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Quantum mechanical study of atomic hydrogen interaction with a fluorinated boron-substituted coronene radical

Hong Zhang[1,2,4], **Sean C Smith**[1], **Shinkoh Nanbu**[2] **and**
Hiroki Nakamura[3]

[1] Centre for Computational Molecular Science, AIBN Building (#75), The University of Queensland, Qld 4072, Brisbane, Australia
[2] Research Institute for Information Technology, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan
[3] Institute for Molecular Science, Myodaiji, Okazaki 444-8585, Japan

E-mail: h.zhang@uq.edu.au

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Abstract
In this work we study the transmission of atomic hydrogen across a fluorinated boron-substituted coronene radical ($C_{19}H_{12}BF_6$) as a model for partially fluorinated and boron-doped nanotubes or fullerenes. Complete active space self-consistent field (CASSCF) and multi-reference configuration interaction (MRCI) methods are employed to calculate the potential energy surfaces for both ground and excited electronic states, and one-dimensional R-matrix propagation is utilized to investigate the transmission/reflection dynamics of atomic hydrogen, through the central six-member ring of the fluorinated boron-substituted coronene radical. The quantum scattering includes resonance effects as well as non-adiabatic transitions between the ground and excited electronic states. Within the sudden approximation, both centre and off-centre approach trajectories have been investigated. Implications for atomic hydrogen encapsulation by carbon nanotube and fullerene are discussed.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Soon after the discovery of the carbon fullerenes, it was found that a variety of atoms can be incorporated into the hollow carbon cages to form endohedral complex structures, which leads to new nanoscale materials with novel physical and chemical properties [1, 2]. Endohedral fullerenes are not only of scientific interest but are also of technological importance in relation to potential applications in fields such as molecular electronics, magnetic resonance imaging, quantum computing and NMR analysis [3, 4]. Several kinds of atoms have been successfully encapsulated into carbon fullerenes, including noble gases such as He and Xe, and some metal atoms such as La and K. Fullerenes are also known to combine with hydrogen, however, the trapping of hydrogen in the C_{60} cage—although theoretically possible—has proven elusive to date experimentally [5, 6]. A non-bonded hydrogen atom in the C_{60} cage would exist in a paramagnetic state and hence could in principle be used as a magnetic detector on the molecular scale. In previous experimental work [6], $C_{60}H_n$ molecules were found, however the evidence suggested that the atoms were in fact bound to the outside of the cage. Through *ab initio* quantum calculations and molecular dynamics simulations, Smith *et al* [7] have shown it is in principle feasible to implant H atoms within the surface layer of fullerene molecules and suggested an experimental procedure for the production of H@C_{60}. Other groups have also performed MD or Monte Carlo simulations to describe the insertion process of atoms into C_{60} and C_{70} [8] as well as carrying out density-functional theory calculations to investigate the endohedral or exohedral complex [9].

Nanotubes are another closely-related carbon nanostructure that have been exploited to encapsulate atoms and molecules. For example, Caesium atoms have been

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[4] Author to whom any correspondence should be addressed.

successfully implanted into single walled nanotubes (SWNT) via plasma ion irradiation [10]. *Ab initio* band structures and density of states studies indicate the possibility of using Cs-doped SWNTs as doped junctions, with potential applications in nanoelectronics [10]. Khare *et al* [11] reported the functionalization of carbon nanotubes using hydrogen atoms, and more recently, Denecke and co-workers characterized the hydrogenation of SWNTs by means of spectroscopy techniques [12]. So far there is no clear experimental evidence that the non-bonded endohedral H@nanotube complex was formed. Rather, it was observed that the C–H bond was formed. For these processes, the underlying mechanism (in particular the hydrogen nuclear dynamics) needs to be explored and some attempts have been made in this direction. For instance, molecular dynamics simulations based upon empirical molecular potentials have been performed to study the injection and/or insertion processes of hydrogen atoms through the hexagonal rings on the sidewalls of the nanotubes [13]. For the (5, 5) CNT it was found that the lowest incident energy needed for the hydrogen atom to penetrate through the hexagonal ring on the tube wall is approximately 14.0 eV. Hydrogen atoms that enter into the SWNT would either be encapsulated to form an endohedral H@nanotube complex, or escape out of it. Quantum dynamics simulations [14] for hydrogen atom transmission across carbon nanotubes have also been reported recently, albeit utilizing a classical interaction potential. We note that other cages such as octasilsesquioxane have been employed to encapsulate atomic hydrogen and have been applied to NMR studies [15]. Additionally, in recent years hydrogen (atomic and molecular) interactions with SWNTs have been widely studied due to the important potential application of these carbon materials for hydrogen storage [11, 16–20].

The functionalization of nano-materials has attracted enormous attention lately [21, 22]. Substitutional doping is a favoured method to modify the chemical activity of carbon nano-materials since it maintains the robust framework and most of its intrinsic properties while at the same time introducing new features. In previous studies, the synthesis and the structures of boron-doped carbon nanotubes have been reported [23], and there is gathering evidence that the boron doping of CNTs can improve the chemisorption of hydrogen atoms [24, 25]. Ferro *et al* [24] investigated the effect of boron substitution on hydrogen adsorption in graphite, and reported that the adsorption energy of hydrogen atoms on graphite could be increased 4–5 times. In a related study, Zhu *et al* [25] pointed out that boron substitution destabilizes the graphene structure, increases the electron density distribution around the substitutional boron atoms, and lowers the electrostatic potential, thus improving the hydrogen adsorption energy on carbon. However, this improvement was only ca 10–20%. Fluorination is another way to change the chemical, electrical and transport properties of the carbon materials. Indeed, experiments on nanotube functionalization started with the fluorination of SWCNTs [26]. Theoretically, DFT and semi-empirical calculations have been carried out to investigate the effects of fluorination in both fullerenes and carbon nanotubes [27, 28], suggesting that functionalization by halogen atoms can modify the electronic properties effectively. Hence, one may postulate that a combination of fluorination and boron substitution might serve as an effective functionalization route to creating designed carbon nanostructures with tailored chemical properties.

An intriguing question with respect to hydrogen transmission/encapsulation through nanostructures relates to the possible role of electronically non-adiabatic phenomena [29–31]. There are numerous examples in nature wherein molecular function is controlled by non-adiabatic transitions. One typical example is photochromism, which involves a photo-induced reversible transformation between two different molecular structures and is usually characterized by a non-adiabatic transition around the conical intersection of the electronically ground and excited states correlated to the two structures [32–34]. Amongst practical applications of photochromism, molecular memory is one of the most important cases. Control of non-adiabatic transitions in such systems is undoubtedly important from the viewpoint of applications. Non-adiabaticity is thus a key phenomenon, not only in the manifestation of molecular function but also in designing strategies to control them.

Previously two of us have proposed an idea of molecular switching which invokes the intriguing phenomenon of complete reflection in periodic non-adiabatic tunnelling type potential systems [30, 31, 35–37]. It was found that under appropriate conditions, the transmission or reflection can be complete. This unique phenomenon is interpreted in terms of the Zhu–Nakamura semi-classical theory of non-adiabatic transitions [38, 39]. However, the phenomena were illustrated only with model potentials at that time. These ideas have subsequently been explored computationally on model five- and six-membered ring systems [40], e.g., hydrogen atom transmission through the cyclic cyclopentadienyl radical (C_5H_5) and pentaboron-substituted corannulenyl (PBC) radical ($C_{15}H_{10}B_5$). These molecules were studied as simplified models for H-encapsulation by fullerenes [41]. The Zhu–Nakamura theory indicates that the complete reflection and complete transmission can occur if (i) the avoided crossing where the two potential curves come close is the non-adiabatic tunnelling type and (ii) the system under consideration has periodicity. The non-adiabatic tunnelling type potential corresponds to the situation in which the signs of gradients of the two diabatic potential curves are opposite to each other.

With the objective of developing a better understanding of the penetration and/or encapsulation mechanism of hydrogen atoms in carbon nanostructures in the presence of fluorination and boron substitution effects, in this paper we study a model six-member ring system to investigate the hydrogen atom scattering process. We employ quantum mechanical theory for both electronic and nuclear motions, including the ground and first excited electronic states. Quantum dynamics calculations on *ab initio* CASSCF-MRCI surfaces are performed to study hydrogen scattering off or through the fluorinated boron-substituted coronene radical ($C_{19}H_{12}BF_6$) (see figure 1). Section 2 below outlines the *ab initio* MO CI methods used to compute the *ab initio* potential energy surfaces as well as our approach used to calculate the transmission

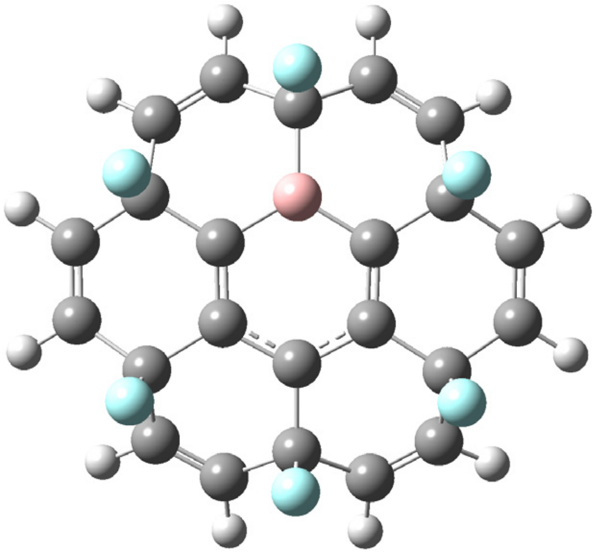

Figure 1. Optimized structure for model six-membered ring system (fluorinated boron-substituted Coronene radical $C_{19}H_{12}BF_6$) at DFT B3LYP/cc-pVDZ level. The fluorine atoms are in cyan (black), the carbon atoms are in (dark) grey, the hydrogen atoms are in white, and the boron atom is in pink (light grey).

probabilities. Section 3 discusses the features of potential energy surfaces and electronic structures of these systems, and presents the quantum dynamical results computed using the ab initio potential energy surfaces. In this section, we also explore the roles played by non-adiabatic transitions for this system and the potential applications of these quantum phenomena for atomic hydrogen trapping and molecular switching. Section 4 concludes.

2. Methodology

Ab initio MO CI calculations. To determine the molecular orbitals (MOs), complete active space self-consistent field (CASSCF) calculations have been carried out. After determining the MOs, we have performed multi-reference (MR) configuration interaction (CI) calculations to obtain low-lying potential energy curves. In this method, multi-reference (MR) single- and double-excitation (SD) CI is employed, in which the configuration state functions (CSFs) were generated by single and double excitations with respect to the reference configuration used in the CASSCF calculations. In the calculations, the quasi-diabatization proposed by Simah, Hartke and Werner has been used to obtain diabatic potential energy surfaces between the ground and excited states [42]. Since the *ab initio* MRCI calculations for a model of this size (figure 1) are quite challenging, we have used a moderate basis set in this paper, i.e., Dunning's cc-pVDZ (correlation consistent, polarized valence, double zeta) basis set [43]. We have tested for the influence of the smaller basis set and the restriction of the active space for several points in the centre approach case, and the results indicate that the general trends for the potential energies are similar, although there are differences in the absolute values of energies.

The geometry optimization of the model system has been carried out for the electronic ground state using the cc-pVDZ basis set at the hybrid density-functional theory (DFT) level of Becke and Lee, Yang, and Parr (B3LYP, which means a hybrid of BLYP with HF exchange) [44–46]. The geometry of the six-member ring system is then fixed during the collision with the H-atom by invoking the sudden approximation. As for CASSCF active space, seven MOs from 103a to 109a should be included in the active space, since they are important to describe the low-lying electronic states and should be occupied by seven electrons in CASSCF (7 MOs/7 electrons). The MOLPRO 2002.6 program package [47]. was used to obtain the potential energy curves for the electronic ground and excited states and to perform the quasi-diabatization of the adiabatic surfaces, while the geometry optimization of the electronic ground state has been done by the GAUSSIAN 03 program package [48].

Quantum dynamics. In line with the rationale of the sudden approximation, namely that the hydrogen atom motion with a moderate collision energy is likely to be fast compared with relaxation of the carbon framework, a one-dimensional model is employed for the simulation of the hydrogen atom transmission. We consider two types of approach path for the atomic H perpendicular to the plane of the carbon framework: firstly H-atom transmission through the centre of the aromatic ring and secondly off-centre H-atom transmission through the ring. In the one-dimensional model, the R-matrix propagation technique [49]. was used to compute the transmission probability with use of the diabatic potential curves provided by the spline interpolation of the original potential energy data. In our calculations, the interaction region was taken from $X = -5.0$ to 5.0 Å (0.0 Å corresponding to the centre of the ring) and the approaching trajectory for the H-atom is perpendicular to the plane of the central ring. The half of the interaction region was subdivided into 100 000 sectors, and the matching condition was applied at the centre of the interaction region. In some cases, the maximum number of the sectors reaches about 250 000 in order to obtain converged results. Note that the hydrogen atom is assumed to attack the model system from outside (e.g., at $X = 5.0$ Å), and then passes through the aromatic six-membered ring.

3. Results and discussion

3.1. PESs

In figure 1 the optimized geometry for the model six-member ring $C_{19}H_{12}BF_6$ system at DFT B3LYP/cc-pVDZ level is shown. In this figure, one carbon atom in the middle hexagonal ring has been replaced with a boron atom, and six fluorine atoms are covalently bonded to the carbon atoms in the surrounding rings, representing partial fluorination of this model nanostructure. The nanostructure is then kept rigid when computing the *ab initio* potential energy curves at the MRCI level for atomic hydrogen interacting with the nanostructure as it passes through the plane of the middle ring. By way of example, in figure 2 we plot some selected molecular orbitals (MOs) for hydrogen interactions with the

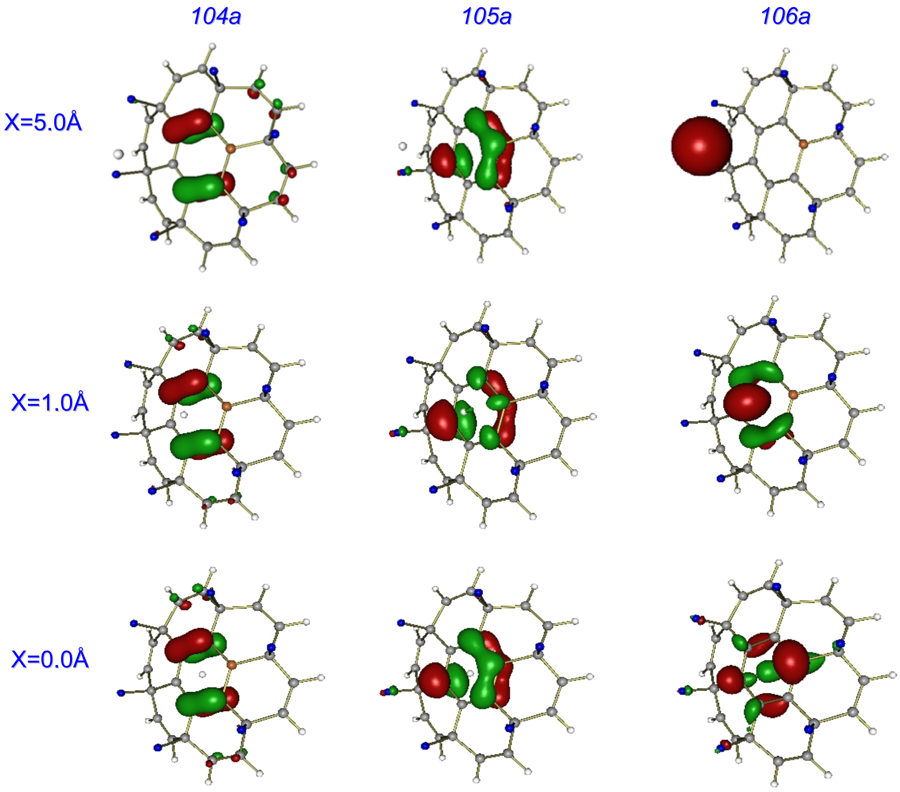

Figure 2. Examples of molecular orbitals (MOs) 104a, 105a and 106a for H-atom interaction with six-membered ring system along the centre approach distance $X = 5.0$, 1.0 and 0.0 Å, calculated with CASSCF.

$C_{19}H_{12}BF_6$ system for the case of on-centre approach. The distances between hydrogen atom and the centre of the middle ring are taken as 5.0 Å, 1.0 Å and 0.0 Å, respectively, which are represent of the qualitative change in the molecular orbitals as the H-atom approaches. The electronic structure around the dissociation limit is characterized by the 104a, 105a and 106a MOs, and in particular the 104a and 105a MOs feature in the π complex conjugate system. Since these two MOs are occupied by only three electrons, the system requires one more electron to become more stable according to the Hückel rule. This leads to a stable anion in the present case. The electronic structures of both neutral and ionic states are strongly mixed when the hydrogen atom approaches the centre of the six-membered ring, especially in the regions near the two avoided crossings around $X = -1.7$ and 1.7 Å, because the neutral state crosses the ionic state at these two points. The neutral state has a repulsive character between the p-orbital and the 1s orbital of the hydrogen atom (see the 106a MO at $X = 1.0$ Å in figure 2). However, once the hydrogen atom comes closer to the ring, the electron of the hydrogen atom transfers to the p-orbital of the model system and the system is characterized as the ionic state, taking the more stable structure of the complete π complex conjugate system (see the 104a and 105a MOs at $X = 1.0$ Å in figure 2). This is similar to the harpoon mechanism. If the hydrogen atom comes much closer to the ring, another potential barrier appears due to the steric hindrance between the σ orbitals and the proton.

We have calculated the potential energy profiles for the case of on-centre approach (atomic hydrogen scattering toward the centre of the middle aromatic ring denoted as $\Delta = 0.0$ Å) and also for the case of off-centre approach. In the latter case, the atomic hydrogen's approach trajectory is still perpendicular to the plane of the middle aromatic ring, but scatters toward a point displaced $\Delta = 0.2$ Å along a line from the centre to the boron atom. Previous studies identified carbon-top sites as preferred sites for atomic hydrogen adsorption [16]. However, for hydrogen atom transmission, the centre approach would seem intuitively to be the most efficient and important case. The computed potential energy curves are shown in figure 3 for the on-centre approach and in figure 5 for the off-centre approach. Note that C_1 symmetry is used in the *ab initio* calculations. As mentioned above, we have performed the quasi-diabatization of the adiabatic surfaces to obtain the diabatic PESs and the off-diagonal coupling elements. The transformations of the corresponding adiabatic PESs to diabatic PESs are implemented using the Molpro package. The adiabatic and diabatic potential energy curves for on-centre approach are shown in figures 3(a) and (b). The excitation energy of the isolated $C_{19}H_{12}BF_6$ radical is found to be 2.46 eV. There are two minima (labelled as β in the ground state PES in figure 3(a)) on either side of the model ring system. However, these minima are metastable, with energies higher than the asymptotic zero. There are two relatively small potential barriers closer to the ring (labelled as α on the ground state PES in figure 3(a)), which correspond to avoided crossings located around $X = 1.7$ and -1.7 Å, where the

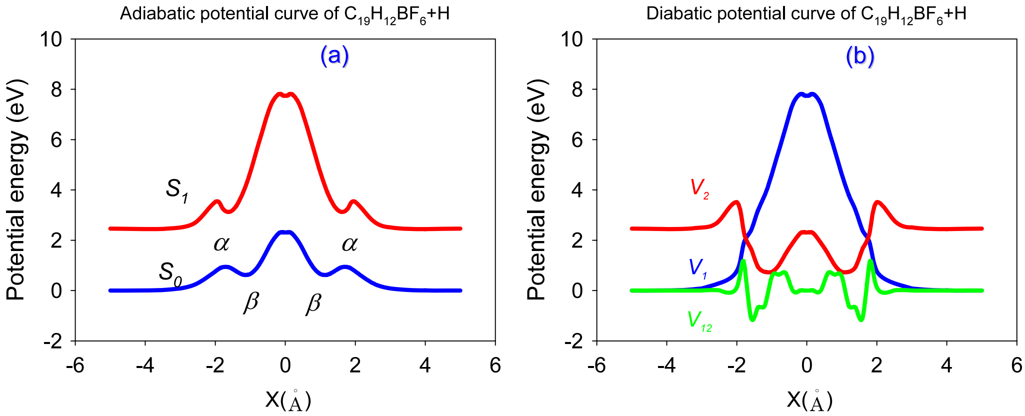

Figure 3. Adiabatic and diabatic potential energy surfaces (PESs) for hydrogen transmission through the six-membered ring of fluorinated boron-substituted Coronene radical. (a) Adiabatic potential curves for the centre approach; (b) diabatic potential curves for the centre approach, in which the green coloured line V_{12} represents the coupling elements. Diabatic potential is obtained by the transformation of the corresponding adiabatic PESs.

non-adiabatic transition mainly occurs. This can be clearly seen in figure 3(b), in which the two diabatic curves (V_1 and V_2) cross each other at $X = 1.7$ and -1.7 Å. Figures 5(a) and (b) show the adiabatic and diabatic potential energy curves for the off-centre approach. The essential features in figures 5 and 3 are similar, namely, for both the ground and the excited electronic states there exist two minima and three potential energy barriers, the middle barrier corresponding to passage of hydrogen across the plane of middle ring and the two outside barriers corresponding to chemisorption of hydrogen approaching from either side. However, the minima on the excited state S_1 are less pronounced for the off-centre scattering case, while the minima on the ground state S_0 are lower in energy (0.0973 eV) and the exterior barriers smaller for the off-centre scattering case compared with the minimum of 0.66 eV for the on-centre approach. This means in effect that the ground state potential energy curve is becoming more attractive as H-atom approaches the boron atom. Moreover, the off-diagonal element (V_{12}) is relatively larger around the two crossing points for off-centre scattering. This is ascribed to the higher symmetry for the on-centre approach and should impact on the transmission probability of the hydrogen atom across the ring (see below), e.g., it should result in the more efficient transmission of the hydrogen atom as shown in the following figures. In addition, the relatively high steric potential barrier close to the ring plane at $X = 0.0$ Å (corresponding to the hydrogen atom crossing of the middle ring) also has effects on the transmission probabilities, as the higher barrier will reduce the transmission probability. We note that the sudden approximation is employed for the relative motions of the radical and H-atom as described above, and the radical moiety is fixed to the optimized geometry in the ground state. The approximation should be reasonable in this case, since the incident energy of the hydrogen atom is relatively high. Finally, we need to mention that it is based upon these diabatic PESs that we study the quantum dynamics for the hydrogen atom transmission through the ring system using our local *R*-matrix program.

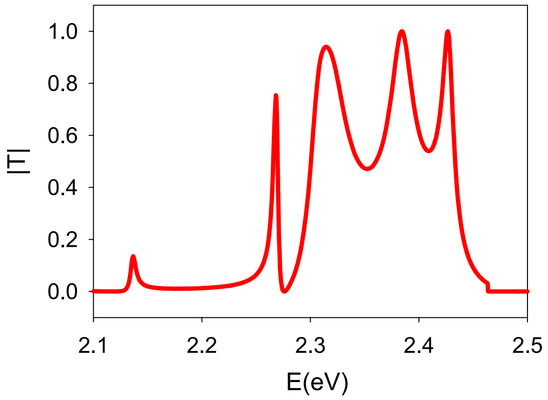

Figure 4. Atomic hydrogen transmission probabilities as a function of total energy (eV) for the centre approaching case through the six-membered ring of fluorinated boron-substituted Coronene radical.

3.2. Hydrogen transmission

Figure 4 shows the transmission probabilities for on-centre approach. In this case the significant transmission probability appears at roughly $E > 2.25$ eV, and there are narrow resonance structures at low energies, which are due to the attractive features in the potential energy surfaces as well as the non-adiabatic transitions between the neutral ground state and the ionic excited state. These resonance structures would not appear for purely repulsive potentials, and the resonance structures indicate that the hydrogen atoms will be trapped in the shallow-well regions to form H@$C_{19}H_{12}BF_6$ complexes for periods of time due to the doped boron atom and fluorination effects. We have analysed one narrow resonance profile around $E = 2.268$ eV in hydrogen transmission probabilities as shown in figure 4. Assuming that the profile has a Lorentzian shape, the resonance lifetime has been estimated to be around 0.01 ps. This indicates that at this energy the resonance complex can exist for a significant period of time, after which the complex dissociates and the hydrogen atom will transmit through the middle ring at a probability of about 75%. As energy increases,

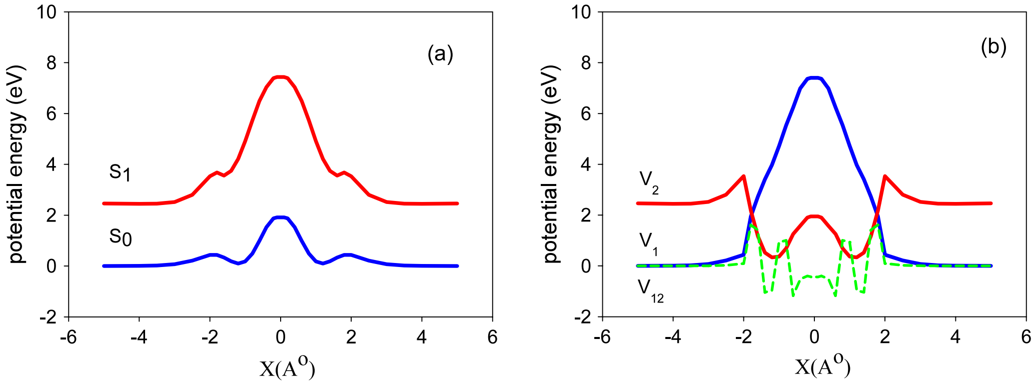

Figure 5. The same as in figure 3, except for atomic hydrogen off-centre approaching the middle ring with small off-centre distance $\Delta = 0.2$ Å.

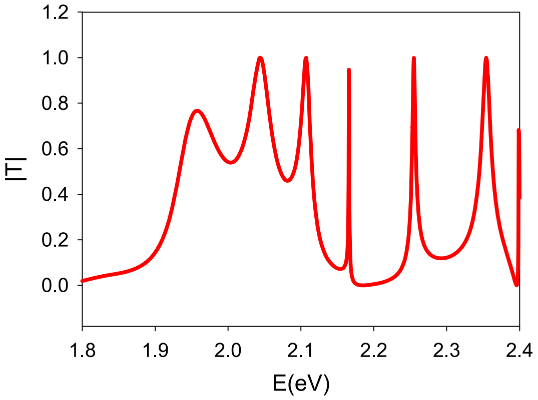

Figure 6. The same as in figure 4, except for atomic hydrogen off-centre approaching the middle ring with $\Delta = 0.2$ Å.

the resonance structures become broader, indicating that the resonance lifetimes are becoming shorter. Similarly, for the off-centre approach the transmission probabilities are shown in figure 6. Significant transmission probabilities for this case appear earlier at roughly $E > 1.9$ eV, and there are more resonance structures on the probability profile. For the narrowest resonance around $E = 2.166$ eV in hydrogen transmission probabilities as shown in figure 6, the resonance lifetime has been estimated to be around 0.1 ps, again assuming that the profile has a Lorentzian shape. Therefore at this energy the resonance complex can exist for even longer time, after which the complex dissociates and the hydrogen atom will transmit through the middle ring nearly completely (the probability is 95%).

Interestingly, the features of the off-centre approach are subtly but noticeably different from the on-centre approach. In the off-centre approach, the off-diagonal coupling elements are relatively large as shown in figure 5(b), so the total transmission probabilities are higher. In addition, the central potential barrier in the off-centre case is a little lower. As a whole, the transmission is more probable for the off-centre approach. In summary, the transmission probability is largely dependent on two physical factors: the non-adiabatic coupling elements and the steric potential barrier at the ring centre.

Another notable feature in the transmission probabilities is that there are peaks corresponding to nearly-complete transmission ($|T| \approx 1$) and also dips corresponding to nearly-complete reflection ($|T| \approx 0$). Such complete reflection and transmission are interesting phenomena with applications in molecular switching. From figures 4 and 6 we can see that the complete transmission is found at several energies (resonance energies), which is predicted by the Zhu–Nakamura theory [38, 39]. As mentioned in the introduction, the complete reflection and complete transmission require two conditions (i) the avoided crossing is the non-adiabatic tunnelling type and (ii) the system considered has a periodicity. If electron transfer between ionic and neutral states occurs in a system, then the first requirement can be met, because the electronic structure should be mixed between the ground and the electronically excited state. For the present system, the ground and excited states are neutral and ionic states, respectively, at large separations of two subsystems, and the electron transfer occurs during their approach. After the electron transfer (i.e., as the two subsystems approach to small distances), the ground state turns to have the ionic character and the excited state becomes the neutral one. Consequently, the non-adiabatic transition between the two states would be a non-adiabatic tunnelling type. Our model system satisfies this requirement, because the radical needs one more electron to become stable π-conjugated system. The strong electro-negativity is realized due to the unstable π-conjugated radical, while the hydrogen atom can be an electron donor easily. The second requirement is also satisfied, since the six-membered ring system has potential energy curves with periodicity (unit $= 2$) for the complete transmission to occur. Here we need to mention that even though theoretically possible, it is still not very straight forward experimentally to tune the incident energy accurately to match the resonance energy in order to get a high transmission probability (e.g, making the hydrogen atom completely transmit through the ring).

The system we have explored here may act as a model for atomic hydrogen encapsulation by fullerenes and carbon nanotubes (or their boron-substituted and fluorinated counterparts). Several groups have investigated properties of the H@fullerene or H@nanotube complex in a different context [50, 51]. As is well known, many experimental studies have been made to search for a possibility of encapsulation of atoms by hollow fullerenes since the discovery of C_{60} by Kroto *et al* [41]. Up to now, several kinds of endohedral fullerenes have been synthesized [3, 52]. Endohedral fullerenes incorporating noble gases or reactive species have been prepared under extreme conditions of high temperatures and high pressures, or through ion implantation, but the yields of these materials are still very low, because such extreme conditions cause serious damage to the hollow framework and most of the fullerene cage is collapsed and cannot accommodate any particles. The extreme conditions have been applied so far to overcome the very high transmission barrier due to stable π-conjugated carbon surfaces (e.g., the barrier height is 14 eV for CNT (5, 5) [13]). Our newly proposed mechanism requires milder conditions with collision energy of about 2 eV. The boron substitution or fluorination of fullerenes or CNT will change the electronic character and as such pave a new route for the encapsulation of a hydrogen atom. Finally, we need to point out that other theoretical work such as impinging neglects the electronically excited states and non-adiabatic transition dynamics, and recently some attempts have been made to address the challenging issue by applying multi-scale quantum-classical molecular dynamics and quantum chemistry approaches [53].

Before concluding, we provide some discussion of how the B substitution and fluorination affect the H transmission through the six-membered ring. We have performed additional exploratory calculations with several types of model systems consisting of carbon, boron and fluorine with the idea being proposed in our previous paper [40]. The all-carbon surface is quite stable and the transmission barrier for atomic H through the five- or six-membered ring is quite high. As one example, we calculated the typical potential energy profile for the six-membered ring + H for coronene ($C_{24}H_{12}$) as a model of carbon surface. The barrier height for the penetration is about 10 eV, and the potential curve is strongly repulsive, although we would expect there is a shallow minimum due to van der Waals force. Thus a high impact energy would be needed in order to transmit the hydrogen atom through such a ring. The result with the five-membered ring is similar to six-membered ring. This has indeed been part of the motivation for proposing the boron substitution and fluorination: in order to activate one part of such a stable carbon surface for hydrogen atom transmission. For the case of additional boron-substitutions surrounding middle six-membered ring, we obtain similar shapes of the MOs to that of the present fluorinated boron-substituted coronene radical, with the barrier height for hydrogen atom transmission through the middle six-membered ring being reduced substantially in comparison with pure carbon. The features of the potential energy curves are very similar, e.g., the two alphas corresponding to the avoided curve crossing points and the two betas corresponding to the minimum positions appear for both cases. We have also performed the calculations for the fluorination case, and these results will be published in a forthcoming paper.

4. Conclusions

We have employed *ab initio* MRCI and quantum dynamics methods to investigate hydrogen transmission through a model ring system ($C_{19}H_{12}BF_6$), which represent a finite periodic potential system with non-adiabatic transition between the ground and excited electronic state. For both on-centre approach and slightly off-centre approach to the middle six-membered ring, transmission and/or reflection of a hydrogen atom are observed since in these cases no stable bond is formed although there exist resonance complexes between H and the ring system (endohedral $H@C_{19}H_{12}BF_6$ complex). These resonances are short-lived from the view point of practical applications. *Complete* reflection from or transmission through the ring system for specific energies is another interesting phenomenon which might find applications in molecular switching. Interesting and ambitious extensions of this work, which may lead to a more complete picture of the likely experimental situation, would involve one-dimensional calculations covering a range of different possible off-centre approaches as well as approach trajectories that are not perpendicular—but rather slanted—with respect to the target ring; or indeed full three-dimensional wavepacket calculations for H-atom scattering across the nanostructured carbon system. The real result for the transmission probabilities can be obtained through such three-dimensional calculation, or through the integration over the off-centre position from one-dimensional calculations.

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