

# Breathing-trap mechanism for encapsulation of atomic hydrogen in C<sub>60</sub>

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## Abstract

Our density-functional-based simulations demonstrate that atomic hydrogen can be encapsulated in C<sub>60</sub> via collisions of either H or H<sub>2</sub> with a C<sub>60</sub> molecule whose breathing mode has been properly excited by an optimized femtosecond-scale laser pulse. The basic mechanism is a “breathing trap”, with the C<sub>60</sub> first expanding, to admit the H, and then contracting, to contain it.

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## 1. Introduction

Immediately after the discovery of C<sub>60</sub> [1], the first endohedral fullerene La@C<sub>60</sub> was produced by laser vaporization [2, 3]. A wide variety of atoms and molecules have now been successfully encapsulated in the C<sub>60</sub> nanocage, with interesting chemical and physical properties [4, 5, 6], using techniques that include high temperature and high pressure treatments [7], atomic collisions in beams [8], and ion implantation [9]. Here we are concerned with the endohedrally hydrogen-filled C<sub>60</sub> system, which has been the subject of many theoretical and computational investigations, focusing on H<sup>+</sup>@C<sub>60</sub> [10, 11], H@C<sub>60</sub> [12, 13, 14, 15, 16, 17], H<sup>-</sup>@C<sub>60</sub> [18], H<sub>2</sub><sup>+</sup>@C<sub>60</sub> [19], H<sub>2</sub>@C<sub>60</sub> [20], H<sub>3</sub><sup>+</sup>@C<sub>60</sub> [21], H<sub>*n*</sub>@C<sub>60</sub> [22], and (H<sub>2</sub>)<sub>*n*</sub>@C<sub>60</sub> [23]. Nevertheless, to our knowledge only molecular hydrogen has been experimentally encapsulated in the C<sub>60</sub> nanocage, with H<sub>2</sub>@C<sub>60</sub> produced by a molecular surgery method [24] and laser excitation [25].

Prima facie, it may be surprising that atomic hydrogen, the lightest and one of the smallest of atoms, has never been successfully encapsulated to form H@C<sub>60</sub>. The reason appears to be that H prefers to bond on the surface of the molecule, with the endohedral site being metastable [12]. In addition, there is a large energy barrier to penetrating the surface [12].

In experiments involving  $\approx 25$  eV hydrogen plasma and C<sub>60</sub> molecules [13, 14], there was no evidence of endohedral H@C<sub>60</sub>, but only exohedral C<sub>60</sub>H<sub>*n*</sub>. The C<sub>60</sub> nanocage,

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which is an active  $\pi$ -electronic system, tends to form C-H covalent bonds more easily on its outside. Although molecular dynamics simulations show that H atoms might be encapsulated in the surface layer of a  $C_{60}$  lattice, the required energy range was found to be extremely narrow (0.1 eV) [13].

Here we explore a different approach, in which a “breathing-trap” is created by excitation via a properly designed femtosecond-scale laser pulse. This mechanism is made possible by the robustness of  $C_{60}$ , which can undergo strong deformations without fragmenting: Laarmann et al. were able to excite large amplitude oscillations of the radially symmetric  $A_g(1)$  breathing mode, using temporally shaped laser pulses [26]. One can then envision the barrier to penetration by an H atom being momentarily lower when the  $C_{60}$  molecule reaches maximum extension, and this atom then being trapped inside by a much larger barrier when the molecule contracts. This “breathing-trap” mechanism is different from the “window” mechanism [7, 27] because no C-C bonds are broken even temporarily.

The breathing mode is one of the ten Raman-active modes of  $C_{60}$ , which can be controlled with properly tailored femtosecond-scale laser pulses, according to several computational investigations with various methods [28, 29, 30, 31, 32] and the experimental studies of Laarmann et al. [26]. Because the H atom has to transfer a large amount of kinetic energy to produce “relaxation” of the  $C_{60}$  nanocage [13], the threshold for H penetration is much higher than the static barrier of 1.87 eV calculated recently with density functional theory (DFT) [17]. It has been shown that one way to lower the penetration energy is to saturate the C-C double bonds by fluorination or bromination [11, 17]. Another way to lower the barrier might be hydrogenation of the guest atomic hydrogen, which just means that it is incorporated in an  $H_2$  molecule and freed during a collision with  $C_{60}$ . Here we will investigate this possibility with the additional feature of a femtosecond-scale laser pulse to produce a “breathing-trap”.

## 2. Method and details of the simulations

We performed simulations for collisions of 8-20 eV H atoms and 4-45 eV  $H_2$  molecules with  $C_{60}$ , both in the ground state and with the breathing mode excited by a laser pulse. Our technique is semiclassical electron-radiation-ion dynamics (SERID), which has been recently reviewed [33]. The radiation field and ion motion are both treated classically (but “ $n$ -photon” and “ $n$ -phonon” processes are still observed in absorption and stimulated emission). The dynamics of the valence electrons is treated with the density-functional-based approach of Frauenheim and co-workers [34, 35]. The electrons are coupled to the radiation field through the time-dependent Peierls substitution [36]. The equations for ion motion were integrated using the velocity Verlet algorithm with a time step of 0.05 fs, and the radiation field for the laser pulse was taken to have the form  $\mathbf{A}(t) = \mathbf{A}_0 \sin(\pi t/2\tau) \cos(\omega t)$  for  $0 \leq t \leq 2\tau$ , where  $\mathbf{A}$  is the vector potential and  $\tau$  is the full-width-at-half-maximum (FWHM) pulse duration. The radiation was taken to be linearly polarized along the  $x$  axis. A series of simulations was performed to optimize the pulse parameters  $A_0$ ,  $\omega$ , and  $\tau$ . It was found (through trial and error) that the amplitude of  $A_g(1)$  is a maximum without any C-C bonds broken when the magnitude of  $\mathbf{A}_0$  is 2.5 Gauss-cm, with  $\hbar\omega = 2.8$  eV and  $\tau = 13.5$  fs. Fig. 1 shows the numerical discrete-time Fourier transform (DTFT) of the total kinetic energy of  $C_{60}$  after completion of the laser pulse, where the breathing mode  $A_g(1)$  and another Raman-active mode  $H_g(1)$  are

clearly visible. The periods of  $A_g(1)$  and  $H_g(1)$  are respectively 70 and 156 fs. The C-C bonds of excited  $C_{60}$  are weaker than those in the ground state, for which the periods are shorter: 59.7 and 125 fs [30]. Vibrating in the  $A_g(1)$  mode, the  $C_{60}$  nanocage reaches its maximum diameter at 45 fs, 115 fs, 185 fs, 255 fs, etc. There is a secondary influence of the  $H_g(1)$  mode, whose period is almost twice that of  $A_g(1)$ , so that the hexagonal ring labeled in Fig. 2 is less distorted at 115 fs, 255 fs, etc.

Since we can perform only a limited number of simulations, we initially chose the most favorable situation for the arrival of the H atom or  $H_2$  molecule. For  $C_{60}$  after laser excitation, the above results imply that this means arrival at the center of the hexagonal ring, with perpendicular velocity, at 115 fs. At this time the C1-C4 distance is 3.13 Å for the breathing-mode-excited  $C_{60}$ , versus 2.86 Å in the ground state. This expansion is substantially smaller than the maximum expansion of approximately 30% reported in Ref. [26], where ionized  $C_{60}$  was also considered.

In order to see whether perfectly optimal conditions are in fact necessary for encapsulation, we also performed simulations with impact angles of 70° and 80° (rather than 90°), and with an impact point midway between the center of a hexagon and one of its vertices.

It should be mentioned that the present mechanism might be generalized to excitation of other vibrational modes, or combinations of modes, using shaped pulses or pulse sequences, but the breathing mode is normally the most strongly excited for pulses with high fluence [26, 28].

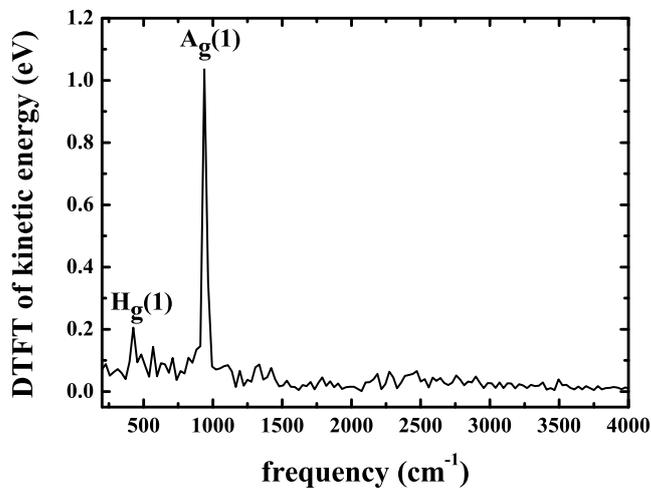


Figure 1: Numerical discrete-time Fourier transform of the total kinetic energy of  $C_{60}$  after being excited by a laser pulse with a FWHM duration of 13.5 fs, photon energy of 2.8 eV, and vector potential amplitude  $A_0$  of 2.5 Gauss-cm. The  $A_g(1)$  and  $H_g(1)$  modes are clearly visible, each with a true angular frequency which is half that exhibited in the figure for the kinetic energy (for the reason given in Ref. [30]).

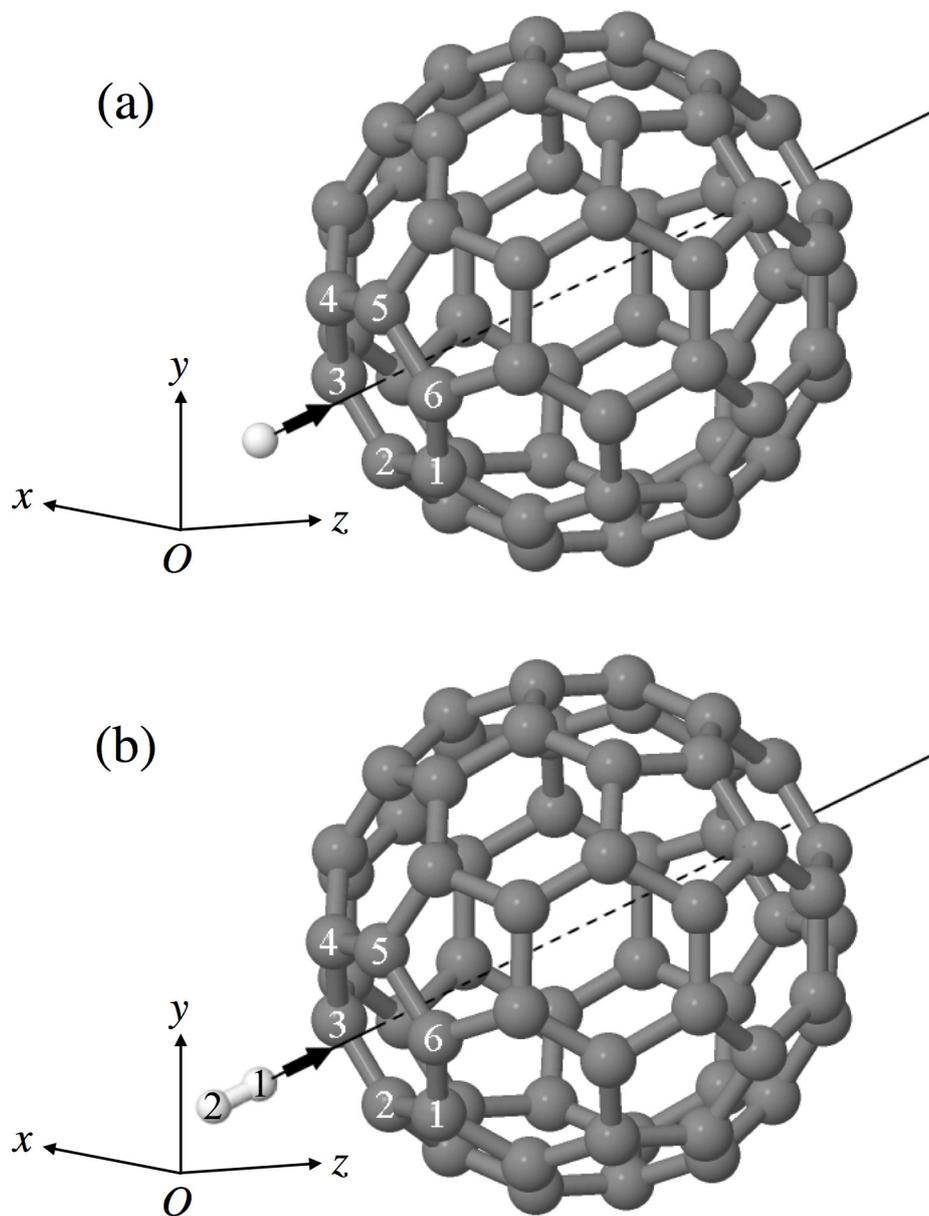


Figure 2: Atomic hydrogen (a) and molecular hydrogen (b) are taken to collide with C<sub>60</sub> at the center of the labeled hexagonal ring, with a velocity perpendicular to its plane.

### 3. Results and discussion

#### 3.1. Collisions between H atom and ground state $C_{60}$

The results of these simulations are summarized in Table 1. In every case, the H atom bounced back or passed through the  $C_{60}$  nanocage, but did not bind either inside or outside. The energy threshold for passing through in our density-functional-based simulations is 17.51 eV, which is higher than the 14 eV reported for simulations with semiempirical many-body potentials [13]. Both are much higher than the static barrier of 1.87 eV calculated with DFT, because a large energy transfer is required for “relaxation” of the  $C_{60}$  [13].

#### 3.2. Collisions between $H_2$ molecule and ground state $C_{60}$

As can be seen in Table 1, neither H nor  $H_2$  was found to be encapsulated in this case. The threshold energy of 6.14 eV for H passing through is (as expected) much lower than the 17.51 eV above, because each H is already bonded. If the kinetic energy of the  $H_2$  is higher than 40.74 eV, then both H atoms pass through.

It is illuminating to calculate the charge transfer when the H or  $H_2$  is near a relaxed  $C_{60}$ , as shown in Fig. 3 and listed in Table 2. The DFT calculations were performed with the SIESTA package [37, 38], using standard values for the parameters (double-zeta basis set with polarization functions and a cutoff of 150 Ryd, with the system placed in a  $20 \text{ \AA} \times 20 \text{ \AA} \times 20 \text{ \AA}$  box). Much more charge is transferred from H than from  $H_2$ , demonstrating the stronger interaction for atomic hydrogen.

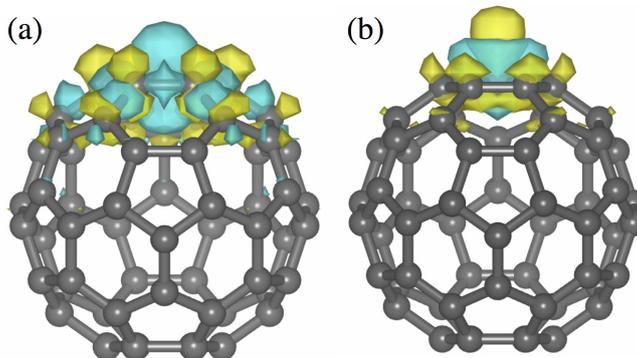


Figure 3: Top views of charge density differences while (a) a hydrogen atom and (b) a hydrogen molecule are crossing the nearest hexagonal ring in  $C_{60}$ . (Online figures with colour: blue and yellow regions respectively indicate electron loss and gain.)

#### 3.3. Collisions between H atom and $C_{60}$ excited into the breathing mode

The most interesting results of this paper are summarized in the various lower panels of Table 1: When the  $C_{60}$  is strongly excited into the breathing mode, by an optimized pulse with the parameters described above, an incident H atom within a wide range of energies, 10.51-15.55 eV, is found to be encapsulated. This is the simplest version of the “breathing-trap” mechanism, and the results demonstrate that it works, at least for favorable trajectories like those chosen here.

	C <sub>60</sub> state	kinetic energy	final state
H	ground	$8.00 \text{ eV} \leq E_k < 17.51 \text{ eV}$	H bounced back
H	ground	$17.51 \leq E_k \leq 20.00 \text{ eV}$	H passed through
H <sub>2</sub>	ground	$4.00 \text{ eV} \leq E_k < 6.14 \text{ eV}$	H1 and H2 bounced back
H <sub>2</sub>	ground	$6.14 \text{ eV} \leq E_k < 40.74 \text{ eV}$	H1 passed through, H2 bounced back
H <sub>2</sub>	ground	$40.74 \text{ eV} \leq E_k \leq 45.00 \text{ eV}$	H1 and H2 passed through
H	excited	$8.00 \text{ eV} \leq E_k < 10.51 \text{ eV}$	H bounced back
H	excited	$10.51 \text{ eV} \leq E_k < 15.55 \text{ eV}$	H was encapsulated
H	excited	$15.55 \text{ eV} \leq E_k \leq 20.00 \text{ eV}$	H passed through
H <sub>2</sub>	excited	$4.00 \text{ eV} \leq E_k < 5.62 \text{ eV}$	H1 and H2 bounced back
H <sub>2</sub>	excited	$5.62 \text{ eV} \leq E_k < 13.94 \text{ eV}$	H1 was encapsulated, H2 bounced back
H <sub>2</sub>	excited	$13.94 \text{ eV} \leq E_k < 18.54 \text{ eV}$	H1 passed through, H2 bounced back
H <sub>2</sub>	excited	$18.54 \text{ eV} \leq E_k < 32.86 \text{ eV}$	H1 passed through, H2 was encapsulated
H <sub>2</sub>	excited	$32.86 \text{ eV} \leq E_k \leq 45.00 \text{ eV}$	H1 and H2 passed through
	angle	collision point	final state
H, 13 eV	70°	center	H passed through
H, 13 eV	80°	center	H was encapsulated
H, 13 eV	70°	midpoint	H was encapsulated
H, 13 eV	80°	midpoint	H passed through
H, 13 eV	90°	midpoint	H passed through
H <sub>2</sub> , 10 eV	70°	center	H1 passed through, H2 bounced back
H <sub>2</sub> , 10 eV	80°	center	H1 was encapsulated, H2 bounced back
H <sub>2</sub> , 10 eV	70°	midpoint	H1 passed through, H2 bounced back
H <sub>2</sub> , 10 eV	80°	midpoint	H1 passed through, H2 bounced back
H <sub>2</sub> , 10 eV	90°	midpoint	H1 passed through, H2 bounced back
H <sub>2</sub> , 20 eV	70°	center	H1 passed through, H2 bounced back
H <sub>2</sub> , 20 eV	80°	center	H1 and H2 passed through
H <sub>2</sub> , 20 eV	70°	midpoint	H1 passed through, H2 bounced back
H <sub>2</sub> , 20 eV	80°	midpoint	H1 and H2 passed through
H <sub>2</sub> , 20 eV	90°	midpoint	H1 and H2 passed through
H <sub>2</sub> , 26 eV	70°	center	H1 passed through, H2 bounced back
H <sub>2</sub> , 26 eV	80°	center	H1 passed through, H2 was encapsulated
H <sub>2</sub> , 26 eV	70°	midpoint	H1 and H2 passed through
H <sub>2</sub> , 26 eV	80°	midpoint	H1 and H2 passed through
H <sub>2</sub> , 26 eV	90°	midpoint	H1 and H2 passed through

Table 1: Results for collisions between atomic H or H<sub>2</sub> molecule and C<sub>60</sub>, either in the ground state or excited into the breathing mode. In the H<sub>2</sub> molecule, H1 is the leading H atom and H2 the trailing one, as shown in Fig. 2. In the upper part of the table, the atom or molecule is incident at the center of a C<sub>60</sub> hexagon, and its velocity makes an angle of 90° with the plane of the hexagon. In the lower part, the C<sub>60</sub> has always been excited into the breathing mode, and the atom or molecule is incident at the indicated energy, angle, and collision point, where “center” means the center of a hexagon and “midpoint” means the point midway between the center and a vertex. The transitional energies in the upper part of the figure were determined by successive interval-halving.

### 3.4. Collisions between $H_2$ molecule and $C_{60}$ excited into the breathing mode

For  $H_2$ , and a  $C_{60}$  again strongly excited into the breathing mode, the range of possibilities is still larger, as can be seen in Table 1. There are actually two large windows for encapsulation, with the leading H trapped for energies in the range 5.62-13.94 eV and the trailing H trapped for 18.54-32.86 eV. The first threshold is lower than that for atomic H, for the reason given above and illustrated in Fig. 3: the interaction with the  $C_{60}$  cage is weaker for  $H_2$ .

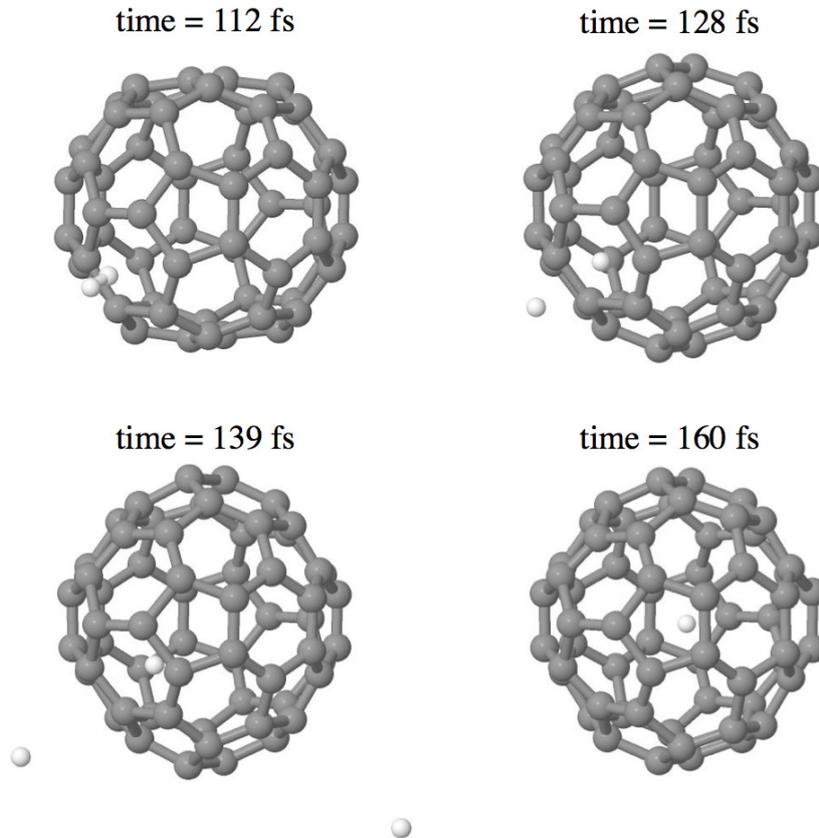


Figure 4: Snapshots of collision between a 5.62 eV  $H_2$  molecule and a breathing-mode-excited  $C_{60}$  nanocage.

Snapshots of a simulation with the  $H_2$  having a kinetic energy of 5.62 eV (i.e. at the threshold) are shown in Fig. 4. The H1 atom “rattles around” inside the  $C_{60}$  cage

Configuration	H1	H2	C1	C2	C3	C4	C5	C6
H- $C_{60}$	0.410		4.114	4.112	4.123	4.080	4.086	4.136
$H_2$ - $C_{60}$	0.769	1.058	4.002	4.007	4.028	3.986	3.999	4.023

Table 2: Charges on H atoms and on C atoms in the nearest hexagonal ring (in units of e).

after its encapsulation [10]. Temporal changes in the kinetic energies of the H1 and H2 atoms (again for a 5.62 eV H<sub>2</sub> molecule) are shown in Fig. 5. The initial kinetic energy of the H1 atom is yielded up to the C<sub>60</sub>, while the H2 atom recoils and has constant speed after all its bonds are broken. The two hydrogen atoms were never observed to be trapped together in the nanocage, since there was always breaking of the H-H bond if H1 passed inside. When the kinetic energy of the H<sub>2</sub> was higher than the bond energy and lower than the threshold for penetration, the H-H bond would break and both hydrogen atoms would bounce back. Thus H<sub>2</sub> was not observed to be encapsulated through this mechanism.

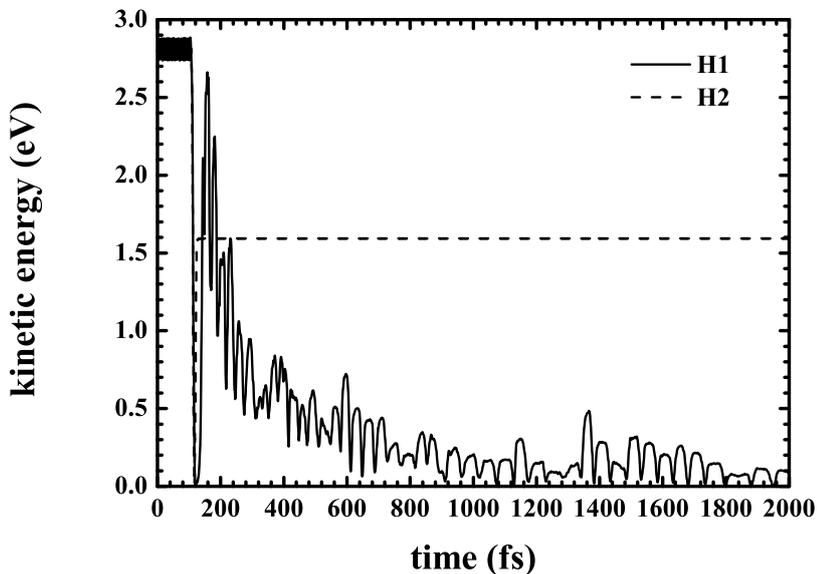


Figure 5: Temporal changes in the kinetic energies of H1 and H2 atoms. The oscillations before 115 fs indicate that the two atoms are bound as an H<sub>2</sub> molecule.

#### 4. Conclusions

Our simulations demonstrate the feasibility of a “breathing-trap” mechanism for producing H@C<sub>60</sub>, which (remarkably) has not yet been achieved experimentally. We propose using an optimized femtosecond-scale laser pulse to strongly excite the C<sub>60</sub> breathing mode. We find that there is then a wide window of incident energies for either atomic H or molecular H<sub>2</sub> to deposit an H atom inside the nanocage (as it expands to maximum size during the breathing-mode vibration), with the H then confined (as the cage subsequently contracts). It is interesting that molecular hydrogen is more promising than atomic hydrogen, as well as experimentally more convenient, because the bonding to the C<sub>60</sub> is weaker and the barrier to penetration is thus lower. This work was motivated by

the experiments of Laarmann et al. [26], who were able to excite the breathing mode with very large amplitude using tailored laser pulses.

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