where the vibrational state changes, ν = 0 → 1. One may ask if the induced electric dipole transitions, ΔN = ±1, can be observed within the vibrational ground state ν = 0. The difference between these two kinds of transitions lies in the dependence of the dipole moment on the proton–proton distance s, represented by the parameter A⁺ₐ₋(R) [Eq. (13)]. The expectation value of R is very similar for both transitions and does not account for the observed difference as explained below. We did not see the transitions of H₂ in far-IR, but can set the upper limit to the dipole moment. The experiment was conducted on a 1.9 mm thick pellet at 20 K. The strongest line expected is the overlap of a para line at 179.5 cm⁻¹ ([0000] → [0111]) and ortho line at 180.4 cm⁻¹ ([1001] → [1112]) (Tables III and IV). The intensity of both lines is given by A₁₀[10]. We simulated the expected absorption using Eq. (17) (note the dependence on ω) and saw that it is at least ten times stronger than would have been possible to detect within our noise level. Thus, in the ground vibrational state, the induced dipole moment must be suppressed at least by a factor of A₁₀[10] / A₀₀[10] ≥ √10. It has been found that the induced dipole moments of a H₂–He pair have an opposite dependence on the vibrational states.25 B₁₀[10] is larger than B₁₀[10].

### VI. SUMMARY

The IR absorption spectrum of endohedral H₂ in C₆₀ is rich, involving several excitations: vibrations, rotations, and translational motions of H₂. The translational motion is quantized because of the surrounding C₆₀ cage and coupled to the rotations of H₂. We used a model of a vibrating rotor in a spherical potential together with the translational motion induced dipole moment theory to explain the positions and intensities of IR absorption lines (Table I). The main effect of temperature on the IR spectra in the studied range 6–900 K is the change of IR line intensities, which is reasonably well accounted for by the Boltzmann distribution in the ground vibrational state ν = 0. The energy levels of H₂@C₆₀ are given in Tables III and IV and were calculated from the model using parameters given in Table II. The potential parameters show clear dependence on the vibrational state, ν = 0 or ν = 1. The potential is divided into an isotropic part, which depends on the center of mass coordinate of H₂ and an anisotropic part which depends on the orientation of H₂ molecule. The IR spectra can be fitted only if both parts of the potential are anharmonic. The induced dipole moment must depend on the vibrational coordinate as well, otherwise we cannot explain why we did not observe far-IR ΔN = 1 transitions in the ground vibrational state ν = 0.

Our study shows that the vibrations and rotations of C₆₀ and the crystal field effects of solid C₆₀ are not important on the energy scale of IR measurements. If these effects are important, their contribution to the IR spectra is the order of 1 wavenumber splitting of few absorption lines. Such small splitting is consistent with the results of heat capacity measurements.

We do not explain how the determined parameters are linked to the molecular structure of the H₂@C₆₀ complex. In principle it should be possible to describe, within a single quantum chemical model of H₂@C₆₀, the potential parameters, induced dipole parameters, the dependence of both on the vibrational state, and the changes of rotational and vibrational constants compared to free H₂ values. Some additional information may come from the IR studies of endohedral D₂ and HD, a work in progress.
ACKNOWLEDGMENTS

This research was supported by the Estonian Ministry of Education and Research (Grant No. SF0690029s09), Estonian Science Foundation (Grant Nos. ETF7011, ETF8170, and JD187), the EPSRC (UK), the University Research Fellowship (Royal Society, UK), and the National Science Foundation (Grant No. CHE-07-17518).