Rotor in a Cage: Infrared Spectroscopy of an Endohedral Hydrogen-Fullerene Complex

S. Mamone,Min Ge,D. H¨uvonen,U. Nagel,A. Danquigny,F. Cuda,M. C. Grossel,Y. Murata,K. Komatsu,M. H. Levitt,T. Rõõm,and M. Carravetta,

School of Chemistry, University of Southampton, Southampton UK SO17 1BJ. E-mail:marina@soton.ac.uk

Related articles by Dr Marina Carravetta can be found below:

A.J. Horsewill, S. Rols, M.R. Johnson, Y. Murata, M. Murata, K. Komatsu, M. Carravetta, S. Mamone, M.H. Levitt, J.Y.-C. Chen, J.A. Johnson, X. Lei and N.J. Turro, (2010) "Inelastic neutron scattering of a quantum translator-rotator encapsulated in a closed fullerene cage: isotope effects and translation-rotation coupling in H2@C60 and HD@C60", Phys. Rev. B 82, 081410(R) (10.1103/PhysRevB.82.081410)

M. Ge, U. Nagel, D. Hüvonen, T. Rõõm, S. Mamone, M.H.Levitt, M. Carravetta, Y. Murata, K. Komatsu, Y.-C. Chen and N.J. Turro, (2011) "Interaction potential and infrared absorption of endohedral H2 in C60", J. Chem. Phys. 134 054507-05451 (DOI:10.1063/1.3535598).

M. Ge, U. Nagel, D. Hüvonen, T. Rõõm, S. Mamone, M.H.Levitt, M. Carravetta, Y. Murata, K. Komatsu, X. Lei and N.J. Turro,(2011) "Infrared spectroscopy of endohedral HD and D2 in C60", J. Chem. Phys. 135 114511. (DOI: 10.1063/1.3637948)

A. J. Horsewill, K. S. Panesar, S. Rols, J. Ollivier, M. R. Johnson, M. Carravetta, S. Mamone, M. H. Levitt, Y. Murata, K. Komatsu, J. Y.-C. Chen, J. A. Johnson, X. Lei and N. J. Turro, (2012) "Inelastic neutron scattering investigations of the quantum molecular dynamics of a H2 molecule entrapped inside a fullerene cage", Phys. Rev. B 85, 205440 (DOI:10.1103/PhysRevB.82.081410)

C. Beduz, M. Carravetta, J. Y.-C. Chen, M. Concistre, M. S. Denning, M. Frunzi, A. J. Horsewill, O. G. Johannessen, R. Lawler, X. Lei, M. H. Levitt, Y. Li, S. Mamone, Y. Murata, U. Nagel, T. Nishida, J. Ollivier, S. Rols, T. Rõõm, R. Sarkar, N. J. Turro, Y. Yang,(2012) "Quantum rotation of ortho and para-water encapsulated in a fullerene cage", Proc. Nat. Acad. Sci. USA 109, 12894-12898 (DOI:10.1073/pnas.1210790109).

S. Mamone, M. Concistre, I. Heinmaa, M. Carravetta, I. Kuprov, G. Wall, M. Denning, X. Lei, J.Y.-C. Chen, Y. Li, Y. Murata, N. J. Turro, M. H. Levitt,(2013) Nuclear Magnetic Resonance of Hydrogen Molecules Trapped inside C70 Fullerene Cages,ChemPhysChem. (DOI:10.1002/cphc.201300269)

Rotor in a Cage: Infrared Spectroscopy of an Endohedral Hydrogen-Fullerene Complex

S. Mamone,[1] Min Ge,[2] D. Hüvonen,[2] U. Nagel,[2] A. Danquigny,[1] F. Cuda,[1] M. C. Grossel,[1] Y. Murata,[3] K. Komatsu,[3] M. H. Levitt,[1] T. Rõõm,[2] and M. Carravetta[1, *]

[1] School of Chemistry, Southampton University, Southampton SO17 1BJ, United Kingdom
[2] National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia
[3] Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan
(Dated: June 25, 2008)

We report an infrared study of molecular hydrogen trapped inside C_{60}-fullerene cages. Narrow absorption lines are observed at a temperature of 6 K, corresponding to vibrational excitations accompanied by changes in the translational and rotational energies of the endohedral H_2 molecules. A theoretical model describes the coupled rotational and translational modes of the confined three-dimensional quantum rotors. The theory provides both the frequencies and the intensities of the infrared transitions. Good agreement with the experimental results is obtained by fitting a small number of empirical parameters to describe the confining potential, as well as the *ortho* to *para* ratio.

PACS numbers: 33.20.Vq, 36.20.Ng, 63.22.+m, 78.30.Na

Endohedral complexes have been synthesized in which freely-rotating H_2 molecules are trapped inside fullerene cages [1–3]. Apart from their chemical interest and importance, these remarkable systems are ideal testbeds for the study of the dynamics of three-dimensional quantum rotors trapped inside a potential well generated by non-bonding atomic interactions. They are highly homogeneous and may be manipulated chemically to change the symmetry of the confining potential[4, 5]. Systems of this type have been studied by a variety of methods including nuclear magnetic resonance [4–6], theoretical calculations [7, 8] and Raman spectroscopy [9]. At first sight, it may seem unlikely that infrared (IR) spectroscopy would be a suitable tool for studying H_2 since it is well-known that isolated homonuclear diatomics have no IR activity [10]. However, H_2 does display IR activity in situations where there are strong intermolecular interactions, such as in the solid and liquid phases [11, 12], in constrained environments [13–15], and in pressurized gasses [16, 17]. The IR spectra of such systems are usually rather broad due to inhomogeneities in the system and the effect of random molecular collisions. These effects are absent for the endohedral $H_2@C_{60}$ complexes in the solid state at low temperature, leading to exceedingly narrow IR lines.

In this Letter we present low temperature IR absorption data for the icosahedral closed-cage complex $H_2@C_{60}$ in the solid state, and present a theoretical model for the confined quantum rotor, using a small number of parameters to describe the confining potential. The potential parameters, and the *ortho/para* ratio of the trapped H_2 molecules, are determined by comparison with the experimental IR spectrum.

The $H_2@C_{60}$ sample (10 mg) was prepared as described in [3] and pressed into a pellet of thickness $d = 0.25$ mm. Transmission measurements were made with an interferometer Vertex 80v (Bruker), halogen lamp, and MCT detector. The unapodized resolution was 0.15 cm^{-1} and Blackman-Harris 3-term apodization was applied. The sample and the open hole as a reference were inside an optical cryostat with KBr windows. The absorbance $\alpha(\omega)$ was calculated from the transmission $T_r(\omega)$ through $\alpha(\omega) = -d^{-1} \ln \left[T_r(\omega)(1-R)^{-2} \right]$ with a reflection coefficient $R = [(n-1)/(n+1)]^2$. A frequency-independent index of refraction $n = 2$ was assumed [18, 19]. The low temperature IR absorption peaks of $H_2@C_{60}$ are located in four narrow spectral bands between 4060 and 4810 cm^{-1} (see Fig. 1). This region corresponds to the H_2 stretching mode and its rotational/translational side-bands. The weak transitions around 4070 cm^{-1} represent pure vibrational excitations of the H_2 molecule without accompanying excitations of the roto-translational modes and are forbidden in the approximate theory presented below. The much stronger peaks in the 4250 cm^{-1}, 4600 cm^{-1} and 4800 cm^{-1} regions are assigned to vibrational excitations of H_2 accompanied by translational and/or rotational excitations.

The position and orientation of H_2 molecule is described using spherical coordinates $\mathbf{R} = \{R, \Theta, \Phi\}$ and $\mathbf{r} = \{r, \theta, \phi\}$ where $\mathbf{R}$ is the vector from the center of the C_{60} cage to the center of mass of H_2 and $\mathbf{r}$ is the internuclear H-H vector. As first approximation we consider decoupled translational, rotational and vibrational movement of H_2. The translation of the confined molecule may be treated using the isotropic three-dimensional harmonic oscillator model. The appropriate translational quantum numbers are $N = 0, 1, \ldots$, the orbital angular momentum quantum number L, which is an integer with the same parity as N and the azimuthal quantum number M_L. The radial form of the wavefunction depends both on N and L. The translational eigenfunctions are

$$\Psi^T_{NLM_L}(R, \Theta, \Phi) = \Psi^T_{NL}(R) \, Y_{LM_L}(\Theta, \Phi) \qquad (1)$$
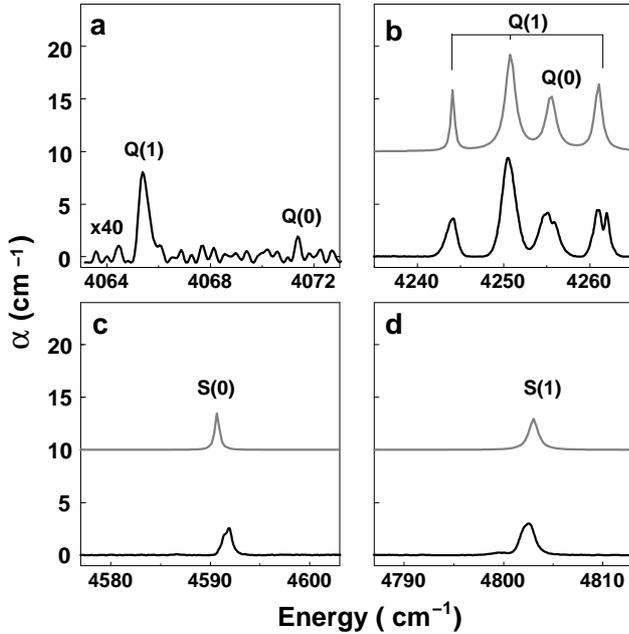
FIG. 1: Baseline-corrected IR absorption spectra (black) of $H_2@C_{60}$ at 6 K and the best fit theoretical spectrum (grey). All transitions are between the vibrational states $v = 0$ to $v = 1$. The labelling scheme uses a letter to indicate the change in J ($\Delta J = 0$ is a Q line and $\Delta J = 2$ is an S line) and the number in parentheses is the initial J value. For the assignment inside a rotational branch, see Table I and Fig. 2. (a) Fundamental vibrational transitions $Q(0)$ and $Q(1)$. (b) $\Delta J = 0$ transitions involving the excitations of one translational quantum, $\Delta N = +1$. (c, d)S transitions with $\Delta N = +1$ and $\Delta J = +2$ for (c) *para*-H_2 and (d) *ortho*-H_2.

where the radial wave function Ψ_{NL}^T and the spherical harmonics Y_{LM_L} are defined in [20]. The rotational wave-functions, defined by the rotational quantum numbers $J = 0, 1 \ldots$ and $M_J = -J, -J + 1 \ldots, +J$, are given by the spherical harmonics $Y_{JM_J}(\theta, \phi)$. It is convenient to introduce a set of coupled angular functions with overall spherical rank Λ and component M_Λ, as follows:

$$F_{\Lambda M_\Lambda}^{LJ}(\Omega) = \sum_{M_L, M_J} \mathcal{C}_{M_L M_J M_\Lambda}^{LJ\Lambda} Y_{LM_L}(\Theta, \Phi) Y_{JM_J}(\theta, \phi) \quad (2)$$

where $\Omega = \{\Theta, \Phi, \theta, \phi\}$ and $\mathcal{C}$ are the Clebsch-Gordan coefficents [21]. The full wave function describing the motion of the H_2 molecule may be written as

$$|vJNL\Lambda M_\Lambda\rangle = \Psi_v^V(r)\Psi_{NL}^T(R)F_{\Lambda M_\Lambda}^{LJ}(\Omega) \quad (3)$$

where $\Psi_v^V(r)$ is the vibrational wavefunction with quantum number v. The complete quantum state of the H_2 molecule also includes the nuclear spin quantum number I. From the Pauli principle, the H_2 molecule is either in a *para* state ($I = 0$ and J even) or in an *ortho* state ($I = 1$ and J odd). Since the spin isomer interconversion is negligible for the endohedral complex [5], the ratio between *ortho* and *para* populations is not in general governed by

the Boltzmann distribution and must be determined empirically. From now on the spin quantum numbers will be ignored, except for noting that the spin degeneracy $g_I = 2I + 1$ influences the amplitudes of the IR transitions.

The Hamiltonian $\mathcal{H}$ for the trapped molecule includes coupling terms between the vibrational, translational, and rotational motion. For simplicity, we neglect all Hamiltonian matrix elements connecting terms with different quantum numbers v and introduce a parametric dependence of the rotation and translation potential on v:

$$\mathcal{H} = {}^v\mathcal{H}^{VR} + \frac{p^2}{2m} + {}^vV(R, \Omega) \quad (4)$$

where ${}^v\mathcal{H}^{VR}$ is the vibration-rotation Hamiltonian, p is the molecular momentum operator and m is the molecular mass. The superscript prefix v is used to indicate an implied dependence on the vibrational quantum number. ${}^vV$ is the potential energy of a molecule at a given position and orientation within the cavity, and includes terms that couple the rotational and translational motion. The vibrational-rotational Hamiltonian ${}^v\mathcal{H}^{VR}$ is diagonal in the basis set $|vJNL\Lambda M_\Lambda\rangle$ with eigenvalues given by ${}^vE_J^{VR} = \hbar\omega_0^V(v + 1/2) + B_vJ(J + 1)$ and rotational constant $B_v = B_e - \alpha_e(v + 1/2)$, where ω_0^V is the fundamental vibration frequency, and α_e is an anharmonicity correction [10]. Below 120 K, the thermally-activated rotational motion of the C_{60} cages is suppressed [5, 22]. The ${}^vV$ potential may be assumed to be time-independent, and is conveniently expressed as follows:

$${}^vV(R, \Omega) = \sum_{n,l,j,\lambda,m_\lambda} {}^vV_{\lambda m_\lambda}^{ljn} R^n F_{\lambda m_\lambda}^{lj}(\Omega) \quad (5)$$

where the functions F are defined in Eq. 2 and n takes even values. Terms with $n = 2$ constitute a harmonic potential energy function, while terms with $n > 2$ represent anharmonic perturbations. Translation-rotation coupling terms have non-zero values for both l and j.

For an icosahedral cavity, and assuming that longer-range intermolecular perturbations are negligible, all terms with odd values of λ vanish, as well as the terms with $\lambda = 2$ and 4. For a homonuclear diatomic molecules, all odd-j terms vanish. For simplicity, we assume all high-order terms are small, and express the potential energy as ${}^vV = {}^vV^0 + {}^vV'$, where the isotropic harmonic term is given by

$${}^vV^0 = {}^vV_{00}^{000}F_{00}^{00} + {}^vV_{00}^{002}R^2F_{00}^{00} \quad (6)$$

and the perturbation due to translation-rotation and anharmonicities coupling is given by

$${}^vV' \cong {}^vV_{00}^{222}R^2F_{00}^{22} + {}^vV_{00}^{004}R^4F_{00}^{00} \quad (7)$$

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

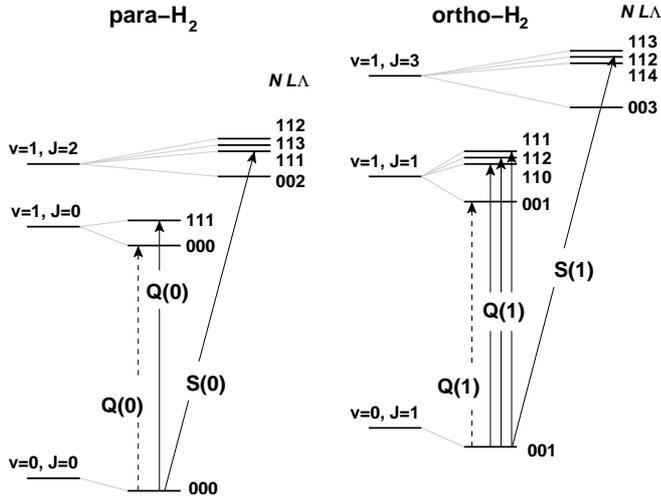$$E_{vJNL\Lambda M_\Lambda}^0 = {}^vE_J^{VR} + \hbar\, {}^v\omega_0^T(N + 1/2) \quad (8)$$

FIG. 2: Qualitative energy level diagram of H_2 trapped inside C_{60} refined against low temperature IR data. Only the ground rotational/translational states of the $v = 0$ level are shown. The energy levels of free H_2 are shown on the left for *para*- and *ortho*-H_2 while the effect of confinement is shown on the right and gives rise to the fine level structure. The arrows show transitions corresponding to the observed low-temperature IR absorption peaks. The dashed lines are forbidden within the approximate theory presented here

where $^v\omega_0^T = \left(^vV_{00}^{002}/(2\pi m)\right)^{1/2}$ is the fundamental frequency for translational oscillations within the cavity.

The matrix elements of $^vV'$ were evaluated analytically in the basis $|vJNL\Lambda M_\Lambda\rangle$ using 100 states with $N \leq 2$ and $J = 1, 3$ for *ortho*-H_2, and using 60 states with $N \leq 2$ and $J = 0, 2$ for *para*-H_2. Matrix diagonalization leads to explicit but cumbersome expressions for the energy levels and eigenstates. A schematic energy level diagram is given in Fig.2. The ordering of the eigenvalues depends on the relative sign and magnitudes of the anharmonic term $^vV_{00}^{004}$ and the translation-rotation coupling term $^vV_{00}^{222}$. The ordering in Fig.2 is consistent with the experimental results.

IR activity in $H_2@C_{60}$ is due to a dipole moment, μ, induced by the constraining environment. The dipole moment operator can be expanded in multipoles depending on the instantaneous H_2 configuration [23]:

$$\mu_q = \frac{4\pi}{\sqrt{3}} \sum_{l,j=0}^{\infty} A^{lj}(R,r)F_{1q}^{lj}(\Omega) \qquad (9)$$

where q denotes the spherical componet and the A coefficients describe the induced dipole moment. Since the dipole moment is a vector, there are restrictions on the allowed j and l values: (i) $j+l$ must be odd, (ii) $l = j\pm1$ from the triangle relation, (iii) for homonuclear molecules only even j terms are allowed. These restrictions imply selection rules for IR spectroscopy of $H_2@C_{60}$. The selection rule for the total angular momentum is $\Delta\Lambda = 0, \pm1$ with the only allowed transitions having even values of

ΔJ and odd values of ΔL. In addition, only the ground rotational/translational states are populated at low temperature. As a result, the allowed transitions observed in the 6 K IR spectrum are from states with $N = L = 0$ to states with $N = L = 1$ (see Fig. 2).

For a transition between an initial state $|i\rangle$ and final state $|f\rangle$ the IR absorption amplitude is [10]:

$$S_{fi}(n_P, T) \propto \omega_{fi}\, p_i(n_P, T) \sum |\langle f|\mu_q|i\rangle|^2 \qquad (10)$$

where p_i is the fractional population of the initial state $|i\rangle$. The populations are determined by individual Boltzmann distributions at the sample temperature T within the separate *ortho* and *para* manifolds, taking in account the nuclear spin degeneracy and also the fractions n_P and n_O of *para* and *ortho*-H_2 respectively, with $n_O + n_P = 1$. Since all the observed transitions are from $L = 0$ to $L = 1$, only terms with $l = 1$ and $j = 0, 2$ are to be considered in the dipole expansion. This implies that only $\Delta J = 0, +2$ transitions are observable. The dipole matrix elements for the observed transitions in $H_2@C_{60}$ between states $|i\rangle$ and $|f\rangle$ can be expressed as

$$\langle f|\mu_q|i\rangle = \frac{4\pi}{\sqrt{3}} \sum_{j=0,2} \rho^j [X_{1q}^{1j}]_{fi} \qquad (11)$$

where

$$\rho^j = \langle \Psi_1^V(r)\Psi_{11}^T(R)|A^{1j}(R,r)|\Psi_0^V(r)\Psi_{00}^T(R)\rangle \quad (12)$$
$$X_{jq}^{fi} = \langle F_f(\Omega)|F_{1q}^{1j}(\Omega)|F_i(\Omega)\rangle. \qquad (13)$$

The matrix elements reduce into a sum of products over radial integrals ρ^j and known angular integrals. Two potential parameters $^1V_{00}^{002}$, $^1V_{00}^{222}$, the rotational constant B_e, ρ^0, ρ^2 and the *ortho-para* ratio, n_O/n_P, have been fitted to match the experimental frequencies and intensities. Since $^1V_{00}^{002}$ and $^1V_{00}^{004}$ cannot be determined independently from the 6 K data, we set $^1V_{00}^{004}=0$. The optimized parameters for the potential in the first vibrational state resulted to be $\{^1V_{00}^{002}, ^1V_{00}^{222}\} = \{25.3 \pm 0.2, 1.4 \pm 0.2\}$ J m^{-2}. The fitted rotational constant is $B_e = 59.3 \pm 0.2$ cm^{-1} while $\alpha_e = 2.98 \pm 0.10$ cm^{-1} is obtained directly from the difference in the fundamental vibrational frequencies for the *ortho* and *para* states. The ratio between the induced dipole moment parameters in given by $\rho^0/\rho^2 = -2.0\pm0.2$ and $n_O/n_P = 2.8\pm0.2$. The *ortho-para* ratio is consistent with equilibration at any temperature warmer than 120K and suggests that there has been negligible spin isomer interconversion since the molecules were synthesized. The experimental and the best fit results are displayed in Fig. 1 and summarised in Table I.

The frequencies of the pure vibrational transitions (see Fig. 1a) are shifted by -90 cm^{-1} from the free H_2 value. The reduction in both the fundamental vibrational frequency and rotational constant [24] are consistent with

TABLE I: Experimental and calculated center frequencies, ω, and absorption line areas, S_ω, of IR-active H_2 modes at $6\,K$ in $H_2@C_{60}$. The forbidden transitions (dotted lines in Fig.2) are used as frequency references for the fitting procedure.

	$NL\Lambda$		Experimental		Fitted	
	initial	final	ω (cm^{-1})	S_ω (cm^{-2})	ω (cm^{-1})	S_ω (cm^{-2})
$Q(1)$	001	001	4065.44	0.093		
$Q(0)$	000	000	4071.39	0.011		
$Q(1)$	001	111	4244.5	5.6	4244.1	4.5
$Q(1)$	001	112	4250.7	18.8	4250.8	20.0
$Q(1)$	001	110	4261.0	8.7	4261.0	10.0
$Q(0)$	000	111	4255.0	10.5	4255.5	11.2
$S(0)$	000	111	4591.5	3.1	4590.7	2.9
$S(1)$	001	112	4802.5	5.6	4803	5.1

a predominantly attractive C-H interaction that slightly stretches the H-H bond.

The results described here are in qualitative agreement with previous theoretical calculations [7, 8]. The energy order of the Λ sublevels is consistent with the numerical calculations of Xu $et\ al.$, even though the splittings are different [8]. The experimental value of $^v\omega_0^T$ is about 12% smaller than that estimated by Cross [7]. It should be recalled, however, that our measurements refer to the $v = 1$ excited state, while the numerical calculations are for the $v = 0$ ground state and that the pairwise C-H potential used in [8] was not optimized for $H_2@C_{60}$.

Deformation of the cage and/or crystal field effects may lower the symmetry, possibly introducing rank 4 terms, and also split lines in the 4240-4265 cm^{-1} region of the spectrum (Fig. 1b). Some degree of mixing among the energy levels may be at the origin of the weak fundamental transitions.

In summary, the low-temperature infrared spectrum of endohedral dihydrogen molecules displays a rich spectral structure due to the coupled translational and rotational modes of the confined quantum rotor. The spectrum may be explained almost quantitatively by a theory involving a multipole expansion of the confining potential, followed by numerical fitting of a small number of parameters. The next targets will be to analyze higher-temperature data in order to extract information on the vibrational ground state, to perform experiments on chemically-modified cages with lower symmetry, and on different dihydrogen isotopomers.

* Electronic address: marina@soton.ac.uk

[1] Y. Rubin, T. Jarrosson, G.-W. Wang, M. D. Bartberger, K. N. Houk, G. Schick, M. Saunders, and R. J. Cross, Angew. Chem. Int. Ed. **40**, 1543 (2001).

[2] K. Komatsu, M. Murata, and Y. Murata, Science **307**, 238 (2005).

[3] M. Murata, Y. Murata, and K. Komatsu, J. Am. Chem. Soc. **128**, 8024 (2006).

[4] M. Carravetta, O. G. Johannessen, M. H. Levitt, I. Heinmaa, R. Stern, A. Samoson, A. J. Horsewill, Y. Murata, and K. Komatsu, J. Chem. Phys. **124**, 104507 (2006).

[5] M. Carravetta, A. Danquigny, S. Mamone, F. Cuda, O. G. Johannessen, I. Heinmaa, K. Panesar, R. Stern, M. C. Grossel, A. J. Horsewill, et al., Phys. Chem. Chem. Phys. **9**, 4879 (2007).

[6] E. Sartori, M. Ruzzi, N. J. Turro, J. D. Decatur, D. C. Doetschman, R. G. Lawler, A. L. Buchachenko, Y. Murata, and K. Komatsu, J. Am. Chem. Soc. **128**, 14752 (2006).

[7] R. J. Cross, J. Phys. Chem. A **105**, 6943 (2001).

[8] M. Xu, F. Sebastianelli, K. Bacic, R. Lawler, and N. J. Turro, J. Chem. Phys. **128**, 011101 (2008).

[9] P. M. Rafailov, C. Thomsen, A. Bassil, K. Komatsu, and W. Bacsa, Phys. Stat. Sol. (b) **242**, R106 (2005).

[10] G. Herzberg, *Molecular spectra and molecular structure, I. Spectra of diatomic molecules* (Van Nostrand Company, Inc. (Princeton), 1950), 2nd ed.

[11] E. J. Allin, W. F. J. Hare, and R. E. MacDonald, Phys. Rev. **98**, 554 (1955).

[12] W. F. J. Hare, E. J. Allin, and H. L. Welsh, Phys. Rev. **99**, 1887 (1955).

[13] S. A. FitzGerald, S. Forth, and M. Rinkoski, Phys. Rev. B **65**, 140302 (2002).

[14] S. A. FitzGerald, H. O. H. Churchill, P. M. Korngut, C. B. Simmons, and Y. E. Strangas, Phys. Rev. B **73**, 155409 (2006).

[15] T. Yildirim and A. B. Harris, Phys. Rev. B **66**, 214301 (2002).

[16] A. Kudian and M. Welsh, Can. J. Phys. **49**, 230 (1971).

[17] A. R. W. McKellar and H. L. Welsh, Can. J. Phys. **52**, 1082 (1974).

[18] C. C. Homes, P. J. Horoyski, M. L. W. Thewalt, and B. P. Clayman, Phys. Rev. B **49**, 7052 (1994).

[19] M. K. Kelly, P. Etchegoin, D. Fuchs, W. Krätschmer, and K. Fostiropoulos, Phys. Rev. B **46**, 4963 (1992).

[20] S. Flügge, *Practical quantum mechanics* (Springer-Verlag (Berlin), 1971).

[21] J. M. Brown and A. Carrington, *Rotational Spectroscopy of Diatomic Molecules* (Cambridge University Press, 2003).

[22] R. Tycko, G. Dabbagh, R. M. Fleming, R. C. Haddon, A. V. Makhija, and S. M. Zahurak, Phys. Rev. Lett. **67**, 1886 (1991).

[23] J. D. Poll and J. L. Hunt, Can. J. Phys. **54**, 461 (1976).

[24] S. Bragg, J. Brault, and W. Smith, The Astrophysical J. **263**, 999 (1982).