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Does H_2 Rotate Freely Inside Fullerenes?

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Calculations were done on H_2 inside of C_{60}, mostly at the level of Hartree−Fock with a basis set 6-31G(d,p). They show a negligible distortion of the fullerene cage. To a high degree of accuracy, one can treat the cage as being spherically symmetric. There is a small torque on the H_2 when it is off center, because of its anisotropy.

For the last several years, we have studied fullerenes with noble gas atoms and other small molecules trapped inside the fullerene cage.[1] These are van der Waals molecules in that there is no chemical bond between the trapped molecule and the fullerene cage. Yet they are very stable, because several C−C bonds must be broken before the molecule can escape. The question then arises as to how to model the motion of the trapped molecule. The answer, of course, depends on the molecule and on the fullerene. Patchkovskii and Thiel[2] have done accurate ab initio calculations of He@C_{60} and found a broad, anharmonic potential that was spherically symmetric. The potential is weakly bonding, because the helium has a small van der Waals attraction to each carbon atom. It is quite likely, however, that Xe@C_{60} is tightly bound and interacts with the carbon cage, although there is no formal chemical bond.

We have not yet made H_2@C_{60}, but H_2 can be put inside a modified C_{60} with a hole opened in the cage by adding groups to the outside.[3] The proton NMR of this compound shows a noticeable broadening of the H_2 resonance, probably due to the short relaxation time for the nuclear spin. We can imagine two limiting models for H_2@C_{60}. At one extreme, the H_2 could be tightly wedged inside the C_{60} so that the cage is severely distorted. Any rotation of the H_2 would then require a concerted motion of the carbon atoms. At the other extreme, there is no distortion of the carbon cage, and the H_2 rotates freely inside, behaving largely as a gas-phase molecule in a small box.

Calculations were done using the electronic structure program Gaussian 98[4] on a Pentium III using the Linux operating system. Unless otherwise noted, they were done using the Hartree−Fock method and the 6-31G(d,p) basis set. For most cases studied, the symmetry is reduced so much that calculations that are more accurate were too time-consuming. First, we calculated a fully optimized structure. From the distance matrix we find that the H_2 bond decreases by only 0.0027 Å. The diameter of the carbon cage increases by 0.0009−0.0014 Å. The maximum change in the pentagon−hexagon single bonds is 0.0009 Å, and the maximum change in the hexagon−hexagon double bonds is 0.0002 Å. We conclude from this that the distortion of hydrogen and the carbon cage is negligible.

With an undistorted carbon cage, there are two sources of torque on the H_2 molecule. If the H_2 is off center, the asymmetry of the H_2 molecule causes a torque. If it is near the cage, it has a lower energy if the H−H bond is parallel to the wall than if it is perpendicular. Second, the nonspherical nature of the cage gives rise to different forces, depending on where on the C_{60} molecule the H_2 is pointing. We first consider the anisotropy of H_2. Figure 1 shows the energy, in kcal/mol, as the H_2 is moved from the center of the C_{60}. The H_2 bond distance is held fixed at 0.732 Å, the Hartree−Fock minimum. The C_{60} cage is icosahedral at the Hartree−Fock minimized structure for empty C_{60}. Two sets of points are shown. The top set (+'s) gives the potential as the H_2 points along a 5-fold axis (between two opposing pentagons) and is moved along that axis. The lower set (×'s) gives the potential as the H_2 is moved perpendicular to the 5-fold axis, while still pointing along that axis. By symmetry, the potential can depend only on even powers of r. The parallel and perpendicular potentials were fit by least squares to give

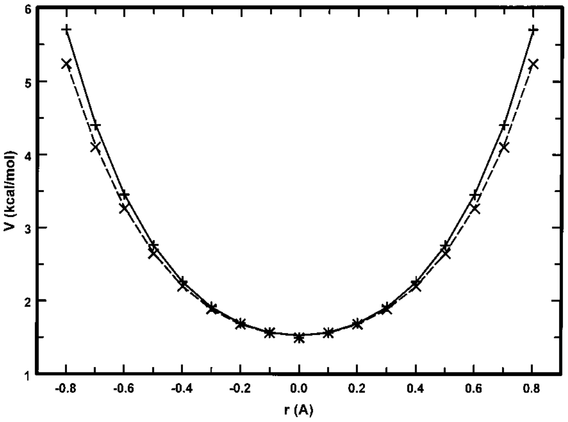

Figure 1. Potential $V(r)$ for H_2 inside C_{60}. The H_2 bond axis is along a 5-fold (pentagon−pentagon) axis. The +'s give $V(r)$ when the H_2 is moved along the 5-fold axis and the ×'s when the H_2 is moved perpendicular to it. Both sets of points were fit by least squares to a quadratic in r^2 to give the curves. The fitted coefficients are given in eqs 1 and 2.

$$V_{\parallel} = 1.52 + 3.91r^2 + 4.08r^4 \tag{1}$$

$$V_{\perp} = 1.52 + 3.62r^2 + 3.41r^4 \tag{2}$$

The fit to the calculated points is good. It is apparent that the H_2 can move fairly freely with the C_{60} cage. It is also clear that the orientation of the H_2 makes very little difference in the potential. If we assume that the potential is spherical (more on this below) and that the H−H distance is held fixed, then the potential depends only on two variables: r, the distance between the center of the C_{60} cage and the center of mass of the H_2 molecule, and γ, the angle between r and the H_2 bond. We expand the potential in terms of Legendre polynomials in cos

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TABLE 1: Effect of Orienting the H_2 Inside C_{60}[a]

orientation	ΔE	CP corr	ΔE_{corr}
pentagon	0.0383	−0.0056	0.0326
hexagon	0.0157	0.0019	0.0176
single	0.0264	−0.0038	0.0226
double	0.0000	0.0000	0.0000
C atom	0.0207	−0.0031	0.0176

[a] The H_2 is moved 0.5 Å off center with the bond pointing toward the center of the cage. The cage is then rotated so that the H_2 points toward the center of a pentagon, the center of a hexagon, the center of a singe bond, the center of a double bond, and a carbon atom. Energies are in kcal/mol and are adjusted so that the double-bond case is zero. ΔE is the energy, CP corr is the counterpoise correction (see text), and ΔE_{corr} is ΔE including the counterpoise correction.

γ, keeping only the leading terms

$$V(r, \gamma) = \nu_0(r) + \nu_2(r)P_2(\cos \gamma) \tag{3}$$

By symmetry, only even terms occur in the expansion. The parallel and perpendicular potentials correspond to $\gamma = 0$ and 90°, respectively. We then have

$$\nu_0(r) = 1.52 + 3.71r^2 + 3.63r^4 \tag{4}$$

$$\nu_2(r) = 0.19r^2 + 0.45r^4 \tag{5}$$

By symmetry, there can be no constant term in υ_2.

To explore the asymmetry introduced by the C_{60} cage, we did a series of calculations with the H_2 pointing toward various features of the C_{60}. The H_2 is moved 0.5 Å off center with the H_2 bond pointing toward the center of the cage (the parallel orientation). The H_2 bond is then rotated to point toward the center of a pentagon, the center of a hexagon, the center of a double and a single bond, and toward a carbon atom. The results are shown in Table 1. The energies are adjusted so that the double bond case is zero. The effect is very small, so small that we should be concerned about the counterpoise correction. When a calculation is done on a system like $H_2@C_{60}$, the energy is calculated as the energy of $H_2@C_{60}$ minus the energies of C_{60} and H_2. However, the calculation on $H_2@C_{60}$ uses a better basis set than those on C_{60} and H_2 because in $H_2@C_{60}$ the hydrogen orbitals can be used for the carbon electrons and visa versa. The counterpoise correction then consists of calculating the energy for C_{60} with the hydrogen orbitals included but without the protons or the extra electrons. A similar calculation is done for H_2 including the carbon orbitals of C_{60} but without the extra electrons or nuclei. The difference is small, only 0.57 kcal/mol out of a total energy of 2000 au. The correction gives an even smaller contribution to the relative potential. The change in energy in H_2 is negligible, as one would expect. The counterpoise correction for C_{60} is shown in Table 1, adjusted so that the double bond case is again zero. The counterpoise correction changes the numbers but not the conclusion that the deviation from spherical symmetry is very small. The deviations are local and correspond to high-order spherical harmonics, rather than the $P_2(\cos \gamma)$ of eq 3. These terms will then give rise to large changes in the rotational angular momentum of H_2, which, in turn, means that the probability will be very low. Furthermore, the deviation from spherical symmetry will be largely averaged out as the H_2 rotates.

The binding energy is the minimum in $V(r)$, 1.52 kcal/mol. This is obviously wrong. The Hartree−Fock calculation does not include correlation and therefore omits the van der Waals attraction between H_2 and the C_{60} cage. We repeated the calculation at $r = 0$ using Møller−Plesset second-order perturbation (MP2). This gives a binding energy of −2.54 kcal/mol, including a counterpoise correction of 1.56 kcal/mol. Patchkovskii and Thiel[2] found for $He@C_{60}$ that the binding energy calculated using MP2 converged slowly as the size of the basis set increased, and their final result used a basis set very much larger than 6-31G(d,p). Because the symmetry of $H_2@C_{60}$ is much lower than I_h, such a calculation is not feasible here.

We find that introducing H_2 into C_{60} causes negligible distortion of the C_{60} cage. The H_2 moves freely inside, undergoing translational and rotational motion. The bonds and rings of the C_{60} cage cause only a very small torque on the H_2 rotation. The largest effect on the H_2 rotation is due to the anisotropy of the H_2 molecule, and even this effect is very small. The calculations were done at a relatively low level of accuracy. The spherically averaged potential $\upsilon_0(r)$ is probably fairly accurate. The anisotropic part $\upsilon_2(r)$ is obtained as a small difference of a larger difference, and this is probably not very accurate. More accurate calculations will probably change $\upsilon_2(r)$ but not the fact that it is much smaller than $\upsilon_0(r)$. Similarly, the numbers in Table 1 are probably not accurate, but the conclusion that the orientation dependence is small probably is.

H_2 moves freely inside C_{60}, rapidly colliding with the fullerene cage. As it moves inside, it rotates freely, but there is a changing torque on the molecule because of the interaction with the carbon cage. This causes rapid changes in the rotational state. Because C_{60} is the smallest fullerene, H_2 will move freely in larger fullerenes. However, in these cases, the greater asymmetry of the cage will cause additional rotational energy changes.

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