

Enhanced ionization of acetylene in strong laser fields

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Introduction. Among recent investigations concerning the ionization of molecules with intense laser light, especially noteworthy are the results presented in Ref. 1. In this experiment, long-wavelength (790 nm), high-intensity ($\sim 10^{15}$ W/cm²) laser pulses of comparatively long duration (27 fs) were employed to ionize small hydrocarbon molecules (CH₄, C₂H₄, C₄H₆ and C₆H₁₄). Surprisingly, it was found that the molecules could be ionized to extremely high charge states. As an example, up to 14 electrons could be removed from 1,3-butadiene. Two conclusions can be drawn from the experimental data in Ref. 1. The first is that the kinetic energy release spectra of the emitted protons is consistent with the Coulomb explosion of the highly charged precursor ion occurring at twice the equilibrium C–H distance. This implies that the main part of the ionization takes place not in the equilibrium configuration, but when the C–H distance is stretched. In addition, many electrons have to be ejected essentially at the same time, since otherwise the protons would end up with lower kinetic energy. For diatomic molecules, the phenomenon of enhanced ionization at a particular internuclear distance is well established [2,3], but for polyatomic molecules a similar mechanism has not yet been thoroughly discussed. The second observation is that, for all of the investigated molecules, the average total charge state measured agrees with that two electrons are lost per C–H bond. It is therefore possible that the observed efficient ionization is common to all hydrocarbon molecules, with the number of ejected electrons being twice the number of C–H bonds in the molecule.

In this contribution, we aim to clarify the experimental findings in Ref. 1. With a simple theoretical model of a hydrocarbon molecule, we confirm that ionization is indeed enhanced when the C–H distance is stretched to twice the equilibrium value.

Theoretical model. For the first confirmation of the mechanism, it is desirable to find a model that is as simple as possible, but still contains all the physics necessary to understand the process. As the target molecule, we choose acetylene (C₂H₂), which is a hydrocarbon molecule with multiple C–H bonds. Because acetylene is a linear molecule, and the electrons are predominantly driven along the laser polarization direction in a strong laser field, we restrict the electronic motion to one spatial dimension, so that this direction coincides with the molecular axis and the laser polarization direction. The positions of the nuclei are kept fixed during the calculation. To describe the time evolution of the system, we employ the time-dependent Hartree-Fock equations in atomic units (a.u.),

$$i \frac{\partial \psi_n(x, t)}{\partial t} = \left[-\frac{1}{2} \frac{\partial^2}{\partial x^2} + V(x) + xE(t) + 2\hat{J} - \hat{K} \right] \psi_n(x, t), \quad (1)$$

for the spatial orbitals $\psi_n(x, t)$ ($n = 1, \dots, 7$). A closed shell electronic configuration is assumed. In Eq. (1), $V(x)$ is the soft-core nuclear potential, $E(t)$ is the electric field of the laser pulse, and \hat{J} and \hat{K} are the Coulomb and exchange operators, respectively. By adjusting the soft-core parameters of the model, we can reproduce the ground state potential energy surface of the three-dimensional molecule, as shown in Fig. 1.

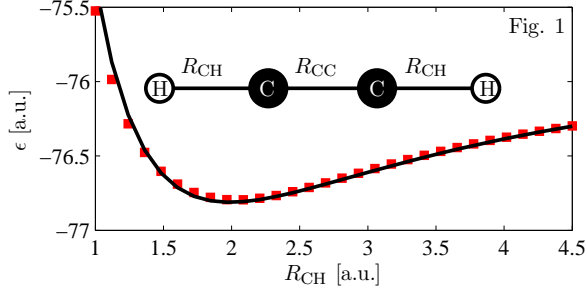


Figure 1: Total energy ϵ as a function of the C–H distance R_{CH} , for fixed C–C distance $R_{\text{CC}} = 2.2$ a.u. The potential energy surface obtained with the one-dimensional model [Eq. (1)] is shown with red squares, and that obtained with GAMESS [4] for three-dimensional acetylene is shown with a solid black line.

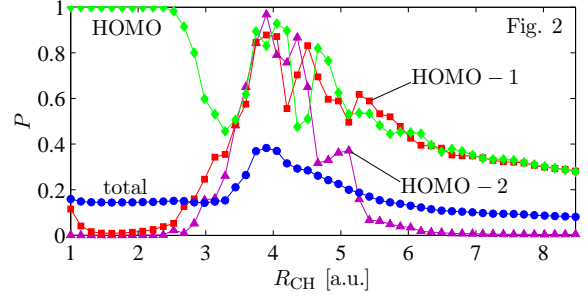


Figure 2: Ionization probability P for the three highest occupied molecular orbitals as a function of the C–H distance. Also shown is the total ionization probability.

Results and discussion. We have solved Eq. (1) numerically, with a laser field of intensity $I = 1.4 \times 10^{15}$ W/cm², wavelength $\lambda = 760$ nm, and pulse length $T = 12.5$ fs, for different values of the C–H distance. The results are shown in Fig. 2, where we show the ionization probability as a function of the C–H distance. Here the orbital ionization probability P_n and the total ionization probability P_{tot} are defined as $P_n = 1 - \eta_n(\tau)$, $P_{\text{tot}} = 1 - \sum_{n=1}^7 \eta_n(\tau)/7$, with $\eta_n(\tau) = \int_{-y}^y |\psi_n(x, \tau)|^2$, $y = 30$ a.u., and $\tau = 3T$.

We see that at the equilibrium C–H distance $R_{\text{CH}} = 2$ a.u., only the HOMO is ionized. Since removing the HOMO implies that the C–H bond is weakened, in a more realistic model where the nuclei are allowed to move, this would mean that the C–H bond starts to stretch. At twice the equilibrium value of R_{CH} , ionization is strongly enhanced. Not only the electrons in the HOMO and HOMO – 1, but also the electrons in the third highest occupied molecular orbital are ejected with a high probability. In total, on average 6 electrons are lost from the molecule, leaving a molecular ion with charge state +6 behind.

The mechanism of the enhanced ionization can be explained in terms of the localization of the electron density to the protons. After concentration of the electron density of an orbital to one of the protons, electron ejection proceeds efficiently by tunneling through the thin barrier created by the combined nuclear and laser electric field. Also an electron in the HOMO–2, which is initially localized to the area in between the two carbon atoms, is ejected from the molecule after first being spatially localized to one of the protons during one half-cycle of the laser pulse.

A very similar mechanism for enhanced ionization has been discussed for H_2^+ [2,3]. The difference is that in the present case, we have four nuclear centers instead of two. Furthermore, in the case of C_2H_2 , we have three orbitals (six electrons) that are strongly influenced by the laser field, instead of only one in H_2^+ .

References.

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