Electronic Supplementary Information

for

"Accidental Resonance Mediated Predissociation Pathway of Water Molecules Excited to the Electronic $\tilde{C}$ State"

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1) The assignment of the 0.3 eV feature

A feature at 0.3 eV is presented in the TRPES data at 244.2 (Fig. 2(b) and Fig. 4(b)), 240.1 (Fig. 4(c)) and 239.0 nm (Fig. 2(c)). During the time delay implemented in these measurements, no decaying of this feature was observed. We have investigated the source of the 0.3 eV feature by systematically changing the pump and probe wavelengths, reaching a conclusion that this feature is actually from H atom. One of the most probable processes proceeds as following, taking H_2O at 244.2 nm as an example,

$$H_2O \xrightarrow{2\times 244.2nm} H_2O(\tilde{D}) \rightarrow OH + H \tag{1}$$

$$H \xrightarrow{2\times 244.2nm} H(n=2) \xrightarrow{332.9nm} H^+ + e^- \tag{2}$$

In this proposed mechanism, the H_2O molecule is excited to the $\tilde{D}$ state by absorbing two pump photons which rapidly dissociates to OH + H during the same pump pulse. The H products then absorb two more pump photon near-resonantly to the n=2 state before the pump laser pulse is off. The metastable H(n=2) atoms are ionized by a single probe photon, generating two color photoelectrons with a kinetic energy around 0.3 eV. The identification of this 0.3 eV feature is further supported by the following factors: (1) It was found that this feature is the most strong at 244.2 nm pump wavelength, and becoming much weaker at 240.1 and 239.0 nm. In Fig. 2(c), this feature is apparently "strong" because other features are much weaker at 239.0 nm and much longer data accumulation time was used. This suggests that H atom might be excited to the n=2 state via two-photon near-resonance excitation (the resonance wavelength is at 243.1 nm). The broad bandwidth (~400 cm^{-1}) of the fs pump pulses facilitates this near-resonant two-photon excitation;[1] (2) By tuning the probe wavelength, it was found that this feature shifts in the kinetic energy by the same amount as the change in the probe photon energy, suggesting that only one probe photon is involved in the photoionization step; (3) All TRPES data showing this feature involves the excitation of the $\widetilde{D}$ state which shows a lifetime shorter than or comparable with the pulse duration of the pump laser. This assures that the $\widetilde{D}$ state can dissociate during the pump laser pulse and the H atom products are still able to absorb two photons from the pump laser pulse to the n=2 state; (4) We have replaced the water molecules with CH_3SH molecule and the same feature was observed, proving that this feature is not from the photoionization of water molecule itself.

2) Comparison of the photoelectron kinetic energy distributions of the $\widetilde{C}$ state with different vibrational excitations

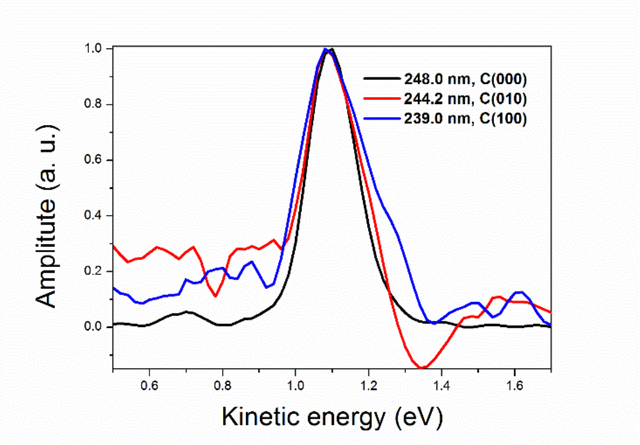

FIG. S1. Comparison of the photoelectron kinetic energy distributions of the $\tilde{C}(000)$, $\tilde{C}(010)$ and $\tilde{C}(100)$ states derived from the 2D global fit.

REFERENCES

1 A. Iqbal, L.-J. Pegg and V. G. Stavros, *J. Phys. Chem. A*, 2008, **112**, 9531.