

Supplemental Material

The observed enhancement of multiple ionization in CHD could potentially be related to the phenomenon of enhanced ionization previously reported in strong-field ionization of diatomic molecules [22, 23]. A pair of charge resonant states [24] coupled by the field can form an asymmetric distribution of the charge around the two nuclei, which can enhance ionization. The stretching of the internuclear separation by the strong field leads to localization of the bonding electron and enhanced tunnel ionization [22, 25]. It is possible that a similar situation arises in the enhanced ionization of the CHD. In the case of CHD the distortion of the molecular geometry from the equilibrium occurs upon UV excitation. Although in the case of the CHD the distortion of the molecular geometry is not as simple as extension of one bond, for the purpose of examining the effect the geometry change can have on the electron localization and consequently enhanced ionization, we will consider primarily the increase in the bond length between the two C atoms between which the bond breaks during the ring opening.

The extension of this idea to polyatomic molecules employs the concept of broken symmetry: When the molecular geometry changes following UV excitation, the original approximate C_{2v} symmetry is broken, and the dipole coupling between S_1 and S_0 may therefore increase (see Fig. S1). Although a full analysis of this is beyond the scope of this paper, we have made a preliminary calculation. The transition dipole moment in Fig. S1 was calculated using the ab initio multiple spawning (AIMS) method, implemented over some 70 runs [18]. The trajectories were population weighted and each run contributed equally. At the conical intersection S_1 and S_0 are degenerate, and the coupling by the field is strongest. If the two C atoms between which the bond breaks are oriented along the field, this coupling can result in an asymmetric distribution of the charge around the uphill and downhill carbons. When the ring starts to open, the increase in the internuclear distance between the two carbons in this proposed mechanism results in a localization of the charge in presence of the strong field on one of the carbons. This localization enables tunneling that enhances the ionization. It is possible that the distortion of other bond lengths and angles contributes to the localization. A calculation of geometry of neutral and cation carried out with SA-2-CAS(6/6)-MSPT2/6-31G* and SA-2-CAS(5/6)-MSPT2/6-31G* methods, respectively, finds a conical intersection in the CHD cation in the vicinity of the geometry for the conical intersection in the neutral (see Fig. S2). A small distortion between these two geometries can easily occur in the strong field. This finding supports a similar mechanism for removal of the second electron.

It is also interesting to consider the possibility of two electrons being ejected simultaneously in the presence of the strong field. When the initial and the final state in the ionization are calculated in its own self-consistent framework [26] there will be non-zero overlaps for double ionization, which only increase in presence of electron correlation. In that case the term in the Hamiltonian for ejection of electrons e_1 and e_2 from orbitals ϕ_1 and ϕ_2 into the continua ε_1 and ε_2 is:

$$\langle \phi_1(e_1) | \dot{E}(t) \cdot \hat{r}_1 | \varepsilon_1(e_1) \rangle \langle \phi_2(e_2) | \varepsilon_2(e_2) \rangle + \langle \phi_1(e_2) | \dot{E}(t) \cdot \hat{r}_2 | \varepsilon_1(e_2) \rangle \langle \phi_2(e_1) | \varepsilon_2(e_1) \rangle, \quad (1)$$

and the observed signal will contain cross terms between the two parts. The cross terms would be maximized when the two parts are of comparable magnitude, which could occur in the vicinity of the conical intersection when strong field coupling leads to charge separation.

Ab initio modeling of strongly nonadiabatic systems in strong fields is currently state of the art. We hope that the experimental observations reported here will be important in testing future models of strong-field ionization of photoexcited polyatomic molecules. The dominant processes in the interaction between atoms and strong laser fields are explained in a framework that uses a single active electron [30-32]. This is the case for non-sequential double ionization as well, where the first emitted electron accumulates enough kinetic energy in the ponderomotive potential of the strong laser field to eject a second electron during a rescattering [33]. Such rescattering may play a role in the explanation of the double ionization enhancement described here, but we cannot rule out a process that requires a breakdown of the single electron approximation. Previously reported quantum resonance rings [28], which arise from strong-field dressing of the crossing states in the vicinity of conical intersections, potentially play an additional role. Future experiments that benefit from higher time resolution and variation of the strong-field laser parameters will help understand the mechanism of the enhanced strong-field multiple ionization in the vicinity of conical intersections.

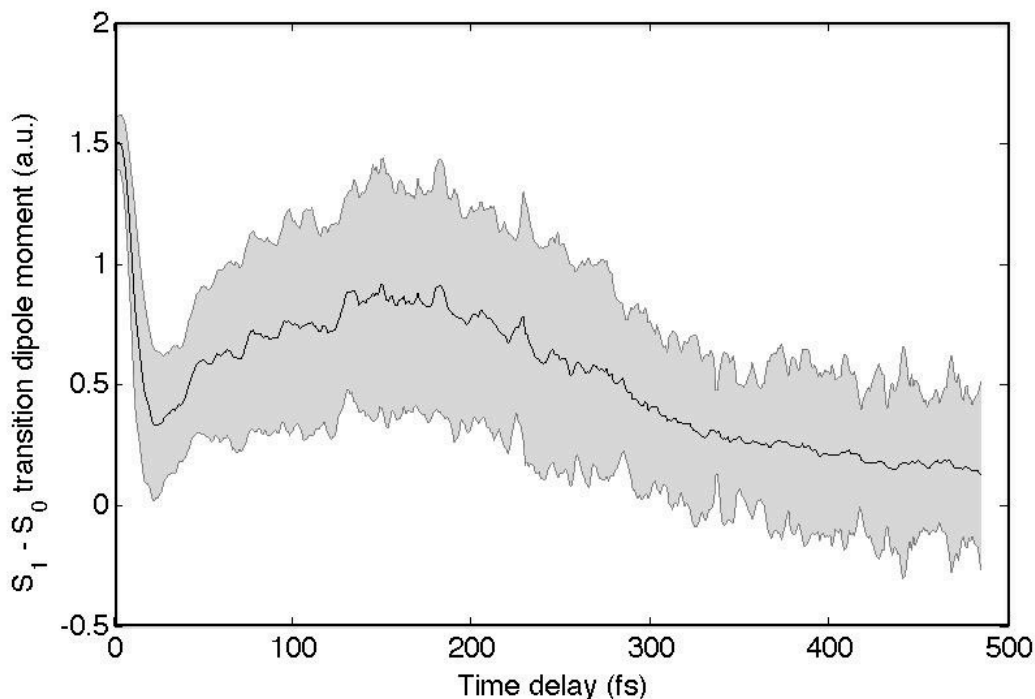


Fig. S1 Transition dipole moment between S_1 and S_0 states as a function of time delay upon the UV excitation, calculated using Ab Initio Multiple Spawning technique (see text for more details).

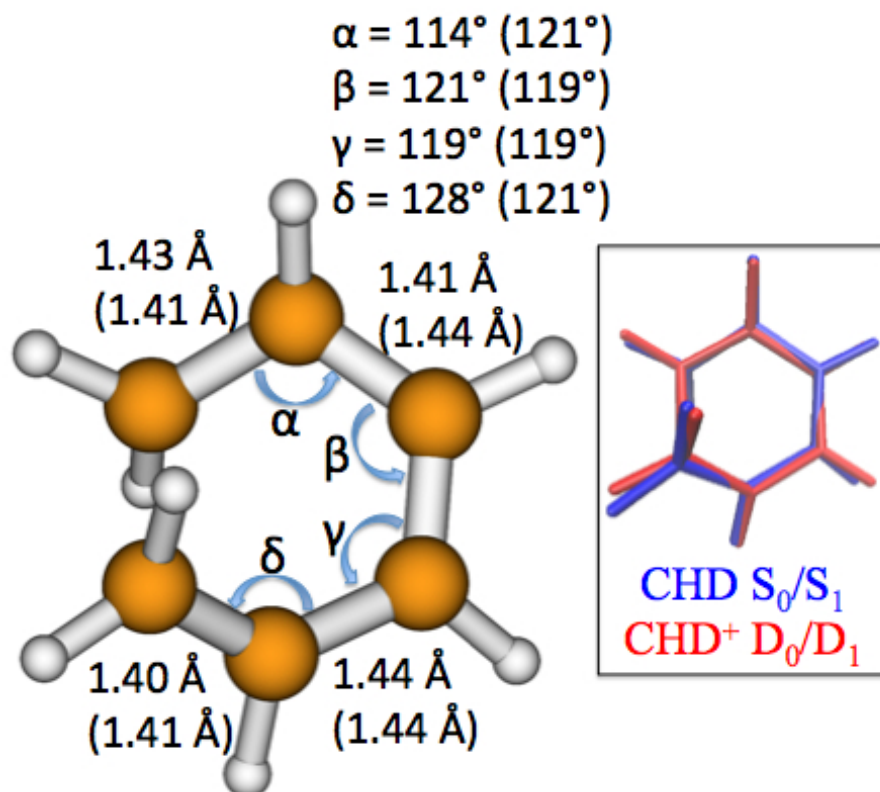


Fig. S2 The geometrical parameters of neutral and cation CHD at minimum energy conical intersection for S_1/S_0 and D_1/D_0 , respectively. The cation parameters are shown in parentheses. The neutral and cation calculations were carried out with SA-2-CAS(6/6)-MSPT2/6-31G* and SA-2-CAS(5/6)-MSPT2/6-31G* methods, respectively. The inset shows a comparison of the geometries of the neutral (blue) and cation (red) CHD.