Electron localization in laser-driven H_3^{2+}

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[**Introduction**] It would be extremely useful if individual valence electrons could be moved in a controllable way from one place to another in a molecule. In this way, chemical bonds could be formed and/or broken at will. Intense, few-cycle laser pulses are a rather new tool which has the possibility to achieve this ambitious aim. Intense is here used to mean laser pulses with an intensity around 10^{14} W/cm² (peak electric field around 10 GV/m). At this high field strength, a large fraction of the valence electron density is influenced; it becomes possible to significantly displace (almost) the whole electron wave function. This is rather different compared to the situation when weak fields are used and only a perturbatively small part of the wave function is affected. Few-cycle implies that the laser-molecule interaction is sensitive to the detailed shape of the electric field such as the carrier-envelope phase (CEP).

In this contribution, we show theoretically that the intra-molecular motion of the bound electron in the molecular ion H_3^{2+} can be controlled by driving the dissociating molecule with a few-cycle, CEP stable intense laser pulse of circular polarization. By varying the value of the CEP, it is possible to select which one of the protons the electron finally binds to in the reaction $H_3^{2+} \rightarrow H^+ + H^+ + H$. Our results extends direct electric field control of electron localization within a molecule to triatomic systems. This kind of control scheme was previously applied to diatomic molecules only [1,2].

[**Theoretical model**] Before the interaction with the laser pulse, the H_3^{2+} molecular ion is assumed to be in the electronic ground state, with the nuclear wave function given by the lowest vibrational state of H_3^+. This situation can be achieved by ejecting one electron from the stable H_3^+ by (for example) an attosecond pulse. The vertical ionization potential is 34 eV. In order to simplify the situation, we furthermore assume that the D_{3h} (equilateral triangle) symmetry of H_3^+ is conserved during the interaction with the laser field. This means that the wave function depends on only one nuclear coordinate, R. Note that this assumption restricts the possible dissociation channels to $H_3^{2+} \rightarrow H^+ + H^+ + H$. At each value of R, we include the three energetically lowest adiabatic electronic states $\psi_n(\boldsymbol{r}, R)$, $n = 1, 2, 3$. Field ionization is not included in the model. The total wave function is thus assumed to be written as

$$\Psi(\boldsymbol{r}, R, t) = \sum_{n=1}^{3} \psi_n(\boldsymbol{r}, R)\chi_n(R, t). \tag{1}$$

By taking an appropriate superposition of the adiabatic eigenstates $\psi_n(\boldsymbol{r}, R)$, we obtain electronic states $\widetilde{\psi}_n(\boldsymbol{r}, R)$ that are localized at either one of the three protons in the limit of large R.

A summary of the theoretical model is shown in Fig. 1.

[**Results and discussion**] Since the three states $\psi_n(\boldsymbol{r}, R)$ are repulsive [see Fig. 1(b)], H_3^{2+} necessarily dissociates. During the dissociation, we drive the molecule with a circularly polarized laser pulse of the form

$$\boldsymbol{E}(t) = E_0 \sin^2(\pi t/\tau) \left[\hat{\boldsymbol{x}} \cos(\omega t + \varphi) + \hat{\boldsymbol{y}} \sin(\omega t + \varphi)\right], \tag{2}$$
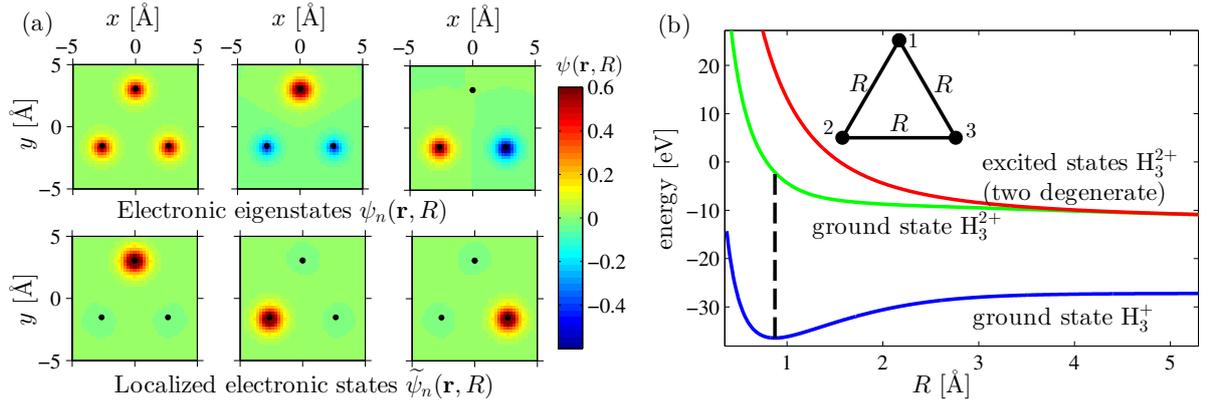
Figure 1: (a) Electronic states at $R = 5.3$ Å. The color scale refers to the value of the wave function in units of Å$^{-3/2}$. (b) Potential energy curves of the adiabatic states ψ_n. Also shown is the electronic ground state of H$_3^+$. The vertical ionization potential H$_3^+ \to$ H$_3^{2+}$ is indicated with a broken, vertical line.

where φ is the CEP. The laser pulse is thus assumed to be polarized in the same plane as the orientation plane of the H$_3^{2+}$ molecule. A laser wavelength of 800 nm and an intensity of around 10^{14} W/cm^2 are employed. The time-dependence of the wave function (1) is calculated by solving the Schrödinger equation for the nuclear wave functions $\chi_n(R, t)$, including the laser-induced dipole couplings. In the talk, it will be shown that by varying the value of φ, we can selectively populate the localized electronic states $\widetilde{\psi}_n$. This means that after the interaction with the laser pulse, the probability for the ejection of an H atom in the positive y direction is different from the probability of ejection in the negative y, negative x direction or negative y, positive x direction. In order to quantify the asymmetry induced by the laser pulse, we introduce the asymmetry measure A, defined as

$$A = P_1 + e^{i2\pi/3}P_2 + e^{-i2\pi/3}P_3, \tag{3}$$

where P_n is the probability that the final electronic state is $\widetilde{\psi}_n$ (the probability that the electron binds to proton n). $A = |A|e^{i\alpha}$ is a complex number, where the amplitude $|A|$ indicates the overall amount of localization: $|A| = 0$ signifies a completely delocalized electron [such as the ground state $\psi_1(\boldsymbol{r}, R)$, see Fig. 1 (a)], while $|A| = 1$ means that the electron is completely localized to one of the protons. The phase α tells us on which proton the electron is localized: $\alpha = 0$ indicates proton 1, $\alpha = 2\pi/3$ proton 2, $\alpha = -2\pi/3$ proton 3, and (for example) $\alpha = \pi/3$ signifies an electron distributed equally on proton 1 and 2.

As a main result of this investigation, we find that by changing the CEP, the asymmetry amplitude $|A|$ can be made to vary periodically with φ (period $2\pi/3$), with a maximum value of ~ 0.5. The phase α changes with φ in a stepwise manner between the values $-2\pi/3$, 0 and $2\pi/3$. This result can be interpreted with a simple model: The proton to which the electron finally binds to is given by the direction of the laser force vector at a particular, critical instant t_c, when the coupling between the states ψ_n is most efficient.

[**References**]
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