Possibility of proton motion through buckminsterfullerene

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Abstract

The possibility of a proton entering a fullerene cage without breaking any C–C bond and undergoing oscillations through the cage is considered. A detailed understanding of the interaction of a proton with the five- and six-membered rings is obtained by examining proton–corannulene interaction, as a prototype. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Following the synthesis of fullerenes and the development of fullerene chemistry [1–5], considerable effort has gone into the production of endohedral fullerenes – represented as M@C60, where M is an atom/ion trapped inside the cage of C60, for example. This has opened up new ways of making materials with specific properties at the molecular level.

One way to make metallo-endohedral fullerenes is to vaporize graphite doped with the appropriate metal oxide or salt [6,7]. An alternative and more specific way is to repeatedly expose monolayers of C60 to an intense beam of alkali ions at an energy such that they penetrate the cage but do not destroy it [8]. Saunders et al. [9] have been able to produce Rg@C60 (Rg = He, Ne, Ar, Kr and Xe) by heating C60 to 650°C under a high pressure (3500 atm) of the rare gas for a few hours. These workers have proposed a ‘window’ mechanism for the formation of endohedral fullerenes. It is envisaged that one C–C bond is broken, the rare gas enters through the resulting window and the cage closes by itself. Jimenez-Vázquez et al. [10] have found evidence for trapping of tritium inside the C60 cage, when the latter was exposed to moderated tritium coming from a nuclear reaction. But, to the best of our knowledge, the interaction of protons with fullerenes has not been examined so far, either theoretically or experimentally.

Therefore, we have undertaken a study of proton–fullerene interactions and found that a proton can easily enter the fullerene cage through either the five- or six-membered ring and that it can oscillate through the cage and also ‘rattle’ inside the cage.

Recently we have pointed out [11] the possibility of a proton oscillating through the benzene ring and also through other aromatic rings such as naphthalene and anthracene. Therefore, it is not unreasonable to expect such a possibility to also exist in the case of fullerenes.

Traditionally, it is believed that protons form a σ-complex with aromatic hydrocarbons like benzene (Bz) but Mason et al. [12] have found mass spectral evidence for the formation of a Bz–H+ σ-complex. Ab initio calculations performed in our laboratory...
showed [11] that there is a potential minimum, corresponding to the \( \pi \)-complex formation, on either side of the benzene ring and that the proton can actually go through the ring without facing any barrier. More refined calculations [13] have reiterated our findings. Although Glukhovtsev et al. [14] have pointed out that the \( \pi \)-complex corresponds to a second-order saddle point, 2.06 eV higher in energy than the \( \sigma \)-complex, there is no reason why the \( \pi \)-complex cannot be formed and the proton cannot oscillate.

![Diagram of corannulene structure](image)

**Fig. 1.** (a) Frontal and (b) side views of the corannulene structure. \( C_s \) indicates the position of the \( C_s \) axis. The numbers 1–3 refer to the particular sites referred to in the text and in Fig. 2b. The \( \sigma \)-complex and \( \pi \)-complex formations are also indicated schematically. The distance of the proton approaching the hexagon/pentagon along a perpendicular direction is labelled \( Z \), with \( Z = 0 \) referring to the centre of the hexagon/pentagon. (c) The ground state interaction potential, \( V \), for \( H^+ - C_{20}H_{10} \) as a function of the approach coordinate, \( Z \), with the zero of energy corresponding to the asymptotically separated \( H^+ \) and \( C_{20}H_{10} \) in its equilibrium geometry. The solid line corresponds to motion through the centre of the hexagon, and the dashed line, motion through the centre of the pentagon. The break in the curves implies that the calculations have been carried out only for a limited range of \( Z \) values and an extrapolation is made to the asymptote.
through the ring, if the incoming proton has sufficient momentum in the direction orthogonal to the plane of the ring.

Before investigating the interaction of a proton with C$_{60}$, we studied the interaction potential between a proton and corannulene which has a bowl shape (see Fig. 1a and b) and for which the carbon framework constitutes the polar cap of buckminster fullerene and the results are summarized below.

2. Results and discussion

Keeping corannulene (C$_{20}$H$_{10}$) in its equilibrium geometry (see Fig. 1a) ($r_{C_1-C_2}$, along the pentagon) = 1.41 Å, $r_{C_3-C_4}$ (along the periphery) = 1.45 Å, $r_{C_5-C_6}$ = 1.36 Å, $r_{C_7-C_8}$ = 1.37 Å, $r_{C_9-H}$ = 1.07 Å) we varied the distance Z of H$^+$ from the centre of a hexagonal ring and for each value of Z, we compute the ground state interaction potential using the 6-31G* basis set and the GAUSSIAN 94 set of programs [15]. It is clear from the potential-energy curve shown in the form of a solid line in Fig. 1c that there are two minima: one corresponding to an exohedral position (convex side) and another to an endohedral position (concave side). It is also clear that the double-well potential is asymmetric, favoring the H$^+$ to be on the endohedral side of corannulene. It should be emphasized that the barrier separating the two minima is well below the zero of energy corresponding to the asymptotically separated proton and corannulene. This means that proton motion through the centre of any one of the hexagonal rings faces no barrier.

Proton interaction with the pentagonal ring (along the C$_5$ axis) (see Fig. 1b) is qualitatively similar to that with any of the hexagonal rings as can be seen from the results shown in the form of a dashed line in Fig. 1c. Although the barrier separating the two minima is larger in the case of the pentagon, it is still below the zero of energy, suggesting a free motion through the pentagon as well. In addition, it can be seen that the proton interaction with the pentagon is stronger than that with the hexagon, at the endohedral as well as the exohedral side of corannulene.

We have reported the potential energy curves for only a limited range of Z as one has to go beyond Hartree–Fock level calculations to get asymptotically correct results.

We have examined the tendency of the proton to bind with one of the carbon atoms (labelled 1) in Fig. 1a of the five-membered ring and so form a σ-complex by plotting the interaction potential as a function of the approach coordinate Z (distance along the line pointing towards the carbon atom and perpendicular to the plane of the ring) in the form of a dashed line, as shown in Fig. 2a. It is clear that the σ-complex at the 1-position is indeed more stable than the interaction along the C$_5$ axis and that the exohedral C–H bond would be stronger than the endohedral bond.

The results shown in Fig. 1c represent the ground state adiabatic potential energy curves and therefore imply that a slow moving proton brought towards the pentagon would tend to form an exohedral C–H σ-complex. However, a fast moving proton directed along the C$_5$ axis can easily pass through the centre of the pentagon and preferentially form an endohedral complex. The barrier to penetration is lowest along the C$_5$ axis and increases as the proton drifts towards one of the carbon atoms labelled 1 in Fig. 1a.

An examination of the interaction potential for the proton approaching any of the peripheral carbon atoms (labelled 2 in Fig. 1b), in the form of a dashed line marked σ in Fig. 2b reveals a minimum corresponding to an exohedral C–H σ-complex. The proton can also form a stable π-complex with any of the 1–2 or 3–3 C=C bonds as shown by the dashed lines labelled π$_{1-2}$ and π$_{3-3}$, respectively in Figs. 1b and 2b. However, this does not preclude the possibility of a proton passing through the center of the hexagon and forming an endohedral complex, as can be seen from the potential plotted in the form of a solid line in Fig. 2b.

Since a single point calculation using the 6-31G* basis set (GAUSSIAN 94) for C$_{60}$–H$^+$ interactions takes nearly two days on our workstation, we have generated potential energy curves for the fullerene–proton interaction using the 4-21G basis set. In any case, our studies on H$^+$–corannulene interaction have shown that calculations using the 4-21G basis set yield qualitatively the same result as do the ones using 6-31G*.

We keep fullerene in its equilibrium geometry ($r_{C-C}$ = 1.45 Å, $r_{C-H}$ = 1.36 Å) and vary the distance Z from the centre of a hexagonal ring as
Fig. 2. (a) The ground state interaction potential for a proton approaching one of the carbon atoms labelled 1 of the pentagon in C$_{20}$H$_{10}$ (Fig. 1a) is plotted in the form of a dashed line. The interaction potential along the C$_{4}$ axis is included as a solid line for comparison. (b) The dashed line marked $\sigma$ shows the interaction potential for the proton approaching carbon atoms labelled 2. The dashed lines marked $\pi_{1-2}$ and $\pi_{3-3}$ represent the interaction potential for proton approaching the 1–2 and 3–3 $\pi$-bonds, respectively. The solid line represents the interaction potential for the proton approaching through the centre of a hexagonal ring, for comparison.

Shown in Fig. 3a. For each value of Z we computed the ground state C$_{60}$ · · · H$^+$ interaction potential. It becomes clear from the results shown in the form of a solid line in Fig. 3b that there are two minima: one corresponding to Z = 1.3 Å and another to Z = −0.9 Å, implying the formation of an exohedral (outside the cage) and an endohedral (inside the cage) complex, respectively.

Although there is a barrier separating the exo- and endohedral complexes, the maximum of the barrier is still below the zero of energy corresponding to the proton asymptotically separated from C$_{60}$. This means that as a proton approaches C$_{60}$, it can easily go through any one of the hexagonal rings. As a matter of fact, it can easily come out on the other side of the cage as well. If it loses some of its energy to the cage, it can result in oscillations through the cage. It is quiet possible that a slow moving proton can form an exohedral $\sigma$-complex with any of the carbon atoms but we would like to emphasize that a fast moving proton can easily pass through the cage and form an endohedral complex.

Results for proton motion through the pentagonal ring are qualitatively similar, as can be seen from the
Fig. 3. (a) Fullerene structure, with a proton approaching along a direction perpendicular to the hexagon/pentagon, with \( Z = 0 \) representing the centre of the hexagon/pentagon. (b) The ground state interaction potential, \( V \), for \( \text{H}^+ - \text{C}_{60} \) as a function of the approach coordinate, \( Z \), with the zero of energy corresponding to the asymptotically separated \( \text{H}^+ \) and \( \text{C}_{60} \) in its equilibrium geometry. The solid line represents the interaction potential schematically as a function of the radial distance, \( r \), through the pentagonal ring, in Fig. 3c. Considering the anisotropy of the fullerene cage, one can anticipate that there might be significant hindered oscillations and rattling of the proton inside the cage.

Although one could argue in favor of more extensive calculations using larger basis sets for determining accurately the \( \text{C}_{60} - \text{H}^+ \) interaction, it is very unlikely that the qualitative findings of our work will change.

Interestingly, our ab initio calculations [16] for the interaction of \( \text{Li}^+ \) and \( \text{He} \) with \( \text{C}_{60} \) show that there is a large barrier to penetration (larger than the \( \text{C-C} \) bond dissociation energy) thus making the penetration route accessible only to proton. Within the local density approximation, Dunlap et al. [17] found \( \text{Li}^+ @ \text{C}_{60} \) to be stable. A similar conclusion was arrived at for \( \text{M} @ \text{C}_{60} \) (\( \text{M} = \text{Li}, \text{K} \) and \( \text{O} \)) by Li and Tománek [18].

When it comes to the \( \text{C}_{60} - \text{H}^+ \) interaction, energetic considerations (ionization potentials for \( \text{H} \) and \( \text{C} \) are 13.6 and 7.54 eV, respectively [22]) suggest that

\[
\text{H}^+ + \text{C}_{60} \rightarrow \text{H} + \text{C}_{60}^* + 6.06 \text{eV}.
\]

This would mean that a lot of energy could potentially be released as \( \text{H}^+ \) approaches \( \text{C}_{60}^* \) and the proton may no longer remain a bare proton. It
could easily be considered to be a hydrogen atom while in the vicinity of the positively charged cage and it can still come out as a proton at the other end. A similar mechanism has been invoked to explain the results of experiments involving high-energy (20–60 eV) projectiles of H⁺ colliding with HCl targets [23]. We only wish to point out that a proton (or a hydrogen atom) could easily be trapped inside or held outside the cage and that it can oscillate between the two minima. Furthermore, it should be pointed out that because of the differences in the interaction of H⁺ with the hexagonal and pentagonal rings and the in-between positions, the proton (or the hydrogen atom) would be expected not only to oscillate radially, but also ‘rattle’ around anisotropically (see above).

It would be interesting to isolate C₆₀H⁺ and other protonated fullerenes in an ion trap [24], for example, and study their spectroscopy.

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