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

Author(s)

Citation
JOURNAL OF CHEMICAL PHYSICS (2011), 134(5)

Issue Date
2011-02

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

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

Type
Journal Article

Textversion
publisher
Kyoto University
Interaction potential and infrared absorption of endohedral H₂ in C₆₀

Min Ge,¹ U. Nagel,¹ D. Huvonen,¹ T. Rööm,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

(Received 1 November 2010; accepted 17 December 2010; published online 2 February 2011)

We have measured the temperature dependence of the infrared spectra of a hydrogen molecule trapped inside a C₆₀ cage, H₂@C₆₀, 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 H₂ and gives rise to an infrared absorption process where one translational quantum is created or annihilated, ∆N = ±1. Some fundamental transitions, ∆N = 0, are observed as well. The rotation of endohedral H₂ 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 H₂. The vibrational frequency and the rotational constant of endohedral H₂ are smaller than those of H₂ in the gas phase. The assignment of lines to para and ortho-H₂ is confirmed by measuring spectra of a para enriched sample of H₂@C₆₀ 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 spectroscopic investigations of the trapped H₂ dynamics and simulated theoretical investigations.⁷–¹² It has been established that H₂ inside a C₆₀ cage is an unhindered vibrating rotor performing translational motion in a nearly spherical potential well.¹³ Similar properties have been predicted theoretically for CO@C₆₀ 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, C₂@Sc₂C₈₄, is two-dimensional and shows hindered rotation.¹⁵, ¹⁶

The H₂@C₆₀ represents a system where the simplest molecule is encapsulated by a molecule with the highest symmetry. The vibrational, rotational, and translational levels of H₂ inside the cage are well separated because of the small mass of the hydrogen atom. The high icosahedral symmetry of the C₆₀ cavity is close to spherical. The local environment of H₂ has a negligible inhomogeneous distribution of parameters, and there is one H₂ per trapping site. The H₂@C₆₀ is a stable complex and can survive a short period of heating up to 500°C under vacuum.³ These properties make H₂@C₆₀ 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 H₂ is not spherical, its interaction potential with C₆₀ depends on the orientation of its molecular axis relative to the inner surface of the C₆₀ 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.⁹, 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 H₂ are relatively large because of its small mass. This makes the potential for H₂ 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-H₂. The two proton spins (I_p = 1/2) are in the antisymmetric I = 0 total nuclear spin state in para-H₂ and in the symmetric I = 1 state in ortho-H₂. Even rotational quantum numbers J are allowed for para-H₂ and odd J for ortho-H₂. As a consequence the ortho-H₂ ground state is above the para-H₂ 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 H₂ 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 H₂@C₆₀ 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 H$_2$@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 $v = 0$ and the excited state $v = 1$. The IR activity of H$_2$ is induced by the translational motion of H$_2$ relative to the C$_{60}$ cage, giving rise to a selection rule $\Delta N = \pm 1$, where $N$ is the translational quantum number. However, the transitions between para and 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 $v = 0, N = 0$ 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 $\Delta v = 1, \Delta N = 0$ para and 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, allows the determination of the energy separation of $N = 0$ and $N = 1$ translational levels in the $v = 1$ 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 H$_2$. The information about the potential in the ground $v = 0$ state is limited, too. The separation of $N = 0$ and $N = 1$ translational levels is known from the INS experiment. The translation–rotation splitting of the $N = 1$ translational state of ortho-H$_2$@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 $v = 0$ state are sufficiently populated to give rise to detectable IR transitions to terminal states connected to the initial states by the selection rules $\Delta v = 1$, $\Delta N = \pm 1$, 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 $v = 0$ and $v = 1$. We have confirmed the assignment of spectral lines to ortho- and para-H$_2$ using an ortho–para converted sample.

II. THEORY

The theoretical work of Olthof et al. is a comprehensive description of the dynamics of a loosely bound molecule inside C$_{60}$. They calculated the dynamics and the IR spectra of CO@C$_{60}$. The main differences between their approach and ours are the following. First, Olthof 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 H$_2$@C$_{60}$ the dipole moment is induced by the translational motion of H$_2$.

A. Five-dimensional spherically symmetric Hamiltonian of H$_2$@C$_{60}$

To describe the motion of H$_2$ inside C$_{60}$ we use the following model. The C$_{60}$ is considered to be rigid, its center of mass is not moving, and it does not rotate. We treat H$_2$@C$_{60}$ as an isolated molecular complex and approximate the true icosahedral symmetry of an isolated C$_{60}$ with spherical symmetry. It means that in this approximation H$_2$ moves in a rigid spherically symmetric binding potential provided by the cavity of C$_{60}$. Besides the translational movement inside C$_{60}$, the 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 ortho-H$_2$ ($J$ odd) and para-H$_2$ ($J$ even) states in our model Hamiltonian. Compared to our earlier work the model has been extended in few points. Here we include the centrifugal correction term $D_c$ to the rotational constant $B_c$ and add an anharmonic term $\nu V^{224}_{00}$ to the anisotropic confining potential. The basis has been extended to $N \leq 7$ for both vibrational states, $v = 0$ and $v = 1$. A more detailed description of the model follows.

The position and orientation of the H$_2$ molecule are given by spherical coordinates $\mathbf{R} = \{R, \Omega\}$, $\Omega = \{\Theta, \Phi\}$ and $\mathbf{s} = \{s, \Omega_s\}$, $\Omega_s = \{\theta, \phi\}$, where $\mathbf{R}$ is the vector from the center of the C$_{60}$ cage to the center of mass of H$_2$ and $\mathbf{s}$ is the internuclear H–H vector, as shown in Fig. 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 $v$:

$$\mathcal{H} = \nu \mathcal{H}^{\text{vib} - \text{rot}} + \frac{p^2}{2m} + \nu V(R, \Omega, \Omega_v),$$

(4)

where $\nu \mathcal{H}^{\text{vib} - \text{rot}}$ is the vibration-rotation Hamiltonian, $p$ is the molecular momentum operator, and $m$ is the molecular mass of H$_2$. Here, $\nu V$ is the potential energy in the vibrational state $\psi_{v}\text{^\nu}(s)$. The vibration-rotation Hamiltonian $\nu \mathcal{H}^{\text{vib} - \text{rot}}$ is diagonal in the basis set $|vJNL\Lambda\mu\rangle$, with eigenvalues given by

$$\nu E_{J}^{\text{vib} - \text{rot}} = \hbar \omega_0 (v + 1/2) + B_r J(J + 1),$$

(5)

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

The potential energy expanded in multipoles is

$$\nu V(R, \Omega, \Omega_v) = \sum_{n, I, J, M, \lambda} \nu V_{nlm}^{ij}(\Omega) F_{i,j}(\Omega),$$

(6)

where the functions $F$ are defined in Eq. (2) and $n$ takes even values. Translation-rotation coupling terms are terms with nonzero $I, J$. 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 $\lambda$ values 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 $\nu V = \nu V^0 + \nu V'$. The isotropic harmonic term is given by $\nu V^0 = \nu V_{0000}^0 R^2 F_{00}^0$, where we have neglected the constant offset $\nu V_{0000}^{00} F_{00}^0$. The perturbation $\nu V'$ consists of translation-rotation coupling $\nu V^{22}_{00}$ and anharmonic corrections $\nu V^{02}_{00}$ and $\nu V^{22}_{00}$ to both isotropic and anisotropic couplings,

$$\nu V' = (\nu V^{22}_{00} R^2 + \nu V^{02}_{00} R^4) F_{22}^0 + \nu V^{02}_{00} R^4 F_{00}^0 + \nu V^{22}_{00} R^4 F_{00}^0.$$

(7)

The unperturbed Hamiltonian eigenvalues in the basis $|vJNL\Lambda\mu\rangle$ are given by

$$E_j^{vJNL\Lambda\mu} = \nu E_{J}^{\text{vib} - \text{rot}} + \hbar \nu \omega_0^f (N + 3/2),$$

(8)

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

$$\nu \omega_0^f = (\nu V_{00}^{00}/(2\pi m))^{1/2}.$$

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 $\Omega_v = [\theta, \phi]$ 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 $\psi_R^{v}(s)$ is different in vibrational states $v = 0$ and $v = 1$. To describe the center of mass translational motion of H$_2$, we use the functions defined in Eq. (2) and $n$ takes even values. Translation-rotation coupling terms are terms with nonzero $I, J$. 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 $\lambda$ values 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 $\nu V = \nu V^0 + \nu V'$. The isotropic harmonic term is given by $\nu V^0 = \nu V_{0000}^0 R^2 F_{00}^0$, where we have neglected the constant offset $\nu V_{0000}^{00} F_{00}^0$. The perturbation $\nu V'$ consists of translation-rotation coupling $\nu V^{22}_{00}$ and anharmonic corrections $\nu V^{02}_{00}$ and $\nu V^{22}_{00}$ to both isotropic and anisotropic couplings,

$$\nu V' = (\nu V^{22}_{00} R^2 + \nu V^{02}_{00} R^4) F_{22}^0 + \nu V^{02}_{00} R^4 F_{00}^0 + \nu V^{22}_{00} R^4 F_{00}^0.$$

(7)

The unperturbed Hamiltonian eigenvalues in the basis $|vJNL\Lambda\mu\rangle$ are given by

$$E_j^{vJNL\Lambda\mu} = \nu E_{J}^{\text{vib} - \text{rot}} + \hbar \nu \omega_0^f (N + 3/2),$$

(8)

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

$$\nu \omega_0^f = (\nu V_{00}^{00}/(2\pi m))^{1/2}.$$
\[ \nu = 1, \text{which are the initial and final states of IR transitions. Second, the initial state is not only the N = 0 state as was the case when the low T spectra were analyzed,} \]

\[ \text{but other states with N > 0 are thermally populated, too. To derive the induced dipole moment for H_2@C_{60}, we assume that it is the sum of dipole moments induced by pairwise interactions between H_2 and ith carbon atom.} \]

An overview of collision induced dipoles in gases and gas mixtures is given in the book by Frommhold. The confinement of the endohedral H_2 introduces two differences as compared to H_2 in the gas. First, the translational energy of H_2 is quantized. In the gas phase it is a continuum starting from zero energy. Second, the variation of the distance between H_2 and the carbon atom is limited to the translational amplitude of H_2 in the confining potential. In the gas phase the distance varies from infinity to the minimal distance given by the collision radius. The selection rule \( \Delta N \pm 1 \) for the endohedral H_2 follows from these two conditions, as shown below. Quantum mechanical calculations of induced dipoles are available for simple binary systems like H_2–He, H_2–Ar, and H_2–H_2. An extensive set of theoretical results for the H_2–He system associated with the roto-translational electric dipole transitions, both in the vibrational ground state \( \nu = 0 \) and accompanying the \( \nu = 0 \rightarrow 1 \) transition of the H_2 molecule, can be found in Refs. 26–30.

The dipole moment operator for H_2 and ith carbon atom can be expanded in spherical harmonics:

\[ d_q(r_i, s) = \frac{4\pi}{\sqrt{3}} \sum_{l,j=0} B^{ij}(r_i, s) F^{ij}_l(\Omega_1, \Omega_2), \tag{10} \]

where \( q = 0, \pm 1 \) denotes the spherical component of the dipole moment vector \( d \) and the spherical functions \( F^{ij}_l(\Omega_1, \Omega_2) \) are described by Eq. (2). The position of the ith carbon atom is defined by \( \mathbf{R}_i = (r_i, \Omega_{C_i}) \), \( \Omega_{C_i} = (\theta_i, \phi_i) \), and the position of the center of mass of H_2 relative to the ith carbon atom by vector \( \mathbf{r}_i = (r_i, \Omega_i) \), \( \Omega_i = (\theta, \phi) \), as shown in Fig. 2. The origin of coordinates of \( \mathbf{R}_i \) and \( \mathbf{R} \) is chosen in the geometric center of C_60. We introduce the dipole moment of the initial state on the initial and the final vibrational states, \( d_{q, \nu_\nu'}(r_i, \Omega_i) \equiv \langle \psi_{\nu_\nu'}^{\text{rb}}(s) | d_q(r_i, s) | \psi_{\nu_\nu'}^{\text{rb}}(s) \rangle \). 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:

\[ B^{ij}_l(r) \equiv \langle \psi_{\nu_\nu'}^{\text{rb}}(s) | B^{ij}_l(r,s) | \psi_{\nu_\nu'}^{\text{rb}}(s) \rangle. \]

Since the dipole moment is a vector, there are restrictions on the allowed \( j \) and \( l \) values of the H_2–C pair: (i) \( j + l \) must be odd, (ii) \( j = \pm 1 \) from the triangle relation, and (iii) for homonuclear molecules only even terms are allowed. We discuss here the first three terms, \( B^{10}, B^{12}, \) and \( B^{32} \). \( B^{10} \) corresponds to the induced dipole moment which is independent of the orientation of H_2 molecular axis. \( B^{12} \) describes the exchange interaction induced dipole which depends on the \( H_2 \) molecular axis orientation. \( B^{32} \) is the term describing the dipole moment induced on the “collision” partner by the quadrupolar moment of H_2 and is called the quadrupolar induction term. In the spherical approximation and in the first order of displacement of H_2 from the C_60 cage center, the quadrupolar induction term is zero (see below).

We expand the dipole moment \( d_{q, \nu_\nu'}(r_i, \Omega_i) \) between the ith C atom and H_2 into a Taylor series in powers of \( \mathbf{R} \) at the center of C_60 and sum over all carbon atoms. The zero order term vanishes because \( R = 0 \) is the center of inversion for \( H_2@C_{60} \). We keep the first nonzero term which is linear in \( R \):

\[ d_{q, \nu_\nu'}^{(1)}(\mathbf{R}, \Omega_i) = \frac{4\pi}{\sqrt{3}} \sum_{l,j} A^{ij}_{q, \nu_\nu'}(R) F^{ij}_l(\Omega_1, \Omega_2) \left. \mathbf{R}_i \right|_{\mathbf{R}} = - \mathbf{R}, \]

where \( \nabla_{\nu_i} \) is the nabla operator in the spherical coordinates of \( \mathbf{R}_i \). 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 \( (\Omega, \Omega_i) \):

\[ d_{q, \nu_\nu'}^{(1)}(\mathbf{R}, \Omega_i) = \frac{4\pi}{\sqrt{3}} \sum_{l,j} A^{ij}_{q, \nu_\nu'}(R) F^{ij}_l(\Omega, \Omega_i). \tag{12} \]

The nonzero coefficients are \( A^{10}_{q, \nu_\nu'} \) and \( A^{12}_{q, \nu_\nu'} \), where

\[ A^{ij}_{q, \nu_\nu'}(R) = 20 R B_{q, \nu_\nu'}|I|, \]

and we have used the notation

\[ B_{q, \nu_\nu'}|I| = \frac{\partial B^{ij}_l(r)}{\partial r} \bigg|_{r=R_0} + \frac{2}{R_0} B^{ij}_l(R_0). \tag{14} \]

The calculation shows that in the spherical approximation of C_60 and in the first order of \( R \) the quadrupolar induction term \( A^{32}_{q, \nu_\nu'} \) vanishes to zero. The selection rules for IR spectroscopy of \( H_2@C_{60} \) follow from the angular and radial dependence of \( d_{q, \nu_\nu'}^{(1)} \) [Eqs. (12), (14)]: \( \Delta N = \pm 1 \) and change of the total angular momentum is \( \Delta L = 0, \pm 1 \) with \( \Delta J = 0, \pm 2 \) and \( \Delta L = \pm 1 \).

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

\[ S(\omega_{ij}) = \frac{N\pi}{V\hbar c_0} p_i \omega_{ij} |\langle f|\mathbf{d}|i\rangle|^2, \]

where \( \mathbf{d} = E/E \) is the unit vector of light electric field \( E \), \( N/V = 1.48 \times 10^{27} \text{ m}^{-3} \) is number density of molecules in solid C_60, \( c \) is the speed of light, \( c_0 \) is the permittivity of vacuum, \( \eta \) is the index of refraction (in C_60 \( \eta = 2 \), Ref. 32), \( h \) is the reduced Planck constant, \( \omega_{ij} = (E_j - E_i)/(2\pi \hbar c) \) is the number of waves in one meter, where \( E_i, E_j \) 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 \( d \) is the dipole moment (unit Cm).

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

\[ |\langle f|\mathbf{d}|i\rangle|^2 = \frac{1}{3} \sum_{\zeta=x', y', z'} |\langle f|d_\zeta|i\rangle|^2, \tag{16} \]

where \( d_\zeta \) 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),

\[ S(\omega_{ij}) = \frac{N\pi}{V\hbar c_0} p_i \omega_{ij} |\langle f|d_{0,0,0}^{(1)}(\mathbf{R})|i\rangle|^2. \tag{17} \]
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 $y(\omega_n)$, 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 $\chi^2 = \sum (y - f(\omega_n, \{k\}))^2$, the numerical values were substituted for symbols and the Hamiltonian diagonalized numerically. Here $f(\omega_n, \{k\})$ is the theoretical spectrum with linewidths and lineshape identical to the synthetic experimental spectrum; $\{k\}$ 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,

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

After the initial determination of reasonable starting values $\{k\}$, 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 $M_A$. Therefore, it is practical to use a reduced basis and reduced matrix elements which are independent of $M_A$. 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 $|vJ\Lambda N\Lambda\rangle$ were $v = 0$ 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 $M_A$ allowed by the initial and final state $\Lambda$. This sum can be reduced to the form of reduced dipole matrix elements, $\langle f|d|\Lambda_i\rangle$, of the dipole operator (12) using the relation,$^{33}$

$$\sum_{M_A_i M_A_j} \left| \langle f|d|\Lambda_i\rangle \langle \Lambda_i|M_A_i \rangle \right|^2 = \frac{1}{3} |\langle f|d|\Lambda_i \rangle|^2, \quad (19)$$

where $|\tau\rangle \equiv |vJ\Lambda N\rangle$. To calculate the IR absorption line area, the formula,

$$S(\omega_f) = \frac{N\pi 10^{-2}}{3V\hbar c\epsilon_0 h} p_t \omega_f |\langle f|d|\Lambda_i \rangle|^2, \quad (20)$$

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

$$p_t = n_k \frac{(2\Lambda_i + 1)e^{-E_i/k_BT}}{\sum_j (2\Lambda_j + 1)e^{-E_j/k_BT}}, \quad (21)$$

where $E_i$ is the energy of the initial state measured from the ground state $v = N = 0$ and $j$ runs over all para- (or ortho-) H$_2$ states in the basis used.

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 $T_r(\omega)$ 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 $T_r(\omega)$ through $\alpha(\omega) = -d^{-1} \ln T_r(\omega)(1 - R)^{-1}$, with the reflection coefficient $R = [(\eta - 1)/(\eta + 1)]^2$ calculated assuming a frequency independent index of refraction.$^{35}$ $\eta = 2$. 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
is an additional group of lines in the 300 K spectrum at about 3850 cm\(^{-1}\).

We compared the C\(_{60}\) 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 C\(_{60}\) 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 H\(_2\)@C\(_{60}\) 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 H\(_2\) absorption lines and were subtracted from the spectra before the fitting of H\(_2\) 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 H\(_2\)@C\(_{60}\) 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
and 4261 cm\(^{-1}\) and one para line at 4255 cm\(^{-1}\), were used as calibration standards to calculate \(n_o/n_p\) 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 \(H_2@C_{60}\) areas 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.\(^{35-37}\) 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 \(\Delta J = 2\).

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 \(\Delta J = 2\), \(\Delta N = -1\) 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 \(\nu V_{000}\), the distance between translational levels increases with the quantum number \(N\). Also, the sign of \(\nu V_{000}\) determines the order of \(L\) levels for given \(N\): the lowest energy level has the largest \(L\). The ordering of \(\Delta\) levels for given \(J, N, L\) is determined by the sign of \(\nu V_{222}\), which is positive in \(H_2@C_{60}\) (Table II).

V. DISCUSSION

A. \(H_2\) dynamics

The potential parameters \(\nu V_{ijm}\) are listed in Table II. The harmonic part of the potential \(\nu V_{002}^{00}\) gives, using Eq. (9), \(0_{o0}^{L} = 138.4\) cm\(^{-1}\) and \(1_{o0}^{L} = 146.1\) 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).
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 $JN\Lambda$ 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>Experiment 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>para lines</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>4255.2</td>
<td>10.60</td>
<td>4255.6</td>
<td>4.29</td>
</tr>
<tr>
<td>4261.3</td>
<td>4.11</td>
<td>4261.8</td>
<td>0.08</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>4592.0</td>
<td>0.90</td>
</tr>
<tr>
<td>4608.9</td>
<td>0.37</td>
<td>4608.9</td>
<td>0.31</td>
</tr>
<tr>
<td>4624.3</td>
<td>0.27</td>
<td>4624.5</td>
<td>0.25</td>
</tr>
<tr>
<td>4630.0</td>
<td>0.10</td>
<td>4629.4</td>
<td>0.12</td>
</tr>
<tr>
<td>ortho lines</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>3876.0</td>
<td>1.13</td>
<td>3874.9</td>
<td>0.27</td>
</tr>
<tr>
<td>3876.3</td>
<td>0.85</td>
<td>3876.3</td>
<td>0.85</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>0.10</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>4261.0</td>
<td>8.86</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>4318.4</td>
<td>0.51</td>
<td>1332</td>
<td>0.68</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>4428.0</td>
<td>0.06</td>
<td>4428.0</td>
<td>0.06</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>1001</td>
</tr>
</tbody>
</table>
The harmonic part $V_{00}^{01}$ is larger in the excited $v = 1$ state than in the ground state, while the anharmonic part $V_{00}^{00}$ 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 the differences between the potential parameters in $v = 0$ and 1 states are even bigger. The translation–rotation coupling $V_{00}^{12}$ in the excited state is two times bigger than $V_{00}^{22}$ in the ground state. This difference is partially eliminated by the reversed magnitudes of anharmonic potential parameters as $V_{00}^{22}$ is about two times smaller than $V_{00}^{24}$. The separation of energy levels in the $J = N = 1$ states is $E_{1}^{00} - E_{111}^{00} = 14.2 \text{ cm}^{-1}$ and $E_{222}^{00} - E_{111}^{00} = 17.0 \text{ cm}^{-1}$ (Table IV). Thus, the translation–rotation splitting remains larger for the $v = 1$ state but not as much as if anharmonic terms $V_{00}^{01}$ 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 $E_{JNL}^{0}$ for all $N > 3$ the translation–rotation splitting is larger in the $v = 0$ state than in the $v = 1$ state. This is because $V_{00}^{24} > V_{00}^{22}$. 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 I. (Continued)

<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>$\omega \ (s^{-1})$</td>
<td>$S_\omega$</td>
<td>$\omega \ (s^{-1})$</td>
<td>$S_\omega$</td>
<td>$JNL$</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>4830.3</td>
</tr>
<tr>
<td>4836.2</td>
<td>0.55</td>
<td>4835.8</td>
<td>0.66</td>
<td>4845.2</td>
</tr>
<tr>
<td>4846.4</td>
<td>0.23</td>
<td>4848.1</td>
<td>0.03</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>4864.8</td>
<td>0.03</td>
<td>1333</td>
<td>0.83</td>
<td>3444</td>
</tr>
</tbody>
</table>

We reported\(^6\) that the vibrational frequency $\omega_0$ is equal to the frequency of the fundamental $\Lambda = 1$ transition at $\omega = 4071.4 \text{ cm}^{-1}$. 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 $\omega_0 = 4062.4 \text{ cm}^{-1}$. The difference of the observed fundamental $\Lambda$ line frequency $\omega = 4071.4 \text{ cm}^{-1}$ from the vibrational frequency $\omega_0$ is determined by the different zero-point

### Table II. Values of the fitted parameters $k_i$.

<table>
<thead>
<tr>
<th>$k_i$</th>
<th>$v = 0$</th>
<th>$v = 1$</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{00}^{00}$</td>
<td>14.277 ± 0.034</td>
<td>15.952 ± 0.032</td>
<td>Jm$^{-2}$</td>
</tr>
<tr>
<td>$V_{00}^{22}$</td>
<td>0.5629 ± 0.0059</td>
<td>1.199 ± 0.012</td>
<td>Jm$^{-2}$</td>
</tr>
<tr>
<td>$V_{00}^{04}$</td>
<td>(2.2105 ± 0.0099)$\times 10^{21}$</td>
<td>(1.920 ± 0.0085)$\times 10^{21}$</td>
<td>Jm$^{-4}$</td>
</tr>
<tr>
<td>$V_{00}^{24}$</td>
<td>(2.211 ± 0.023)$\times 10^{20}$</td>
<td>(1.030 ± 0.011)$\times 10^{20}$</td>
<td>Jm$^{-4}$</td>
</tr>
<tr>
<td>$\delta_{00}$</td>
<td>4062.37 ± 0.28</td>
<td>cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{v}$</td>
<td>59.865 ± 0.074</td>
<td>cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{v}$</td>
<td>2.974 ± 0.025</td>
<td>cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$D_{v}$</td>
<td>(4.832 ± 0.051)$\times 10^{-2}$</td>
<td>cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>$B_{00}[10]$</td>
<td>(4.53 ± 0.13)$\times 10^{-3}$</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>$B_{00}[12]$</td>
<td>(2.13 ± 0.21)$\times 10^{-3}$</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>$n_{s}$/n$_{p}$</td>
<td>2.890 ± 0.045</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 para and 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 para, panel (d), or ortho, panels (c) and (e), components of the fit are shown, as the other component does not have any contribution.
translation energies in \( v = 0 \) and 1 states. In the harmonic approximation the difference is \( \frac{1}{2}(\omega_0^2 - \omega^2) = 11.6 \text{ cm}^{-1} \), but is reduced to 9.0 cm\(^{-1}\) because of anharmonic corrections \( \omega_0 \). The vibrational frequency \( \omega_0 \) 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 \( B_r \) and the vibrational correction \( \alpha_v \) of H\(_2\) inside C\(_{60}\), Table II, are smaller than the gas phase values,\(^{36} \) 60.853 and 3.062 cm\(^{-1}\). We found that it is necessary to include a centrifugal correction \( D_r \) to the rotational constant, that is 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. 1 of Ref. 6. The value of \( B_r \) 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 \( B_r \sim \langle 1/s^2 \rangle \). 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 redshifts of \( \omega_0 \) (Ref. 39). However, the correction \( \alpha_0 \) 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.\(^{11} \) 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 para \( J = 0 \) and ortho \( J = 1 \) states. When compared to energies listed in Tables III and IV, their energies \( E_{\text{para}}^1 \) and \( E_{\text{ortho}}^1 \) are higher by 10 cm\(^{-1}\) and \( E_{\text{ortho}}^0 \) by 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 ortho line at 4267 cm\(^{-1}\) (Table I). This experimental line is split into two components, about 2 cm\(^{-1}\) apart [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 ortho or para lines within 2 cm\(^{-1}\) [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 C_{60} crystal. The prominent features in the exohedral H_{2} IR spectra\textsuperscript{40} are the translational, \Delta N = \pm 1, sidebands to the fundamental transitions, \Delta v = 1 and \Delta J = 0, 2. The redshift of the fundamental vibrational frequency is about 60 cm\(^{-1}\), which is less than that in H_{2}@C_{60} 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 H_{2}@C_{60}. It is likely that the main contribution to the latter difference comes from the larger van der Waals volume available for H_{2} in the octahedral site than in the C_{60} cage.

### B. Dipole moment

The dipole moment parameters \( B_{10}[10] \) and \( B_{10}[12] \) are given in Table II. The numerical values are consistent with our previous result,\textsuperscript{6} where only the ratio of the two dipole moment parameters, \(-2.0 \pm 0.2\), 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 \( B_{10}[|j|] \) depend on the pairwise H_{2}–C induced dipole parameter \( B^{ij} \) and its derivative [Eq. (14)]. A theoretical calculation of \( B^{ij} \) for H_{2}–C is outside the scope of the current study. The general trend is consistent with the theoretical calculations for H_{2}–He pairs, where the signs of \( B^{10} \) and \( B^{12} \) are opposite and \( B^{12} \) has the smaller absolute value.\textsuperscript{25}

Herman and Lewis\textsuperscript{41} calculated the dipole moment of interstitial H_{2} at the octahedral site in solid C_{60} using H_{2}–He interaction data. They considered the isotropic exchange (overlap) induced dipole \( B^{(10)} \) at short range and the quadrupole induced dipole \( B^{(32)} \) at short and long ranges. We showed in Sec. II that \( B^{32} \) does not contribute to \( \Delta N = \pm 1 \) electric dipole transitions in endohedral H_{2}.

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 \( d = 3.28 \times 10^{-32} \) C m. For example, the permanent dipole moment of a free HD molecule\textsuperscript{42} corresponding to \( \nu = 0 \to 1, J = J + 1 \) transitions is only \( 5 \times 10^{-5} \) D. To estimate an effective charge associated with the 4255 cm\(^{-1}\) transition, we use \( q = 20B_{10}[10] \) [see Eq. (13)] and get \( q = 9.1 \times 10^{-22} \) C after substituting the fitted value for \( B_{10}[10] \) from Table II. This is about 0.006 electron charges. However, the displacement \( \langle R \rangle_{10} = d/q = 0.36 \) 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 H_{2}@C_{60}, when H_{2} experiences translational motion in the C_{60} cage.

The IR transitions reported here are the transitions where the vibrational state changes, \( \nu = 0 \to 1 \). One may ask if the induced electric dipole transitions, \( \Delta N = \pm 1 \), can be observed within the vibrational ground state \( \nu = 0 \). 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 parameters \( A_{j0}^{(10)}(R) \) [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 H_{2} 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\(^{-1}\) (\( 0000 \to 0111 \)) and ortho line at 180.4 cm\(^{-1}\) (\( 1001 \to 1112 \)) (Tables III and IV). The intensity of both lines is given by \( A_{10}^{(10)} \). We simulated the expected absorption using Eq. (17) (note the dependence on \( \omega \)) 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 \( A_{10}/A_{00} \geq \sqrt{10} \). It has been found that the induced dipole moments of a H_{2}–He pair have an opposite dependence on the vibrational states.\textsuperscript{25} \( B_{10}^{(10)} \) is larger than \( B_{10}^{(10)} \).

### VI. SUMMARY

The IR absorption spectrum of endohedral H_{2} in C_{60} is rich, involving several excitations: vibrations, rotations, and translational motions of H_{2}. The translational motion is quantized because of the surrounding C_{60} cage and coupled to the rotations of H_{2}. 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 6–300 K is the change of IR line intensities, which is reasonably well accounted for by the Boltzmann distribution in the ground vibrational state \( \nu = 0 \). The energy levels of H_{2}@C_{60} 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, \( \nu = 0 \) or \( \nu = 1 \). The potential is divided into an isotropic part, which depends on the center of mass coordinate of H_{2} and an anisotropic part which depends on the orientation of H_{2} 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 \( \Delta N = 1 \) transitions in the ground vibrational state \( \nu = 0 \).

Our study shows that the vibrations and rotations of C_{60} and the crystal field effects of solid C_{60} are not important on the energy scale of IR measurements. If these effects are important, their contribution to the IR spectra is the order of 1 wavenumber splitting of few absorption lines. Such small splitting is consistent with the results of heat capacity measurements.\textsuperscript{43}

We do not explain how the determined parameters are linked to the molecular structure of the H_{2}@C_{60} complex. In principle it should be possible to describe, within a single quantum chemical model of H_{2}@C_{60}, 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 H_{2} values. Some additional information may come from the IR studies of endohedral D_{2} 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).