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Vibration−Rotation Spectroscopy of Molecules Trapped inside C_{60}

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A simple model is developed to treat the energy levels and spectroscopy of diatomic molecules inside C_{60}. The C_{60} cage is treated as spherically symmetric, and the coupling to the C_{60} vibrations is ignored. The remaining six degrees of freedom correspond to the vibrations and rotations of the diatomic molecule and the rattling vibration of the molecule inside the cage. By using conservation of angular momentum, we can remove two of these motions and simplify the calculations. The resulting energy levels are simple and can be labeled by a set of quantum numbers. The IR and Raman spectra look like those of gas-phase diatomic molecules at low temperatures. At higher temperatures, hot bands due to the low-frequency rattling mode appear, and the spectrum becomes congested, looking like a solution spectrum.

Introduction

We have developed several techniques for putting nonmetal atoms and small molecules inside fullerenes, where they remain trapped.[1–4] These species are van der Waals molecules, because there are no formal chemical bonds between the guest and the fullerene cage, but the guest cannot escape without breaking several C−C bonds. We have used a high-pressure technique[2] to put He, Ne, Ar, Kr, Xe, CO, and N_2 inside C_{60}[1,5] and, in some cases, higher fullerenes. Komatsu et al. have developed a way to chemically open a hole in C_{60} and C_{70} that is large enough to admit He and H_2.[6] They were then able to fill C_{60} with H_2 and remove the outside groups, closing the hole.[7] The result was $H_2@C_{60}$: C_{60} where almost every molecule contained H_2. Iwamatsu has made two derivatives of C_{60} with larger holes that can admit H_2O, CO, N_2, and larger noble gases.[8–11] There is currently no known way to close these larger holes, but it is quite likely that one will be found, and the list of molecules that can be trapped inside fullerenes will grow.

These unusual molecules can be expected to have unusual spectra. What does the IR spectrum of $CO@C_{60}$ look like? With 62 atoms and a nonstandard structure, it is very difficult to treat accurately. Olthof et al. have done a model calculation on $CO@C_{60}$,[12] and more recently, Xu et al. have done one on $H_2@C_{60}$.[13] Furthermore, as explained below, the most interesting spectra will have to be done in the solid state at low temperatures; therefore, interactions with neighboring molecules could be important. Here, we develop a simple model to explore this spectroscopy in the case of a diatomic molecule inside C_{60}. Although the results are unlikely to give an accurate description of the true spectra, the model may help explain the basic features of the spectra and point the way to more complicated and accurate models. Electronic structure calculations on $H_2@C_{60}$ show that, if the H_2 is placed at the center of the C_{60} cage, there is almost no torque on the molecule as it points to the various bonds and rings of the C_{60}.[14] Similar calculations were done for $CO@C_{60}$ with the same results.[15] This suggests that we can treat C_{60} as having spherical symmetry rather than only I_h symmetry. The frequencies associated with the atom or molecule vibration inside C_{60} are thought to be fairly low, around 100 cm^{-1},[16–18] and well below the normal modes of the C_{60} cage.[19] This suggests that the coupling to the cage vibrations is small, and we can get away with neglecting it, at least to a first approximation. We are then left with studying the motions of a molecule inside a rigid, spherically symmetric cage with some sort of potential between the molecule and the cage. This system has only six degrees of freedom and is tractable. We use a suitable basis set in the six variables and compute and diagonalize the Hamiltonian matrix to get the allowed energies. Both Olthof et al.[12] and Xu et al.[13] ignore the coupling to the cage vibrations. They do not make the approximation of spherical symmetry. However, this approximation allows us to use the full power of angular momentum theory and to partially diagonalize the Hamiltonian, thus greatly simplifying the calculations. We can then take the electric dipole matrix elements between states to get the IR spectrum or the matrix elements of the polarizability tensor to get the Raman spectrum. The results show that the energy levels are regular and can be assigned to a simple set of quantum numbers. The computed IR spectrum of $CO@C_{60}$ at low temperatures looks very much like the gas-phase spectrum. As the temperature is raised, more and more lines appear. As a result, we get a gas-phase spectrum at low temperature and a solution-like spectrum at high temperature.

Computational Details

The six coordinates required to define the positions of the two atoms inside a spherical cavity are best defined by two vectors. Let $\mathbf{r} = (r,\theta,\phi)$ be the vector between the two atoms. Let $\mathbf{R} = (R,\Theta,\Phi)$ be the vector between the center of the cavity and the center of mass of the molecule. Then, motion along r is basically the vibration of the molecule, whereas θ and ϕ describe its rotation. The coordinates R, Θ, and Φ describe the rattling vibration as the molecule moves inside the cage.

Because of the spherical symmetry, we can rotate both $\mathbf{R}$ and $\mathbf{r}$ by any angle without changing the potential. The potential is then

$$V = V(R, r, \gamma) \qquad (1)$$

where γ is the angle between $\mathbf{R}$ and $\mathbf{r}$. At $R = 0$, V is independent of γ. The form of the potential and much of the following theory are very similar to the quantum mechanics of the scattering of an atom from a diatomic molecule.[20–22] We

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TABLE 1: Energies of the States in the Lowest Level for CO@C_{60}

J	parity	E cm^{-1}	$E/J(J+1)$ cm^{-1}
0	+	0	
1	−	3.75	1.875
2	+	11.36	1.893
3	−	22.68	1.890
4	+	37.93	1.897
5	−	56.62	1.887
6	+	79.63	1.896
7	−	105.88	1.891
8	+	136.37	1.894

start by expanding the potential in a series of Legendre polynomials.

$$V(R, r, \gamma) = \frac{1}{2}k_0(r - r_0)^2 + V_0 + \sum_{\lambda=0}^{\infty} v_\lambda(R, r)\, P_\lambda(\cos\gamma) \quad (2)$$

where k_0 and r_0 are the force constant and the bond length for the free diatomic, respectively, and $V_0 = V(0,r_0,\gamma)$. V_0 defines the energy zero for the calculation, and we can ignore it, thus setting $E = 0$ to be the energy at $R = 0$ and $r = r_0$. For homonuclear diatomics, v_λ is zero for odd λ because of symmetry.

We could determine the potential by doing a series of ab initio electronic structure calculations by using any of a number of popular programs. In practice, it is not so simple. A major part of the interaction is due to the van der Waals force. Including this requires correlation and a large basis set. Because most cases lack symmetry, this amounts to a very long calculation. Having made some severe approximation to define the model, it seems more appropriate to use a simple potential. We assume a Lennard-Jones potential between each atom of the diatomic and each of the sixty carbons on C_{60}. Both Olthof et al.[12] and Xu et al.[13] use similar potentials.

$$V = \frac{1}{2}k_0(r - r_0)^2 + \sum_{i=1}^{60}\left\{4\varepsilon_A\left[\left(\frac{\sigma_A}{\rho_{Ai}}\right)^{12} - \left(\frac{\sigma_A}{\rho_{Ai}}\right)^{6}\right] + 4\varepsilon_B\left[\left(\frac{\sigma_B}{\rho_{Bi}}\right)^{12} - \left(\frac{\sigma_B}{\rho_{Bi}}\right)^{6}\right]\right\} \quad (3)$$

where ρ_{Ai} is the distance between atom A in the diatomic and carbon i in C_{60} and ε and σ are the Lennard-Jones parameters for the interaction of A and B and a carbon atom (see the Supporting Information). The values of these parameters are, at best, only an educated guess, and the results of the calculation depend rather strongly on them. We can then determine $v_\lambda(R,r)$ by integrating $VP_\lambda(\cos\gamma)$ over γ. In practice, we need terms only through $\lambda = 5$. For most diatomics, the force constant is sufficiently large that only small changes in r occur. We can expand $v_\lambda(R,r)$ in a power series in $(r - r_0)$ by keeping only the constant and linear terms. We then expand $v_\lambda(R,r)$ in a power series in R, but now, we have to keep more terms. Because the potential is not strictly spherically symmetric, $v_\lambda(R,r)$ depends slightly on the orientation of the C_{60} molecule, particularly for large λ and large R. Calculations of the energy levels (see below) with the C_{60} oriented with a pentagon, a double bond, or a carbon atom along the z-axis show differences of at most a few tenths of a percent. In contrast, increasing the two Lennard-Jones σ parameters by 1% causes changes in energies larger by an order of magnitude.

We must calculate the matrix elements of the Hamiltonian by using some basis set of functions. For five of the six coordinates, the choice is obvious and routine. For r, we use harmonic-oscillator wave functions $u_\nu(r)$, where ν is the quantum number. We need not use the force constant (frequency) and r_0 for the free molecule. In fact, changing these values slightly from the values for the free molecule can result in faster convergence, meaning that we can use fewer basis functions.

For the four angular variables, we can use spherical harmonics, $Y_{jm_j}(\theta,\phi)$ and $Y_{lm_l}(\Theta,\Phi)$. The resulting matrix elements contain an ugly mess of Clebsch−Gordan coefficients (see the Supporting Information). Because of the spherical symmetry, there is no torque on the system as a whole, and the total angular momentum must be conserved. We can couple the rotational angular momentum (j and m_j) and the orbital angular momentum (l and m_l) to get basis functions in $|JMjl\rangle$. The magnitude of the total angular momentum is given by J and its z component by M. The resulting Hamiltonian matrix contains an even uglier mess of Clebsch−Gordan and 6-j coefficients, but it is diagonal in J and M and independent of M. There is one further symmetry. Because of parity, Δj and Δl must be either both even (even parity) or both odd (odd parity). Blocks of different parity are uncoupled. For $J = 0$, only the even parity block is present. This sort of basis set is standard in the theory of molecular scattering. Without the assumption of spherical symmetry, these diagonalizations are impossible.

This leaves the variable R. A natural choice of basis set is a set of harmonic oscillator wave functions about $R = 0$. However, because of the three-dimensional nature of the problem, these are not the usual Hermite polynomials described in every book on quantum mechanics. We look at the problem of an atom inside a spherical cage with a harmonic potential. The Schrödinger equation is immediately soluble in Cartesian coordinates. It separates into three degenerate one-dimensional Schrödinger equations for the harmonic oscillator. The energies are

$$E = (n_x + n_y + n_z + 3/2)h\nu \quad (4)$$

Unfortunately, this solution is of little use because we need spherical coordinates to do the angular momentum coupling. We can also separate the Schrödinger equation in spherical coordinates. The process is very similar to what is done for the hydrogen atom. The details are given in the Supporting Information. The angular part of the wave function is a spherical harmonic with quantum numbers l and m_l, where $m_l = -l, -l + 1, ..., l$. With some substitutions, the radial equation can be transformed to Laguere's differential equation. Well-behaved solutions give rise to a quantum number $n = 0, 1, 2,...$ Unlike the hydrogen atom, the energies depend on both n and l (but not m_l), and there is no restriction on l. The energy is

$$E_{nl} = (2n + l + 3/2)h\nu \quad (5)$$

The ground state corresponds to $n = l = 0$ and is nondegenerate. The first excited state corresponds to $n = 0$, $l = 1$ and is 3-fold degenerate ($m_l = \pm 1, 0$). One quantum goes into the x, y, or z mode. The next state is 6-fold degenerate corresponding to $n = 1$, $l = 0$ and $n = 0$, $l = 2$. The energy depends on a single quantum number $k = 2n + l$, and the degeneracy is given by

$$g_k = \frac{1}{2}(k + 1)(k + 2) \quad (6)$$

If anharmonic terms are included in the potential, the degeneracy in k is lost, but the degeneracy in m_l is retained. Matrix elements in R are obtained as integrals over the Laguerre functions, as described in the Supporting Information.

For each value of J and parity, we can calculate a Hamiltonian matrix with quantum numbers j, l, ν, and n. For the case of

CO@C_{60}, the dimension ranges from a few hundred for $J = 0$ to a few thousand for larger J. All the Hamiltonian matrices for $J = 0-8$ can be diagonalized in less than an hour of computer time on a standard PC.

Results and Discussion

After diagonalizing the Hamiltonian matrix, we are left with long tables of eigenvalues, one for each J and parity. We must now try to make sense of the data. For CO@C_{60}, this is not hard. By starting with the lowest energies, we find a series of states with even parity for even J and odd parity for odd J which have the energies

$$E = E_0 + BJ(J+1) \tag{7}$$

where B is close but not equal to the gas-phase rotation constant for CO. The energies are shown in Table 1.

About 100 cm^{-1} higher is a second series with both even and odd parities but without a state with $J = 0$. The odd and even parity states for a given J are close in energy but not degenerate. This series is followed by a series like the first series. Then, there is a gap and a series with both even and odd parities but only for states with $J \geq 2$. The value of B differs from state to state but is almost always within 20% of the gas-phase value. The fit to eq 7 gets worse as the energy gets larger, because there are often two or more states with the same J and parity which are close together, causing small interactions between them. Nature needs not be so accommodating. The system might have been chaotic. Then, we would have gotten a series of seemingly random energies. Making small changes in the potential parameters would then have produced a very different series of energies. Fitting or interpreting experimental data would be nearly impossible.

Clearly, we must devise an approximate set of quantum numbers to assign to the various states and thus simplify the classification. As mentioned above, the form of the potential and the angular momentum coupling are similar to those used in the calculation of the scattering of an atom and a diatomic molecule. Here, we also have rotational and orbital angular momentum that couple. Again, the total J and parity are conserved. There are various coupling schemes used in the scattering problem. The one described above is known as the space-fixed (SF) representation. The quantum numbers are v, n, J, M, j, and l. A second representation is the body-fixed (BF) representation.[23] Here, we get the projection of the rotational angular momentum along the vector $\mathbf{R}$. The quantum numbers are v, n, J, M, j, and μ, where μ is the projection quantum number. The transformation between SF and BF representations mixes states of different l. In the BF representation, the potential matrix is simpler, but the kinetic energy is no longer diagonal. In the scattering problem, generally $R \gg r$, and the energy difference between states of different l are much smaller than between states of different j. Here, $r \gg R$, and the energy spacings are reversed. It makes sense, therefore, to couple states of different j to get the projection of l on the vector $\mathbf{r}$. The quantum numbers are v, n, J, M, l, and μ. The state for $\mu = 0$ has only even parity. All others have both even and odd parity. Also, $\mu = 0, 1, 2, ..., l$. Taking sums and differences of odd and even parity states for $\mu > 0$ gives a representation with both positive and negative values of μ and no parity. The lowest states are shown in Table 2. The energies of the states for different J are fit to eq 7.

The lowest series of states has $v = n = l = \mu = 0$. Only even symmetry (even parity for even J and odd parity for odd J) is allowed. The second series has one quantum of energy in the rattling mode such that $v = n = 0$, $l = \mu = 1$. Both even and odd symmetries are allowed, but because μ and l are 1, J cannot be zero. The next series at a slightly higher energy has $v = n = 0$, $l = 1$, $\mu = 0$. Again, only even symmetry is allowed. This is followed by a series of states with two quanta in the rattling mode characterized by $n = 0$ and $l = 2$, $\mu = 2, 1, 0$ and a state with $n = 1$, $l = \mu = 0$. As the energy gets higher, the various series of states get closer in energy, and the assignment gets increasingly more difficult. Nevertheless, we can assign a few dozen series comprising several hundred quantum states. The energies go up to 600 cm^{-1}. If the potential parameters are changed, the energies change, and the ordering of closely spaced levels change, but the general assignment scheme still works.

TABLE 2: Lowest Energy Levels for CO@C_{60}

level	sym[a]	quant[b]	l	μ	n	v	E_0[c]	B[d]
1	e	0	0	0	0	0	0	1.89
2	e	1	1	1	0	0	120.6	1.71
3	o	1	1	1	0	0	121.2	1.89
4	e	1	1	0	0	0	186.4	2.16
5	e	2	2	2	0	0	243.0	1.59
6	o	2	2	2	0	0	244.4	1.52
7	e	2	0	0	1	0	250.5	1.72
8	e	2	2	1	0	0	314.1	1.81
9	o	2	2	1	0	0	314.2	2.09

[a] Even symmetry, e, is even parity for even J and odd parity for odd J. Odd symmetry, o, is the opposite. [b] The nominal number of quanta in the rattling mode is $l + 2n$. [c] Energy in cm^{-1} above the lowest state, as fit to eq 7. [d] Rotation constant in cm^{-1}, as fit to eq 7. B for gas-phase CO is 1.9313 cm^{-1}.

Calculations were also done on N_2@C_{60} and H_2@C_{60}. In both cases, the calculations are simplified by the symmetry. Only terms in even λ are allowed in the expansion of the potential. Matrix elements between even and odd j are zero. The states for N_2@C_{60} are quite similar to those for CO@C_{60}. H_2 has a much larger rotation constant than CO and N_2. The energy spacing between states of different J is now comparable to the spacing between the different series of states. With fewer J states in the basis set, it is harder to make the assignments, but the general scheme described above still holds.

When the Hamiltonian matrix is diagonalized, we get not only the energies but also the matrix of the eigenvectors. This is the unitary matrix that transforms the original basis set to the eigenfunctions. It is then a simple matter to compute the matrix elements of the electric dipole operator in the original basis set and then transform it to the eigenfunction basis set. Squaring the matrix elements and multiplying by a Boltzmann factor gives the computed IR spectrum. The selection rules are $\Delta J = \pm 1$, 0, and the parity must change. Figure 1 gives the IR spectrum for CO@C_{60} at three different temperatures. At 20 K, the spectrum looks remarkably similar to the gas-phase spectrum of CO. There is a P and an R branch and a missing Q branch. The vibrational frequency and the rotational constant are slightly different. If you look closely, you will see that the rotational lines are not spaced exactly right. This spectrum is due to excitations from the lowest series of states, $v = n = l = \mu = 0$. At 100 K, we now see hot bands from states with one quantum in the rattling mode. We now have a small Q branch, and the lines in the P and R branches are doublets, corresponding to odd and even parity. At still higher temperatures, the spectrum becomes highly congested. Given the experimental line broadening due to the spectrometer and to various interactions not included in this model, we will probably loose most or all of the structure in the peak. Thus, we get a gas-phase spectrum at low temperatures and a solution-like spectrum at high temperatures.

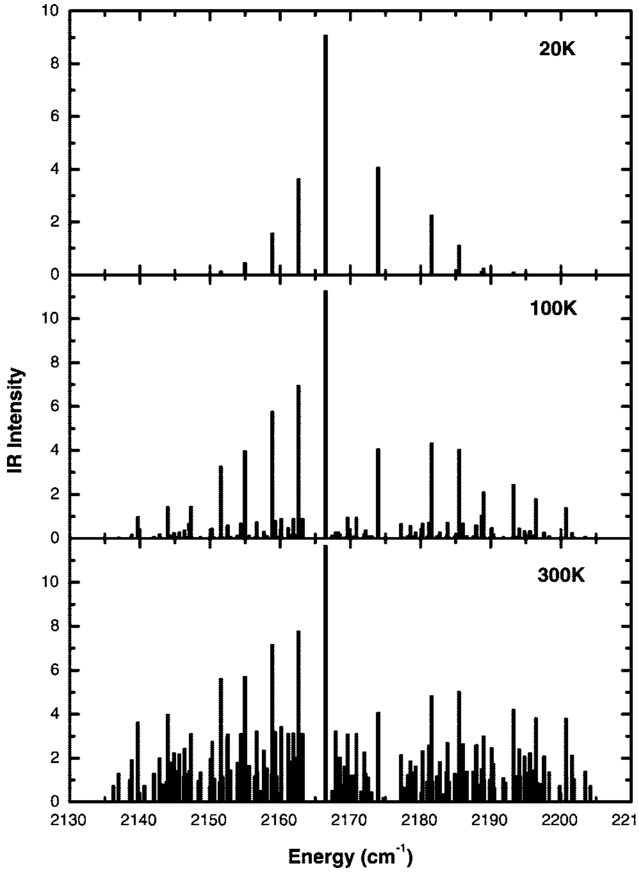

Figure 1. Calculated IR spectrum for CO@C_{60} at three temperatures.

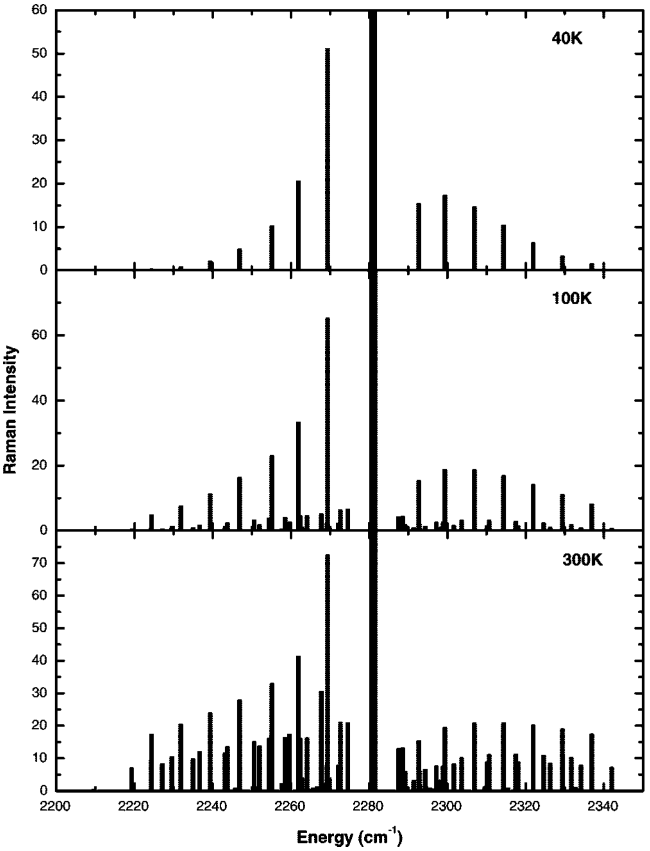

Figure 2. Calculated Raman spectrum for N_2@C_{60}.

The rattling mode is IR active, and there are many weak lines around 100 cm^{-1} in the spectrum. However, the intensities are low, and this is a difficult region (far IR) to do spectroscopy. There are no obvious lines corresponding to combination bands involving the rattling mode and the CO stretch. This is disappointing, because it means that it will be difficult to observe the rattling mode by any means other than studying the temperature dependence of the lines for the CO stretch.

N_2, of course, has no IR spectrum. It does have an intense Raman spectrum, and this can be calculated by transforming the matrix for the polarizability tensor into the eigenfunction basis set. Figure 2 shows some calculated spectra. As in the case of CO, the low-temperature spectrum looks similar to the gas-phase spectrum. There are O and S branches and a very pronounced Q branch, going way off scale in Figure 2. As the temperature increases, we get contributions from the hot bands, but the Q lines are very closely spaced. The most pronounced feature of an experimental spectrum is likely to be the Q branch.

What are the consequences of the assumptions made in deriving the model? The most severe limitation is our almost complete ignorance of the potential for the interaction of the molecule and the C_{60} cage. Accurate ab initio calculations would be very expensive. The four Lennard-Jones parameters used in eq 3 are only slightly educated guesses, and the results are affected by even small changes in these parameters. We assumed that the C_{60} cage is spherically symmetric, when, in reality, it has I_h symmetry. If we decompose various J states into the representations of the I_h group, we see that $J = 0$ goes into A_g, $J = 1$ goes into $T_{1u,g}$, and $J = 2$ goes into $H_{g,u}$. $J = 3$ decomposes into $T_{2u,g}$ and $G_{u,g}$, and it is the lowest state that goes into two different representations. One manifestation of the I_h symmetry is likely to be that rotational lines with $J \geq 3$ will split, whereas those with $J \leq 2$ will not. Small splittings (1 cm^{-1}) are seen in the calculations of Olthof et al.[12] and Xu et al.[13] It is harder to see the consequences of ignoring the coupling between the motions of the diatomic molecule and the vibrations of the C_{60} cage. There are no close frequency matches, but there may be coupling to the cage vibrations.

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Supporting Information Available: Table of van der Waals parameters and matrix elements for the vibrational, angular, and radial modes. This information is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Poreda, R. J. *Science* **1993**, *259*, 1428–1430.

(2) Cross, R. J.; Khong, A.; Saunders, M. *J. Org. Chem.* **2003**, *68*, 8281–8283.

(3) Jiménez-Vázquez, H. A.; Cross, R. J.; Saunders, M.; Poreda, R. J. *Chem. Phys. Lett.* **1994**, *229*, 111–114.

(4) Shimshi, R.; Cross, R. J.; Saunders, M. *J. Am. Chem. Soc.* **1997**, *119*, 1163–1164.

(5) Peres, T.; Cao, B. P.; Cui, W. D.; Khong, A.; Cross, R. J.; Saunders, M.; Lifshitz, C. *Int. J. Mass Spectrom.* **2001**, *210*, 241–247.

(6) Murata, Y.; Murata, M.; Komatsu, K. *Chem. Eur. J.* **2003**, *93*, 1600–1609.

(7) Komatsu, K.; Murata, M.; Murata, Y. *Science* **2005**, *307*, 238–240.

(8) Iwamatsu, S.; Murata, S. *Kagaku Kogyo* **2004**, *55*, 124–128.

(9) Iwamatsu, S.-i.; Murata, S. *Synlett* **2005**, *211*, 7–2129.

(10) Iwamatsu, S.; Uozaki, T.; Kobayashi, K.; Re, S.; Nagase, S.; Murata, S. *J. Am. Chem. Soc.* **2004**, *126*, 2668–2669.

(11) Iwamatsu, S.; Stanisky, C. M.; Cross, R. J.; Saunders, M.; Mizorogi, N.; Nagase, S.; Murata, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 5337–5340.

(12) Olthof, E. H. T.; vanderAvoird, A.; Wormer, P. E. S. *J. Chem. Phys.* **1996**, *104*, 832–847.

(13) Xu, M. Z.; Sebastianelli, F.; Bacic, Z.; Lawler, R.; Turro, N. J. *J. Chem. Phys.* **2008**, 128.

(14) Cross, R. J. *J. Phys. Chem. A* **2001**, *105*, 6943–6944.

(15) Stanisky, C. M. *Studies of Fullerenes Encapulating Atoms and Small Molecules*; Yale University: New Haven, CT, 2008.

(16) Pang, L.; Brisse, F. *J. Phys. Chem.* **1993**, *97*, 8562–8563.

(17) Jiménez-Vázquez, H. A.; Cross, R. J. *J. Chem. Phys.* **1996**, *104*, 5589.

(18) Patchkovskii, S.; Thiel, W. *J. Chem. Phys.* **1997**, *106*, 1796.

(19) Schettino, V.; Salvi, P. R.; Bini, R.; Cardini, G. *J. Chem. Phys.* **1994**, *101*, 11079–11081.

(20) Child, M. *Molecular Collision Theory*; Academic Press: New York, 1974.

(21) Cross, R. J. *J. Chem. Phys.* **1988**, *88*, 4871.

(22) Bernstein, R. B. *Atom-Molecule Collision Theory: A Guide for the Experimentalist*; Plenum: New York, 1979.

(23) Khare, V.; Kouri, D. J.; Hoffman, D. K. *J. Chem. Phys.* **1982**, *76*, 4493–4501.

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