

## Supporting Information

Electron-Withdrawing Effects in the Photodissociation of  $\text{CH}_2\text{ICI}$  To Form  $\text{CH}_2\text{CI}$  Radical,  
Simultaneously Viewed Through the Carbon K and Chlorine  $L_{2,3}$  X-ray Edges

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## Experimental Methods

In a typical transient absorption experiment, a neutral density filter combined with a 45-cm lens is used in the path of the pump beam to control the energy of 266 nm so that  $\sim 15\text{-}20 \mu\text{J/pulse}$  radiates on the sample gas, corresponding to peak intensity of  $3 \times 10^{11}\text{-}4 \times 10^{11} \text{ Wcm}^{-2}$  at the focus. The  $\text{CH}_2\text{ClI}$  introduced into the gas cell is heated to  $\sim 60 \text{ }^\circ\text{C}$  to obtain a vapor pressure of  $\sim 100 \text{ Torr}$ . The entire path is heated to prevent deposition at cold regions.

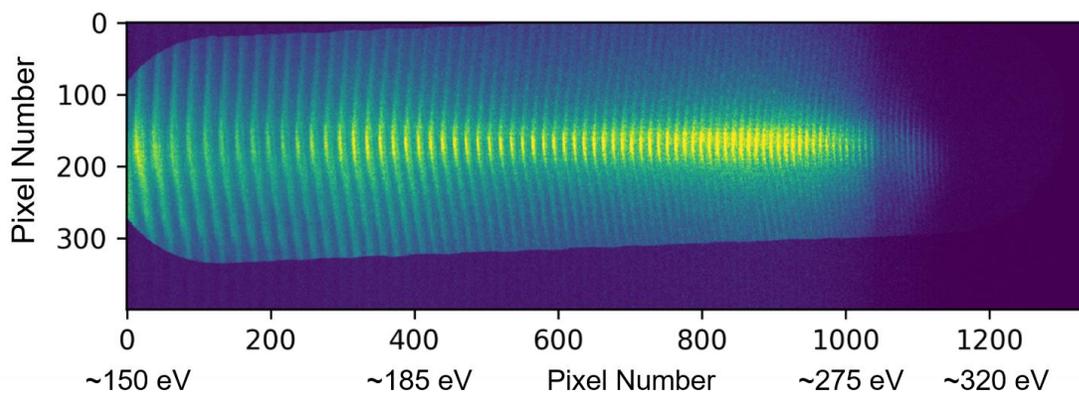


Figure S1. A chip image of the high harmonics generated, dispersed onto the 1340x400-pixel CCD camera. The energy range after calibration is as indicated along with the horizontal axis.

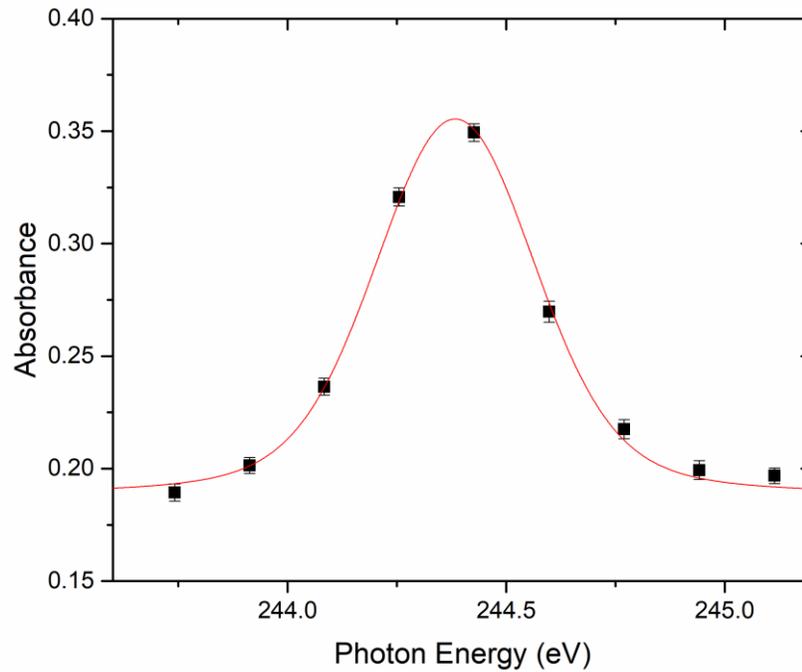


Figure S2. Determined spectral resolution ( $360 \pm 20$  meV). The peak represents the transition of  $2p_{3/2} \rightarrow 4s$  in argon which is fitted with a Voigt function with a Lorentzian width fixed at 120 meV, i.e. the reported core-hole lifetime of  $2p_{3/2}^{-1}$ .<sup>1</sup> The Gaussian width and the error thus obtained is taken as the spectral resolution of the apparatus.

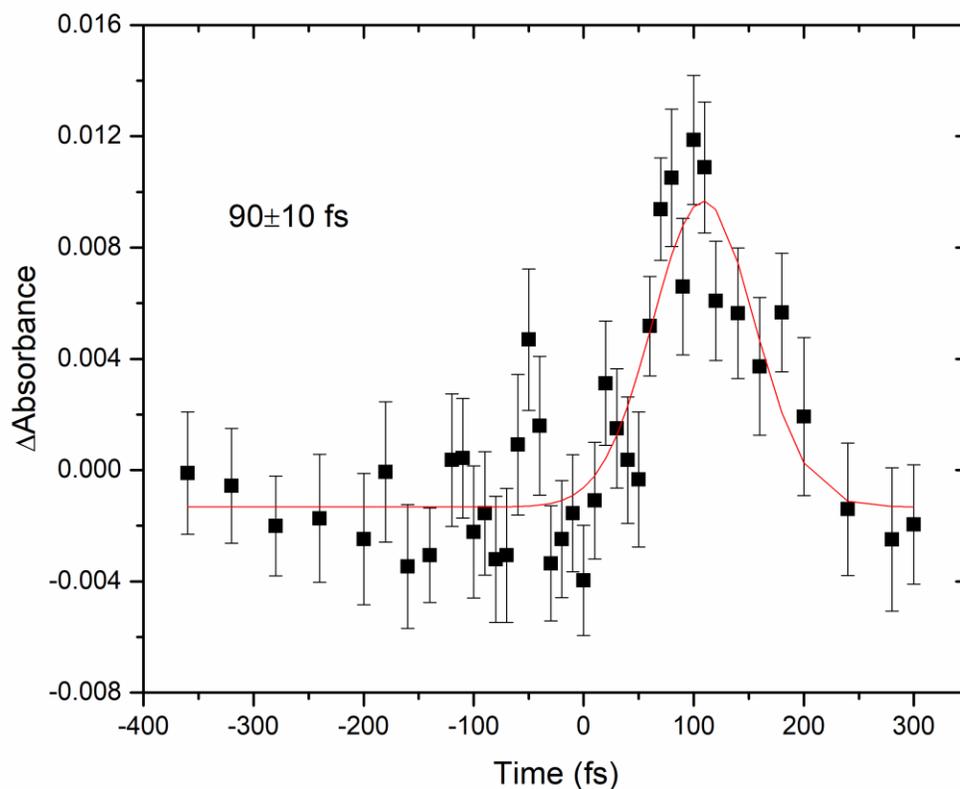


Figure S3. Temporal resolution determined by using the ponderomotive shift of the  $2p_{3/2} \rightarrow 4s$  transition<sup>1</sup> in argon in the presence of a strong UV field (i.e. 266 nm). The transition is slightly shifted in time from 244.4 eV to 244.6 eV when the soft-ray beam is overlapped with an intense UV beam and the figure plots the change in absorbance observed at 244.6 eV as a function of delay time between the two beams. The determination gives a temporal resolution of  $90 \pm 10$  fs.

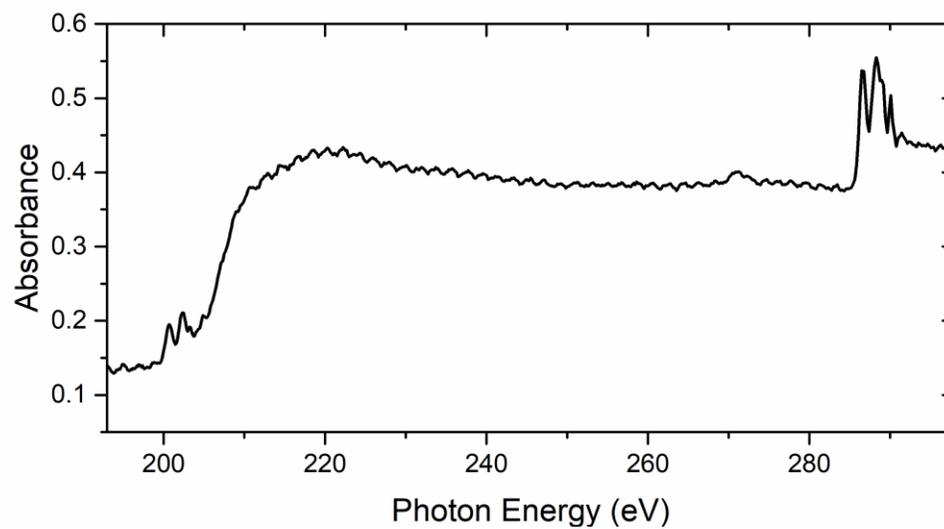


Figure S4. An overview of the CH<sub>2</sub>ICl absorption spectrum across the whole spectral range to demonstrate the overall absorption structure. Figure 1(a) and 1(b) zoom into the 284-292 eV and the 199-207 eV respectively.

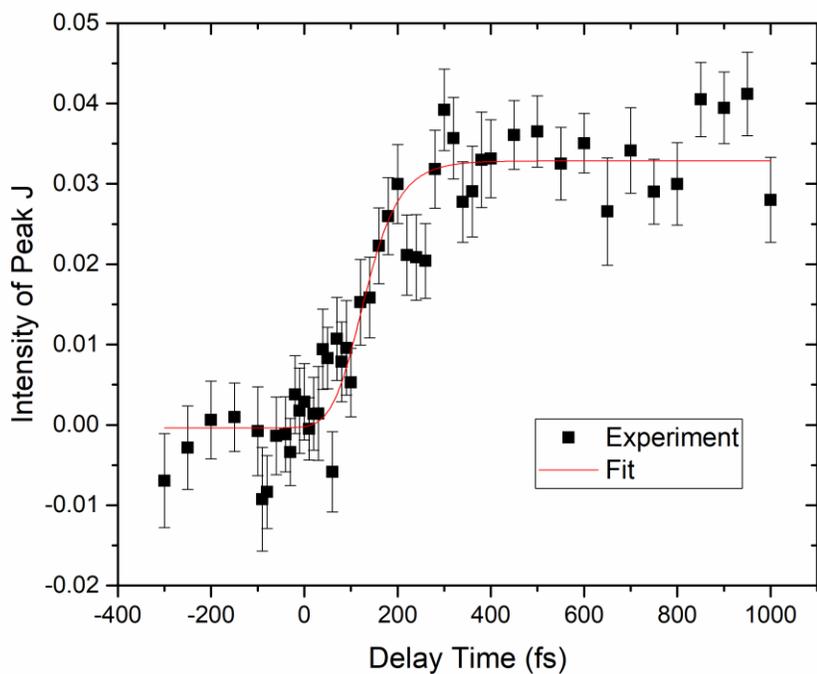


Figure S5. Temporal Dependence of peak J, which is fit with an exponential rise convoluted with a 90-fs instrumental response as determined in Fig. S3. The photodissociation is complete after ~150 fs. The spectra at intermediate delay times (50-150 fs) greatly resemble the spectra at the asymptotic limit but with less intensity. Results from 400 fs to 1000 fs are averaged to get electronic structures of the product. The spectrum is obtained 32 times *in situ* with data taken at all the delay time points and co-added. The whole acquisition time is about 2 hours in total.

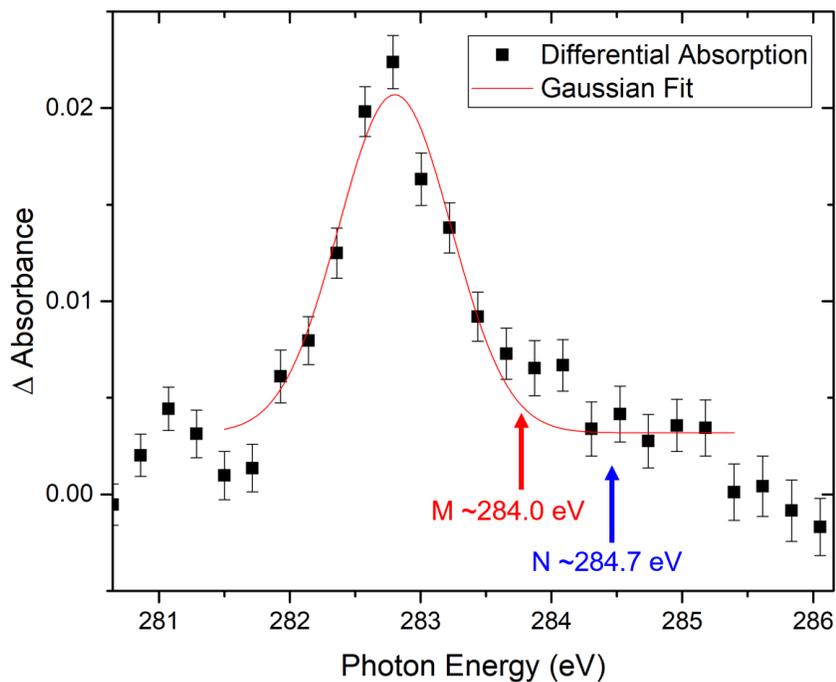


Figure S6. A representative spectra used to obtain an added back spectrum such as Fig. 4; only a moderate UV power is used (15-20  $\mu\text{J}$ ) and ion signals (M at  $\sim 284.0$  eV and N at  $\sim 284.7$  eV) are suppressed. Peak N completely disappears, while there is only a small contribution from Peak M.

## Reference

1. King, G. C.; Tronc, M.; Read, F. H.; Bradford, R. C., Investigation of Structure near  $L_{2,3}$  Edges of Argon,  $M_{4,5}$  Edges of Krypton and  $N_{4,5}$  Edges of Xenon, Using Electron-Impact with High-Resolution. *J Phys B-at Mol Opt* **1977**, *10* (12), 2479-2495.