## Nanocapillarity in Fullerene Tubules

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Fullerene tubules are shown to be highly polarizable "molecular straws" capable of ingesting dipolar molecules. Local-density-functional calculations on HF molecules within a finite-length tubule, of size 144 atoms, demonstrate this effect. The energy of incarceration is several times the thermal ambient at room temperature. These calculations, now feasible on desktop workstations, open the way to the study of nanoscale capillarity and to, perhaps, precise control over shielding of specific "guest" compounds from external electric and magnetic fields.

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The recent discovery in electron micrographs of graphene microtubules [1,2], prepared by arc-discharge evaporation and having diameters of order nanometers, suggests that under more carefully controlled conditions, perhaps by deliberate synthesis, tubules of specific diameter and topology may be attainable. The tubules are believed to be comprised of unsaturated hexagonal hydrocarbon rings, similar to those found in the aromatics, graphite, and the fullerenes. The winding of the hexagons around the longitudinal axis of the tubule has been categorized by Hamada, Sawada, and Oshiyama [3] and by Saito et al. [4]. Different topologies, with similar radii, can produce insulating or metallic behavior depending upon how the winding cuts the graphitic Brillouin zone [3,4]. Mintmire, Dunlap, and White [5] performed a calculation, within the framework of the local-density approximation (LDA), on an infinite-length fullerene tubule and found metallic behavior in accord with the classification scheme of Hamada, Sawada, and Oshiyama [3].

Given the similarities to graphite and fullerene molecules (which recently have been shown to have high polarizabilities [6] even though the gap is 1.7 eV) such tubules are expected to be highly polarizable along the tube axis. Further, given the longitudinal internal cavity dictated by their topology, these systems will be natural container compounds [7]. In addition to charged and dipolar species, van der Waals molecules will easily migrate into their interior [8].

While aromatic and unsaturated hydrocarbons are known to be reactive to hydrogen halides (addition occurs), we have explored these ideas by performing localdensity-functional calculations on a system consisting of a finite-length hydrogen-terminated graphitic tubule and a pair of HF molecules constrained to travel collinearly along the axis. We expect less reactive dipolar molecules to behave similarly. Experimentally, the tubules are often capped and may exist concentrically within one another [3]. However, looking to the day of greater synthetic control, we considered a single, open-mouthed tubule pictured in Fig. 1. The model consists of a 120-atom cylindrical carbon cage with 24 H atoms tying off the C atoms at the mouth of the tubule. This tubule is 12.8 Å long, 8.2 Å in diameter, has  $S_{12}$  symmetry, and belongs to the A(12,6) class of tubules that are metallic when of infinite length [3]. Each C-C bond length is 1.423 Å in length (the C-C graphite bond length or alternatively, the mean fullerene C-C bond lengths [6]). Each C-H bond length is 1.10 Å long.

To perform the calculations we employed an allelectron Gaussian-orbital cluster code developed by ourselves [9]. There are no shape approximations in this code and the basis sets used are of high quality (four stype and three p-type contracted orbitals on each C and F and two s-type and one p-type contracted orbitals on each H with the exponents of Huzinaga [10]).

The ability to fabricate such tubules is related to the



FIG. 1. The fullerene tubule consists of 120 C atoms and 24 H atoms. Two HF molecules were constrained to move along the axis of symmetry.

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energetic stability and the reactivity of the system. To address quantitatively the question of energetic stability, we have calculated the LDA atomization energies for the fullerene molecule ( $C_{60}$ ), two tubules of different lengths  $(C_{120}H_{24} \text{ and } C_{72}H_{24})$ , benzene  $(C_6H_6)$ , and napthalene  $(C_{10}H_8)$  with the basis sets described above. Assuming that the resulting cohesive energies are reproduced by additive bond energies, we find the tubule C-C bonds to be more stable than those of  $C_{60}$  by 0.16 to 0.19 eV [11]. This energy difference is 5 times larger than the deviations in C-C bond energies obtained for the four nonspherical conjugated hydrocarbon systems  $(C_{120}H_{24},$  $C_{72}H_{24}$ ,  $C_6H_6$ , and  $C_{10}H_8$ ). However, since an ideal graphene tubule has 24 dangling bonds, a short tubule is energetically less stable than C<sub>60</sub> on a per carbon-atom basis. Neglecting the additional stabilization that occurs due to passivation or reconstruction of the tubule mouth, an ideal graphene tubule will not be energetically stable with respect to a set of C<sub>60</sub> molecules until it consists of approximately 360-420 C atoms. If the LDA passivation/reconstruction-induced stabilization is on the order of 1.7 eV/(dangling bond) or greater, our 120-atom graphene tubule will be more stable than two C<sub>60</sub> molecules.

Recently, Kaxiras [12] has noted that the reactivity of a cluster is qualitatively related to the size of the HOMO-LUMO gap (HOMO denotes highest occupied and LUMO lowest unoccupied molecular orbital). The tubule gap of 1.15 eV is smaller than that of an isolated fullerene molecule (1.7 eV) but still large compared to the gapless infinite tubule. Thus, we expect that finitelength graphene tubules of our winding topology will be slightly more reactive than a fullerene molecule. Since the gap decreases with tube length, the polarizability of the tubule may be a sensitive function of the length. Hydrogenation of some or all of the C  $\pi$  bonds could lead to a more stable and less reactive tubule although puckering of the atoms will almost certainly occur due to the bondangle strains. While surface hydrogenation may be desirable (and difficult to avoid) from the standpoint of fabrication, this will undoubtedly decrease the polarizability of the resulting tubule. Additional calculations, within the generalized gradient approximation [13] (GGA) rather than LDA, and which include geometrical relaxation of the tubule mouth, are necessary to understand fully the relative stabilities and reactivities.

The calculations provide insight into how longer and/or wider tubules would interact with (or catalyze interactions between) less chemically aggressive and perhaps larger dipolar molecules. Comparison is made between the bare interaction for a pair of HF molecules and that obtained when the tubule is either sandwiched by, or enveloping, the molecules. Simulational models, based on the LDA results described below, are in progress for much larger systems.

The energy of two HF molecules, one at either end of

the tubule (see Fig. 1) and oriented with the fluorines nearest, has been studied as a function of the distance along the tube axis. This orientation is chosen because the interaction of the HF molecule with the tubule at long range is expected to be dipole-induced-dipole type which varies as  $-1/r^6$ . The LDA obtains the asymptotic behavior of static fields with polarizable media correctly. Broughton and Bagus [14] have shown, for dipoles of finite length, that the interaction is stronger when the negative end is nearest the polarizable medium. Before further discussing the bimolecular-tubule system, we turn to the bare bimolecular interaction.

The bond length of the HF is kept fixed throughout these calculations at the experimental value of 0.92 Å. The calculated dipole moment of the HF molecule is 0.71 a.u. which indicates an ionic bond with a charge transfer of approximately 0.41 electron [15]. As expected from classical electrostatics, we have verified that for large values of r, LDA predicts a bare (HF)<sub>2</sub> dipole-dipole repulsion of  $2(0.71)^2/r^3$ . This interaction is depicted in Fig. 2(a). The origin is taken as the point midway between the fluorines and will coincide, below, with the midpoint of the tubule. We define the position of the HF by its midpoint and the longitudinal axis as the z direction. The energy scales in these systems are on the order of 0.1 eV or alternatively 1160 K. That is, the interac-



FIG. 2. (a) Interaction of two HF molecules with and without the presence of the A(12,6) tubule according to the local-density approximation. (b) The classical model described in the text: Extended dipoles interacting with (1) long tube of small radius, (2) short tube of small radius, (3) long tube of large radius, and (4) short tube of large radius.

tions are indeed "physical" as opposed to "chemical" in nature. We note that the potential energy minimum near 1.7 Å on the rising background in Fig. 2(a) for the bare (HF)<sub>2</sub> is real and is due to correlation energy. To verify that the dip is not due to superposition error, we have ascertained that the dip is present even for a very extensive basis set consisting of eighteen s-type (four of which have an  $r^2$  prefactor), nine p-type, and four d-type even tempered single Gaussians (with exponents lying between 0.05 and 5000 bohr<sup>-2</sup>) on each atom. Dips of similar magnitude have been observed in applications of the LDA to Ar<sub>2</sub> and [K<sup>+</sup>]<sub>2</sub> [16]. For the [HF]<sub>2</sub> case discussed here, the dip is also partially due to induction in one HF molecule by the dipole field of the other.

Figure 2(a) also presents the full interaction when the HF molecules are brought together in the presence of the tubule. The resulting interactions have a similar energy scale but differ dramatically. At long range, the energy decreases due to the dipole-induced-dipole interaction. This attractive interaction defeats the relatively small HF-FH  $1/r^3$  repulsion because the dipoles are so far apart (at extremely long range, this term will again dominate). However, as the HF molecules approach the mouth of the tube, the energy rises due to an overlapinduced increase of the kinetic energy. It coincidentally reaches an energy maximum of about the infinite separation limit. In addition to the interactions discussed above, a small permanent dipole exists at the tubule mouth due to charge transfer between neighboring C and H atoms. Its magnitude and sign have yet to be determined, but this also may contribute to the energy bump at the mouth.

Once the HF molecules are within the tube, the full polarizability of the tubule comes into effect and overcomes any overlap repulsions. The energy decreases by 0.1 eV per molecule, or approximately 4 times room-temperature ambient. As the HF molecules approach one another, the energy again rises as the repulsive dipole-dipole term begins to dominate. The same correlation-energy dip observed in the bare HF bimolecular interaction is also seen.

To address whether or not our constraint of a fixed HF bond length will affect our results, we note that the repulsion between two isolated HF molecules is simply decreased by a factor of  $1+2q^2/kr^3$ , with q=0.41 unit of charge, k the HF molecular spring constant, and r the center-to-center separation between the HF molecules. Even for separations as small as 3.0 Å, the repulsion is only reduced by a factor of 1.003 compared to the rigid calculation. The isolated dipolar molecules will be purely repulsive even if the HF bond length is relaxed. In addition to interactions between dipolar molecules, the tubule may also induce HF bond relaxation upon incarceration. Such a relaxation will increase the incarceration energy but is expected to be negligible. To estimate the magnitude of this effect a single HF molecule was placed in a tubule half as long as that pictured in Fig. 1. The resulting HF bond length changed by less than 1% relative to the free molecule.

In Fig. 3, we present a difference electron density plot for the case of incarcerated HF molecules (separated by 6.7 Å). The isosurface is drawn at a level of 0.03 electron per bohr<sup>3</sup> which is close to the maximum difference (0.032). The isosurface is hollow with tubular symmetry. The small change in electron redistribution again points to a "physical" interaction. The tubule's  $\pi$ -electron density polarizes in response to the dipole field of the diatomics. Electron density is pushed away from the fluorines and from the tubule z origin, in a fluted manner. In the figure, the F of the HF's exist at the inner mouth of the two flutes. The interaction has atomistic components, as indicated by the "lumpy" character of the isosurface, as well as a cylindrically symmetric smooth background. The electron density of the molecular HF moeity is expected and found to be unpolarizable.

How dipoles interact with tubules of different length and radius may be understood by treating the HF molecules as extended dipoles with charge ( $\pm 0.41$ ) and bond length (0.92 Å) equal to those of the LDA calculations and the tubule as a structureless cylinder with an isotropically polarizable surface. The polarization energy of the system is proportional to the integral of the square of the field (E) along the tubule surface:

$$U(L,R) = U_0 + U_{dip-dip} - \frac{1}{2} (2\pi R) \alpha \int_{-L/2}^{L/2} dz |\mathbf{E}(z,R)|^2,$$
(1)

where L is the length of the tubule, R is the radius,  $\alpha$  is the effective polarizability per unit area, and  $U_{dip-dip}$  represents the repulsive energy between the two HF molecules. The model neglects overlap repulsion effects and hence cannot describe the energy maximum at the mouth of the tubule. Results are shown in Fig. 2(b) using an  $\alpha$ value of 3.4 Å. This polarizability approximates the en-



FIG. 3. Electronic density difference  $(\rho^{\text{SCF}}[C_{120}\text{H}_{24}(\text{HF})_2] - \rho^{\text{SCF}}[C_{120}\text{H}_{24}] - \rho^{\text{SCF}}[(\text{HC})_2])$  isosurface of the interacting (HF)<sub>2</sub>-tubule system. See text.

ergy of interaction of HF within the tubule but is 6 times larger than the LDA value of  $C_{60}$  [6]. Four situations are depicted; tube lengths equal to and 1.5 times that used in the LDA calculations, and radii for the present and A(16,8) tubules (approximately 4 and 5 Å, respectively). If the tubule is made longer, the well depth increases slightly and a more gently sloping plateau region within the tubule is observed. Thus the z range over which the dipolar molecules are fully incarcerated would be extended. If the radius of the tubule is increased, the number of atoms at the perimeter increases linearly, but the charge-induced-dipole interaction (within the tubule, C atoms nearest the H or F are normal to the dipolar axis) varies as  $1/r^4$ , and hence the incarceration energy decreases in magnitude. Increasing the tubule radius will also lower the overlap repulsion activation barrier at the mouth of the tube; i.e., the maximum at the tubule's mouth observed in Fig. 2(a) would diminish. More complex models are being examined but the simple model given here captures the essential physics.

The ramifications of these observations are manyfold. Our calculations, by computational necessity, have involved dipolar molecules constrained to collinearity with the tubule's axis. While lower energy states may exist for molecules off axis, the following points have been demonstrated. Tubules are clearly container compounds. They act as "molecular straws" for many systems, capable of withdrawing molecules from the vapor or fluid phases by interactions akin to those in wetting and capillarity. In principle, they may be tailored to incarcerate different guest molecules. The screening within the tubule may also lower reactive activation barriers between entrapped charged molecules. Further, the degree of screening from outside fields may also be tailored, due to the selectivity of metallic or insulating behavior [3,4]. Indeed, as our calculations show, the band gap of the tubule and therefore the polarizability per C atom is a function of tube length. Applications such as nanoscale solenoids and piezoelectric devices are being pursued.

In addition to the potential for new technologies, these calculations represent a new size regime for local-orbital basis sets since the overlap between the most diffuse basis functions on a pair of well-separated atoms vanishes. It is this size regime where the advantages of local-orbital basis sets can be most dramatic. All (about 30) calculations discussed here have been performed on IBM RISC-320 workstations in approximately 200 workstation days, a nontrivial but increasingly accessible amount of computer time. With the continued availability of faster desktop computers and new algorithms which exploit the characteristics of this and larger size regimes, we expect the first-principles calculations on significantly larger molecules, clusters, and unit cells to become ever more routine.

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