Quantum dynamics of coupled translational and rotational motions of H₂ inside C₆₀

Minzhong Xu, Francesco Sebastianelli, and Zlatko Bačić[a)]
Department of Chemistry, New York University, New York, New York 10003, USA

Ronald Lawler
Department of Chemistry, Brown University, Providence, Rhode Island 02912, USA

Nicholas J. Turro[b)]
Department of Chemistry, Columbia University, New York, New York 10027, USA

We report rigorous quantum calculations of the translation-rotation (T-R) eigenstates of the H_2 molecule in C_{60}. The resulting level structure can be explained in terms of a few dominant features. These include the coupling between the orbital and the rotational angular momenta of H_2 to give the total angular momentum λ, and the splitting of the sevenfold degeneracy of T-R levels with $\lambda = 3$ by the nonsphericity of C_{60}, according to the rules of the icosahedral I_h group. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2828556]

I. INTRODUCTION

The fascinating endohedral H_2-C_{60} complex, denoted $H_2@C_{60}$, in which the H_2 molecule is trapped inside the C_{60} cage, has been synthesized recently in macroscopic quantities.[1,2] This has prompted the investigations of the dynamical properties of the endohedral H_2 in C_{60} and related fullerenes using NMR spectroscopy,[3–5] as well as of its photophysical characteristics.[6] The confinement of H_2 inside C_{60} leads to the quantization of its translational degrees of freedom. Due to the small mass of H_2, and the rather small fullerene cavity, the translational energy levels are well separated in energy. The same is true for the rotational levels of H_2 because of its large rotational constant (≈ 60 cm^{-1}). This combination makes the dynamics of the confined H_2 molecule highly quantum mechanical. Consequently, $H_2@C_{60}$ provides a unique opportunity for elucidating the key features of the quantum dynamics of the coupled translational and rotational motions of a light molecule inside a cage of high symmetry. So far, the dynamics of this intriguing system has been treated extremely approximately[5] by solving the textbook one-dimensional (1D) radial Schrödinger equation for a structureless particle (H_2) inside a spherical box. This approach leaves out entirely the H_2 rotations and their coupling to the translational motions. The only quantum mechanical calculations to date of the translation-rotation (T-R) eigenstates of a molecule in C_{60} were performed for $CO@C_{60}$.[7] The interaction potential of $CO@C_{60}$ is qualitatively different from that of H_2 in C_{60}, and the masses and the rotational constants of the two guest molecules differ greatly as well, resulting in substantially different T-R dynamics.

In this paper, we report the results of the study where for the first time the quantum dynamics of the three translational

and the two rotational degrees of freedom of the H_2 molecule inside C_{60} is treated rigorously, as fully coupled, while C_{60} and H_2 are taken to be rigid. The analysis of the calculated T-R energy levels and wave functions reveals the basic facets of the dynamics of the endohedral H_2 molecule.

II. METHODOLOGY

The Raman and infrared spectra of the C_{60} molecule[8,9] show some rather low-frequency modes, starting at 273 cm^{-1}. But, the H_2-C_{60} interaction is weak and the disparity between the masses of H_2 and C_{60} is large. Therefore, the coupling between the vibrations of C_{60} and the T-R motions of H_2 is expected to be weak, and its neglect should not introduce significant errors, thus justifying the treatment of C_{60} as rigid. C_{60} has icosahedral (I_h) symmetry, and the geometry used in our calculations is virtually identical to the experimental one.[10] The five dimensional (5D) T-R eigenstates of the endohedral H_2 molecule are calculated using the bound-state approach developed by us earlier to treat the quantum T-R dynamics of H_2 inside the cages of the clathrate hydrates.[11] The set of five coordinates (x, y, z, θ, ϕ) is employed; x, y, and z are the Cartesian coordinates of the center of mass (c.m.) of H_2, while the two polar angles θ and ϕ specify its orientation. The coordinate system is aligned with three orthogonal C_2 axes of C_{60}, and its origin is at the c.m. of the cage. The rotational constants of C_{60}, a spherical top, are only 0.0028 cm^{-1},[7] and therefore, the fullerene can be treated as nonrotating. Then, the 5D Hamiltonian for the T-R motions of the trapped H_2 molecule is

$$H = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + B\mathbf{j}^2 + V(x, y, z, \theta, \phi). \quad (1)$$

In Eq. (1), μ is the reduced mass of $H_2@C_{60}$ (only 0.3% smaller than the mass of H_2), while B (equal to 59.322 cm^{-1}) and $\mathbf{j}^2$ are the rotational constant and the angular momentum operator of the diatomic, respectively. $V(x, y, z, \theta, \phi)$ in

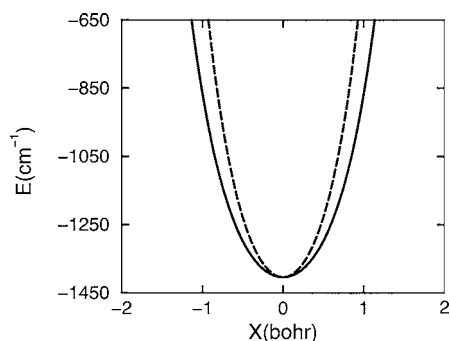a)Electronic mail: zlatko.bacic@nyu.edu.
b)Electronic mail: njt3@columbia.edu.

FIG. 1. One-dimensional cuts through the 5D interaction potential of H_2 inside C_{60} along a C_2 axis of C_{60} for H_2 perpendicular (full line) and parallel (dashed line) to the axis.

Eq. (1) is the 5D potential energy surface (PES) described below. The energy levels and wave functions of the Hamiltonian in Eq. (1) are obtained utilizing the efficient computational methodology whose detailed description is available.[11,12] The final Hamiltonian matrix, its size drastically reduced by the sequential diagonalization and truncation procedure,[13] is diagonalized yielding the T-R eigenstates which are numerically exact for the 5D PES employed.

The dispersion interactions between H_2 and the fullerenes cannot be computed reliably by density functional theory, while the *ab initio* calculation of the 5D PES at a higher level of theory would be prohibitively time consuming. Therefore, the intermolecular 5D PES for H_2 inside C_{60} is constructed as a sum over the pairwise interaction of each H atom of H_2 with each C atom of C_{60}, as was done in the theoretical investigations of H_2 in single-walled carbon nanotubes[14,15] and on graphite.[16] The two-body H–C interaction is modeled with the Lennard-Jones (LJ) 12-6 potential

$$V_{LJ}(r) = 4\epsilon_{HC}\left[\left(\frac{\sigma_{HC}}{r}\right)^{12} - \left(\frac{\sigma_{HC}}{r}\right)^{6}\right], \quad (2)$$

where ϵ_{HC} is the well depth of the potential and σ_{HC} is related to its equilibrium distance r_e, as $r_e = 2^{1/6}\sigma_{HC}$. In this

work, we employ the set of LJ parameters referred to in Ref. 14 as FB,[15] in which $\epsilon_{HC} = 19.2$ cm^{-1} and $\sigma_{HC} = 3.08$ Å. They generate a 5D PES for $H_2@C_{60}$, with the well depth of -1403.87 cm^{-1}, whose 1D cuts along a C_2 axis of C_{60}, for H_2 perpendicular and parallel to the axis, respectively, are shown in Fig. 1.

In the calculations reported here, the dimension of the sine discrete variable representation (DVR) was 15 for each of the three Cartesian coordinates x, y, and z, and it spanned the range -2.83 bohr $\leq \lambda \leq 2.83$ bohr ($\lambda = x, y, z$). The angular basis included functions up to $j_{max} = 7$. The energy cutoff parameter for the intermediate three-dimensional (3D) eigenvector basis[12] was set to 5000 cm^{-1}, resulting in the final full 5D Hamiltonian matrix of dimension 20 264.

III. RESULTS AND DISCUSSION

Molecular hydrogen exists in two species, parahydrogen (p-H_2) and orthohydrogen (o-H_2), for which the rotational quantum number j has only even ($j = 0, 2, 4, \ldots$) and odd ($j = 1, 3, \ldots$) values, respectively. The lower-lying quantum 5D T-R energy levels of o-H_2 and p-H_2 in C_{60} are given in Tables I and II, respectively. They display a conspicuous pattern of degeneracies, which must reflect certain basic features of the quantum T-R dynamics. To the endohedral H_2, C_{60} provides an environment of very high symmetry. This suggests that the model of the 3D isotropic harmonic oscillator (HO) for the translational degrees of freedom of the c.m. of H_2, and of the rigid rotor for the rotation of H_2 about its c.m., may constitute the starting point for developing the complete physical picture behind the intriguing calculated level structure. The energy levels of the 3D isotropic HO are labeled by the principal quantum number n and the orbital angular momentum quantum number l, whose allowed values are $n, n-2, \ldots, 1$ or 0 for odd or even n, respectively. Their degree of degeneracy, denoted here g_n^{HO}, is

TABLE I. Translation-rotation energy levels of o-H_2 inside C_{60} from the quantum 5D calculations. The excitation energies ΔE are relative to the ground-state energy $E_0 = -1012.009$ cm^{-1}, and g denotes their degeneracy. $\langle R \rangle$ (in a.u.) is the mean value of the distance between the centers of mass of H_2 and C_{60}. n and l are the principal and the orbital angular momentum quantum numbers, respectively, of the 3D isotropic harmonic oscillator, j is the quantum number of the dominant H_2 rotational basis function, and $c(j)$ is its contribution to a T-R eigenstate. λ is the quantum number of the total angular momentum operator $\lambda = \mathbf{j} + \mathbf{l}$. The values of l shown in the last column are those allowed for the given n.

ΔE	g	$\langle R \rangle$	λ	n	j	$c(j)$	l
118.45	3	0.57	1	0	1	0.999	0
378.56	3	0.72	1	1	1	0.999	1
402.73	5	0.71	2	1	1	0.996	1
445.52	1	0.69	0	1	1	0.998	1
665.11	5	0.84	2	2	1	0.996	0,2
683.78	3	0.82	1	2	1	0.995	0,2
686.52	4	0.75	3	2	1	0.636	0,2
687.05	3	0.75	3	2	1	0.618	0,2
726.79	4	0.66	3	0	3	0.643	0
727.73	3	0.66	3	0	3	0.625	0
765.32	3	0.79	1	2	1	0.992	0,2

TABLE II. Translation-rotation energy levels of p-H$_2$ inside C$_{60}$ from the quantum 5D calculations. The excitation energies ΔE are relative to the ground-state energy $E_0 = -1012.009$ cm^{-1}. Other symbols have the same meaning as in Table I.

ΔE	g	$\langle R \rangle$	λ	n	j	$c(j)$	l
0.00	1	0.57	0	0	0	0.998	0
279.47	3	0.71	1	1	0	0.990	1
354.92	5	0.57	2	0	2	0.994	0
574.52	5	0.82	2	2	0	0.975	0,2
593.27	1	0.81	0	2	0	0.968	0,2
615.58	5	0.72	2	1	2	0.999	1
640.02	4	0.72	3	1	2	0.984	1
640.36	3	0.72	3	1	2	0.983	1
662.28	3	0.70	1	1	2	0.985	1
883.64	4	0.91	3	3	0	0.956	1,3
883.97	3	0.91	3	3	0	0.954	1,3
…	…	…	…	…	…	…	…
914.13	3	0.90	1	3	0	0.944	1,3

$\frac{1}{2}(n+1)(n+2)$, i.e., 3 for $n=1$, 6 for $n=2$, and 10 for $n=3$. For the rigid rotor (RR) level with the quantum number j, the degeneracy g_j^{RR} is $2j+1$.

Among the quantities listed in Tables I and II are $\langle R \rangle$, the mean value of the distance between the centers of mass of H$_2$ and C$_{60}$, and $c(j)$, the contribution of the dominant H$_2$ rotational basis state j to a T-R eigenstate. The latter is obtained by projecting the eigenstate onto the rotational basis, taking the modulus squared and integrating over x, y, and z. Table I shows that the lowest T-R level of o-H$_2$ at 118.45 cm^{-1}, which is threefold degenerate ($g=3$), is a pure $j=1$ level. Moreover, its energy is very close to that of the $j=1$ level of the freely rotating H$_2$ at $2B=118.64$ cm^{-1}. Therefore, this level is assigned as $n=0$, $j=1$. The second excited level of p-H$_2$ in Table II, at 354.92 cm^{-1}, with fivefold degeneracy ($g=5$), is a pure $j=2$ level, whose energy is virtually equal to the $j=2$ level of the gas-phase H$_2$ at $6B=355.93$ cm^{-1}, and is assigned as $n=0$, $j=2$. Thus, for lower rotational excitations, j is a good quantum number. However, as discussed below, this behavior does not necessarily extend to higher energies. For the first excited T-R level of p-H$_2$ at 279.47 cm^{-1}, which is threefold degenerate ($g=3$), the predominant rotational contribution is from $j=0$. Consequently, this level must represent the fundamental translational (radial) excitation, which confirmed by its value of $\langle R \rangle$, 0.71 bohr, significantly larger than that of the p-H$_2$ ground state, 0.57 bohr. Therefore, this level is assigned as $n=1$, $j=0$.

That the translational and rotational degrees of freedom of H$_2$ in C$_{60}$ *are coupled* emerges from the examination of the group of three excited T-R levels of o-H$_2$ in Table I, at 378.56 ($g=3$), 402.73 ($g=5$), and 445.52 cm^{-1} ($g=1$). Based on the values of $\langle R \rangle$, energy consideration, and the dominant rotational state contribution $c(1) \geqslant 0.996$, their assignment is $n=1$, $j=1$, i.e., all three levels are excited both translationally and rotationally. The total number of $n=1$, $j=1$ states is

9, as expected from $g_{n=1}^{\mathrm{HO}} \times g_{j=1}^{\mathrm{RR}} = 3 \times 3$. But what is the cause of the peculiar $3+5+1$ degeneracy pattern?

A natural and simple explanation is that the orbital angular momentum $\mathbf{l}$ of the c.m. of H$_2$ and the H$_2$ rotational angular momentum $\mathbf{j}$ *couple* to give the *total* angular momentum $\lambda = \mathbf{l} + \mathbf{j}$. For given l and j, λ can take values $\lambda = l + j, l + j - 1, \ldots |l-j|$, with the degeneracy of $2\lambda + 1$. For $n=1$, the only value of l is $l=1$. Consequently for the T-R states with $n=1$, $j=1$, λ has values 2, 1, and 0, whose degeneracies are 5, 3, and 1, respectively, thus matching the degeneracy pattern of the three $n=1$, $j=1$ levels. The implication is that the level at 378.56 cm^{-1} ($g=3$) has $\lambda=1$, the level at 402.73 cm^{-1} ($g=5$) has $\lambda=2$, and the level at 445.52 cm^{-1} ($g=1$) has a $\lambda=0$ level. In other words, the T-R states having the same values of n, j split according to λ values into degenerate blocks (i.e., levels) of dimension (degeneracy) $2\lambda + 1$, which differ considerably in energy.

This scheme accounts for the degeneracies of *all* calculated T-R levels of o- and p-H$_2$. A group of four excited T-R levels of p-H$_2$ in Table II, ranging in energy from 615.58 to 662.28 cm^{-1} and assigned as $n=1$, $j=2$, exhibits some new features. Taking into account the degeneracies of these levels, there are 15 $n=1$, $j=2$ states, equal to $g_{n=1}^{\mathrm{HO}} \times g_{j=2}^{\mathrm{RR}} = 3 \times 5$. For $n=1$, the associated value of l is 1, and since $j=2$, λ takes values 3, 2, and 1, with respective $(2\lambda+1)$-fold degeneracies 7, 5, and 3. Therefore, the level at 615.58 cm^{-1} ($g=5$) has a $\lambda=2$ level, while the level at 662.28 cm^{-1} ($g=3$) has $\lambda=1$.

The seven $\lambda=3$ states, which should all be degenerate, appear instead as two closely spaced levels at 640.02 ($g=4$) and 640.36 cm^{-1} ($g=3$). This is in accordance with the group-theoretical prediction[17] that the "crystal field" of the icosahedral I_h symmetry should split a septet of $\lambda=3$ states into two sets of degenerate states of dimensions 4 and 3, respectively. It is readily verified that all $\lambda=3$ states in Tables I and II are split into a pair of levels of three- and

fourfold degeneracies, respectively. This type of splitting was also found in the calculations of CO @ C$_{60}$.[7]

We highlight the pair of $\lambda=3$ levels of o-H$_2$ in Table I, at 726.79 ($g=4$) and 727.73 cm^{-1} ($g=3$), assigned as $n=0$, $j=3$. Although they are nominally $j=3$ levels, j is not a very good quantum number, since $c(3)$ is only ~0.6, and the energies differ substantially from the $j=3$ level of the freely rotating H$_2$ at $12B=711.86$ cm^{-1}. This is probably due to the interaction with the pair of $\lambda=3$ levels at 686.52 and 687.05 cm^{-1} with $n=2$, $j=1$, whose $c(1)$ is ~0.6. Thus, the picture of H$_2$ rotating freely in C$_{60}$ (Ref. 18) is not necessarily valid at higher levels of rotational excitation.

The quantum numbers n and l of the 3D isotropic HO are essential for the assignment of the T-R levels. However, the translationally excited states are *not* harmonic since, as Table II shows, their energies depend not only on n but also on l. Thus, there are two $n=2$, $j=0$ levels of p-H$_2$, at 574.52 ($g=5$) and 593.27 cm^{-1} ($g=1$), corresponding to l (or λ, since $j=0$) equal to 2 and 0, respectively. The same is true for the $n=3$, $j=0$ levels of p-H$_2$, at the bottom of Table II. Moreover, the energy separation between the neighboring translational levels with $n=1$, 2, and 3 (and $j=0$) *increases* with n, demonstrating their *negative* anharmonicity.

The 5D T-R levels of H$_2$ in C$_{60}$ were also calculated by us for another set of LJ parameters for the H–C interaction, designated NW (Ref. 16) in Ref. 14. The 5D PES which they generate has a much smaller well depth, −1068.11 cm^{-1}, is softer, and gives rise to very different T-R excitations. Nevertheless, the T-R level structure computed on this PES can be understood completely utilizing the concepts discussed above. Therefore, the emergent physical picture of the factors which govern the T-R dynamics of the endohedral H$_2$ appears to be robust, insensitive to the details of the PES employed.

IV. CONCLUSIONS

Our study shows that the T-R energy level structure of the H$_2$ molecule inside C$_{60}$, from rigorous quantum 5D calculations, can be understood in terms of a few key features. (1) The orbital angular momentum **l** of the c.m. of H$_2$ and the rotational angular momentum **j** of H$_2$ couple to give the total angular momentum $\lambda=\mathbf{l}+\mathbf{j}$, with $\lambda=l+j, l+j-1, \ldots, |l-j|$. The values of l are those allowed for the quantum number n of the 3D isotropic HO. Introduction of the quantum number λ, with its $(2\lambda+1)$-fold degeneracy, accounts for the intricate pattern of degeneracies of the calculated T-R levels. (2) The $\lambda=3$ levels of H$_2$, which should be sevenfold degenerate, are each split into two closely spaced levels of fourfold and threefold degeneracies, respectively, by the icosahedral I_h environment of C$_{60}$, as predicted by group theory.[17] (3) The translationally excited levels are not harmonic, since their energies depend not only on n but also on l. The energy separation between the neighboring purely translational levels having $n=1$, 2, and 3 (and $j=0$) increases with n, evidence of their negative anharmonicity. The quantum dynamics calculations for HD and D$_2$ in C$_{60}$, and for H$_2$/HD/D$_2$ in C$_{70}$, are in progress in our group. What is most needed now are measurements of the translational and rotational excitations of H$_2$ inside C$_{60}$, which we hope our work will motivate. In conjunction with high-level quantum dynamics calculations, they would be used to determine accurately the H$_2$−C$_{60}$ interaction potential, which remains poorly characterized at the present time.

[1] K. Komatsu, M. Murata, and Y. Murata, Science **307**, 238 (2005).
[2] M. Murata, Y. Murata, and K. Komatsu, J. Am. Chem. Soc. **128**, 8024 (2006).
[3] 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).
[4] M. Carravetta, A. Danquigny, S. Mamone, F. Cuda, O. G. Johannessen, I. Heinmaa, K. Panesar, R. Stern, M. C. Grossel, A. J. Horsewill, A. Samoson, M. Murata, Y. Murata, K. Komatsu, and M. H. Levitt, Phys. Chem. Chem. Phys. **9**, 4879 (2007).
[5] 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 (2007).
[6] J. Lopez-Gejo, A. A. Marti, M. Ruzzi, S. Jockusch, K. Komatsu, F. Tanabe, Y. Murata, and N. J. Turro, J. Am. Chem. Soc. **129**, 14554 (2007).
[7] E. H. T. Olthof, A. van der Avoird, and P. E. S. Wormer, J. Chem. Phys. **104**, 832 (1996).
[8] D. S. Bethune, G. Meijer, W. C. Tang, H. J. Rosen, W. G. Golden, H. Seki, C. A. Brown, and M. de Vries, Chem. Phys. Lett. **179**, 181 (1991).
[9] Z. H. Dong, P. Zhou, J. M. Holden, P. C. Eklund, M. S. Dresselhaus, and G. Dresselhaus, Phys. Rev. B **48**, 2862 (1993).
[10] K. Hedberg, L. Hedberg, D. S. Bethune, C. A. Brown, H. C. Dorn, R. D. Johnson, and M. de Vries, Science **254**, 410 (1991).
[11] M. Xu, Y. Elmatad, F. Sebastianelli, J. W. Moskowitz, and Z. Bačić, J. Phys. Chem. B **110**, 24806 (2006).
[12] S. Liu, Z. Bačić, J. W. Moskowitz, and K. E. Schmidt, J. Chem. Phys. **103**, 1829 (1995).
[13] Z. Bačić and J. C. Light, Annu. Rev. Phys. Chem. **40**, 469 (1989).
[14] T. Lu, E. M. Goldfield, and S. K. Gray, J. Phys. Chem. B **110**, 1742 (2006).
[15] S. J. V. Frankland and D. W. Brenner, Chem. Phys. Lett. **334**, 18 (2001).
[16] A. D. Novaco and J. P. Wroblievski, Phys. Rev. B **39**, 11364 (1989).
[17] B. R. Judd, Proc. R. Soc. London, Ser. A **241**, 122 (1957).
[18] R. J. Cross, J. Phys. Chem. A **105**, 6943 (2001).