

Enhanced ionization of acetylene in intense laser pulses is due to energy upshift and field coupling of multiple orbitals

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Synopsis We describe a new enhanced ionization mechanism for polyatomic molecules. It works via a significant energy up-shift of valence orbitals for stretched bonds and a strong concomitant increase in the coupling between multiple molecular orbitals.

Laser-ionization of molecules is one of the most important processes in the strong-field and attosecond sciences. A key mechanism governing molecular ionization is enhanced ionization, where for diatomic molecules the ionization probability becomes strongly enhanced at a critical internuclear distance [1,2].

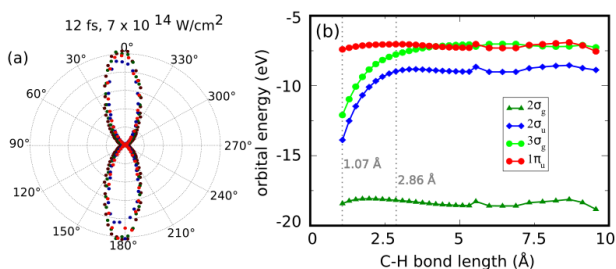


Figure 1. (a) Polar plots of measured proton yields ejected from $C_2H_2^{2+}$ during four-body fragmentation into $C^m/C^n/H^+/H^+$, $z=m+n+2$. Laser parameters are indicated, polarization direction vertical. Colours brown, green, blue and orange indicate charge states $z=\{+4,+5,+6,+7\}$. (b) Binding energy of the four most loosely bound valence orbitals as a function of the C-H internuclear distance (symmetric stretch mode) calculated by DFT.

Experiments on polyatomic molecules have revealed remarkably high charge states and indicated the existence of a different ionization-enhancement mechanism [3-5]. However, until now this mechanism has not been fully understood and has been a subject of intense debate.

We present the results of a combined experimental and numerical study on strong-field ionization of acetylene performed with the aim of identifying the mechanism behind the reported surprisingly large multi-electron ionization probabilities of polyatomic molecules [3-5]. Using coincidence momentum imaging techniques

and TDDFT simulations, we show that the strong ionization enhancement measured for molecules aligned parallel to the laser polarization [Fig. 1(a)] is due to the combined action of (i) a significant energy up-shift of the most relevant valence orbitals as the C-H distance increases [Fig. 1(b)], and (ii) a concomitant strong increase in the coupling between multiple molecular orbitals. Both processes lead to a strong effective reduction of the binding energy and an enhancement of the emission probability for lower-valence orbitals, making their ionization contributions even the dominant ones. For molecules aligned perpendicularly to the laser polarization direction this mechanism is inhibited because of a dominant emission of π electrons at low charge states, which in turn suppresses the C-H stretch motion and therewith prohibits entering the regime of the enhanced ionization.

To express these two key-ingredients in this mechanism we refer to it as EIC-MOUSE (Enhanced Ionization from laser-Coupled Multiple Orbitals that are Up-Shifted in Energy). We argue that the EIC-MOUSE mechanism, which – as we will show in our presentation – is different from the usually considered CREI mechanism [1,2] in many ways, is relevant for a large class of polyatomic molecules.

References

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