Time-dependent density functional theoretical studies on the photo-induced dynamics of an HCl molecule encapsulated in C_{60} under femtosecond laser pulses*

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By using first-principles simulations based on time-dependent density functional theory, the chemical reaction of an HCl molecule encapsulated in C_{60} induced by femtosecond laser pulses is observed. The H atom starts to leave the Cl atom and is reflected by the C_{60} wall. The coherent nuclear dynamic behaviors of bond breakage and recombination of the HCl molecule occurring in both polarized parallel and perpendicular to the H–Cl bond axis are investigated. The radial oscillation is also found in the two polarization directions of the laser pulse. The relaxation time of the H–Cl bond lengths in transverse polarization is slow in comparison with that in longitudinal polarization. Those results are important for studying the dynamics of the chemical bond at an atomic level.

Keywords: time-dependent density functional theory, femtosecond laser pulse, photo-induced dynamics, chemical reaction

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1. Introduction

The study of molecular dynamics in the femtosecond time domain (1 fs = 10^{-15} s) is one of the most vigorously pursued research topics in nonperturbative light matter interaction physics. There are some examples of the photo-induced dynamical phenomena such as the simple optical response,[1] multi-photon ionization,[2–4] the various scenarios of Coulomb explosion of clusters,[5–7] charge resonance-enhanced ionization,[8,9] bond softening,[10] and bond hardening (light-induced bound states or vibrational trapping).[11] In particular, the dynamics of chemical reaction induced by an optimal femtosecond pulse has attracted particular attention recently.[12–14] Miyamoto *et al.*[14] showed the dynamics of HCl molecules encapsulated in nanotubes under the irradiation of a short laser pulse. The dynamics induced by subsequent laser pulses is different, depending on the initial orientation of the HCl molecule. In the present work, we consider a completely enclosed structure with a large nanometer space in order to study the photochemistry of molecules in those confined spaces under femtosecond laser pulses.

We select the fullerene C_{60} molecule to exemplify the dynamical theory induced by femtosecond pulses. C_{60} is a very special subject because of its highly symmetric structure and its large number of electronic and nuclear degrees of freedom. With its 60 essentially equivalent, delocalized π electrons, it may be seen as a prototype of a large, finite system for studying the photodynamics in a strong laser field.[15–17] And a variety of experimental studies and model calculations have been devoted to a detailed understanding of ionization and fragmentation dynamics in C_{60}.[18] The large empty spaces between the molecules are freely available for smaller atoms, ions or molecules, which is often described by the term of 'doped fullerene'. The varieties of chemical properties and the modifications of those 'doped fullerenes' induced by the C_{60} confinement have opened a new avenue of research linked to the nanoconfined chemistry. Understanding the confinement effect in the photophysics and photochemistry of encapsulated molecules is of fundamental and practical interest.

In this paper, for the first time, we report on the systematic studies of the photo-induced dynamics of an HCl molecule encapsulated in C_{60} under laser pulses. At present the most practical scheme is an effective description of the photo-induced dynamics in terms of the time-dependent density functional theory (TDDFT).[19] The TDDFT has been very successful in describing the optical spectra of small nanostructure materials,[20] including high-intense laser-induced electronic-ion dynamics.[21] For the exchange–correlation potential, we use the adiabatic local density approximation (LDA). The TDLDA was used to study the dynamics of metal clusters and isolated molecules[21,22] in the presence of a strong laser pulse. The dynamics of the HCl molecule encapsulated in C_{60} is calculated under the pulse laser with a wavelength of 800 nm and full with at half maximum of 2 fs. These conditions make the duration time of the pulse reach only 4 fs and make the pulse

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shape strongly asymmetric in the direction of the alternating optical E field as shown in Fig. 1. Such a short pulse is indeed experimentally available.[23]

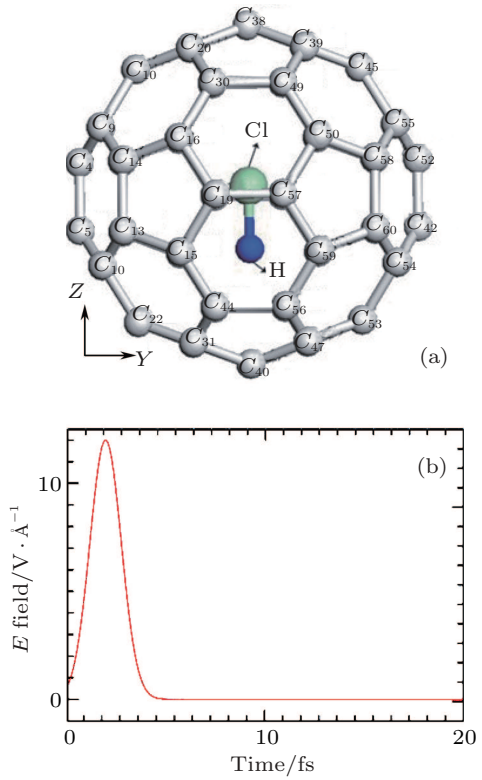


Fig. 1. (color online) Schematic diagram of the ground state for an HCl molecule encapsulated in C_{60} (panel (a)), in which the H–Cl bond is along the Z axis. The biggest ball denotes the Cl atom, the second biggest ball refers to the H atom, and the remaining balls (with numbers) represent the C atoms. The C atoms are numbered for the sake of discussion in text. The pulse shape of the laser pulse used in the current simulation is shown in panel (b). The maximum field intensity is 12 V/Å with a wavelength of 800 nm and full width of half maximum of 2 fs.

2. Computational methods

In the present simulation, the photo-induced dynamics is described by the coupling TDDFT for the electron time evolution with classical molecular dynamics for the ions. The motions of the electrons and the nuclei are described by the following equation derived from the Lagrangian:

$$L = \sum_{\alpha}\left[\frac{1}{2}m_{\alpha}\dot{R}_{\alpha}^{2}+Z_{\alpha}R_{\alpha}\varepsilon(t)\right] - \sum_{\alpha<\alpha'}\frac{Z_{\alpha}Z_{\alpha'}}{|R_{\alpha}-R_{\alpha'}|} + \sum_{i}\langle\phi_{i}|\mathrm{i}\hbar\frac{\partial}{\partial t} - ex\varepsilon(t)|\phi_{i}\rangle - E_{\mathrm{DFT}}(\{\phi\},\{R\}), \quad (1)$$

where m_{α} and Z_{α} are the nuclear mass and charge quantity, respectively, E_{DFT} is the usual Kohn–Sham density functional, depending on the electron orbital $\{\phi\}$ and the nuclear coordinates $\{R\}$, and $\varepsilon(t)$ is the time-dependent electric field from the laser pulse. Variation of the Lagrangian then yields Newton's equation for the nuclear coordinates,

$$m_{\alpha}\frac{\mathrm{d}^{2}R_{\alpha}}{\mathrm{d}t^{2}} = -\nabla R_{\alpha}E_{\mathrm{DFT}} - \sum_{\alpha'}\frac{(R_{\alpha}-R_{\alpha'})Z_{\alpha}Z_{\alpha'}}{|R_{\alpha}-R_{\alpha'}|^{3}} + Z_{\alpha}\varepsilon(t), \quad (2)$$

and the usual TDDFT equations for the orbital variables.[24] We then solve the time-dependent Kohn-Sham equation with the Newton equations. And the TDKS equation is as follows:

$$\mathrm{i}\hbar\frac{\mathrm{d}\phi_{i}(R,t)}{\mathrm{d}t} = [H_{\mathrm{KS}}(R,t)+\varepsilon(R,t)]\,\phi_{i}(R,t), \quad (3)$$

where $H_{\mathrm{KS}}(R,t)$ is the Kohn–Sham Hamiltonian. The forces exerted on it are calculated with the help of a generalized Hellmann–Feynman theorem,

$$-\nabla_{R_{\alpha}}E_{\mathrm{DFT}} = -\sum_{i}\langle\phi_{i}|\nabla_{\alpha}H_{\mathrm{KS}}|\phi_{i}\rangle. \quad (4)$$

The interaction between valence electrons and ions is described by norm-conserving Troullier–Martins pseudopotentials.[25] The computational details are as follows: we start with the systems in its ground state. The ground state Kohn–Sham wave-functions are then propagated with a unitary scheme.[26] The simulation zone is a sphere of radius 20 Å (1 Å = 0.1 nm). The space is discrete using a uniform grid spacing of 0.3 Å and for the time evolution we use a time-step of $0.002\hbar$ eV^{-1} $\approx$ 0.0013 fs.

3. Results and discussion

The optimized ground-state configuration of an HCl molecule encapsulated in C_{60} is presented in Fig. 1 (panel (a)). The diameter of a sphere inscribed into C_{60} is roughly 7.09 Å, and the two different C–C bond lengths are 1.452 Å along pentagon edges and 1.392 Å along hexagon edges. The H–Cl bond is along the Z axis. We mainly investigate the dynamics of an HCl molecule with the short pulse shown in Fig. 1(b). We perform calculations by setting the polarization direction of the pulse, separately, to be parallel to the H–Cl bond, i.e., along the Z axis, and perpendicular to the H–Cl bond, i.e., along the Y axis. Our extensive calculations are also performed with the same shape but different strengths of the pulse in Fig. 1(b). The structure of C_{60} is found to be maintained when the maximum field strength is 12 V/Å and the laser intensity I is 1.9×10^{15} W/cm^2. Such a high intensity of the E-field is experimentally available. For example, the laser intensity I available experimentally for 5-fs duration is 4×10^{15} W/cm^2,[27] with corresponding electric field $E = 17.4$ V/Å according to the formula $I = 1/2\varepsilon_0 cE^2$, where ε_0 and c are the dielectric function of vacuum and the velocity of light, respectively.

We now investigate the dynamics of an HCl molecule encapsulated in C_{60} under the irradiation of the pulse shown in Fig. 1(b) with polarization direction parallel to HCl molecule axis. Figure 2 shows the snapshots of deformation

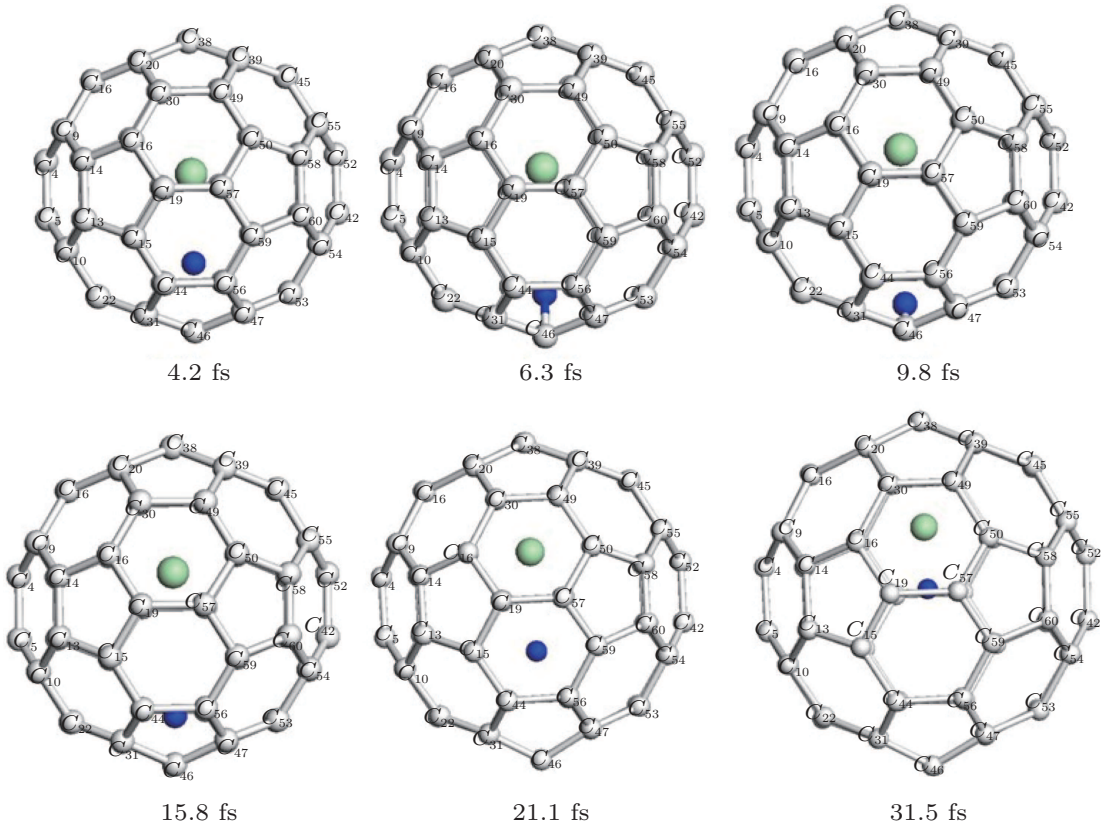


Fig. 2. (color online) Deformation of the C_{60} and dynamics of an HCl molecule under the pulse of Fig. 1(b) with polarization direction parallel to the H–Cl bond (Z axis). The biggest ball denotes the Cl atom, the second biggest ball refers to the H atom, and the remaining balls (with numbers) represent the C atoms.

of the C_{60} and dynamics of an HCl molecule at different moments. The initial velocity of the HCl molecule is negligibly small compared with the velocity induced by the laser pulse. After the time evolution, the H atom starts to leave the Cl atom with the orientation along Z axis (paralleling to the pulse). In addition, chemical bonds should be formed between the H atom and the C_{46} (C_{27}) atom with a minimal bond length of 0.93 Å (0.94 Å) at 9.8 fs. The collision takes place between the C_{46} and C_{27} atoms. Then H atom is reflected by the C_{60} wall. The incident angle of the H atom with respect to C_{60} wall is just 90°. On the other hand, the Cl atom does not obtain considerable kinetic energy compared with the H atom. As we can find from Fig. 2, the orders of occupied and empty bands are alternated and this alternation tends to dissolve the indicated recovery of electronic ground state at early time of pulse irradiation. We obviously find that the significant expansion of the diameter of C_{60} presents asymmetric distortion in the radial direction. In other words, the diameter of C_{60} in the direction parallel to pulse irradiation is larger as expected. A similar expansion was found in the nanotube in the radial direction.[14]

To gain more insight into the dynamics of an HCl molecule encapsulated in C_{60}, we examine the influence of the pulse (Fig. 1) with the polarization perpendicular to the H–Cl bond, i.e., along the Y axis. As shown in Fig. 3, the H atom again leaves Cl with the orientation roughly along Y axis if negligible displacement is ignored. Then the H atom is also reflected by the C_{60} wall and the minimal distance between C atom (C_6) and the ejected H atom is 0.87 Å in this case, causing strong reflection, while this distance is much longer (0.93 Å) in Fig. 2. Meanwhile, the radial oscillation appears after the pulse has decayed. Calculations for our system have also been performed with the same shape as but different strengths of the pulse from their counterparts in Fig. 1, which shows qualitatively similar results. In the beginning of pulse irradiation, the dynamics of the HCl molecule is found to be almost the same as the case of an isolated HCl molecule with the same pulse irradiation. This manifests no interference between the electronic excitations of the C_{60} and the HCl molecule. At the end of the simulation the internuclear H–Cl is larger than 3.3 Å, providing evidence for the complete fragmentation of the HCl molecule.

Figure 4 shows the time evolutions of kinetic energy of H and Cl atoms for the dynamics of an HCl molecule in isolation and in C_{60} under the pulse of Fig. 1(b). Figures 4(a) and 4(b) correspond to the polarization directions parallel and perpendicular to the H–Cl bond, respectively. At a very early time of pulse irradiation, the H (Cl) atom obtains almost the same kinetic energy for the HCl molecule both in isolation and inside C_{60} under the same pulse. Starting from about 2 fs, the kinetic energy of the H (Cl) atom in C_{60} was slightly higher than that of H (Cl) atom in isolatation until 4.3 (9.0) fs in Fig. 4(a) (Fig. 4(b)). These differences can be qualitatively attributed to the competition between intra-atomic confinement and inter-atomic coupling. A comparison between Figs. 4(a) and 4(b)

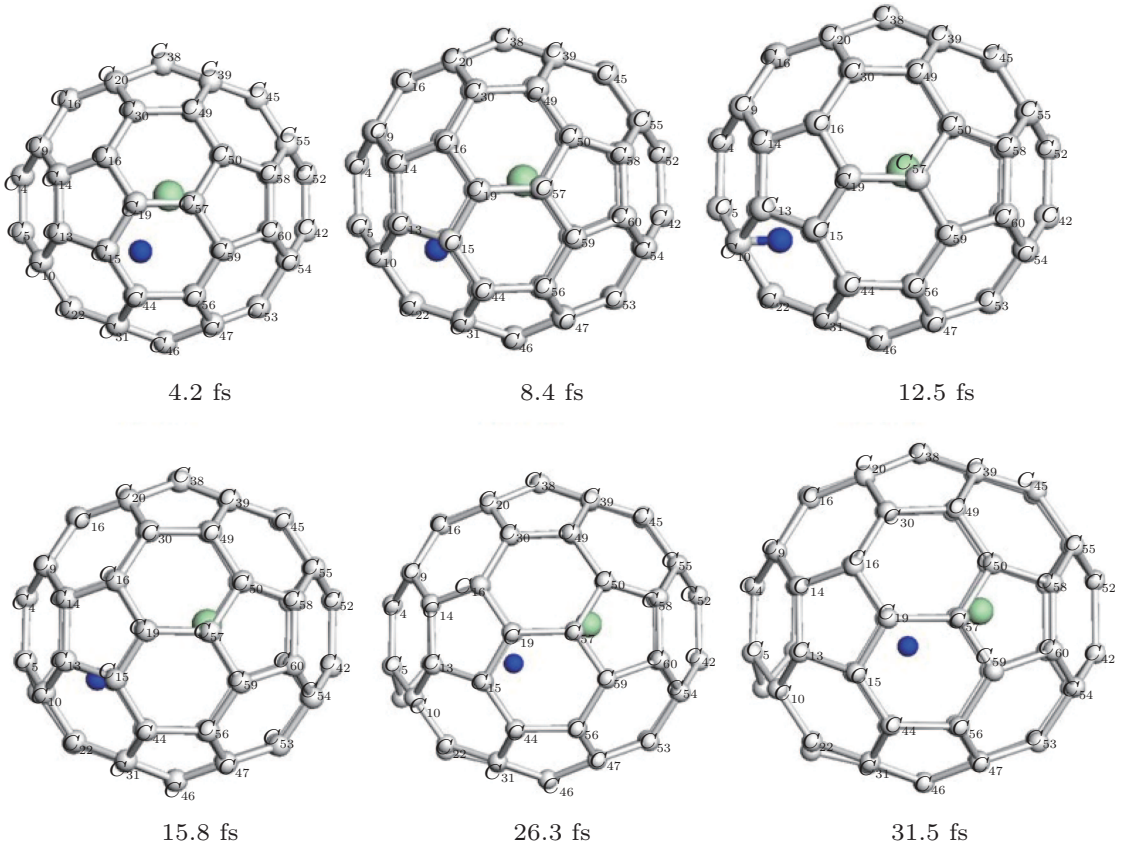


Fig. 3. (color online) Deformations of the C_{60} and dynamics of an HCl molecule under the pulse of Fig. 1(b). The polarization direction of the pulse is perpendicular to the H–Cl bond, along the *Y* axis. The biggest ball denotes the Cl atom, the second biggest ball refers to the H atom, and the remaining balls (with numbers) represent the C atoms.

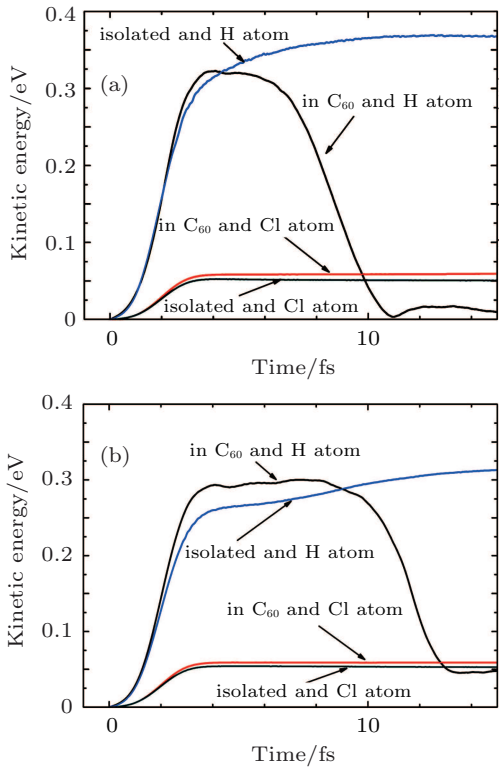


Fig. 4. (color online) Time evolutions of kinetic energies of H and Cl atom for the dynamics of HCl molecule in isolation and in C_{60} under the pulse in Fig. 1(b). The directions of pulse irradiation are parallel (a) and perpendicular (b) to the H–Cl bond (*Z* axis).

shows that in the case of the pulse orientation parallel to the molecule axis the kinetic energy of the H atom inside C_{60} is 0.03 eV higher than that in the case of the pulse orientation perpendicular to the molecule axis, while the Cl atom obtained almost the same kinetic energy in the two cases. This suggests that the kinetic energy given to the H atom is dependent on the pulse polarization direction. Similar dependences were found in Ref. [28]. During the time interval of 0–3 fs, the rate of decline for the kinetic energy of the H atom inside C_{60} in Fig. 4(b) would be gentler than that in Fig. 4(a). Meanwhile, the kinetic energy of the H atom inside C_{60} in Fig. 4(a) is close to zero at 10.9 fs, but not in Fig. 4(b). This difference can be understood from the incident angle of the H atom with respect to the C wall. This again confirms that the incident angle is 90° for the pulse parallel to the molecule axis and less than 90° for the pulse perpendicular to the molecule axis.

In order to further investigate the mechanism of the dynamics of the HCl molecule under a femtosecond laser pulse, we analyze the H–Cl bond lengths in isolation and in C_{60} with different irradiation intensities and polarization directions as shown in Fig. 5. We focus on the initial velocity of the H–Cl elongation as a measure of pulse intensity. We can observe that the initial velocities of the H–Cl elongation are the same as

those of isolated HCl molecules with an irradiation intensity of 1.9×10^{15} W/cm^2, while the initial velocities are faster (at an irradiation intensity of 3.4×10^{15} W/cm^2). Such a dependence of intensity on initial velocity is a common phenomenon. During some time interval, the curves of the H–Cl bond lengths suggest that relaxation time in transverse polarization is slow in comparison with in longitudinal polarization. As shown in Figs. 2 and 3, the H atom is reflected by the C_{60} wall and moves back. Afterwards, the C_{60} should start to shrink and recover to its ground state.

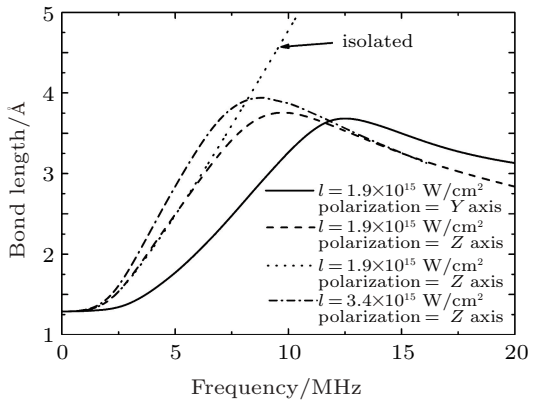


Fig. 5. Time evolutions of H–Cl bond lengths in isolation and in C_{60} with the pulse of Fig. 1(b). The intensity and the polarization direction are indicated in the bottom right corner. The dotted line denotes the isolated case, while the other three lines represent the case inside C_{60}.

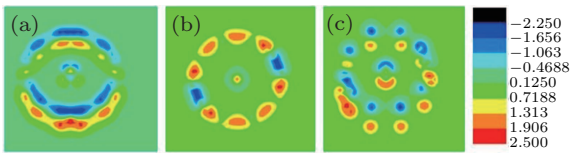


Fig. 6. (color online) Charge density redistributions at $t=9.8$ fs. The redistribution is obtained by subtracting charge density at $t=0$ from that at $t=9.8$ fs. The pictures obtained through XZ plane (a) and XY plane (b) under the polarization direction parallel to Z axis, but picture (c) is obtained through XY plane under the polarization direction parallel to Y axis. In all the cases, the simulations are the pulse of Fig. 1(b).

The dynamic charge density redistributions are monitored with the polarization directions: along the Z axis and the Y axis. As shown in Fig. 6, the picture in Fig. 6(a) is obtained through the XZ plane and the picture in Fig. 6(b) is obtained through the XY plane under the polarization direction parallel to the Z axis, while the picture in Fig. 6(c) is obtained through the XY plane under the polarization direction parallel to the Y axis. The pictures of charge redistribution are taken at $t=9.8$ fs, which is the moment when the H–C bond in minimal. The redistribution is obtained by subtracting charge density at $t=0$ from that $t=9.8$ fs, i.e., $\rho(\boldsymbol{r},t=9.8\text{ fs})-\rho(\boldsymbol{r},t=0\text{ fs})$. When the plane of the charge density redistribution is parallel to the polarization direction of the pulse, such as Figs. 6(a) and 6(c), the negative charge tends to spread upward from the original position of C_{60}, which is consistent with the history of the decayed pulse, with average polarity pushing negative charge in that direction. Meanwhile, for the polarization plane shown in Fig. 6(b), we obtain the cross section of positive charge distribution around C atoms as a result of the negative charge spreading upward from the original position of C_{60}. The negative charge density point occurs at the position where the overlap takes place between the static state charge density and the time evolution of charge density.

4. Conclusions

We investigated in detail the photo-induced dynamics of an HCl molecule encapsulated in C_{60} under the irradiation of a short laser pulse with the polarization direction parallel and perpendicular to the H–Cl bond separately. The coherent nuclear dynamic behaviors of bond breakage and recombination of the HCl molecule occurring in both cases are studied. The significant expansion of C_{60} structure and the vector of H atom movement are found to be dependent on the polarization direction of the pulse. The relaxation time of the H–Cl bond length in transverse polarization is hysteresis in contrast with longitudinal polarization. This fact hints at efficient hydrogen extraction from hydrogenated molecules of any kind. The control of various parameters, such as shape, intensity, frequency, and type of molecules, would offer us the different photo-induced dynamics. We hope that the results presented here will help to highlight further experiment study.

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