Interaction of Low-Energy Ions and Atoms of Light Elements with a Fluorinated Carbon Molecular Lattice

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Received: September 22, 2006; In Final Form: December 20, 2006

The mechanism of interaction of low-energy atoms and ions of light elements (H, H+, He, Li, the kinetic energy of the particles 2–40 eV) with C6H6, C8F12, C60, and C60F48 molecules was studied by ab initio MD simulations and quantum-chemical calculations. It was shown that starting from 6 Å from the carbon skeleton for the “C6H6 + proton” and “C60 + proton” systems, the electronic charge transfer from the aromatic molecule to H+ occurs with a probability close to 1. The process transforms the H+ to a hydrogen atom and the neutral C6H6 and C60 molecules to cation radicals. The mechanism of interaction of low-energy protons with C8F12 and C60F48 molecules has a substantially different character and can be considered qualitatively as the interaction between a neutral molecule and a point charge. The Coulomb perturbation of the system arising from the interaction of the uncompensated proton charge with the Mulliken charges of fluorine atoms results in an inversion of the energies of the electronic states localized on the proton and on the C8F12 and C60F48 molecules and makes the electronic charge transfer energetically unfavorable. On the different levels of theory, the barriers of the proton penetration for the C8F12 and C60F48 molecules are from two to four times lower than those for the corresponding parent systems (C6H6 and C60). The penetration barriers of the He atom and Li+ ion depend mainly on the effective radii of the bombarding particles. The theoretical penetration and escaped barriers for the “Li+ + C60” process qualitatively explain the experimental conditions of synthesis of the Li@C60 complex.

1. Introduction

Development of an effective method of synthesis of endohedral fullerene complexes and nanotubes remains a priority in the chemistry of nanostructures. There are only a few ways to prepare such nanostructures: (1) high-temperature synthesis in a carbon plasma,1,2 (2) processing of carbon nanostructures to prepare such nanostructures: (1) high-temperature synthesis from the carbon plasma or as a result of high-energy radioactive decay with really low chemical yield.1,2,7 To optimize the synthesis conditions of the endohedral complexes with light elements,3–6 one needs to manipulate the penetration barriers of the species through the carbon wall of the C60 molecule. A practical way to achieve the goal is a chemical modification of the C60 molecule to decrease the electronic density of active π-states localized perpendicular to the C6 and C5 fragments.8

Earlier, the potential barrier to the penetration of a proton into a fullerene molecule was calculated by quantum-chemical PRD0 and DFT methods9 (3.8 eV) as the difference between the total energies of a neutral C60H molecule (hydrogen covalently bonded to one of the carbon atoms on the external side of the C60 molecule) and a neutral transition complex where the proton is at the center of a relaxed carbon hexagon. The potential barriers for a He atom have been calculated by the molecular mechanics method (9.4 eV),10 semiempirical MNDO method11 (11.5 eV), or using the second-order Möller–Plesset perturbation theory (MP2) with the 6-31G** basis set12 (10.7 eV for the C60H6 molecule).

The main reason for the high penetration barriers for some ions and atoms through a molecular carbon lattice is an active π-electronic system, which tends to form new covalent bonds at the external side of the objects. Hence, the best way to lower this potential barrier could be to neutralize this system by saturation of the carbon–carbon double bonds, for example, by fluorination. At present the most fluorinated derivative of the C60 is the C60F48 molecule.13 Previously, the electronic
II. Atomic and Electronic Structures of C\textsubscript{60}F\textsubscript{48} and Details of the Calculations

The C\textsubscript{60}F\textsubscript{48} molecule has S\textsubscript{6} symmetry (the Schlegel diagram for the C\textsubscript{60}F\textsubscript{48} molecule is presented in Figure 1).\textsuperscript{13} There are 3 types of carbon hexagons in the C\textsubscript{60} atomic lattice: 2 hexagons with 6 fluorine atoms each, 12 hexagons with 5 fluorine atoms, and 6 hexagons with 4 fluorine atoms. There are also two types of carbon pentagons: with five fluorine atoms (six pentagons) and with three fluorine atoms (six pentagons). Single carbon–carbon bonds are divided into four types (the ab initio 6-31G\* level): 1.49, 1.54, 1.56, and 1.59 Å. The length of six double carbon–carbon bonds is 1.31 Å, and the length of a fluorine–carbon bond is 1.34 Å.

To study the process of interaction of low-energy (~10–100 eV) ions and atoms with molecular targets, the kinetic energy of the projectiles should be taken into account. The kinetic energy of the projectiles to penetrate the carbon cage of the C\textsubscript{60} and its derivatives. Moreover, because of the large difference in the effective speed of the projectiles and vibration movements of the atoms composing a molecule, an achievement of a number of specific points on the molecular potential energy surface is not evident and should be clarified using a combination of quantum-chemical and molecular-dynamics calculations.

![Schlegel Diagram for the C\textsubscript{60}F\textsubscript{48} Molecule](image)

Figure 1. Schlegel diagram for a C\textsubscript{60}F\textsubscript{48} molecule. The blue circles denote fluorine atoms, and the black dots represent carbon atoms not connected with fluorine. Red shaded regions reflect regions on the surface of C\textsubscript{60}F\textsubscript{48} accessible for low-energy protons.

TABLE 1: Theoretical (Calculated Using the Coopmans Theorem) and Experimental Ionization Potentials of H, He, Li, C\textsubscript{60}, and C\textsubscript{60}F\textsubscript{48} (in Electronvolts)

<table>
<thead>
<tr>
<th>object</th>
<th>UHF PM3 (eV)</th>
<th>ab initio UHF-6-31G* (eV)</th>
<th>experiment (eV)</th>
</tr>
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<tr>
<td>H</td>
<td>13.1</td>
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<td>13.6</td>
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<td>He, 1st IP</td>
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<td>24.56\textsuperscript{18}</td>
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<tr>
<td>He, 2nd IP</td>
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<tr>
<td>Li</td>
<td>5.30</td>
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<td>5.39</td>
</tr>
<tr>
<td>C\textsubscript{60}</td>
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<td>7.6\textsuperscript{17}</td>
</tr>
<tr>
<td>C\textsubscript{60}F\textsubscript{48}</td>
<td>14.2</td>
<td>13.8</td>
<td>12.3\textsuperscript{13}</td>
</tr>
</tbody>
</table>

The mechanisms of the interaction of low-energy protons, helium atom and Li\textsuperscript{+} ion (the kinetic energy of the particles is in the range of 2–40 eV) with aromatic C\textsubscript{6}H\textsubscript{6} and C\textsubscript{60} molecules (carbon nanostructures (CNS)) and fluorine derivatives C\textsubscript{6}F\textsubscript{12} and C\textsubscript{60}F\textsubscript{48} (fluorinated carbon nanostructures (FCNS)) were also investigated using the unrestricted semiempirical UHF PM3 and ab initio 6-31G* quantum-chemical methods using the Gaussian code\textsuperscript{13} and molecular-dynamics simulations as well. The optimization of the geometry was performed by the analytical gradient method. All potential barriers were calculated taking into account the basic set superposition error (BSSE). The potential curves for the interaction of a proton with optimized CNS and FCNS were calculated as functions of the distance between the proton and the center of the carbon hexagon lying strictly normal to the direction of motion of the H\textsuperscript{+} ion. The penetration of low-energy protons and Li\textsuperscript{+} ions through carbon hexagons and pentagons was simulated by the molecular-dynamics method using the UHF PM3 (MD/PM3) and ab initio 6-31G* (MD/6-31G*) potentials.

The applicability of one-determinant wave functions to the description of the electronic structure of fullerenes and their derivatives was confirmed earlier in the work of ref 16. An analysis of the UHF wave function for all different proton positions with respect to the C\textsubscript{60}F\textsubscript{48} molecule has shown that the spin contamination of the wave function vanishes in a wide range of distances (0–5 Å). At chemically significant distances from the proton to the center of the carbon hexagon (from 0 to 6 Å), the energy difference between the HOMO and LUMO levels of the “C\textsubscript{60} + proton”, “C\textsubscript{60}F\textsubscript{48} + proton”, “C\textsubscript{6}H\textsubscript{6} + proton”, and “C\textsubscript{6}F\textsubscript{12} + proton” systems varied from 5 to 8 eV (depending on the method, system, and distance); this might also argue for the applicability of one-determinant wave functions to the description of such processes. The same difference for the C\textsubscript{60} + Li\textsuperscript{+} and C\textsubscript{60}F\textsubscript{48} + Li\textsuperscript{+} is sufficiently higher (~10 eV). It should be noted that because of the presence of a uncompensated positive charge in the systems under study the occupied electron levels are displaced to lower energies to a much greater degree than the unoccupied ones and the number of electrons is always even (according to the condition of the problem). Calculations show that in all cases the electronic states are actually doubly occupied (because the orbitals with spin up and spin down in the UHF method have close energies and have the same characteristic of spatial distribution) and, therefore, the electronic shells are closed.

The unrestricted Hartree–Fock method was chosen for the description of the electronic structure of such dynamic systems because the restricted Hartree–Fock method (RHF, or ROHF in the case of open electronic shells) and various versions of the DFT method incorrectly describe the self-interaction of the hydrogen 1s electron (in these methods, the hydrogen 1s eigenvalues are ca. –6 to 8 eV, whereas the experimental and theoretical (UHF) values of the ionization potential are equal to approximately 13.5 eV; Table 1). This feature of the RHF
and DFT methods does not allow one to correctly describe the initial electronic state of the $C_6F_{12}^+ + \text{proton}$ and $C_6F_{48}^+ + \text{proton}$ systems at infinity, which is formally excited: the hydrogen 1s state with an energy of about $-13.5$ eV is vacant, and the HOMO level in CNS/FCNS with an energy higher than $-12$ eV is occupied.

**a. Interaction of the Low-Energy Protons with CNS and FCNS.** To illustrate the results of direct MD simulations of the “$H^+ + \text{CNS/FCNS}$” interactions, let us develop a simplified perturbation model of the collision process. In the most complex case, the initial state of the “carbon nanostructure plus proton” system (proton–target distance $R_{\text{HI}} = \infty$) is unstable and excited: the low-energy proton at infinity and the neutral molecule as a target (Figure 2). Because of the substantial energy difference (6 eV for the proton + CNS system and 1.3 eV for the proton + FCNS system; Table 1), an electron transition should occur from the occupied electronic states of the carbon nanoparticle to the unoccupied 1s state of the positive hydrogen ion (which is essentially a proton) as the proton approaches the carbon nanostructure sufficiently closely. For the systems $H^+ + \text{CNS}$ and $H^+ + \text{FCNS}$ (with the proton moving along the Z axis to the center of the carbon hexagon bonded to the six fluorine atoms and oriented normal to the direction of the proton motion), we can write (in the first order of perturbation theory)

$$H = H_0^{\text{HI}} + H_0^{\text{CN}} + V_N(R_{\text{HI}}) - \frac{\nabla^2 R_{\text{HI}}}{2m_p} + V_S(R_{\text{HI}})$$  

(1)

Here, $H_0^{\text{HI}}$ and $H_0^{\text{CN}}$ are the Hamiltonians of the unperturbed electronic systems of the proton (having an unoccupied 1s orbital) and of the carbon nanostructure and $R_{\text{HI}}$ is the radius vector of the proton, which is parallel to the proton velocity and whose length $|R_{\text{HI}}| = t\sqrt{2E_p/m_p}$ is equal to the distance between the proton and the center of the carbon hexagon. The time $t$ changes from $-\infty$ to 0; $-\nabla^2 R_{\text{HI}}/(2m_p)$ is the operator of the proton kinetic energy; $E_p$ is the proton kinetic energy ($\approx 10$ eV in our case); and $V_N(R_{\text{HI}})$ and $V_S(R_{\text{HI}})$ are the operators of the Coulomb perturbation for the electronic and nuclear subsystems, respectively, describing the interaction of the uncompensated charge of the proton ($H^+$) with the Mulliken charges of the atoms of CNS or FCNS.

Modern ab initio molecular dynamics\textsuperscript{19} describes the motion of nuclei only for the Born–Oppenheimer potential surfaces, for which one can write the relationship $\sqrt{2E_p/m_p} \approx \sqrt{2E_{p}/m_e}$, where $E_p$ is the electron kinetic energy and $m_p$ and $m_e$ are the proton and electron masses, respectively. Taking into account the relationship between the masses $m_p/m_e \approx 2 \times 10^3$ and the average kinetic energy of the valence electrons ($E_k \sim 1/10$ eV), this approximation can be applied to the description of the interaction of low-energy protons with matter if the proton kinetic energy is not higher than $E_k \sim 10^2/10^3$ eV. In our case, $E_k \sim 10$ eV.

If the kinetic energy is below this limit, then we can separate the electronic and nuclear parts of eq 1. For the electronic part, in the first order of perturbation theory we can write

$$\epsilon_{\text{H}}(R_{\text{HI}}) = \epsilon_{\text{H}}^0 + \Delta \epsilon_{\text{H}}(R_{\text{HI}})$$  

(2)

$$\epsilon_{\text{CN}}^0(R_{\text{HI}}) = \epsilon_{\text{CN}}^0 + \Delta \epsilon_{\text{CN}}(R_{\text{HI}})$$  

(3)

where $\epsilon_{\text{H}}(R_{\text{HI}})$ and $\epsilon_{\text{CN}}(R_{\text{HI}})$ are the excited electron energy eigenvalues corresponding to the unperturbed value $\epsilon_{\text{H}}^0$ (the energy of the hydrogen 1s level) and to the unperturbed value $\epsilon_{\text{CN}}^0$ (the HOMO level of CNS/FCNS) localized on the proton and on the carbon nanocluster, respectively. For $C_60$ and $C_60F_{48}$, we have $\epsilon_{\text{CN}}^0 = -E_{\text{CN}}^0 = -7.6$ eV and $\epsilon_{\text{CN}}^0 = -E_{\text{CN}}^0 = -12.3$ eV, respectively (where the $E_{\text{CN}}^0$ are the experimental ionization potentials,\textsuperscript{20,13} see Table 1).

Qualitatively, we can interpret the interaction of a low-energy proton with carbon (fluorine–carbon) nanoclusters in terms of perturbation theory. Disregarding the effects of orbital overlap, we can write the perturbation operator of the electronic system as

$$V_{\text{e}}(R_{\text{HI}}) = V_{\text{H}}(R_{\text{HI}}) + V_{\text{C}}(R_{\text{C}}) + V_{\text{F}}(R_{\text{F}})$$  

(4)

where $\textbf{r}_H$, $\textbf{r}_C$, and $\textbf{r}_F$ are the radius vectors of the electronic wave functions belonging to the hydrogen, carbon, and fluorine atoms, respectively; $V_{\text{H}}(R_{\text{HI}}) = -\textstyle{\sum_{N_C} (q_C)/(|r_{\text{H}} - r_{\text{C}}|)} + \textstyle{\sum_{N_F} (q_F)/(|r_{\text{H}} - r_{\text{F}}|)}$ operates only on the $\textbf{r}_H$ coordinate of the electron wave function ($N_C$ and $N_F$ are the numbers of carbon and fluorine atoms in the system, respectively; $V_{\text{C}}(R_{\text{C}}) = -\textstyle{\sum_{N_C} (1)/(|r_{\text{C}} + r_{\text{C}}|)}$ operates on the $r_{\text{C}}$ coordinate; and $V_{\text{F}}(r_{\text{F}}) = -\textstyle{\sum_{N_F} (1)/(|r_{\text{F}} + r_{\text{F}}|)}$ operates on the $r_{\text{F}}$ coordinate. The vectors $R_{\text{C}}$ and $R_{\text{F}}$ are directed from the proton to the carbon and fluorine atoms, respectively, and their lengths (for the nearest six neighbors) are $|R_{\text{C}}| = \sqrt{R_{\text{H}}^2 + A^2}$ and $|R_{\text{F}}| = \sqrt{R_{\text{H}}^2 + B^2}$, where $A$ and $B$ are the distances between the centers of the carbon and fluorine nanoclusters.

![Figure 2. Schematic representation of the interaction of a low-energy proton with (a) C$_{60}$ and (b) C$_{60}$F$_{48}$ molecules.](image-url)
Interaction of Ions and Atoms

\[ \sqrt{(R^2 - B)^2 + C^2}. \]

The geometrical parameters \( A = 1.4 \text{ Å}, B = 1.1 \text{ Å}, \) and \( C = 2.4 \text{ Å} \) are determined by the features of the atomic structure of the object: \( q_C \) and \( q_C \) are the Mulliken charges of the carbon (\( q_C \) is zero for \( C_6 H_6 \) and \( C_{60} \) and is equal to \( -0.1 \) for \( C_6 F_{12} \) and \( C_{60} F_{48} \) and fluorine (\( q_F \approx -0.1 \) atoms).

The interaction \( V_{S}(R_{ni}) \) between the uncompensated proton charge and the Mulliken charges of the atoms of the target molecule also contributes to the energy of the system. For nonfluorinated structures, we have \( V_{S}(R_{ni}) = 0 \) because the carbon Mulliken charges are equal to zero. For fluorinated molecules (\( C_{60} F_{48}, C_{6} F_{12} \)), the quantity \( V_{S}(R_{ni}) = \sum \left( q_C(r)(1-R_{ni}) \right) + \sum \left( q_F(r)(R_{ni}) \right) \) describes the contribution to the energy due to the interaction of the Mulliken charges of the carbon and fluorine atoms with the uncompensated charge.

The electronic structure of the system in the initial state of the process (neutral target molecule + proton at infinity) is quasi-excited (the energy of the unoccupied H1s state is \( -13.6 \text{ eV} \), and the energy of the HOMO level of the target molecule \( \approx 5.8 \text{ Å} \), the overlap integrals vary from 0 to 0.5. In this interval, the interaction of the Mulliken charges of the carbon and fluorine atoms with the uncompensated charge.

For a low-energy proton (~2 eV), the transit time for a distance of \( 6 \text{ Å} \) is \( T = \frac{5 \times 10^{-14}}{s} \) for the \( (C_{60} + \text{proton}) \) system with \( R_{ni} = 6 \text{ Å} \), the number of periods of the electronic transition from the occupied state \( \psi_{\text{CN}}(r_{\text{CN}}) \) to the unoccupied state \( \psi_{\text{CN}}(r_{\text{CN}}) \) (Figure 2) is \( 10^2 \). For \( C_{60} \), we have \( \Delta_{\text{CN}} = 0 \text{ eV} \) and \( \Delta_{\text{CN}} = 1.4 \text{ eV} \) (the new \( \epsilon_{\text{CN}} = -13.5 \text{ eV} \) and \( \epsilon_{\text{CN}} = -13.7 \text{ eV} \) values were obtained using the theoretical energy shifts and correspondent experimental ionization potentials, Table 1). Thus, at distances of \( 6 \text{ Å} \), the “\( C_{60} F_{48} + \text{proton} \)” configuration becomes the ground state of the system and the fluorinated carbon nanostructure interacts with a proton as does a neutral molecule with a point charge.

For a low-energy proton (~2 eV), the transit time for a distance of \( 6 \text{ Å} \) is \( T = \frac{5 \times 10^{-14}}{s} \) for the \( (C_{60} + \text{proton}) \) system with \( R_{ni} = 6 \text{ Å} \), the number of periods of the electronic transition from the occupied state \( \psi_{\text{CN}}(r_{\text{CN}}) \) to the unoccupied state \( \psi_{\text{CN}}(r_{\text{CN}}) \) (Figure 2) is \( 10^2 \). For \( C_{60} \), we have \( \Delta_{\text{CN}} = 0 \text{ eV} \) (the Mulliken charge of the carbon atoms is zero) and \( \Delta_{\text{CN}} = 1.15 \text{ eV} \) (\( \epsilon_{\text{CN}} = -13.6 \text{ eV} \), \( \epsilon_{\text{CN}} = -8.7 \text{ eV} \)). In this case, the transition probability from the molecular level into the unoccupied H1s state (with regard for the number of periods of the electronic transition) is close to 1. The lifetime of the excited electronic state (\( \tau \approx 5 \times 10^{-15} \text{s} \)) can be estimated from the experimental width of the photoelectron spectra (0.2–0.3 eV for \( C_{60} F_{48} \) and \( C_{60} F_{48} \)). This lifetime is an order of magnitude shorter than the proton transit time of the distance of \( 6 \text{ Å} \) at which the overlap integral between the wave functions of the carbon nanoparticle and the proton becomes nonzero. On the basis of these estimations, we may assert that the aromatic systems like \( C_{60} \) and \( C_{60} H_6 \) interact with a low-energy proton as do positive ion radicals (\( C_{60} H^{+} \) and \( C_{60} H_6^{+} \)) with a radial (neutral hydrogen atom). This will certainly facilitate the formation of a new covalent carbon—hydrogen bond on the external side of the carbon nanoparticle.

Both theoretical quantum-chemical methods (UHF PM3 and ab initio UHF/6-31G*) correctly describe the initial “\( \text{FCNS} + \text{proton} \)” state because the first ionization potential of \( C_{60} F_{48} \) is overestimated (Table 1) and, therefore, the H1s state in the \( C_{60} F_{48} + \text{proton} \) system remains unoccupied and all \( C_{60} F_{48} \) levels are occupied. This feature allowed us to perform molecular-dynamics simulation of the interaction of protons with FCNS (\( C_{60} F_{48} \) and \( C_{60} F_{48} \)) using both the semiempirical and ab initio quantum-chemical potentials. For comparison, we performed a molecular-dynamics simulation of the interaction of protons with aromatic carbon molecules (\( C_{60}, C_{60} H_6 \) with one difference: to avoid an error in describing the initial state (neutral molecule + proton at infinity), the initial distance between the proton and the carbon nanoparticle was chosen to be 2 Å. Thus, we assumed that, at this distance, the electron from the carbon nanoparticle has already passed to the proton with the formation of a hydrogen atom. We used the MD/PM3 and MD/UHF 6-31G* methods to simulate the interaction of a proton with \( C_{60} H_6 \) and \( C_{60} F_{12} \) and only the MD/PM3 method to simulate the interaction with \( C_{60} F_{48} \) molecules.

b. Interaction of Helium with CNS and FCNS. It is well known that helium has really high first (24.56 eV experiment and 24.87 eV ab initio RHF/6-31G*) and second (54.25 and 54.42 eV respectively) ionization potentials (Table 1). Because of this, the \( \text{He}^+ \) and \( \text{He}^{2+} \) (α-particle) ions are really strong oxidizers, and both CNS and FCNS systems should interact with low-energy \( \text{He}^+ \) and \( \text{He}^{2+} \) as positively charged radicals with neutral helium atoms. Because of this, here we studied only the interactions of the helium atom with CNS and FCNS objects.

c. Interaction of the Low-Energy Lithium Ions with CNS and FCNS. In contrast with helium, lithium has a really small ionization potential (5.39 eV experiment, 5.50 eV UHF PM3 and 5.33 eV ab initio UHF/6-31G*, Table 1). Taking into account the ionization potentials of both types of objects (CNS and FCNS, Table 1), the probability of the charge transfer from the targets (CNS and FCNS) to the \( Li^+ \) ions can be estimated close to 0. Evidently, in this situation the quantum-chemical methods can describe correctly the initial state of the process (neutral target molecule and low-energy positive ion on infinity). Because of this, we have performed the ab initio MD/PM3 simulations of interactions of \( Li^+ \) with CNS and FCNS in the same way as for the \( \text{H}^+ + \text{FCNS} \) (see the above paragraph).

III. Results and Discussion

The potential curves for the interaction of a proton with \( C_{60} F_{48} \) and \( C_{60} \) molecules calculated by the UHF PM3 and ab initio UHF/6-31G* methods are shown in Figure 3. The distance \( R_{ni} \) was measured from the proton to the center of the carbon hexagon (completely fluorinated in the case of \( C_{60} F_{48} \) lying on the trajectory of the approaching proton. The solid and dashed lines represent the results obtained by the ab initio UHF/6-31G* method for the \( C_{60} F_{48} \) and \( C_{60} \) molecules correspondingly, whereas the solid squares and dots correspond to the UHF PM3 method. The filled upward and downward triangles (the ab initio UHF/6-31G* method) and the open upward and downward ones (the UHF PM3 method) at infinity (\( R = \infty \)) denote the total
energy of the neutral C_{60}F_{48} and C_{60} molecules in the gas phase. Solid (the ab initio UHF/6-31G* method) and open (UHF PM3 method) diamonds denote the total energy of the optimized H−C_{60}F_{48}− complex with the hydrogen placed at the center of the carbon hexagon, R = 0 Å, and the hydrogen covalently bonded to an sp² carbon inside the carbon polyhedron, R = 5 Å. The cross (+) (the ab initio UHF/6-31G*) and X character (UHF PM3) denote the optimized structure of the H−C_{60}+ complex with the hydrogen covalently bonded to an sp² carbon outside the C_{60} molecule, R = 1 Å.

For the C_{60}F_{48} + H⁺ system, the potential curves are typically smooth and do not exhibit high potential barriers or wells outside the carbon nanostructure or at the wall. For the C_{60} + H⁺ system, two deep potential wells outside the carbon nanostructure, corresponding to the initial state (a neutral C_{60} molecule, R = −∞) and to the hydrogen covalently bonded to a carbon atom (R = −1 Å), and one high potential barrier at the center of the carbon hexagon (R = 0 Å) exist. For the C_{60}F_{48} + H⁺ system, a deep potential well exists inside the carbon polyhedron (R = 5 Å), corresponding to the hydrogen covalently bonded to an sp² carbon atom. This bond forms when the incident proton passes through the center of the carbon hexagon and collides with a nonfluorinated carbon atom located on the opposite side of the molecule.

The potential barriers to the penetration of the proton were calculated as the difference between the energies of the intermediate state (a guest atom at the center of the carbon hexagon) and of the free C_{60} molecule. The choice of the former initial state of the process of proton penetration through the carbon polyhedron is related not only to compare our data with the results of the work of ref 9 but also to the obvious fact that this configuration corresponds to the global energy minimum of the system, to which the system will tend in the case where the proton kinetic energy is close to zero.

Using molecular dynamics, we calculated the kinetic energy of the penetration of a proton or Li⁺ ion as the minimum kinetic energy required for the particle to penetrate into the molecule through the center of the carbon hexagon. In the case of the C_{60}F_{48} molecule, the center of the completely fluorinated carbon hexagon was chosen as a target. The calculated penetration barriers are listed in Tables 2 and 3 (ab initio UHF/6-31G* and UHF PM3 methods, respectively).

The ab initio UHF/6-31G* calculations (Table 2) show a significantly lower barrier (by up to four times in the case of C_{60}H_{6}/C_{60}F_{12} molecules) for the penetration of a proton through the carbon hexagon of FCNS (C_{60}F_{12} and C_{60}F_{48}) as compared to the barriers of nonfluorinated C_{60} and C_{60}H_{6} molecules. We explain this result in terms of a substantial decrease in the density of valence π-electrons on fluorinated nanobjects, which precludes the formation of new covalent hydrogen−carbon bonds on the external side of the carbon polyhedron.

### Table 2: Potential Barriers and Kinetic Energies Required for a Proton to Penetrate through the Center of a Carbon Hexagon (Results of Ab Initio UHF/6-31G* Calculations)

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<tr>
<th>object</th>
<th>potential barrier (eV)</th>
<th>kinetic energy (eV)</th>
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</thead>
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<td>6.7</td>
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<tr>
<td>C_{60}F_{12} + H⁺</td>
<td>1.4</td>
<td>2.6</td>
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<tr>
<td>C_{60} + H⁺</td>
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<td>C_{60}F_{48} + H⁺</td>
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<td>C_{60} + He</td>
<td>14.0</td>
<td>15.6</td>
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<tr>
<td>C_{60}F_{48} + He</td>
<td>10.5</td>
<td>12.1</td>
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</tbody>
</table>

*Note: The potential barrier was calculated as the difference between the energies of the intermediate state (with a proton at the center of the hexagon) and of the free C_{60} molecule, indicated in parentheses. The calculations were performed taking into account the BSSE error.

### Table 3: Potential Barriers and the Kinetic Energies Required for a Proton to Penetrate through Carbon Hexagons (Results of the UHF PM3 Calculations)

<table>
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<th>object</th>
<th>potential barrier (eV)</th>
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<tr>
<td>C_{60}H_{6} + H⁺</td>
<td>6.5</td>
<td>6.6</td>
</tr>
<tr>
<td>C_{60}F_{12} + H⁺</td>
<td>4.8</td>
<td>5.7</td>
</tr>
<tr>
<td>C_{60} + H⁺</td>
<td>6.5 (12.0)</td>
<td>12.6</td>
</tr>
<tr>
<td>C_{60}F_{48} + H⁺</td>
<td>1.8</td>
<td>2.6</td>
</tr>
<tr>
<td>C_{60} + Li⁺</td>
<td>18.6</td>
<td>20.6</td>
</tr>
<tr>
<td>C_{60}F_{48} + Li⁺</td>
<td>17.6</td>
<td>19.6</td>
</tr>
</tbody>
</table>

*The meaning of the parenthetical value is explained in the footnote of Table 2.
structures (Table 2); this fact can be explained by the 12.5% lengthening of the carbon—carbon distance in a C$_6$F$_{48}$ molecule (1.59 Å) as compared to that in a C$_6$$_{60}$ molecule (1.40 Å) and by the decrease in the density of π clouds at the center of the carbon hexagon.

For C$_6$H$_6$ and C$_6$F$_{12}$ molecules, we performed the molecular-dynamics simulation using the ab initio UHF/6-31G* potential (MD/6-31G*). The proton kinetic energy at which the H$^+$ penetrates through the C$_6$ fragment turned out to be 2.6 times lower for a C$_6$F$_{12}$ molecule (2.6 eV) than that for a benzene molecule (6.7 eV; Table 2). We did not study the potential curves for the interaction of a proton with a C$_6$F$_{12}$ molecule because of the substantial distortion of the C$_6$ fragment in this case and the impossibility of defining its center uniquely.

Similar results for the C$_6$H$_6$ + H$^+$ and C$_6$F$_{12}$ + H$^+$ systems were also obtained by the semiemirical PM3 method (Table 3). The potential barrier for a C$_6$O$_{68}$ molecule (1.8 eV) turned out to be 3.6 times lower than that for a C$_6$$_{60}$ molecule (6.5 eV). This ratio for the pair C$_6$F$_{12}$ (4.8 eV) and C$_6$H$_6$ (6.5 eV) is much lower (~1.4) because the PM3 method predicts that the C—C bond in the C$_6$F$_{12}$ molecule can be broken by the proton. Simulation of the (C$_6$O + H$^+$)(C$_6$O$_{68}$ + H$^+$) and (C$_6$H$_6$ + H$^+$)/(C$_6$F$_{12}$ + H$^+$) processes using the MD/PM3 method showed that fluorination lowers the penetration barriers by factors of 4.1 and 1.5, respectively. It should be noted that after the penetration into the carbon polyhedron of the C$_6$F$_{48}$ molecule the proton forms a new C—H bond with an sp$^2$ carbon atom inside the carbon skeleton. Subsequent collisions with protons form either new carbon—hydrogen bonds inside the C$_6$O$_{68}$ molecule or H$_2$ molecules via the breaking of the earlier formed carbon—hydrogen bonds.

The MD/PM3 simulations of the processes C$_6$O + Li$^+$ and C$_6$O$_{68}$ + Li$^+$ (Table 3) show that there is no significant difference between penetration barriers for the C$_6$O$_{68}$ (17.6 eV) and C$_6$O (18.6 eV). The Li$^+$ ion is chemically passive in both cases because of low ionization potential. The escape barrier for both molecules remains high and practically the same (the initial kinetic energy of the ions is 31.4 and 32.3 eV for C$_6$O$_{68}$ and C$_6$O, respectively). The high value of the escape barrier can explain quantitatively the experimental data of E.E.E. Campbell described shortly in the introduction. According to this data, the endohedral complexes of the C$_6$O can be created using Li$^+$ ion beams with the kinetic energy around 30 eV. The consequent increasing of the kinetic energy of the Li$^+$ ions during our MD simulations leads to a destroying of the carbon cage of the C$_6$O/C$_6$F$_{48}$ and escape of the Li$^+$ ions from both molecules.

Collisions of the low-energy He and Li$^+$ with C$_6$O and C$_6$O$_{68}$ as well as the H$^+$ + C$_6$O$_{68}$ ones can be rated as the interactions of chemically passive particles with neutral molecules. Increasing of the potential barriers in the line H$^+$, He, and Li$^+$ can be explained by increasing of the ionic/atomic radii of the species (Table 4).

We also studied other channels of inelastic scattering of protons by a C$_6$O$_{68}$ molecule using the MD/PM3 method. As a target, we chose (i) a carbon atom not bonded to a fluorine atom, (ii) the center of the double carbon—carbon bond, (iii) the center of the carbon pentagon, (iv) a fluorine atom, (v) the center of the carbon—fluorine bond, and (vi) a series of points on an imaginary surface of carbon pentagons and hexagons lying far from their centers.

Molecular-dynamics simulation showed that there are several channels of inelastic scattering of protons with a kinetic energy of about 2 eV:

1. Breaking of a C—F bond with the formation of a HF molecule (collisions with a carbon atom, with the centers of the carbon—carbon and carbon—fluorine bonds).

2. Penetration into a C$_6$O$_{68}$ molecule (through a number of points on the imaginary surface of carbon pentagons and hexagons).

3. Reflection of the proton with partial absorption of its kinetic energy via the excitation of molecular vibrations of the C$_6$O$_{68}$ molecule (in particular, due to collisions with fluorine atoms).

The same trajectories were also studied for the Li$^+$ + C$_6$O$_{68}$ collisions with kinetic energy close to 30 eV. The MD simulations also demonstrate some alternative channels of inelastic scattering of the Li$^+$ ions with breaking the C—F bonds and consequent formation of the LiF molecules or breaking the C$_6$O cage itself.

The results of the MD/PM3 calculations showed that, on the imaginary surface of carbon hexagons in C$_6$O$_{68}$, there are regions with a reduced electronic density that are open for proton penetration. For example, for a kinetic energy of 2 eV, the diameter of such a region is ~1.5 Å. Therefore, approximately 25% of the imaginary surface of the carbon polyhedron of fluorinated nanoobjects is open for proton penetration through the walls. The schematic representation of the accessible proton areas are presented in Figure 1 by shaded red regions.

VI. Conclusions

In this study we have shown that starting from a distance of ~6 Å the electronic charge transfer determines the character of interaction of low-energy protons with aromatic molecules and transforms a proton into a hydrogen atom and a neutral target molecule into a cation radical. In turn, this circumstance facilitates the formation of a new covalent carbon—hydrogen bond outside the carbon nanoparticle and determines the nature of the potential barrier to the penetration of a proton through carbon pentagons and hexagons.

The presence of substitutional fluorine atoms suppresses the electronic charge transfer from C$_6$F$_{12}$ and C$_6$O$_{68}$ due to the Coulomb perturbation of the electronic structure of an interacting system. In this case, the neutral C$_6$F$_{12}$/C$_6$O$_{68}$ molecule + proton state becomes the ground state and, therefore, the low-energy proton interacts with fluorinated carbon nanoparticles as a point charge does with a neutral molecule. At short (chemically significant) distances of ~2 Å, the absence of the π-electron density on the external side of the carbon polyhedron precludes the formation of a new C—H bond. In turn, this lowers the barriers to the penetration of low-energy protons through the carbon cage by a factor of 2—4.

Molecular-dynamics simulations using the ab initio UHF 6-31G* and semiempirical potentials have shown that, for a proton kinetic energy of 2 eV, a quarter of the imaginary surface of the carbon cage of the fluorine-substituted carbon molecules is open for the penetration of low-energy protons. However, the barrier to the escape of a proton from such molecules remains high because of the formation of new covalent carbon—hydrogen bonds inside the systems under study. Other scattering channels result either in the carbon—fluorine bond breaking (with the formation of HF molecules) or in the reflection of a
proton from the molecules with a loss of part of the kinetic energy due to the excitation of molecular vibrations in the fluorine–carbon nanoparticle.

The He atoms and Li$^+$ ions are chemically passive for both types of molecules, and the barrier heights depend only on the effective radii of the bombardment particles.

Acknowledgment. Work at Rice University was supported by the Office of Naval Research, by the Robert Welch Foundation, and by the Nanoscale Science and Engineering Initiative of the National Science Foundation (CBEN). Research at ASRC was supported by JAERI/JAEA project “Materials Design with New Functions Employing Energetic Beams” and JAERI/JAEA Research fellowship (P.V.A.). P.V.A. also thanks Prof. Yoshihito Maeda and the personnel of JAERI/JAEA Research Group for Atomic-scale Control for Novel Materials under Extreme Conditions for hospitality and fruitful discussions.

References and Notes