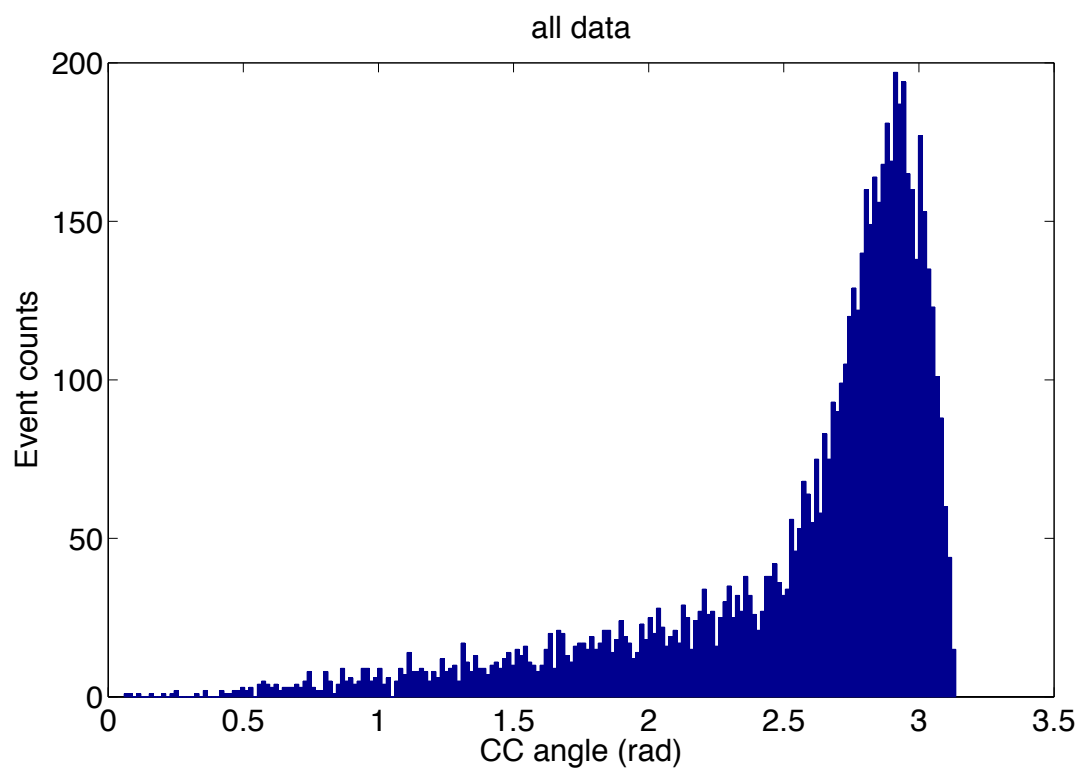
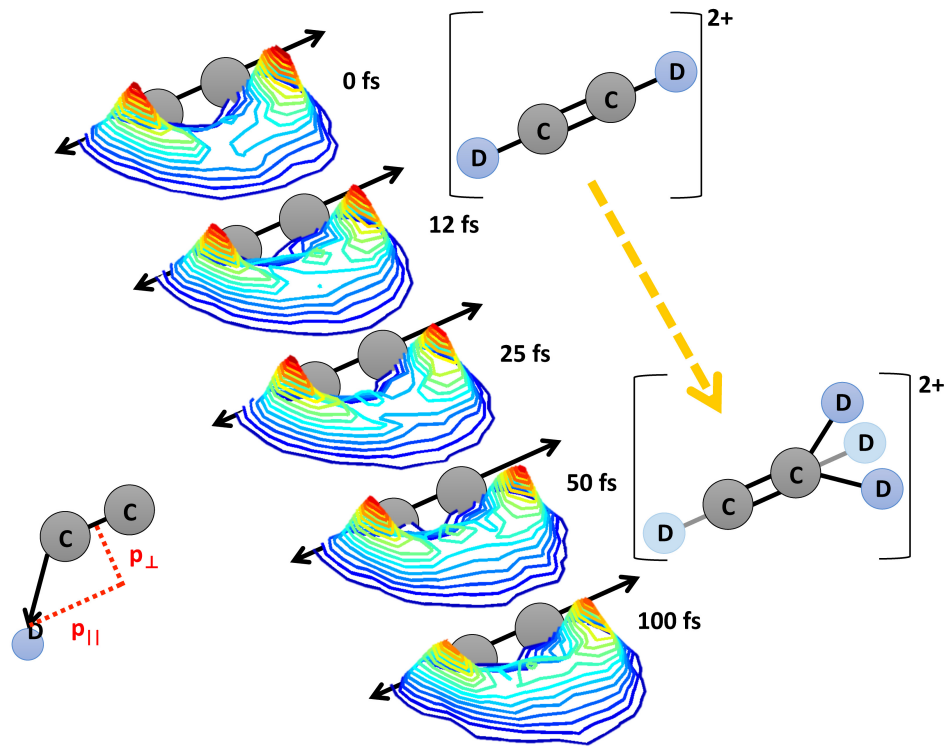


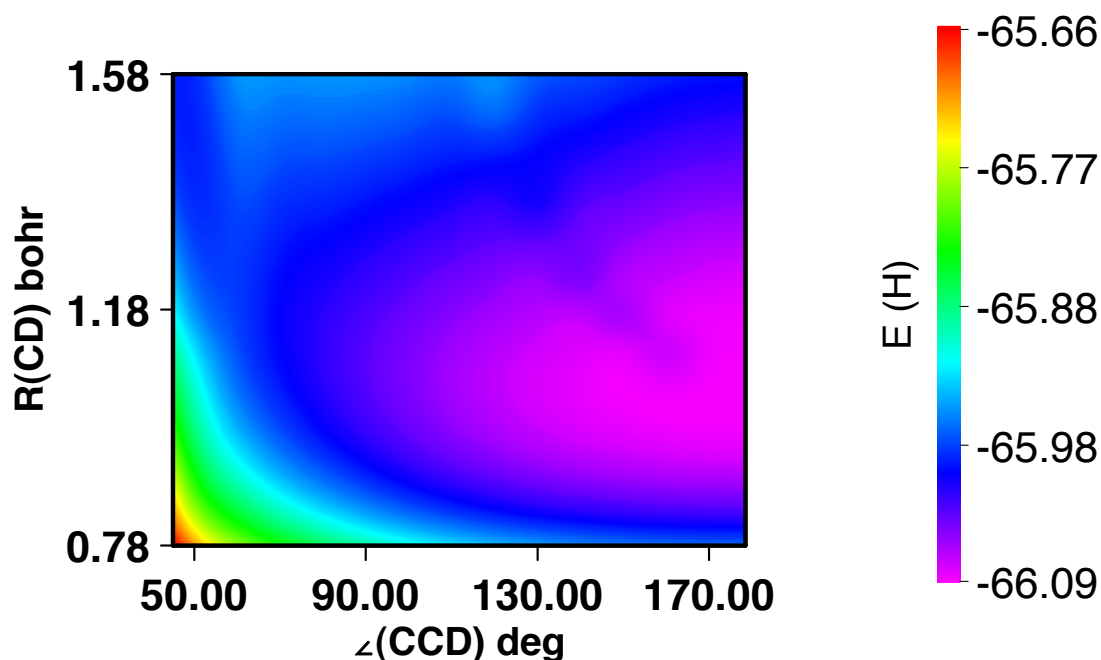
Supplementary Figures



Supplementary Figure 1. Carbon fragment momenta. Plotted is the distribution of angles among the two carbon fragments defining the effective C-C axis.



Supplementary Figure 2. Temporal evolution of the deuteron momenta in three-particle coincidences. Similar to Fig. 3 in the main text, but for events in which only three particles, C^+ , C^+ , and D^+ , are detected: temporal evolution of the distribution of the deuteron momentum components parallel and perpendicular to the C-C axis at 0 fs (a), 12 fs (b), 25 fs (c), 50 fs (d) and 100 fs (e). Three particles are detected more often than all four, resulting in a larger number of events for analysis. However, with only three particles the requirement that the momentum sum is near zero cannot be used as a filter. This leads to a larger dilution of the signal with false coincidences as compared to Fig. 3.



Supplementary Figure 3. Potential energy surface of the $^2\Sigma_u^+$ state of the 1s core-ionized $C_2D_2^+$. Potential energy is plotted as a function of the CCD bending angle and the CD internuclear distance ($^2\Sigma_g^+$ is almost isoenergetic; comparison to the potential energy of the $1\Sigma_g^+$ ground state of neutral given is in the main text, Fig. 3(i)). The potential energy surface of C_2D_2 was obtained at the Hartree-Fock (HF) level of theory using Dunning's double-zeta basis (DZP) [1]. For $C_2D_2^+$ we first carried out the HF/DZP calculation on the C_2D_2 ground state. We then started with two reference ion configurations, $(1a'12a'^23a'^24a'^25a'^21a''^22a''^2)$ and $(1a'^22a'^13a'^24a'^25a'^21a''^22a''^2)$, with a single vacancy in the C1s orbital, and performed an all-singles configuration-interaction calculation, constraining the maximum combined electron occupancy of the core molecular orbitals, $1a'$ and $2a'$, to three. Note that the bond distances and angles, other than those being plotted, are fixed at the equilibrium geometry of the neutral C_2D_2 . Evolution of the molecular geometry begins on this potential energy surface prior to Auger relaxation. Increased flexibility of the bending mode in core-ionized acetylene could facilitate geometry change during the Auger lifetime. Auger lifetime of the 1s hole in carbon is approximately 6 fs [2].

Supplementary References

- [1] Dunning, T. H., Gaussian basis functions for use in molecular calculations. I. Contraction of (9s5p) atomic basis sets for the first-row atoms. J. Chem. Phys. 53 2823 (1970).
- [2] Schlachter, S. et al. Lifetime of a K-shell vacancy in atomic carbon created by $1s \rightarrow 2p$ photoexcitation of C^+ . J. Phys. B 37, 103 L103 (2004).