J|A|C|S
ARTICLES

Hydrogen Molecules inside Fullerene C_{70}: Quantum Dynamics, Energetics, Maximum Occupancy, And Comparison with C_{60}

Francesco Sebastianelli,[‡] Minzhong Xu,[‡] Zlatko Bačić,*[,†,‡] Ronald Lawler,[§] and Nicholas J. Turro*[,||]

State Key Laboratory of Precision Spectroscopy and Department of Physics, Institute of Theoretical and Computational Science, East China Normal University, Shanghai 200062, China, Department of Chemistry, New York University, New York, New York 10003, Department of Chemistry, Brown University, Providence, Rhode Island 02912, and Department of Chemistry, Columbia University, New York, New York 10027

Received April 12, 2010; E-mail: zlatko.bacic@nyu.edu; njt3@columbia.edu

Abstract: Recent synthesis of the endohedral complexes of C_{70} and its open-cage derivative with one and two H_2 molecules has opened the path for experimental and theoretical investigations of the unique dynamic, spectroscopic, and other properties of systems with multiple hydrogen molecules confined inside a nanoscale cavity. Here we report a rigorous theoretical study of the dynamics of the coupled translational and rotational motions of H_2 molecules in C_{70} and C_{60}, which are highly quantum mechanical. Diffusion Monte Carlo (DMC) calculations were performed for up to three *para*-H_2 (p-H_2) molecules encapsulated in C_{70} and for one and two p-H_2 molecules inside C_{60}. These calculations provide a quantitative description of the ground-state properties, energetics, and the translation−rotation (T−R) zero-point energies (ZPEs) of the nanoconfined p-H_2 molecules and of the spatial distribution of two p-H_2 molecules in the cavity of C_{70}. The energy of the global minimum on the intermolecular potential energy surface (PES) is negative for one and two H_2 molecules in C_{70} but has a high positive value when the third H_2 is added, implying that at most two H_2 molecules can be stabilized inside C_{70}. By the same criterion, in the case of C_{60}, only the endohedral complex with one H_2 molecule is energetically stable. Our results are consistent with the fact that recently both $(H_2)_n@C_{70}$ ($n = 1,\ 2$) and $H_2@C_{60}$ were prepared, but not $(H_2)_3@C_{70}$ or $(H_2)_2@C_{60}$. The ZPE of the coupled T−R motions, from the DMC calculations, grows rapidly with the number of caged p-H_2 molecules and is a significant fraction of the well depth of the intermolecular PES, 11% in the case of p-$H_2@C_{70}$ and 52% for $(p\text{-}H_2)_2@C_{70}$. Consequently, the T−R ZPE represents a major component of the energetics of the encapsulated H_2 molecules. The inclusion of the ZPE nearly doubles the energy by which $(p\text{-}H_2)_3@C_{70}$ is destabilized and increases by 66% the energetic destabilization of $(p\text{-}H_2)_2@C_{60}$. For these reasons, the T−R ZPE has to be calculated accurately and taken into account for reliable theoretical predictions regarding the stability of the endohedral fullerene complexes with hydrogen molecules and their maximum H_2 content.

I. Introduction

In this paper, we present the results of the first rigorous treatment of the quantum translation−rotation (T−R) dynamics of up to three H_2 molecules inside C_{70} and, for comparison, of one and two H_2 molecules in C_{60}. Our studies of the quantum dynamics of molecular hydrogen in C_{60} and C_{70} to date[1−3] have considered only a single H_2 (HD, D_2) molecule in confinement. But, the synthesis of $(H_2)_2@C_{70}$ (ref 4), as well as $(H_2)_2$@open-cage C_{70} (ref 5), has provided fresh impetus for investigating the quantum T−R dynamics of two or more H_2 molecules confined inside fullerenes, which has not been attempted prior to the present work.

Endohedral complexes of C_{60} and C_{70} with multiple hydrogen molecules have been the subject of recent *ab initio* quantum chemical calculations,[6,7] focused on the stability and binding energies of the complexes. Because of the high computational cost, in these and similar studies, the interaction potentials were calculated at only a few select geometries of the H_2 molecule(s) in the fullerene. However, quantum effects associated with the T−R dynamics of the caged H_2 molecules play a large role in the energetic, structural, spectroscopic, and other properties of $(H_2)_n$@fullerene complexes. Consequently, they must be accurately taken into account in order to make a meaningful and quantitative comparison of theoretical predictions with the experimental values of the physical and chemical properties of

---

[†] East China Normal University.
[‡] New York University.
[§] Brown University.
[||] Columbia University.

(1) Xu, M.; Sebastianelli, F.; Bačić, Z.; Lawler, R.; Turro, N. J. *J. Chem. Phys.* **2008**, *128*, 011101.
(2) Xu, M.; Sebastianelli, F.; Bačić, Z.; Lawler, R.; Turro, N. J. *J. Chem. Phys.* **2008**, *129*, 064313.
(3) Xu, M.; Sebastianelli, F.; Gibbons, B. R.; Bačić, Z.; Lawler, R.; Turro, N. J. *J. Chem. Phys.* **2009**, *130*, 224306.
(4) Murata, M.; Maeda, S.; Morinaka, Y.; Murata, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2008**, *130*, 15800.
(5) Murata, Y.; Maeda, S.; Murata, M.; Komatsu, K. *J. Am. Chem. Soc.* **2008**, *130*, 6702.
(6) Korona, T.; Hesselmann, A.; Dodziuk, H. *J. Chem. Theory Comput.* **2009**, *5*, 1585.
(7) Kruse, H.; Grimme, S. *J. Phys. Chem. C* **2009**, *113*, 17006.

10.1021/ja103062g

these complexes. This demands, at minimum, solving the multidimensional Schrödinger equation for the coupled T−R motions of the guest hydrogen molecules, on the best available full intermolecular potential energy surfaces (PESs) of dimensionality $5n$ (for H_2 and the fullerene treated as rigid), where n is the number of trapped H_2 molecules.

When the H_2 molecule is confined inside the fullerene cage, the dynamics of the translational motions of the center of mass (cm) of the molecule and its overall rotation is strongly coupled. Nanoscale confinement gives rise to discrete translational energy levels, which are well separated in energy, due to the small mass of H_2. The same holds for the quantized rotational levels of H_2, because of its large rotational constant. The resulting T−R energy level structure is sparse. It is even sparser for the homonuclear isotopologues H_2 and D_2, where the symmetry constraints on the total wave function lead to the existence of two distinct species, one having only even-j rotational states, p-H_2 and o-D_2, and the other with exclusively odd-j rotational states, o-H_2 and p-D_2. As a result, the T−R, or “rattling”, dynamics of the guest hydrogen molecule(s) is inherently highly quantum mechanical, in particular at the low temperatures, generally well below 100 K, at which most of the spectroscopic measurements of these systems are performed.

The confining nanocage shapes the quantum T−R dynamics not only through its size but also through its symmetry. The latter leaves a strong imprint on the overall T−R energy level structure, including the quantum numbers required for assignment of the translational excitations, the splittings of the rotational excitations, and the nature of coupling between the angular momenta associated with the translational and rotational motions, respectively. This was initially brought to light by our quantum five-dimensional (5D) calculations of the T−R eigenstates of H_2 trapped inside the small[8,9] and large cages[10,11] of the structure II (sII) clathrate hydrates, which are formed by a 3D network of hydrogen-bonded water molecules; the dimensions of these cavities are comparable to those of the fullerenes. Subsequently, we broadened our rigorous theoretical investigations of the dynamics of nanoconfined molecular hydrogen to the endohedral H_2−fullerene complexes, first $H_2@C_{60}$ (refs 1 and 2) and later $H_2@C_{70}$ (ref 3). They revealed intricate patterns of level degeneracies, which are very different for the two systems. These could be understood in terms of the rather elegant picture of the quantum T−R dynamics,[1,3] which for the translational excitations invokes the harmonic oscillator model, in 3D for C_{60} and in 2D for C_{70}, and involves the coupling of the angular momenta associated with the translational and rotational motions of the guest molecule, respectively, the T−R coupling being qualitatively different for H_2 in C_{60} and C_{70}. The levels predicted to arise from the T−R coupling for H_2 inside C_{60} (ref 1) were observed in the recent infrared (IR) spectroscopic study of $H_2@C_{60}$.[12] The IR spectra of $H_2@C_{70}$ have also been measured[13] and are in the process of being analyzed with the help of our published results[3] and additional calculations of higher-lying T−R energy levels. The IR spectrum of $H_2@C_{60}$ (ref 12) has allowed us to develop and refine the novel three-site H_2−C pair potential.[3] For optimal values of its three parameters, the pairwise additive 5D intermolecular PES of $H_2@C_{60}$ constructed using this two-body potential, when employed in the fully coupled quantum bound-state calculations, reproduced all six T−R energy levels observed in the IR spectra of this endohedral complex to within 1−2 cm^{-1} (0.6%) or better.[3] This success was attributed primarily to the greatly improved description of the angular anisotropy of the H_2−fullerene interaction afforded by the three-site H_2−C pair potential relative to its standard two-site counterpart.

The significance of the quantum effects arising from the T−R dynamics of the guest H_2 molecules is becoming apparent with the growing number of experimental studies of the spectroscopy and chemical reactivity of $(H_2)_n@$fullerene complexes. In addition to the IR spectroscopic study of $H_2@C_{60}$ (ref 12) mentioned above, transitions between the quantized T−R states were observed also in the recent inelastic neutron scattering investigation of the endohedral complex of H_2 with aza-thia-open-cage fullerene (ATOCF).[14] The extent to which H_2 inside C_{60} is able to communicate with the outside world, as measured by the quenching of $^1O_2$ outside the cage,[15] the spin−lattice relaxation rates,[16] and the interconversion of parahydrogen (p-H_2) and orthohydrogen (o-H_2),[17] has been studied in the past couple of years.[18] NMR spectroscopy has been used to probe the dynamic properties of H_2 in C_{60};[19−21] it has also revealed the positional exchange of two H_2 molecules trapped inside an open-cage C_{70}.[5] In a more chemical example, it was observed that $H_2@C_{70}$ and $(H_2)_2@C_{70}$ exhibit measurable difference in reactivity;[4] the equilibrium constant for the Diels−Adler reaction of 9,10-dimethylanthracene (DMA) with $(H_2)_2@C_{70}$ was found to be about 15% smaller than that with $H_2@C_{70}$ in the temperature range considered, 30−50 °C.

The quantum dynamics calculations presented in this paper, as well as in our previous work,[1−3] have a broad range of potential applications. For example, it has been observed[17] that the lifetime of the *ortho* and *para* allotropes of H_2 is lengthened substantially by encapsulation in C_{60}. This, and the well-defined, relatively sparse T−R energy level structure, suggest that endohedral fullerene complexes with H_2 might be promising candidates for testing the proposed use of a resonant laser radiation field for selective enrichment of the nuclear spin

---

(8) Xu, M.; Elmatad, Y.; Sebastianelli, F.; Moskowitz, J. W.; Bačić, Z. *J. Phys. Chem. B* **2006**, *110*, 24806.

(9) Xu, M.; Sebastianelli, F.; Bačić, Z. *J. Chem. Phys.* **2008**, *128*, 244715.

(10) Sebastianelli, F.; Xu, M.; Bačić, Z. *J. Chem. Phys.* **2008**, *129*, 244706.

(11) Xu, M.; Sebastianelli, F.; Bačić, Z. *J. Phys. Chem. A* **2009**, *113*, 7601.

(12) Mamone, S.; Ge, M.; Hüvonen, D.; Nagel, U.; Danquigny, A.; Cuda, F.; Grossel, M. C.; Murata, Y.; Komatsu, K.; Levitt, M. H.; Rõõm, T.; Carravetta, M. *J. Chem. Phys.* **2009**, *130*, 081103.

(13) Rõõm, T., National Institute of Chemical Physics, Estonia, private communication, 2009.

(14) Horsewill, A. J.; Panesar, K. S.; Rols, S.; Johnson, M. R.; Murata, Y.; Komatsu, K.; Mamone, S.; Danquigny, A.; Cuda, F.; Maltsev, S.; Grossel, M. C.; Carravetta, M.; Levitt, M. H. *Phys. Rev. Lett.* **2009**, *102*, 013001.

(15) Lopez-Gejo, J.; Marti, A. A.; Ruzzi, M.; Jockusch, S.; Komatsu, K.; Tanabe, F.; Murata, Y.; Turro, N. J. *J. Am. Chem. Soc.* **2007**, *129*, 14554.

(16) Sartori, E.; Ruzzi, M.; Turro, N. J.; Komatsu, K.; Murata, Y.; Lawler, R. G.; Buchachenko, A. L. *J. Am. Chem. Soc.* **2008**, *130*, 2221.

(17) Turro, N. J.; Marti, A. A.; Chen, J. Y. C.; Jockusch, S.; Lawler, R. G.; Ruzzi, M.; Sartori, E.; Chuang, S. C.; Komatsu, K.; Murata, Y. *J. Am. Chem. Soc.* **2008**, *130*, 10506.

(18) Turro, N. J.; Chen, J. Y. C.; Sartori, E.; Ruzzi, M.; Marti, A.; Lawler, R.; Jockusch, S.; Komatsu, K.; Murata, Y. *Acc. Chem. Res.* **2010**, *43*, 335.

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

(20) Carravetta, M.; Danquigny, A.; Mamone, S.; Cuda, F.; Johannessen, O. G.; Heinmaa, I.; Panesar, K.; Stern, R.; Grossel, M. C.; Horsewill, A. J.; Samoson, A.; Murata, M.; Murata, Y.; Komatsu, K.; Levitt, M. H. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4879.

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

modifications of molecules.[22] Planning such an experiment, however, requires accurate knowledge of the excited T−R states of the *ortho* and *para* allotropes, in order to identify resonant excited states of the two allotropes at experimentally accessible wavelengths. The presence of an externally supplied relaxant or even the magnetic moment of a naturally occurring ^{13}C nucleus in the fullerene cage could then provide the magnetic catalysis for the conversion.

Finally, elucidating the role of quantum effects in the energetics and the spatial distribution of H_2 molecules inside fullerenes and the maximum H_2 occupancy of their cavities, which is the main objective of this work, is highly relevant for the important problem of molecular hydrogen storage by physisorption in carbon nanotubes[23,24] and other forms of nanostructured carbon.[25] Moreover, the reported computations provide additional validation of our three-site H_2−C pair potential, [3] suggesting that it can be applied successfully to describe the interactions of H_2 with curved carbon nanosurfaces in general, about which there is presently a great deal of uncertainty. [26]

In the calculations reported here the total intermolecular PESs for the endohedral fullerene complexes with multiple H_2 molecules are constructed in a pairwise additive fashion, utilizing the spectroscopically optimized three-site H_2−C pair potential[3] and a high-quality *ab initio* 4D (rigid-monomer) PES of the H_2−H_2 weakly bound complex.[27] The quantum diffusion Monte Carlo (DMC) calculations are performed of the ground-state properties, energetics, and T−R zero-point energies (ZPEs) of the confined H_2 molecules and, in the case of C_{70}, of their vibrationally averaged spatial distribution within the cage. The issue of the maximum number of H_2 molecules that can occupy C_{60} and C_{70}, respectively, is discussed by considering both the energies of the global minima of the intermolecular PESs and the quantum ground-state energies from the DMC calculations. Explicit comparison is made with the recent *ab initio* quantum chemical calculations as well as the experimental results.

II. Theoretical Methodology

A. Cage Geometries and Intermolecular Potential Energy Surfaces. As in our earlier studies,[1−3] the fullerenes, C_{60} and C_{70}, are taken to be rigid, and their geometries used in our calculations have been determined experimentally, from the gas-phase electron diffraction study of C_{60}[28] and the neutron diffraction measurements of solid C_{70}.[29] Encapsulation of a small number of H_2 molecules causes negligible distortions of the fullerene geometries, as shown by the density functional theory (DFT) calculations with the MPWB1K functional[30] for $(H_2)_n@C_{70}$ ($n = 1, 2$)[4] and $H_2@C_{60}$.[30] Therefore, treating the two fullerenes as rigid is not expected to have an appreciable effect on the accuracy with which the properties of interest are calculated. The bond lengths of the guest H_2 molecules are also held fixed; this is justified by the fact that the fundamental frequency of the H_2 intramolecular vibration, ~4100 cm^{-1}, is much higher than the frequencies of the T−R modes.

All interactions, between n hydrogen molecules and the fullerene nanocage, as well as those between the confined hydrogen molecules (when $n > 1$), are treated as pairwise additive.[3,9,10] The 5D interaction potential, $V_{H_2-\text{fullerene}}$, between the hth confined H_2 molecule and N carbon atoms of the fullerene ($N = 60$ or 70 in this work) is written as[3]

$$V_{H_2-\text{fullerene}}(\mathbf{q}_h) = \sum_{w=1}^{N} V_{H_2-C}(\mathbf{q}_h, \boldsymbol{\Xi}_w) \qquad (1)$$

where $\mathbf{q}_h$ are the coordinates of the endohedral H_2 molecule, V_{H_2-C} is the pair interaction specified below between H_2 and a carbon atom of the fullerene, and the index w runs over all fullerene C atoms, whose coordinates, $\boldsymbol{\Xi}_w$, are fixed. The total intermolecular PES for n H_2 molecules inside the fullerene cavity has the form[9,10]

$$V_{\text{TOT}}(\mathbf{Q}) = \sum_{h=1}^{n} V_{H_2-\text{fullerene}}(\mathbf{q}_h) + \sum_{h<k}^{n} V_{H_2-H_2}(\boldsymbol{\Omega}_{hk}) \qquad (2)$$

where $\mathbf{Q}$ is the vector defining the coordinates of all the guest molecules. In eq 2, the first term accounts for the (additive) interaction of n H_2 molecules with the fullerene cage, $V_{H_2-\text{fullerene}}(\mathbf{q}_h)$ being defined in eq 1. The second term of eq 2 represents the interactions between all pairs of H_2 molecules; $\boldsymbol{\Omega}_{hk}$ are the intermolecular diatom−diatom Jacobi coordinates for the pair of H_2 molecules h and k. As before,[9,10] the H_2−H_2 pair potential is described by the *ab initio* 4D (rigid monomer) PES by Diep and Johnson.[27]

The three-site V_{H_2-C} pair potential appearing in eq 1 was introduced in ref 3, and its detailed description can be found there. In addition to the two Lennard-Jones (LJ) H−C sites centered on each atom of H_2, our three-site H_2−C pair potential has the third LJ interaction site at the midpoint of the H−H bond. The weight factor associated with this interaction site effectively controls the angular anisotropy of the H_2−fullerene interaction PES and allows it tuning to the degree that cannot be achieved with the standard two-site H_2−C pair potential.[3] As mentioned already in the Introduction, with the pairwise additive 5D intermolecular PES based on the three-site H_2−C pair potential, it was possible to simultaneously fit with excellent accuracy the six T−R excitations observed in the IR spectra of $H_2@C_{60}$, corresponding to the translational fundamental and the excitations split into a triplet due to the coupling between the rotational and translational modes of H_2;[3] this could not be done with the two-site H_2−C pair potential. We have good reasons to believe that this three-site H_2−C pair potential, which was optimized for H_2 in C_{60} and describes quantitatively its T−R energy level structure, provides an accurate description of the interaction between H_2 and other fullerenes as well.

B. Diffusion Monte Carlo Calculations of Ground-State Properties. The ground-state properties of $(p\text{-}H_2)_n@C_{70}$ and $(p\text{-}H_2)_n@C_{60}$, such as the ground-state energies and the ZPEs, are calculated rigorously for the intermolecular PESs described above employing the DMC method originally developed by Anderson.[31,32] The DMC treatment of the quantum T−R dynamics of the guest hydrogen molecules includes full coupling between all of their intermolecular degrees of freedom, as well as the potential anharmonicities and anisotropies, angular and radial. The calculations are restricted to the T−R ground state, since the calculation of excited states by the DMC requires the knowledge of their nodal surfaces, which are known or can be guessed with reasonable accuracy only in special cases. Detailed descriptions of the DMC

---

(22) Shalagin, A. M.; Il̆ichev, L. V. *JETP Lett.* **1999**, *70*, 508.
(23) Schlapbach, L.; Züttel, A. *Nature* **2001**, *414*, 353.
(24) Henwood, D.; Carey, J. D. *Phys. Rev. B* **2007**, *75*, 245413.
(25) Kuchta, B.; Firlej, L.; Pfeifer, P.; Wexler, C. *Carbon* **2010**, *48*, 223.
(26) Ngyen, T. X.; Bae, J. S.; Wang, Y.; Bhatia, S. K. *Langmuir* **2009**, *25*, 4314.
(27) Diep, P.; Johnson, J. K. *J. Chem. Phys.* **2000**, *112*, 4465.
(28) Hedberg, K.; Hedberg, L.; Bethune, D. S.; Brown, C. A.; Dorn, H. C.; Johnson, R. D.; de Vries, M. *Science* **1991**, *254*, 410.
(29) Nikolaev, A. V.; Dennis, T. J. S.; Prassides, K.; Sopper, A. K. *Chem. Phys. Lett.* **1994**, *223*, 143.
(30) Slanina, Z.; Pulay, P.; Nagase, S. *J. Chem. Theory Comput.* **2006**, *2*, 782.
(31) Anderson, J. B. *J. Chem. Phys.* **1975**, *63*, 1499.
(32) Anderson, J. B. *J. Chem. Phys.* **1976**, *65*, 4121.

Table 1. Global Minima, V_{min} (Interaction Energies), of the Endohedral Complexes Considered[a]

	V_{min}	$V_{tot}(H_2-\text{fullerene})$	$V_{tot}(H_2-H_2)$	$r_{eq}(H_2-H_2)$
$H_2@C_{70}$	−1337.95	−1337.95		
$(H_2)_2@C_{70}$	−1824.52	−2148.90	324.38	4.70
$(H_2)_3@C_{70}$	2836.88	−11.44	2848.32	4.02 (2),4.95 (1)
$H_2@C_{60}$	−1498.71	−1498.71		
$(H_2)_2@C_{60}$	2878.02	589.17	2288.85	3.73

[a] Also shown for each endohedral complex are $V_{tot}(H_2-\text{fullerene})$, the total (additive) interaction energy of the caged H_2 molecules with fullerene interior, and $V_{tot}(H_2-H_2)$, the total energy of the interactions between all pairs of H_2 molecules. V_{min} is the sum of $V_{tot}(H_2-\text{fullerene})$ and $V_{tot}(H_2-H_2)$. All energies are in cm^{-1}. In the last column, $r_{eq}(H_2-H_2)$ is the equilibrium H_2-H_2 distance at the global minimum. In the case of $(H_2)_3@C_{70}$, there are two such distances, since $(H_2)_3$ forms an isosceles triangle. The distances are in au.

method are available.[33−36] Our implementation of the DMC methodology has been discussed previously.[37,38] Most recently, we used it to investigate small $(p\text{-}H_2)_n$ and $(o\text{-}D_2)_n$ clusters inside the large cage of the sII clathrate hydrate.[10] The bond lengths of the H_2 molecules are held fixed by means of the constraint dynamics method of Sarsa and co-workers.[39] The effective rotational constant $B_1 = 54.83$ cm^{-1} appropriate for the $\nu = 1$ vibrational state of the encapsulated H_2 is used in our calculations for consistency, since the three-site H_2-C pair potential employed was optimized by fitting to the IR spectra of H_2 ($\nu = 1$) in C_{60} (ref 3). This should not affect significantly our quantum results regarding the energetics and stability of the endohedral complexes considered, since we do not expect a large change in the H_2−fullerene interaction with the intramolecular vibrational excitation of the guest molecule. The vibrationally averaged spatial distribution of the $p\text{-}H_2$ molecules within C_{70} is characterized by means of the probability distribution functions (PDFs) of the two coordinates, $\vec{R}_i$ and $\vec{r}_{ij}$; $\vec{R}_i$ is the vector connecting the cm of the cage with the cm of the ith H_2 molecule, while $\vec{r}_{ij}$ is the vector connecting the centers of mass of H_2 molecules i and j (for $n > 1$). The 3D PDF of the Cartesian coordinates of the centers of mass of n H_2 molecules, $P(x, y, z)$, is also computed. These three PDFs are defined in ref 10.

The DMC calculations reported here used an ensemble of 3000 walkers and the time step of 1.0 au For each cluster size considered, the simulations involved eight independent runs. In every run, after the initial equilibration, the ensemble is propagated in 110 blocks consisting of 2000 steps each.

III. Results and Discussion

A. Energetics and Implications for Maximum H_2 Occupancy of C_{70} and C_{60}. 1. Interaction Energies. Energies of the global minima, V_{min}, on the intermolecular PESs of $(H_2)_n@C_{70}$ ($n = 1-3$) and $(H_2)_n@C_{60}$ ($n = 1,\ 2$), determined by the method of simulated annealing, are given in Table 1. In the following, the values of V_{min} will often be referred to as the interaction energies; they are also called complexation[7] or encapsulation energies.[30] The equilibrium geometries of one and two H_2 molecules in C_{70} are shown in Figure 1. In the case of a single H_2 in C_{70}, the PES has two symmetrically equivalent global minima,[3] each corresponding to the H_2 molecule lying on, and parallel to, the long axis of C_{70}, which coincides with its C_5 axis of rotation, with the cm of H_2 at (0.00, 0.00, ±1.09 au). In the global minimum for $n = 2$, the centers of mass of both H_2 molecules lie on the long axis of C_{70}. The two H_2 molecules are placed symmetrically relative to the center of the cage; they are 4.70 au apart, and each is 2.35 au from the cage center. Both molecules are perpendicular to the long axis of C_{70}, and have a “crossed” mutual orientation.

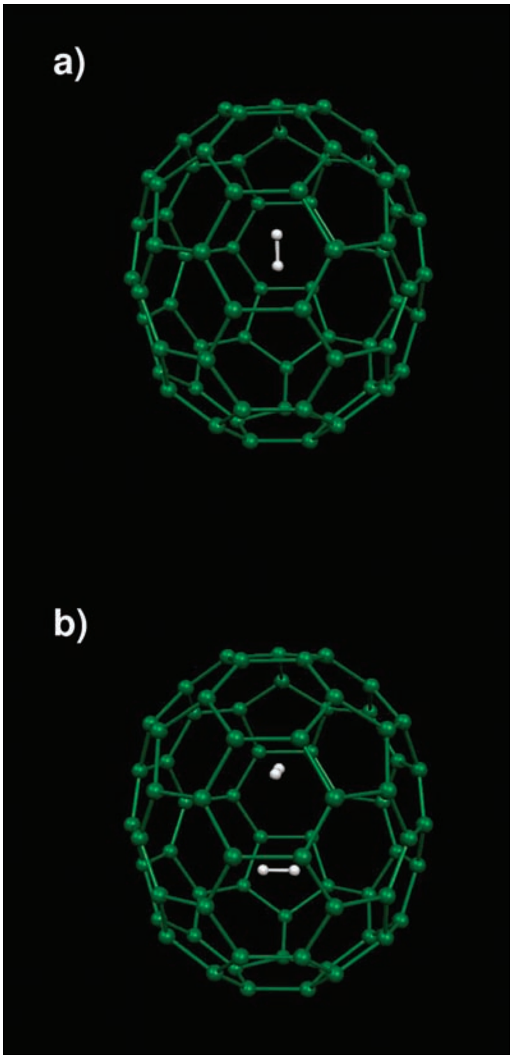

Figure 1. The equilibrium geometries of (a) one and (b) two H_2 molecules in C_{70}.

For one and two H_2 molecules in C_{70}, the interaction energy is substantially negative, that is, the energy of the molecules inside the fullerene is lower than when they are at a large distance outside the cage (where the interaction energy is essentially zero). In other words, one and two H_2 molecules are stabilized by encapsulation in C_{70}. In fact, $(H_2)_2@C_{70}$ is considerably more stable than $H_2@C_{70}$; the interaction energy of the former, −1825 cm^{-1}, is 36% greater (in absolute value) that of the latter, −1338 cm^{-1}. This trend reverses completely with the addition of the third H_2 molecule in the cavity of C_{70}, when the interaction energy sharply rises to a high positive value

---

(33) Hammond, B. L.; Lester., W. A., Jr.; Reynolds, P. J. *Monte Carlo Methods in Ab Initio Quantum Chemistry*; World Scientific: Singapore, 1994.

(34) Suhm, M. A.; Watts, R. O. *Phys. Rep.* **1991**, *204*, 293.

(35) Gregory, J. K.; Clary, D. C. Diffusion Monte Carlo studies of water clusters. In *Advances in Molecular Vibrations and Collision Dynamics*; Bowman, J. M., Bačić, Z., Eds.; JAI Press Inc.: Stamford, CT, 1998; Vol. 3.

(36) Whaley, K. B. Spectroscopy and microscopic theory of doped helium clusters. In *Advances in Molecular Vibrations and Collision Dynamics*; Bowman, J. M., Bačić, Z., Eds.; JAI Press Inc.: Stamford, CT, 1998; Vol. 3.

(37) Jiang, H.; Bačić, Z. *J. Chem. Phys.* **2005**, *122*, 244306.

(38) Sebastianelli, F.; Elmatad, Y.; Jiang, H.; Bačić, Z. *J. Chem. Phys.* **2006**, *125*, 164313.

(39) Sarsa, A.; Schmidt, K. E.; Moskowitz, J. W. *J. Chem. Phys.* **2000**, *113*, 44.

of 2837 cm^{-1}. Having three H_2 molecules encapsulated in C_{70} is energetically highly unfavorable, virtually ruling out the experimental preparation of $(H_2)_3@C_{70}$. These results are consistent with the recent synthesis of the endohedral complexes of C_{70} with one and two H_2 molecules, but not three.[4]

The interaction energy of $H_2@C_{60}$ is negative, -1499 cm^{-1}, implying that the formation of this endohedral complex is favorable on energetic grounds. In contrast, for C_{60} with two H_2 molecules in its cavity, the interaction energy is positive, 2878 cm^{-1}, which means that this complex is very destabilized. These findings are in agreement with the fact that unlike $H_2@C_{60}$,[40,41] $(H_2)_2@C_{60}$ has not been synthesized and we do not expect that it will be, in the light of our results above and those discussed in the following section.

In order to gain a better understanding of the trends in the interaction energies with the increasing number of incarcerated H_2 molecules, listed in Table 1 are the two components of the (total) interaction energy, the interaction energy of the guest H_2 molecule(s) with the interior of C_{70} and C_{60}, the first term in eq 2, and the energy of the interactions among all pairs of the caged H_2 molecules, represented by the second term in eq 2. Insertion of the third H_2 molecule in C_{70} raises the interaction energy by 4662 cm^{-1}, from -1825 cm^{-1} for $n = 2$ to 2837 cm^{-1} for $n = 3$. The two components of the interaction energy, the total H_2-C_{70} interaction and the total H_2-H_2 interaction, contribute rather evenly to this large change, increasing by 2138 and 2524 cm^{-1}, respectively. Clearly, the three encapsulated H_2 molecules are crowded inside C_{70}, pushed too close to the walls of the cage and to each other. In particular, the distances between the caged H_2 molecules, 4.02 and 4.95 au, are much shorter than the equilibrium H_2-H_2 separation of 6.34 au on the intermolecular PES of the free H_2 dimer.[27,42] This places them on the strongly repulsive part of the dimer PES, which results in the substantial positive total H_2-H_2 interaction energy.

The situation is very similar for the endohedral H_2-C_{60} complexes. The interaction energy of $(H_2)_2@C_{60}$, 2878 cm^{-1}, is 4377 cm^{-1} higher than that of $H_2@C_{60}$, -1499 cm^{-1}. This energy jump is caused in equal measure by the increase in the total H_2-C_{60} interaction of 2088 cm^{-1} and by the H_2-H_2 interaction of 2289 cm^{-1}. The minimum-energy distance between two H_2 molecules in C_{60} is only 3.73 au, just 59% of that on the PES of the gas-phase H_2 dimer. Thus, the encapsulated H_2 molecules are highly compressed; hence the interaction between them is very repulsive. Incidentally, the H_2-H_2 separation in C_{60} calculated by us, 3.73 au, is close to the value of 3.78 au obtained using the *ab initio* method, which combines the DFT with the symmetry-adapted perturbation theory (SAPT).[6]

Table 2. Comparison of the Interaction Energies Determined in This Work ($V_{\min}$ Values in Table 1) with Those from Two Recent Quantum Chemical Calculations[a]

	this work	DFT−SAPT (ref 6)	MP2-based (ref 7)	DFT[f] (ref 4)
$H_2@C_{70}$	−1337.95	−1210[b]	−2273[c]	−2414
$(H_2)_2@C_{70}$	−1824.52	−1655[d]	−3917[c]	−3253
$H_2@C_{60}$	−1498.71	−1618	−2553[e]	
$(H_2)_2@C_{60}$	2878.02	2065	210[e]	

[a] All energies are in cm^{-1}. For additional explanations see the text. [b] For the cm of H_2 on the z axis, 0.945 au from the center of the cage (Tatiana Korona, private communication). [c] SCS−MP2 method. [d] Estimate based on the additive part of the interaction energy only. [e] MP 2.5/CBS′(2,3) method. [f] MPWB1K functional.

Table 3. Translation−Rotation (T−R) Ground-State Energies, E_0, of the Endohedral Complexes Considered, from the DMC Calculations[a]

	E_0	$V_{\min}$	ZPE
$H_2@C_{70}$	−1192.33 ± 0.09	−1337.95	145.62
$(H_2)_2@C_{70}$	−884.22 ± 0.33	−1824.52	940.30
$(H_2)_3@C_{70}$	5622.55 ± 0.89	2836.88	2785.67
$H_2@C_{60}$	−1257.34 ± 0.11	−1498.71	241.38
$(H_2)_2@C_{60}$	4763.48 ± 0.48	2878.02	1885.46

[a] Also shown for each endohedral complex are the global minimum, $V_{\min}$, and the T−R zero-point energy (ZPE); ZPE is the difference between E_0 and $V_{\min}$. All energies are in cm^{-1}.

In Table 2, the interaction energies determined in this work for $(H_2)_n@C_{70}$ and $(H_2)_n@C_{60}$ ($n = 1, 2$) are compared with the results of three recent *ab initio* quantum chemical calculations[4,6,7] [two in the case of $(H_2)_n@C_{60}$]. All the calculations are in a qualitative agreement that up to two H_2 molecules are stabilized in C_{70} and only one inside C_{60}. However, there are substantial quantitative differences. For the complexes considered, the interaction energies calculated with the DFT−SAPT method[6] are the closest to our results. The overall level of agreement between the two sets of results is actually remarkable, in view of how completely different these two approaches are. The calculations[7] based on the second-order Møller−Plesset perturbation theory (MP2) for $H_2@C_{70}$ and $H_2@C_{60}$ give interaction energies that are about 70% larger than ours or the DFT−SAPT values. This is consistent with the known tendency of the MP2-based approaches to overestimate the energies of the noncovalent interactions.[43] The same holds for the DFT−MPWB1K calculations[4] of $H_2@C_{70}$. As a result, for $(H_2)_2@C_{60}$, the MP2.5/CBS′(2,3) calculation[7] predicts a slightly positive interaction energy of just 210 cm^{-1}, which is more than 10 times smaller than the results of our and DFT−SAPT calculations. Moreover, the SCS−MP2 interaction energy for $(H_2)_2@C_{70}$, -3917 cm^{-1}, is more than a factor of 2 greater than our value of -1825 cm^{-1} or the DFT−SAPT result, -1655 cm^{-1}. Given these trends, for $(H_2)_3@C_{70}$, it is not clear whether the MP2-based methods employed in ref 7 (or the DFT−MPWB1K approach[4]) would give a negative (stabilizing) or positive (destabilizing) interaction energy.

2. Quantum Mechanical Ground-State and Zero-Point Energies. The interaction energies in Table 2 discussed in the previous section are static, based on the consideration of the PES alone, and do not reflect the quantum T−R dynamics of the encapsulated H_2 molecules. Table 3 gives the ground-state energies, E_0, and the ZPEs of the T−R motions for the endohedral complexes investigated in the present study, $(p\text{-}H_2)_n@C_{70}$ ($n = 1-3$) and $(p\text{-}H_2)_n@C_{60}$ ($n = 1,\ 2$), from the DMC calculations. Also shown to facilitate comparison are the global minima, $V_{\min}$, or the interaction energies. The ground-state energies of the endohedral complexes of C_{70} with one and two $p\text{-}H_2$ molecules are negative, -1192 and -884 cm^{-1}, respectively, implying that they are stable, while the ground-state energy of $(p\text{-}H_2)_3@C_{70}$ is highly positive, 5623 cm^{-1}, making the triple H_2 occupancy of C_{70} extremely improbable. For C_{60}, the ground-state energy is negative, -1257 cm^{-1}, with one $p\text{-}H_2$ molecule inside but has a high positive value of 4763

---

(40) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238.

(41) Murata, M.; Murata, Y.; Komatsu, K. *J. Am. Chem. Soc.* **2006**, *128*, 8024.

(42) Patkowski, K.; Cencek, W.; Jankowski, P.; Szalewicz, K.; Mehl, J. B.; Garberoglio, G.; Harvey, A. H. *J. Chem. Phys.* **2008**, *129*, 094304.

(43) Pitonak, M.; Neogrady, P.; Cerny, J.; Grimme, S.; Hobza, P. *ChemPhysChem* **2009**, *10*, 282.

cm^{-1} when two p-H_2 molecules are encapsulated, all but precluding the synthesis of $(H_2)_2@C_{60}$.

It is evident from the above and from Table 3, which shows E_0 and V_{min} having the same sign for all endohedral complexes considered, that in this instance the inclusion of the ZPE does not change the conclusions based on the interaction energies regarding the maximum H_2 occupancy of the two fullerenes, double for C_{70} and single for C_{60}. But the ZPE has a *major impact* on the energetics of the H_2 encapsulation in C_{70} and C_{60}, especially if two or more H_2 molecules are involved, when it represents a *large* fraction of the global minimum of the PES. As shown in Table 3, the ZPE increases rapidly with the number of caged p-H_2 molecules, both in magnitude and in comparison to the global minimum V_{min}. In the case of C_{70}, for one p-H_2 the ZPE (146 cm^{-1}) amounts to 11% of the global minimum (i.e., its absolute value) and grows more than 6-fold to 940 cm^{-1} or 52% of the global minimum for two p-H_2 molecules. One consequence of this fast growth of the ZPE is that while judging by the (much) larger interaction energy (V_{min}) $(H_2)_2@C_{70}$ is more stabilized than $H_2@C_{70}$, the ground-state energy of $(p\text{-}H_2)_2@C_{70}$ is appreciably higher than that of p-$H_2@C_{70}$, making it energetically the *less stable* of the two. For $(p\text{-}H_2)_3@C_{70}$, the ZPE of 2786 cm^{-1} is comparable to the interaction energy of 2837 cm^{-1}; hence the inclusion of the ZPE almost doubles the energy by which this complex is destabilized.

For p-$H_2@C_{60}$, the ZPE (241 cm^{-1}) represents 16% of the well depth of the global minimum. The ZPE increases nearly 8-fold to 1885 cm^{-1} for $(p\text{-}H_2)_2@C_{60}$; when added to the interaction energy of 2878 cm^{-1}, the ZPE increases the energetic destabilization of the complex by 66%.

Our results discussed in this section demonstrate that the ZPE of the coupled T−R motions is in general a significant fraction of the well depth of the intermolecular PES. Therefore, the ZPE must be calculated accurately and included in any quantitative investigation of the stabilization, or lack of it, of the endohedral fullerene complexes with H_2 molecules. Prior to this study, we are aware of only one attempt to calculate, in the harmonic approximation, the ZPE of $(H_2)_n@C_{60}$ ($n = 1, 2$).[7] The harmonic ZPEs obtained for $n = 1$ and $n = 2$ were 175 and 2170 cm^{-1}, respectively. Their comparison with the corresponding DMC values in Table 3 is not straightforward, since very different PESs were used in the two calculations.

B. Vibrationally Averaged Spatial Distribution of H_2 Molecules in C_{70}. Figure 2a displays the PDF $P(R)$ for $(p\text{-}H_2)_n@C_{70}$ ($n = 1, 2$) from the DMC calculations; R is the distance from the cage center to the cm of H_2 molecule. Going from $n = 1$ to $n = 2$, the peak of $P(R)$ shifts from 0.9 to 2.3 au, and its width decreases markedly. This narrowing of $P(R)$ shows that, not surprisingly, two H_2 molecules have much less room to move than one, which diminishes the amplitude of their motions inside C_{70}. In addition, the fact that $P(R) \approx 0$ for $R <$ 1.5 au reveals that the two guest molecules are virtually excluded from the central region of the cage and are confined to a narrow range of R values, which is only about 1 au wide. A complementary view of the spatial distribution of two p-H_2 molecules in C_{70} is provided by the PDF $P(r)$ in Figure 2b, r being the distance between their centers of mass. $P(r)$ peaks around 4.7 au, close to the equilibrium H_2−H_2 separation, and its width is comparable to that of $P(R)$.

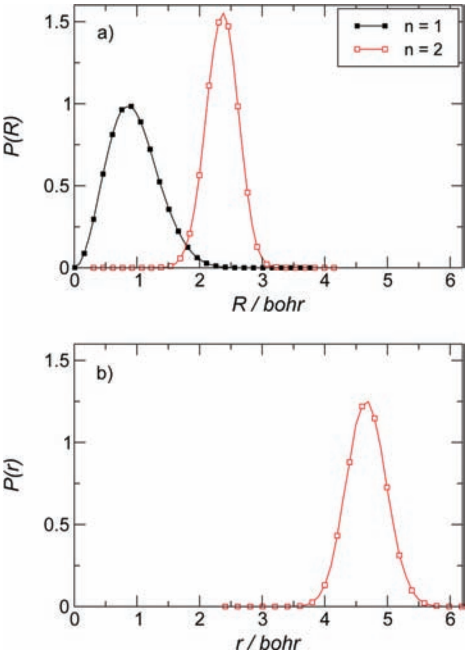

Figure 2. (a) The cage center to guest H_2 cm distance (R) probability distribution, $P(R)$, for one and two p-H_2 molecules in C_{70}. (b) The p-H_2—p-H_2 cm distance (r) probability distribution, $P(r)$, for two p-H_2 molecules in C_{70}, from the DMC calculations.

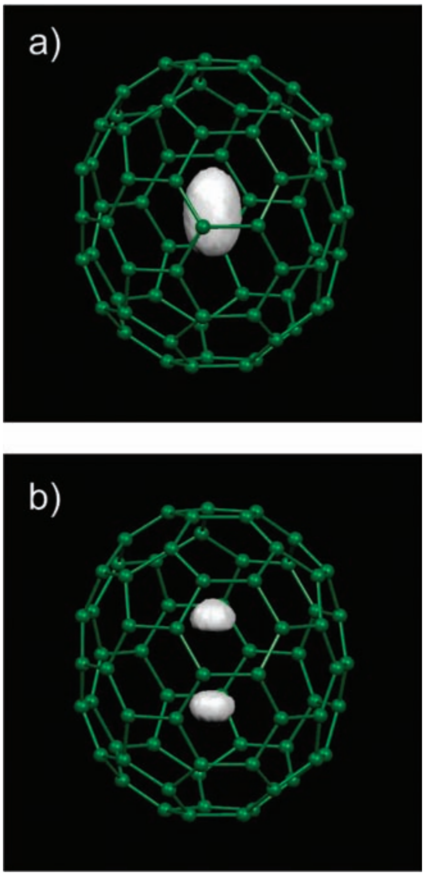

Figure 3. The 3D H_2 cm probability distribution, $P(x, y, z)$, of (a) one and (b) two p-H_2 molecules in C_{70}, from the DMC calculations.

Finally, Figure 3 shows the 3D PDF, $P(x, y, z)$, for $n = 1, 2$. For $n = 1$, the egg-shaped $P(x, y, z)$ occupies the center of the cage and is elongated in the direction of the long (C_5) axis of C_{70}. This is due to the far greater softness of the PES along the long molecular axis than in the directions perpendicular to it.[3] For $n = 2$, $P(x, y, z)$ has two distinct lobes lying on the C_5 axis of rotation of C_{70}, located symmetrically on both sides of the cage center. The parts of the two lobes that face each other are flattened, evidence of the repulsion between the two molecules. All three PDFs convey that, in the T−R ground state, the two guest p-H_2 molecules are spatially rather localized inside the cavity of C_{70}, despite the fact discussed earlier that their ZPE is 52% of the global minimum for $n = 2$. This means that the potential for the translational displacements away from the minimum-energy H_2−H_2 distance is stiff as a result of rapidly increasing repulsive H_2−H_2 and H_2−cage interactions, limiting the amplitudes of the H_2 excursions from their equilibrium positions.

IV. Conclusions

We have rigorously investigated the quantum T−R dynamics of up to three p-H_2 molecules encapsulated in C_{70} and, for comparison purposes, of one and two p-H_2 molecules inside C_{60}. The fullerenes were treated as rigid, and experimentally determined geometries were used in the calculations. The H_2 bond lengths were held fixed as well. The objective was to characterize, with the help of the DMC method, the ground-state properties of these endohedral complexes: their energetics, the T−R ZPEs, the number of H_2 molecules that can be stabilized in the fullerene cages, and for C_{70}, also the spatial distributions of one and two confined p-H_2 molecules. Pairwise additive intermolecular PESs were employed, constructed from the three-site H_2−C pair potential[3] optimized by fitting to the recently measured[12] IR spectra of $H_2@C_{60}$ and an accurate *ab initio* PES of $(H_2)_2$.[27]

In the first step of the study, for the endohedral complexes considered, the global minima of the intermolecular PESs, referred to here as the interaction energies, were determined by simulated annealing. In the case of C_{70}, the interaction energy is negative for one and two H_2 molecules, implying that they are stabilized by the encapsulation, relative to being at large distances outside the cage. Upon addition of the third H_2 molecule to the C_{70} cavity, the interaction energy jumps to a high positive value. This signals that there is a considerable energetic penalty for trying to squeeze three H_2 molecules inside C_{70}. When C_{60} is considered, only the endohedral complex with one H_2 is stable, that is, its interaction energy is negative. With two H_2 molecules in the cage of C_{60}, the interaction energy is large and positive, meaning that the complex is significantly destabilized. The H_2−H_2 distances in both $(H_2)_2@C_{70}$ (4.7 au) and $(H_2)_2@C_{60}$ (3.7 au) are much shorter than the minimum-energy H_2−H_2 separation of 6.3 au on the PES of the free $(H_2)_2$, resulting in substantial repulsive interaction between the guest molecules. In addition, there is considerable repulsion between the H_2 molecules and the respective fullerene cages. The predictions that at most two H_2 molecules can stably occupy C_{70} and just one can be accommodated by C_{60} are in accord with the recent experimental preparation of $(H_2)_n@C_{70}$ ($n = 1$, 2)[4] and $H_2@C_{60}$.[40,41]

The ground-state energies from the DMC calculations are negative for one and two p-H_2 molecules in C_{70} and for one p-H_2 inside C_{60}. Insertion of an additional p-H_2 molecule in either C_{70} or C_{60} results in highly positive ground-state energies. Consequently, the quantum dynamics effects accounted for by the DMC calculations leave unchanged the above conclusions concerning the at most double H_2 occupancy of C_{70} and the single H_2 occupancy of C_{60}. However, the ZPE of the coupled T−R motions does play a major role in the energetics of the encapsulated p-H_2 molecule(s), since it typically amounts to a large fraction of the well depth of the intermolecular PES. Thus, in the case of $(p\text{-}H_2)_n@C_{70}$, the ZPE represents 11% of the global minimum for $n = 1$, and 52% for $n = 2$. For $H_2@C_{60}$, the ZPE is 16% of the potential well depth. Moreover, the inclusion of the ZPE greatly increases the energetic penalty (and the resulting destabilization) for adding the third p-H_2 molecule in C_{70} by almost a factor of 2 and for the second p-H_2 in C_{60} by 66%. Consequently, accurate calculation of the T−R ZPE is essential for a reliable and quantitative assessment of the stability, or instability, of the endohedral fullerene complexes with a varying number of H_2 molecules and for a meaningful comparison with experiments. Judging from several DMC-computed PDFs, in the ground T−R state the two p-H_2 molecules in C_{70} are quite confined to the vicinity of their equilibrium positions, although their ZPE exceeds 50% of the potential well depth.

We are currently working on the development of the computational methodology for the fully coupled 10D calculations of the T−R energy levels of two (rigid) diatomic molecules in nanoconfinement, which will be applied to the dynamics of two H_2 molecules inside C_{70} in their excited T−R states.

Acknowledgment. Z.B. is grateful to the National Science Foundation for partial support of this research, through Grant CHE-0315508. The computational resources used in this work were funded in part by the NSF MRI Grant CHE-0420870. Acknowledgment is made to the donors of the American Chemical Society Petroleum Research Fund for partial support of this research. N.J.T. thanks the NSF for support of this research through Grant CHE-0717518.

Supporting Information Available: The global minimum energies (in hartree) of the endohedral complexes $(H_2)_n@C_{70}$ ($n = 1-3$) and $(H_2)_n@C_{60}$ ($n = 1,\ 2$) and the equilibrium coordinates of the H_2 molecules for each of the complexes, and the atomic coordinates of C_{60} and C_{70}. This material is available free of charge via the Internet at http://pubs.acs.org.

JA103062G