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The interaction of hydrogen with C₆₀ fullerenes

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Abstract. Experiments and molecular dynamics (MD) simulations of low-energy (10–30 eV) H interactions with the C₆₀ molecule have been carried out in order to investigate the possible chemical combinations at these energies. It is found that the preferred minimum-energy state is for the H atom to be attached to the outside of the molecule but that some trapping of the H atom within the cage should be possible if the C₆₀ molecule has only a small initial energy. As the excitation of the molecule increases, trapping becomes less likely. The trajectories calculated by MD show a number of different interactions: (i) reflection of the H atom, (ii) transmission of the H atom through the structure, (iii) implantation within the molecule, (iv) attachment of the H atom to the outside of the structure and (v) initial implantation and attachment of the H atom to the inside of the structure followed by bond-breaking of the C atoms and final attachment of the H atom externally. The experimental results of the interaction process with ‘energetic’ C₆₀ molecules so far have shown no evidence of the existence of a trapped H atom at the centre of the C₆₀ cage, but indicate strong evidence for externally bonded H atoms.

1. Introduction

Although the ability of carbon atoms to form large stable clusters has been known for some time, interest in the C₆₀ molecule was stimulated by experiments which showed that 60-atom carbon clusters were heavily dominant in the mass spectra of laser-vapourized graphite [1]. Since then techniques have been developed for synthesizing the C₆₀ molecule and other fullerenes [2–4] and collision experiments of charged fullerene molecules with silicon and graphite surfaces [5] have revealed little fragmentation at impact energies up to a few hundred eV. This was subsequently verified by molecular dynamics (MD) simulations [6–8]. Thus experiments and simulation with different semi-empirical potential functions have indicated the stability of the C₆₀ molecule in collision processes. The stability and size of the C₆₀ molecule suggests that it might be possible to produce new materials by implantation of atoms into the caged C₆₀ structure. Indeed, within a short time after the discovery of the C₆₀ molecule, evidence was obtained that a single lanthanum atom could be trapped inside the cage [9]. The same group who reported this result has also shown that other species such as potassium could also be implanted [10]. The evidence for the existence of the metal atom trapped within the cage was a combination of FT-ICR mass spectra and experiments which showed that externally attached metal atoms behave in a radically different way, i.e. they react easily and are readily knocked off the molecule. The reported success with metal atoms suggests that it might be possible to implant other species within the C₆₀ structure. We report here on the results of some experiments and associated computer simulations concerned with the attempt to implant hydrogen into the C₆₀ cage. Endohedral complexes

would provide a unique possibility to tailor specific properties of C_{60} systems on a molecular level. Modifications in the electronic and phonon spectrum of these materials are expected. Moreover, a non-bonded hydrogen atom inside a C_{60} cage would be a paramagnetic state of the doped fullerene and could be used as a magnetic detector on a molecular scale. Another essential reason for this development is the vision of a new type of chemistry based on stabilized carbon cages. Endohedral $H@C_{60}$ and exohedral $C_{60}H_n$ molecules (where n is an integer equal to or less than 60) could have potential applications for hydrogen storage and they have also been suggested as one of the infrared emission sources in interstellar space [11–13].

The MD simulations are carried out using empirical many-body potentials. Although the empirical potential models the static-energy configurations of small C–H clusters and bulk crystalline carbon well, it is clearly less preferable to use such potentials than to calculate the interactions using *ab initio* methods. However, this would be a prohibitively expensive process in terms of computing time for the number of cases considered here. The approximation using empirical potentials should at least enable us to obtain a qualitative if not quantitative view of the dynamic interaction process.

The optimum energy for implantation is calculated but static potential calculations show that it is more favourable for the hydrogen atom to attach on the outside, rather than the inside, of the cage. The simulations show evidence that it should be possible to implant H into 'cold' C_{60} molecules, but that the probability of this occurring reduces with increased excitation of the molecule. This seems to be confirmed by experiments that show no evidence of trapping of hydrogen inside (excited) molecules.

2. Experimental results

Raw fullerenes were produced by evaporating graphite rods in a 150–200 Torr He atmosphere using an electric arc welder. The soot produced by vapourization of the graphite rods was collected from the chamber. From this soot the fullerenes were extracted with about a 10% yield by dissolving the soot in toluene and filtering it to yield a red solution. The toluene extract from the carbon soot contains about 75–85% C_{60} and 10–15% C_{70} , with the remainder being the higher fullerenes and impurities. To obtain C_{60} free from the higher molecular weight fullerenes, a flash chromatographic purification method was used. The residual was then redissolved in toluene. After the toluene was evaporated, the blackish powder of C_{60} was outgassed in a quartz tube at 250°C and 10^{-3} – 10^{-4} Torr. In order to obtain a high degree of purity of C_{60} , the powder was sublimated in a quartz tube with a pressure of 10^{-4} Torr at 540°C. The vapour condensed on a water-cooled glass substrate with a temperature of 80°C. The C_{60} powder produced in this way was analysed to ensure that a pure substance was obtained, and then used for the hydrogen interaction experiments.

One of the promising avenues in C_{60} research is the synthesis of new compounds from the addition of atoms or radicals to the molecule either inside or externally on the cage. The fullerene synthesis is very sensitive to the presence of hydrogen. Formation of C_{60} stops after adding only a few per cent of hydrogen to the helium quenching gas. A previous attempt to hydrogenate C_{60} in the gas phase was unsuccessful because C_{60} is unreactive to molecular hydrogen. All the fullerene ions could not be hydrogenated in the H_2 atmosphere as shown in the FT-ICR experiments [10]. However, both the mono-cations and the di-cations of C_{60} and C_{70} can be hydrogenated in the gas phase by reactions with atomic hydrogen yielding $C_{60}H_n$ molecules indicated in the quadrupole mass spectrometer [14]. The dihydride derivative $C_{60}H_2$ is formed by the reaction of C_{60} with BH_3 tetrahydrofuran

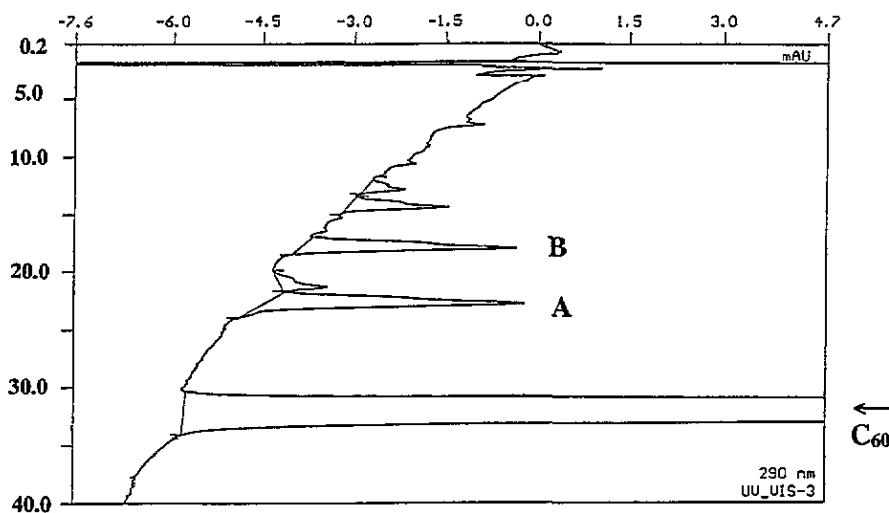


Figure 1. ^1H NMR spectrum of hydrogenated C_{60} molecules.

in toluene followed by hydrolysis [15]. $C_{60}H_{36}$ is a product of Birch reduction [16] and can be generated with transfer hydrogenation as well as [17, 18] $C_{60}H_{18}$.

We tried to produce endohedral hydrogenated fullerenes by hydrogenation of C_{60} in a hydrogen plasma, thus having atomic hydrogen for the reaction in the plasma atmosphere and energetically excited states of the reacting species. The experiments were carried out by placing the C_{60} powder in a quartz tube with a high vacuum (i.e. less than 10^{-5} Torr). The quartz tube was heated to 250°C in a furnace and then filled with hydrogen gas. Although molecular hydrogen gas is used, in the plasma atomic hydrogen is produced. The pressure increases to $5\text{--}10 \times 10^{-4}$ Torr. Because of this gas pressure, a plasma can be ignited between the concave cathode and a 'ring' anode at about 20 cm distance. The whole plasma system is placed in a furnace and slowly heated to around $550\text{--}600^\circ\text{C}$ and held at this temperature until the C_{60} powder is completely sublimated. During the sublimation process, the H plasma glows with a violet colour.

The plasma properties are estimated by Langmuir probe measurements. The electrons of the low-pressure plasma have an energy of 10–25 eV. The estimated energy range depends on the potential difference between the anode and the cathode. These electrons are capable of dissociating and ionizing neutral species at high rates at quite a low gas temperature and therefore of causing a high-temperature chemistry in a cold non-equilibrium glow discharge plasma. The gas phase reactions of these chemically active C_{60} and hydrogen species are used for endohedral and exohedral hydrogenation of the fullerenes. After interaction with the hydrogen plasma, the sublimated C_{60} condenses on a water-cooled copper finger at the end of the quartz tube outside the furnace. The H- C_{60} powder was collected and analysed by various methods.

The C_{60} powder was first analysed using x-ray diffraction and Raman spectroscopy in order to ensure that C_{60} was indeed being produced. The spectra from these experiments for the H- C_{60} powder were identical to pure C_{60} . Further analyses were carried out using electron spin resonance (ESR) and nuclear magnetic resonance (NMR). If a single H atom were to be trapped at the centre of the C_{60} molecule then ESR should indicate both a fullerene line in the spectrum and two additional lines at ± 50 mT, symmetric around the fullerene signal. No evidence of these signals was obtained. Proton-NMR (^1H NMR) at a 300 MHz

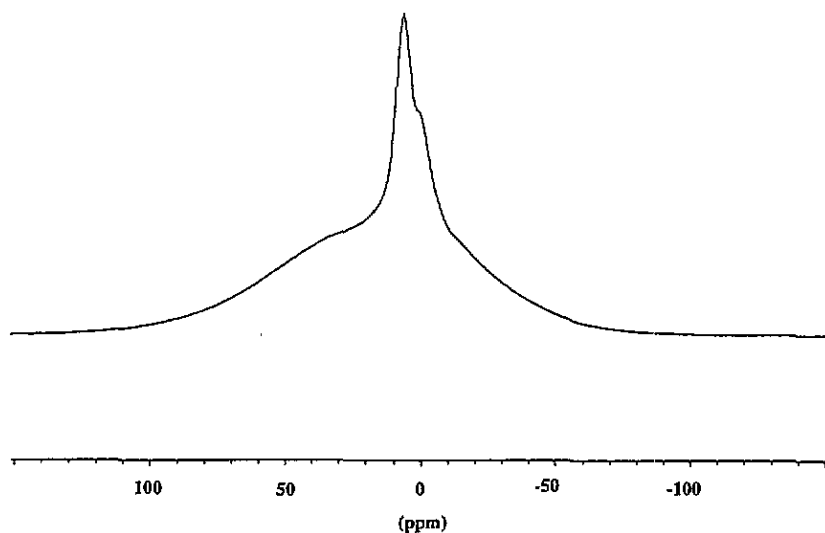


Figure 2. HPLC profiles of hydrogenated C_{60} fullerenes dissolved in toluene, absorbance at 290 nm against retention time.

frequency shows a broad signal from the C_{60} molecule after interaction with the H. The signal shown in figure 1 is a narrow peak with a shoulder. The maximum of the peak is located at about 6 ppm. Comparison with earlier results indicates that the peak is located at the position corresponding to $C_{60}H_2$. The shoulder on the NMR peak has not been observed before, and seems to be evidence of other $C_{60}-H$ bonds. However, it is not clear precisely what kind of bond is indicated by this shoulder.

Finally, experiments were undertaken with high-performance liquid chromatography (HPLC). Both the unhydrogenated C_{60} and the $H-C_{60}$ powder were investigated. In both cases the powder was dissolved in toluene. Figure 2 shows that there are two additional peaks in the spectra of the $H-C_{60}$ powder compared to the pure C_{60} . The two peaks are labelled A and B in figure 2. Measurements on a mixture of $C_{60}H_2$, $C_{60}H_4$ and $C_{60}H_6$ indicates that peak A appears at a time corresponding to $C_{60}H_2$. The comparisons with HPLC measurements on a sample of $C_{60}H_n$ prepared chemically, indicates that the peak B is indicative of $C_{60}H_4$. Mass spectroscopy measurements on the sample show strong signals at masses 722 and 724. The measurements also show the presence of $C_{60}H_{18}$ and $C_{60}H_{36}$. These cannot be seen in the HPLC diagrams. One must be careful in interpreting these measurements because of the isotope carbon 13. However, the 722 and 724 signals are enhanced by between 20% and 25% compared to what would be expected by the natural abundance of carbon 13. In order to determine bonding arrangements liquid chromatography mass spectroscopy measurements are in preparation, and these measurements will provide further information for the correct interpretation of these peaks.

3. Molecular dynamics simulations

Simulations involving C_{60} interactions have all been carried out using semi-empirical many-body potentials. We have computer codes available for three such potentials [19,20] but only the Brenner potential deals with C-H interactions. The Brenner potential reproduces the optimal structures of small C and C-H structures and gives a better description of bond breaking and forming than the Tersoff potential. Table 1 gives a comparison of

these potentials for the minimum-energy C₆₀ structure. All the potentials give a stable C₆₀ structure, and it can be seen that the first parametrization of the Brenner potential (Brenner 1) gives a reasonable agreement with the reported experimental measurements for the size and structure of the C₆₀ cage. The first parametrization of this potential is used throughout this paper. Although Brenner's hydrocarbon potential appears to be the best empirical potential available, it does have some drawbacks, notably the C–C interactions cut off after 2.0 Å, the C–H interactions cut off after 1.8 Å and H–H interactions cut off after 1.7 Å. Non-bonded interactions are therefore ignored.

Table 1. Calculated radii, bond lengths and potential energy of the C₆₀ structure for different empirical potentials. The radius refers to the average distance of the C atoms from their centre of mass.

Potential	Radius (Å)	Bond 1 (Å)	Bond 2 (Å)	Potential/atom (eV)
Brenner 1	3.564	1.419	1.449	7.04
Brenner 2	3.634	1.451	1.476	6.99
Tersoff	3.683	1.460	1.501	6.75
Experiment [21, 23]	3.55	1.401	1.45	6.91–6.94 ^a
<i>Ab initio</i> [22, 23]	—	1.36–1.41	1.43–1.47	6.74–6.96 ^a

^a Deduced from the heats of formation given in [23].

Some static minimum-energy structures of H–C₆₀ and H₂–C₆₀ were also calculated using the Brenner potential and a number of these configurations are shown in figure 3. For the H–C₆₀ cases shown in figure 3(a), the H atom was placed initially in an approximate bonding position and the local minimum-energy configuration was found by small random changes to the atomic configuration (i.e. not by MD). In the three cases where the H atom bonded within the molecule the potential energy of the system was raised by between 0.3 and 1 eV compared to the raw C₆₀ structure. These results are summarized in table 2.

Table 2. Local potential-energy minima calculated using the Brenner potential. The nomenclature is that given in the caption to figure 3. A bond between two atoms is defined to be broken when the distance is outside the range of the interaction potential. The base potential is taken as that of the isolated C₆₀ molecule (–422.6 eV). An isolated H atom is taken to have zero potential energy.

C ₆₀ H	Potential (eV)	C ₆₀ H ₂	Potential (eV)
NE	–1.6	NEE	–3.3
NI	0.3	NHPEE	–4.0
HE	–0.3	NHHEE	–4.0
HI	1.0	HPEE	–5.9
PE	–1.0	NHPEI	–2.4
PI	0.6	HPEI	–4.2

In the case of a single H atom interaction with C₆₀, the minimum-energy state is for the H atom to be bound externally to the molecule and this was often the final state predicted by the MD simulations described below when the H atom became trapped by the molecule. From the table it can be seen that for the H atom bound outside the structure, the energy is lowered by between 0.3 and 1.6 eV implying that the preferred bonding position is external to the molecule. Thus it appears that any H atom trapped inside the C₆₀ cage would prefer to be located away from an internal bonding location. The atom might be free within the structure or located at the centre of the cage. The potential value of a H atom located at the

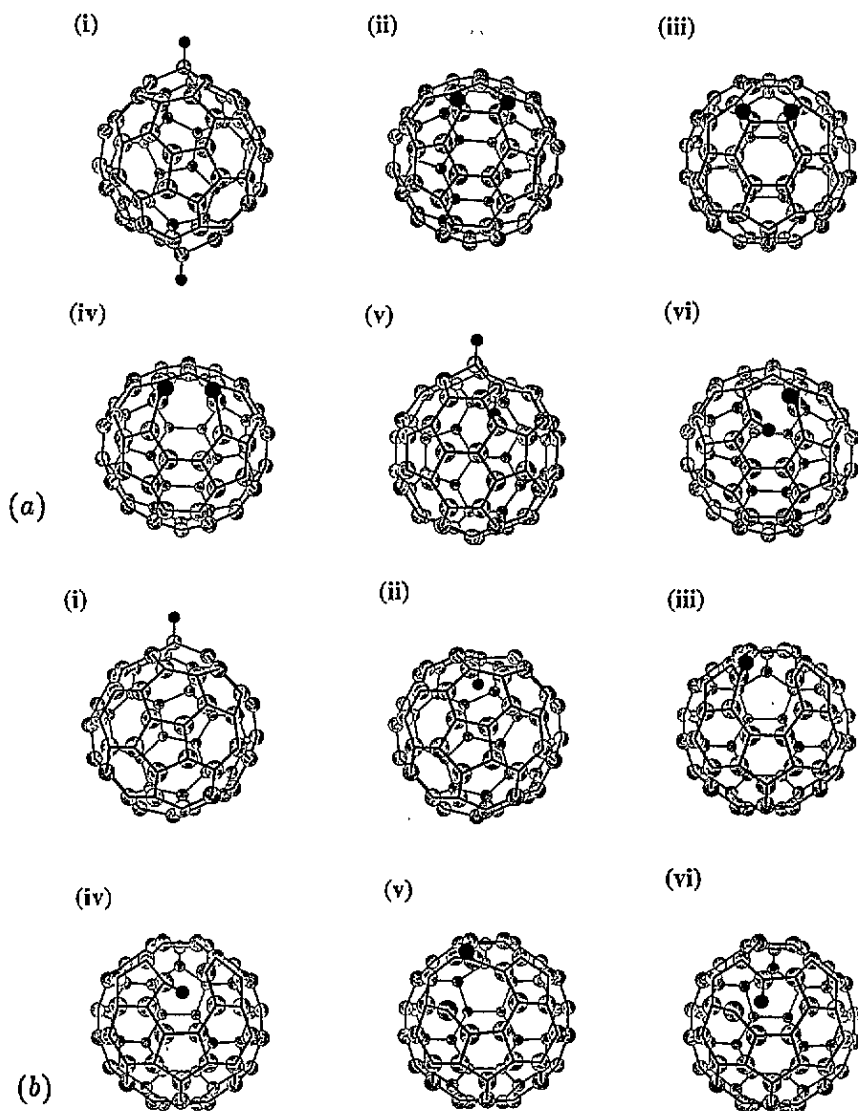


Figure 3. Local minimum-energy structures calculated using the Brenner 1 potential. The dark circles represent the hydrogen atoms, the light circles are carbon. (a) Local minimum-energy structures for $H-C_{60}$ combinations. (i) H atom bonded externally with no C bonds broken (NE). (ii) H atom bonded internally with no C bonds broken (NI). (iii) H atom bonded externally with a hexagonal-hexagonal C bond broken (HE). (iv) H atom bonded internally with a hexagonal-hexagonal C bond broken (HI). (v) H atom bonded externally with a pentagonal-hexagonal C bond broken (PE). (vi) H atom bonded internally with a pentagonal-hexagonal C bond broken (PI). (b) Local minimum-energy structures for H_2-C_{60} combinations. (i) Two isolated externally bonded H atoms with no bonds broken (NEE). (ii) Two H atoms bonded externally to adjacent hexagonal-pentagonal C atoms with the bond unbroken (NHPEE). (iii) Two H atoms bonded externally to adjacent hexagonal-hexagonal C atoms with the bond unbroken (NHHEE). (iv) (HPPEE) is the same as (ii) but with the hexagonal-pentagonal C bond broken. (v) Two H atoms, one bonded externally, one internally to adjacent hexagonal-pentagonal C atoms (NHPEI) and (vi) (HPEI) same as (v) but with the hexagonal-pentagonal C bond broken.

centre of the cage cannot be estimated with the empirical potential used in our calculations because the H-C interactions cut off at distances $> 1.8\text{\AA}$ and therefore there is a volume of approximately one eighth of the cage located at the centre of the molecule in which the C-H potential is assumed to be zero. If the energetics were to be such that

$$E(C_{60} - H)_{\text{external bond}} < E(C_{60} - H)_{\text{centre}} < E(C_{60}) < E(C_{60} - H)_{\text{internal bond}}$$

they would be consistent with *ab initio* calculations for deuterium- C_{60} interactions which have been reported [24]. Further evidence for the possible existence of unbonded H within the cage comes from muon experiments with both C_{60} ²⁵ and C_{70} ²⁶. This work indicates that the muonium can be either free within the cage or bonded externally.

For the H_2 - C_{60} cases, the results are also summarized in table 2. If the H atoms are bound externally and well separated, at positions corresponding to that shown in figure 3(b)(i) then the potential energy is decreased by 3.3 eV compared to the isolated C_{60} energy (i.e. two times that corresponding to figure 3(a)(i)). The most stable configuration (-5.9 eV) turned out to be the case where two H atoms were externally bonded on adjacent C atoms where the C-C hexagonal-pentagonal bond is broken. However MNDO calculations [27] indicate that the NHHEE configuration is the preferred minimum-energy state. The short cut-off distance of the Brenner potential between adjacent H atoms might well be responsible for the erroneous results in the minimum-energy structures for H_2 - C_{60} .

The initial motivation for this study, however, was the hypothesis that it might be possible to implant a H atom within the molecule and so some computer experiments were set up to examine the feasibility of this by projecting H atoms at different energies towards C_{60} molecules.

Any implantation of the H atom within the structure will require it to traverse an energy barrier and in so doing lose energy itself and impart excitational energy to the C_{60} molecule. The MD simulations described below were designed to try to understand this process. A similar MD code has been used before to study a number of interactions of energetic particles with crystals [28, 29].

4. H interaction with 'cold' C_{60}

C_{60} molecules condense to form a face-centred cubic (FCC) structure known as fullerite. This has a cell edge of 14.1 \AA and a nearest-neighbour spacing of 9.97 \AA . In order to carry out the interaction simulations, it was assumed that the incoming H atoms were incident normally on an irreducible symmetry zone of the FCC fullerite lattice at zero temperature. This zone is shown in figure 4(a). Only the three neighbouring C_{60} molecules are considered in this simulation, and these were assumed to be orientated randomly with respect to each other. This random orientation was altered before the start of each trajectory. A total of 500 simulations were run at each of 12 different energies between 11-44 eV. For the purpose of generating the statistics, the simulations were run until the H atom had entirely escaped from the system or for 1 ps, whichever was the greater. This was sufficient for most of the interactions considered, however some special cases were also analysed where the trajectories were continued for longer than 1 ps. In these cases the final equilibrium configuration is only reached after times of the order of a few picoseconds.

The results are shown in table 3. In this table, space is divided into three regions: the plane above the three molecules, the plane below and the internal region of the molecules. The C atoms are all assumed to have zero kinetic energy initially. It can be seen from table 3 that there is some implantation for particles with initial energy of 14 eV or more,

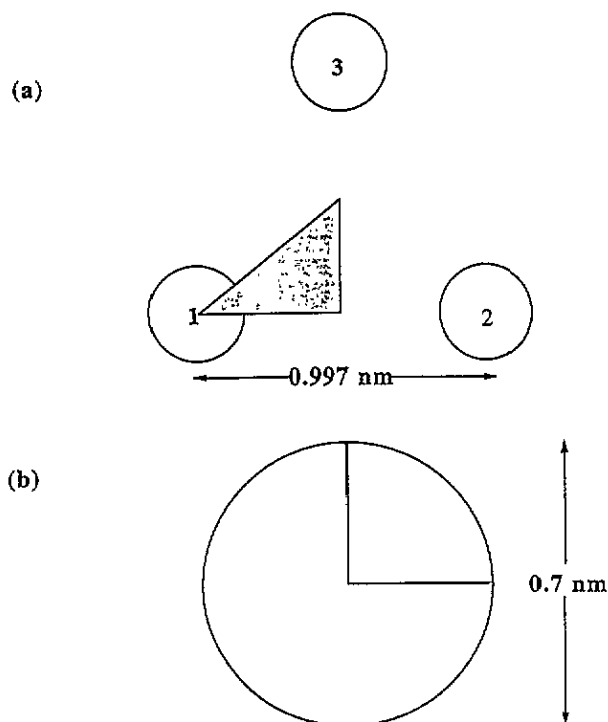


Figure 4. (a) The irreducible symmetry zone for the FCC fullerite surface, depicted by the triangle. The molecules are labelled 1, 2 and 3, consistent with the nomenclature used in table 3. (b) The impact zone for H interactions with the 'energetic' C₆₀ molecules. The centre of mass of the molecule is the centre of the circle.

but that the preferred energy for implantation is 23 eV, where nearly 5% of the H atoms are predicted to implant and stay within the molecules for excess of 1 ps. It can also be seen that not all atoms implant into molecule 1, which is the molecule adjacent to the irreducible symmetry zone. There are a number of H atoms which reflect off molecule 1, but end up being trapped by molecules 2 and 3. As expected, as the energy increases, the backscattering reduces and transmission straight through increases.

Table 3. Table of H implantation of 500 trajectories at various energies into the fullerite lattice first layer. The second column (Back) refers to the H atoms backscattered and the last column (Forward) to those H atoms that pass through the layer. The third column is the total number of H atoms which implant within any of the three C₆₀ molecules. The next three columns is the number implanting within molecules 1, 2 and 3 respectively (see figure 4(a)). The 'On' column refers to those H atoms that attach to the outside of a molecule.

Energy (eV)	Back	In	In1	In2	In3	On	Forward
11.0	214	0	0	0	0	1	285
14.0	197	3	3	0	0	1	299
17.0	185	11	9	2	0	2	302
20.0	136	21	14	7	0	0	343
23.0	139	24	18	3	1	1	338
26.0	126	19	11	7	1	5	350
29.0	117	16	11	4	1	5	362
32.0	106	16	10	3	3	9	369
35.0	79	16	11	1	1	2	405
38.0	88	5	2	3	0	7	400
41.0	96	3	1	2	0	4	397
44.0	90	5	4	1	0	3	402

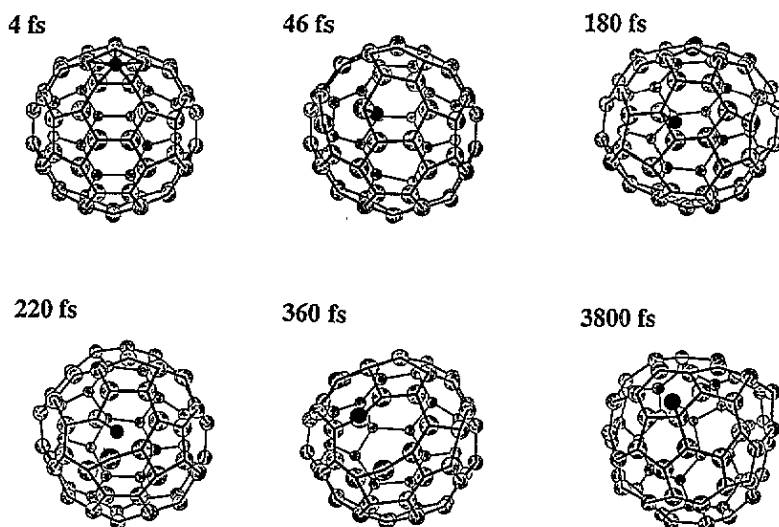


Figure 5. Various stages in the interaction of a H atom with the C_{60} molecule which shows the H atom attaching externally to the molecule after first implanting. The H atom is projected towards the centre of the pentagonal face at an angle of 5° to the normal with an initial kinetic energy of 20 eV. The times are (a) 4 fs, (b) 46 fs, (c) 180 fs, (d) 220 fs, (e) 360 fs and (f) 3.8 ps.

Figure 5 shows various stages in one especially interesting interaction of a 20 eV H atom with the C_{60} molecule for times up to 3.8 ps. The interesting point about this trajectory is that although the H atom initially implants, it eventually attaches to the outside of the molecule. The H atom is initially incident on the pentagonal face at 15° to the normal. The interaction causes a C–C bond to break after about 220 fs. In all the simulations conducted where a bond breaks, it has been the weaker bond between the hexagonal and pentagonal faces that has broken. After the bond has broken, the H atom is adjacent to an under-coordinated C atom and attaches to it. At a later time the broken C–C bond reforms but another hexagonal–pentagonal bond breaks. As it does so the C–H bond flips to the outside of the cage. The molecule vibrates for a considerable amount of time until finally, after about 3.8 ps, the C–C bond reforms. The final state of the attached H atom is close to the minimum-energy structure shown in figure 3(a). This final externally bonded state took one of the longest times to achieve of any of the simulations run, but illustrates the point that if a H atom is initially bonded internally to a C_{60} molecule then this bond can easily switch to an external bond. Examples of all the various cases have been animated and a computer video depicting these events is available on request from the authors [30].

Figure 6 shows the energy change of the H atom and C_{60} molecule for a trajectory where the H atom is predicted to implant within the structure. The excess energy (i.e. above the equilibrium state) for the isolated H atom and cold C_{60} molecule is plotted as a function of time for a H atom with initially 22 eV of kinetic energy. The energy of the H atom rapidly decreases below the threshold for escape from the molecule (around 14 eV). After 0.5 ps the kinetic and potential energy of the H atom is almost zero. The H atom now spends a lot of time near the centre of the molecule, but the C–H potential does not take into account Van der Waals forces so the H potential never drops below zero there. The kinetic and potential energy transferred to the molecule equilibrates rapidly, reaching a quasi-steady state after about 300 fs. Figure 7 shows the same interaction except for a trajectory at 14 eV where the H atom bonds to the outside of the structure, losing most of its kinetic energy within

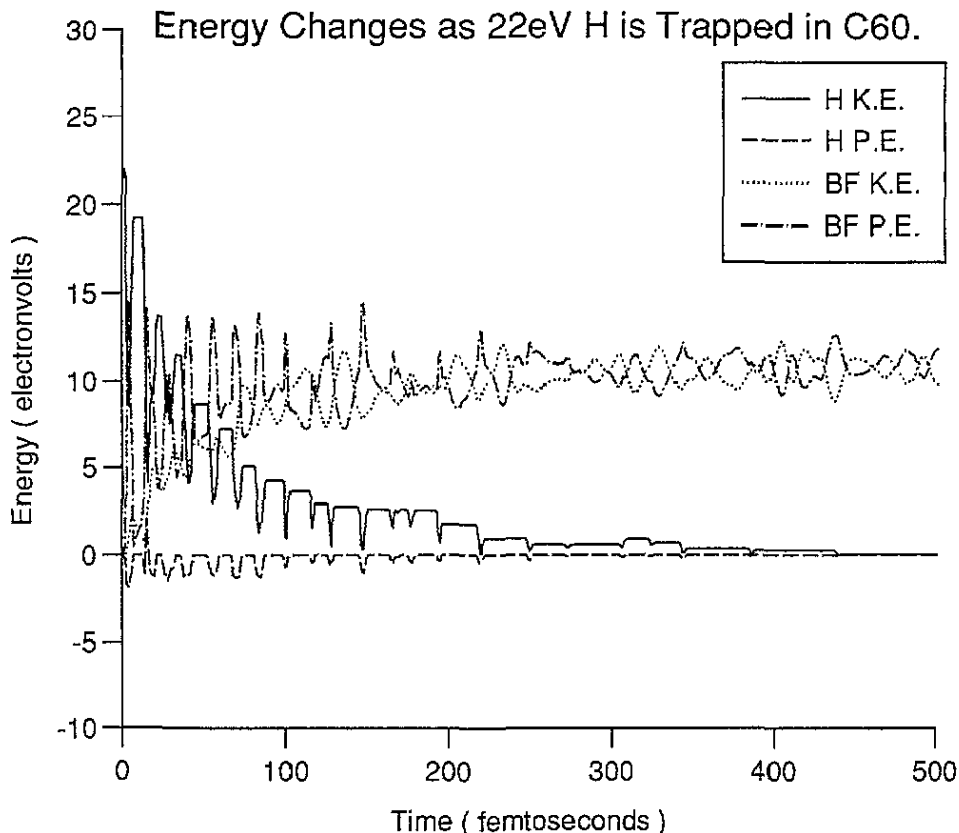


Figure 6. The potential and kinetic energy changes plotted as a function of time for the case where a 22 eV H atom is trapped within the molecule.

7 fs. Figure 8 is for a 24 eV H atom which passes through the molecule. In this case the interaction is over within 25 fs, with 16 eV being transferred to the molecule. It can be seen that, as in figure 6, rapid equilibration between potential and kinetic energy within the molecule takes place.

In addition to the interaction statistics generated in table 3, the threshold energies for the H atom to cross into the cage were calculated. In these calculations, the H atom is assumed to be incident normally at the centre of one of the hexagonal faces of the C₆₀ molecule. From table 3 it can be seen that the energy threshold appears to be around 14 eV. The calculations show that at 13.9 eV, the H atom is repelled by the molecule. At 14.0–14.1 eV the H atom binds externally to the molecule and at > 14.2 eV, the H atom enters the molecule. Static *ab initio* calculations give a figure of 3.9 eV [31] which seems much smaller. However the two values are not exactly comparable because the figure of 3.9 eV was the calculated *static* potential energy of a H atom at the centre of a relaxed hexagonal ring. In the *dynamic* simulations, energy would have to be imparted by the incoming H atom as it approaches the molecule to cause that relaxation. Figure 9 plots the equivalent *static* potential energy using the Brenner potential as the H atom passes through the hexagonal face. It can be seen that the potential energy increases by 3.9 eV when the particle is located at the centre of the relaxed hexagonal ring, in good agreement with the *ab initio* calculations. For a H atom to escape from out of the cage, repulsion of the atom is found up to 14.1 eV. At 14.2 eV it binds on the inside of the cage. At 14.3 eV it binds

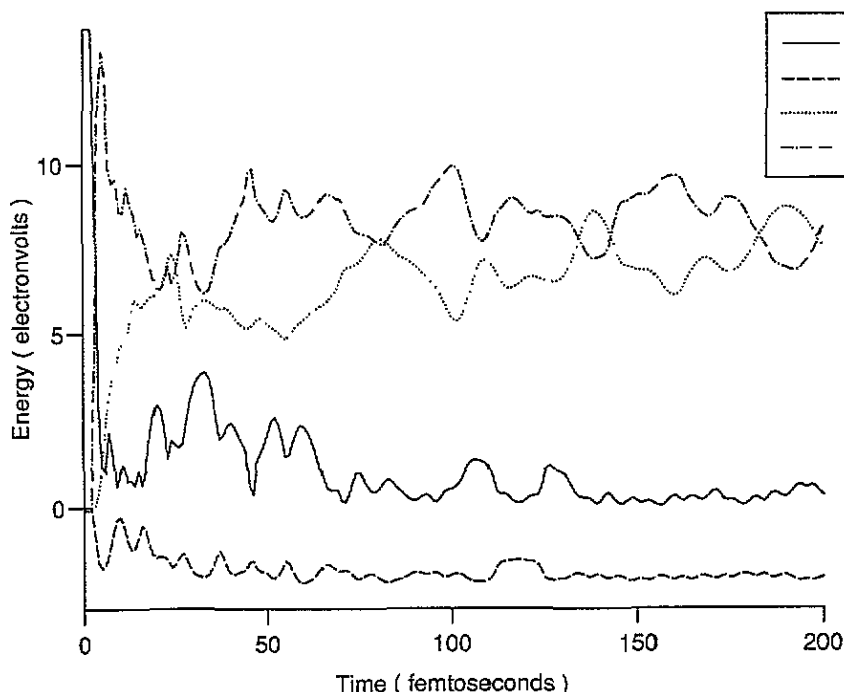
Energy Changes as 14eV H Reacts With C_{60} .

Figure 7. The potential and kinetic energy changes plotted as a function of time for the case where a 14 eV H atom becomes externally bonded to the molecule.

on the outside of the cage and for energies of 14.4 eV and more the H atom escapes.

The evidence from table 3 and the above detailed trajectories shows that it should be possible for a H particle to implant within an initially cold C_{60} structure and to transfer its kinetic energy by collisions with the C atoms until it has insufficient energy to escape from the cage. This suggests that a possible technique for producing H-implanted C_{60} is to bombard the FCC fullerene lattice at normal incidence at the optimum energy for implantation and then to remove the material layer-by-layer after sufficiently large H doses. It would then be necessary to strip off any H attached to the outside of the molecule which, being externally bonded, would be more amenable to chemical reaction than the internally implanted H.

The experimental results described previously were not of the form described above, but where sublimated C_{60} molecules were passed through a H plasma. As a result, calculations were also carried out of 25 eV H interactions with energetic C_{60} molecules.

5. H interaction with 'heated' C_{60}

In the experiments described in section 2, sublimated C_{60} molecules are passed through a H plasma. The mean energy of the plasma is estimated to be 10–25 eV. These ions will transfer energy through collision with C_{60} molecules as the molecules pass through the plasma. Since the collision process occurs primarily with a single C atom of the C_{60} structure, it is possible for the molecule itself to have a total internal vibrational energy

Energy Changes as 24eV H Passes Through C60.

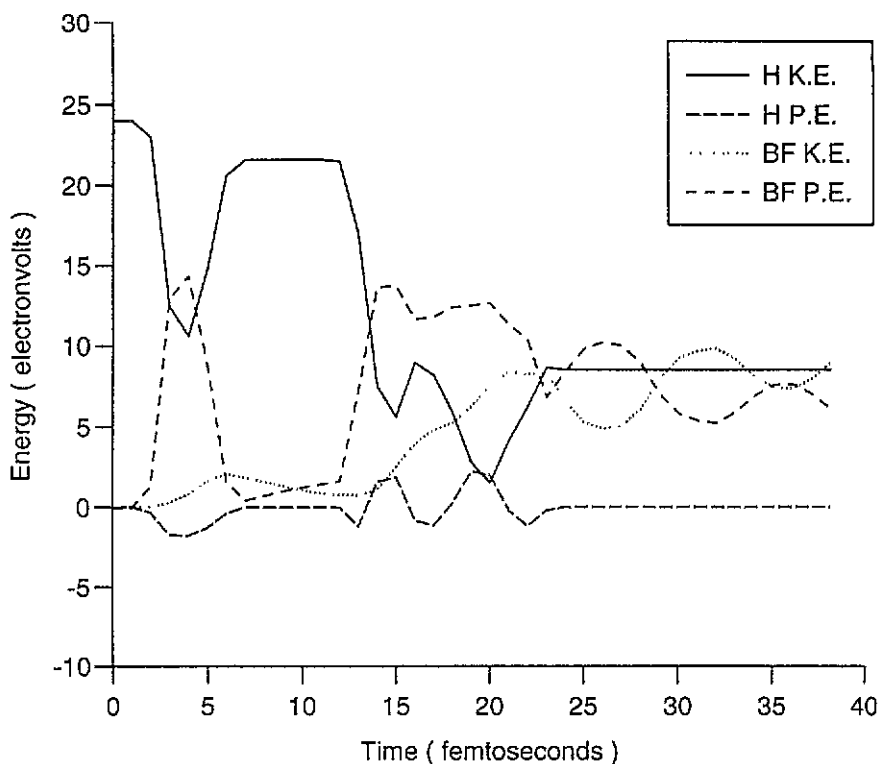


Figure 8. The potential and kinetic energy changes plotted as a function of time for the case where a 24 eV H atom passes through the molecule.

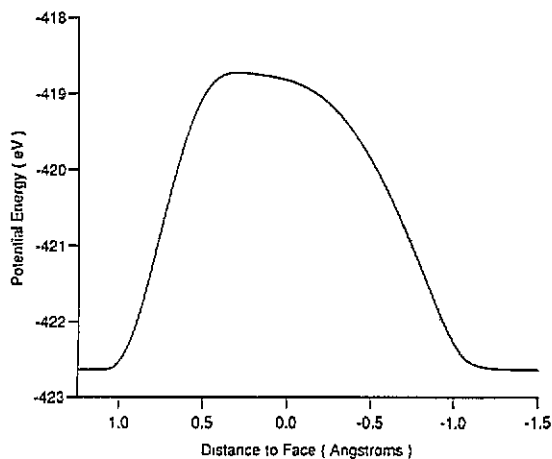


Figure 9. The static potential energy calculations for a H atom passing through the centre of a hexagonal face from outside to inside the molecule.

in excess of 25 eV. In the experiments, the C_{60} is sublimated at an estimated temperature of 650°C. We have calculated that this corresponds to a total internal energy of around 14 eV, in agreement with the estimates of Mowray and co-workers [6]. Thus simulations

were run of H interaction with C_{60} which had internal energies of 14 and 33 eV, i.e. at an energy corresponding to the estimated sublimation temperature and slightly greater than the estimated mean ion energy.

A system consisting of a single H atom and an isolated energetic C_{60} molecule was studied in the MD simulations. To introduce the energy into the C_{60} molecule one sixtieth of the total energy required to be added was given to each C atom with the velocity in a random direction. The C_{60} was allowed to equilibrate for 1 ps before the H atom was introduced into the simulation. Using this method, the added energy is mainly in the form of internal vibrational energy rather than rotational or linear kinetic energy of the molecule as a whole. The H atom is now assumed to be incident over the region given by the quarter circle centred on the C_{60} molecule shown in figure 4(b) and projected downwards. The simulations were run for 8 ps or until the H atom escaped from the system. 200 trajectories were run at the two internal energies of 14 and 33 eV. A set of simulations were also run for an internal energy of 52 eV. However, at this energy any H that bonded to the molecule caused severe damage to the molecule. If the internal energy is further increased to 90 eV, any H atom incident at 25 eV causes the molecule to disintegrate. For the 14 eV internal-energy case, it was still found that five of the incident H atoms became trapped within the molecule. However 14 formed external bonds but maintained the C_{60} structure. A further H atom bonded in such a way as to cause a breaking of one of the hexagonal-pentagonal bonds and one H bonded but caused multiple bond-breaking in the molecule. At 33 eV no H atom implanted within the molecule although 1/200 bonded on the inside of the cage, four bonded externally with no broken bonds, two with single bonds broken and seven with multiple bond breaking. Thus trapping of H by a heated C_{60} molecule is much less likely than trapping by a molecule at 0 K.

6. Conclusions

The calculated static potential energy configurations analysed seem to indicate that $C_{60}H_2$, where the H atoms are attached to adjacent C atoms from a broken hexagonal-pentagonal bond is one of the preferred minimum-energy states with a potential energy of 5.9 eV less than that of the isolated C_{60} molecule. Further H atoms added in pairs at other similar but separated bonding sites on the molecule would be expected to reduce the potential energy further by similar amounts. These might well be the most common structures for $C_{60}H_4$ and $C_{60}H_6$. However, the addition of further atoms would also increase the strain energy of the cage (figure 3(b)(i) shows a considerable strain to the molecule) and it is known that $C_{60}H_4$ and $C_{60}H_6$ decompose over a long time, whereas $C_{60}H_2$ is stable. Whether the addition of internally bonded H atoms within the cage could stabilize $C_{60}H_n$ molecules is a question that has not been considered here.

The experimental results showed no evidence of a single H atom located at the centre of the C_{60} molecule. Since this would be a paramagnetic state it would be easily detected in ESR even in small quantities. The explanation presented here is that the excitation of the C_{60} molecule as it passes through the plasma prevents the formation of this state as indicated in the 'warm' molecule simulations carried out. However, it is suggested that if the experimental process were to be such that single energetic H atoms interact with 'cold' C_{60} molecules then implantation within the structure should be possible with the minimum-energy state at the centre of the molecule. The main experimental difficulty would appear to be how to do this without imparting too much energy to the molecule, since it would appear that it is more difficult both to implant and to contain the H atom within the vibrating C_{60} structure. One possibility might be by producing a Langmuir-Blodgett film of C_{60} and

irradiating with a low-dose low-energy proton beam. Such experiments will be reported on at a later date.

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