

Supplementary Information: Signature of a conical intersection in the dissociative photoionization of formaldehyde

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1 Time-of-Flight Ion Mass Spectra

Figure 1 presents the time-of-flight (TOF) ion mass spectra recorded following excitation at 17 and 18.5 eV. Besides the H_2CO^+ parent ion at $m/z=30$, several fragment ions are observed: the H-loss channel leading to HCO^+ , which is the major DPI channel and the molecular channels producing CO^+ and the minor H_2^+ . At 18.5 eV, the H^+ channel is opened as observed. The branching ratio between these different ion fragments for both excitation energies are really similar as observed in Table 1. The photoelectrons produced in coincidence with the H_2CO^+ parent ion are characterized by a high kinetic energy ($E_e > 4$ eV) and are not properly detected taking into account the repeller voltage selected to study DPI processes.

An additional structure is observed in Fig 1 around $m/z = 18$ reflecting the photoionization of residual water although some amount of water is coming from the supersonic jet. Besides, the residual nitrogen from the chamber is also photoionized as reflected by the enhancement in the background signal around $m/z=28$, in particular at 18.5 eV. In order to ensure a proper further analysis of the (ion,electron) coincident events in this TOF area, in particular CO^+ (at $m/z=28$) and HCO^+ ions, the analysis software was slightly modified and only the left half of the ions images (coincident with the corresponding electrons) was analyzed. The thermal ions are centered at different positions (more to the right) than the supersonic ions, by using only one half of the image, we can completely suppress the thermal ions, in particular the nitrogen and properly analyze the fragment ions of interest.

2 Results following dissociative photoionization at $h\nu=18.5$ eV

The electron-ion kinetic energy correlation diagram (KECD), *i.e.* the ion kinetic energy release (KER) *vs.* the photoelectron energy (E_e), for the three DPI channels, (HCO^+ , e^-), (CO^+ , e^-) and (H_2^+ , e^-) coincident events following excitation at 18.5 eV is presented in Figure 2 along with the corresponding photoelectron spectra, which are compared to the HeI α photoelectron spectrum reported by Carlsson-Göthe and Karlsson.[1]

Table 1: Branching ratios between the different fragments following DPI at $h\nu=17$ and 18.5 eV.

Ion fragment	Branching ratio ($\pm 1\%$)	
	$h\nu = 17$ eV	$h\nu = 18.5$ eV
HCO^+	71.6	74.9
CO^+	27.7	24
H_2^+	0.7	1
H^+	–	0.1

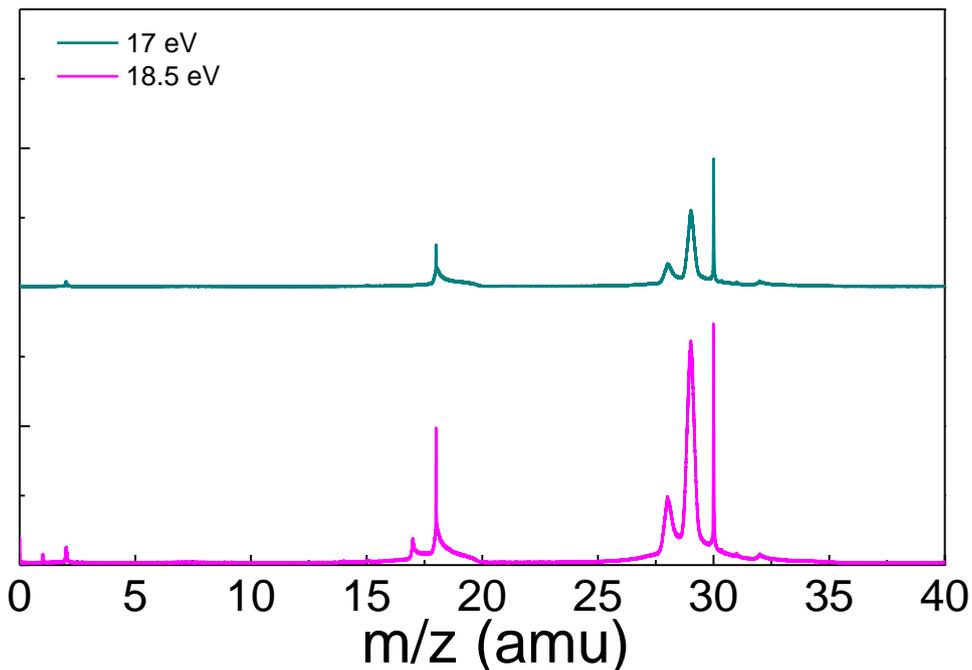


Figure 1: Time-Of-Flight ion mass spectra following photoionization of Formaldehyde at $h\nu = 17$ and 18.5 eV .

The KECD and PES measured for the H-loss DPI channel at higher energy, 18.5 eV is characterized by a low ion translational energy and a series of resolved structures in the PES reflecting in this case the photoionization to the B^2A_1 and C^2B_2 excited states, in agreement with the reported HeI PES spectrum.

The KECD and PES recorded for (CO^+, e) coincident events present a low ion translational energy distribution and a series of resolved peaks in the PES assigned to the vertical photoionization into H_2CO^+ (B^2A_1, ν) while a broad structure is also observed at higher binding energies associated with vertical FC photoionization into H_2CO^+ (C^2B_2). A non Franck-Condon photoionization leading to H_2CO^+ (A^2B_1) vibrationally excited in the 15.8 - 15 eV range is clearly observed reflecting the role of the conical intersection in this binding energy region, in agreement with our results at 17 eV.

The second molecular channel, (H_2^+, e) channel is characterized by a broad Boltzmann-type ion energy distribution and a PES reflecting ionization into H_2CO^+ (B^2A_1, ν). At 18.5 eV, an additional structure is observed at binding energies higher than 17 eV reflecting the population of H_2CO^+ (C^2B_2). In contrast to CO^+ and HCO^+ , all the structures observed in the PES are due to direct Franck-Condon photoionization.

The KECD for the H^+ channel, opened at 18.5 eV photon energy, is reported in Figure 3. This channel presents a really low signal and is characterized by a threshold ion and electron energy. The experimental threshold for the $\text{HCO} + \text{H}^+$ channel has indeed been reported at 17.41 ± 0.07 eV.

3 Theoretical Information

The active space selected includes 10 active orbitals corresponding to the the $2s$ and $2p$ orbitals of C and O atoms and the $1s$ orbitals of both H atoms. The six outer active orbitals (including five occupied and one virtual) are depicted in Fig. 4, along with the electronic configuration of the ground state of the cation H_2CO^+ . The first four excited states considered are valence states due to the following excitations:

- A state: $(^1b_1) \rightarrow (^2b_2)$
- B state: $(^4a_1) \rightarrow (^2b_2)$
- C state: $(^2b_2) \rightarrow (^2b_1)$
- D state: $(^1b_2) \rightarrow (^2b_2)$

The geometries associated with the stationary points from Fig. 4, including relevant transition states and

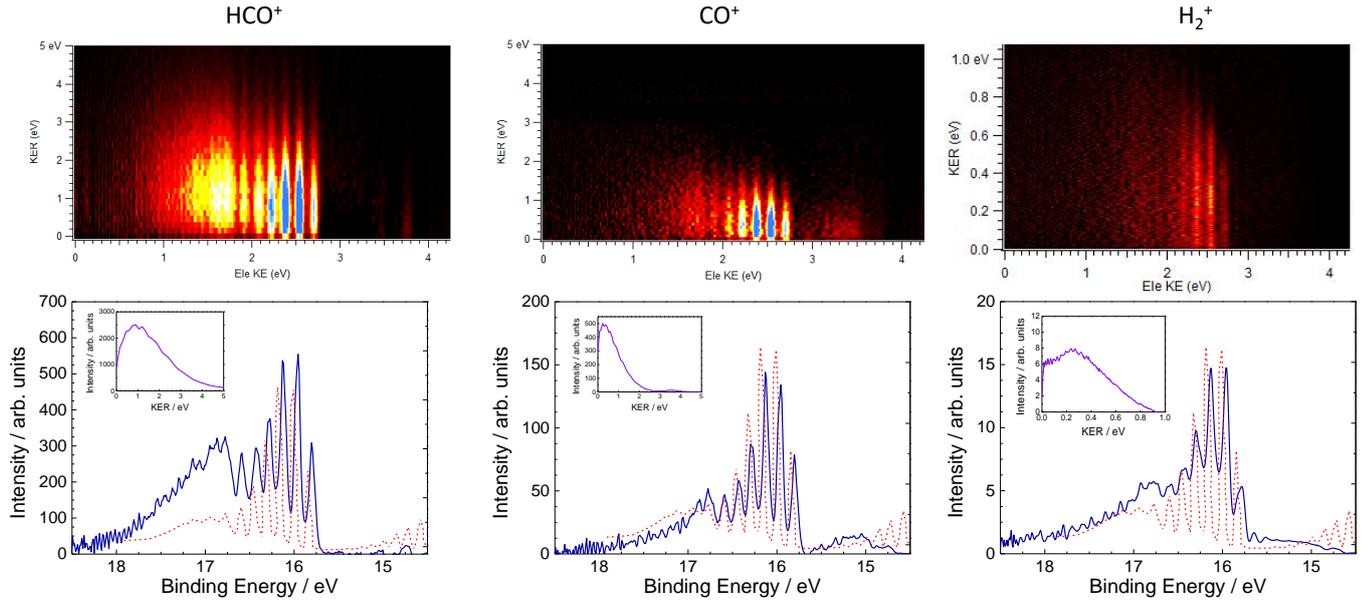


Figure 2: Electron-ion kinetic energy correlation diagram, KER *vs.* E_e , for (HCO^+ , e^-), (CO^+ , e^-) and (H_2^+ , e^-) coincident events following excitation at 18.5 eV and corresponding photoelectron spectrum (blue line) compared to the reported HeI α PES (red dashed line). The corresponding ion translational energy distributions are represented in the insets.

dissociation limits, are represented in Fig. 5.

References

- [1] M. C. Göthe and L. Karlsson, *A High Resolution HeI Excited Photoelectron Spectrum of the H₂CO Molecule*, Uppsala university, sweden technical report, 1990.

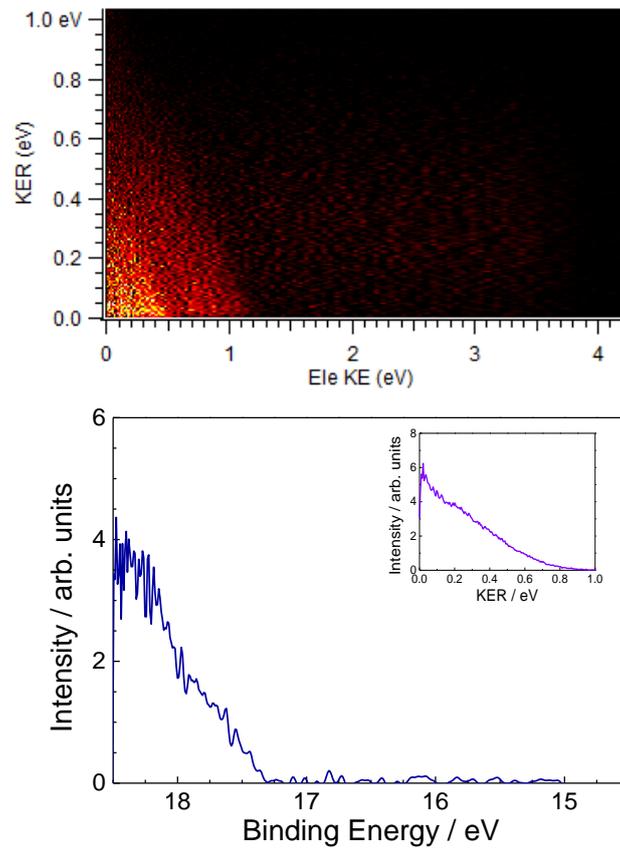


Figure 3: Electron-ion kinetic energy correlation diagram, KER *vs.* E_e , for (H^+ , e^-) coincident events following excitation at 18.5 eV and corresponding photoelectron spectrum (blue line). The corresponding ion translational energy distribution is represented in the inset.

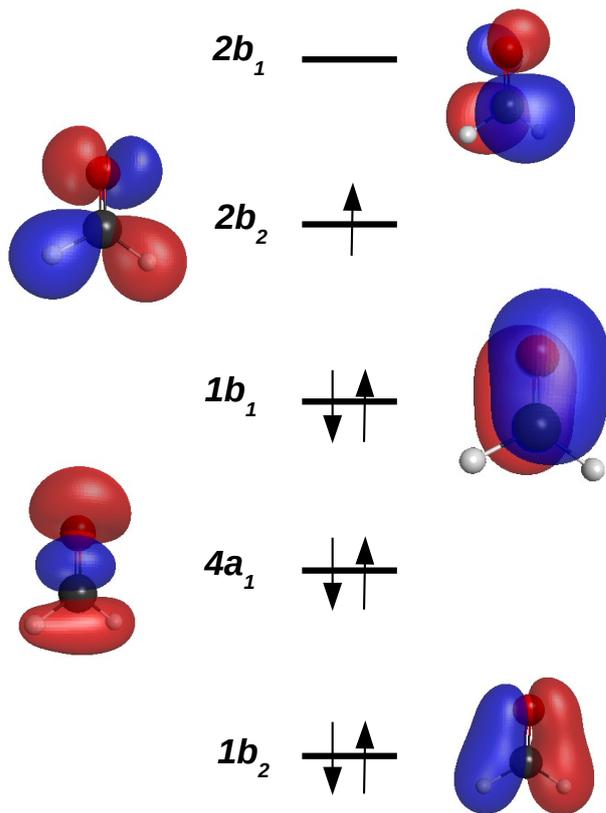


Figure 4: Six active orbitals included in the calculations. From the 10 active orbitals, the four inner are not shown.

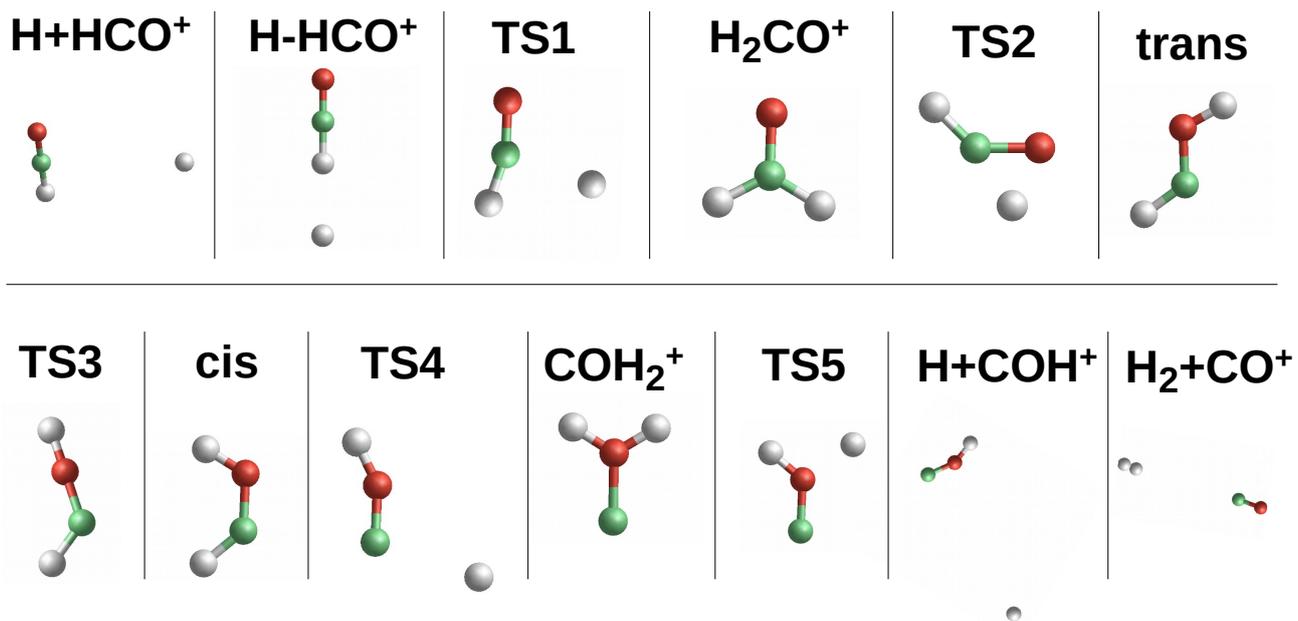


Figure 5: Computed geometries for stationary points in Fig. 4.