

## **Electronic Supplementary Information (ESI)**

### **Mechanisms of methyl formate production during electron-induced processing of methanol–carbon monoxide ices**

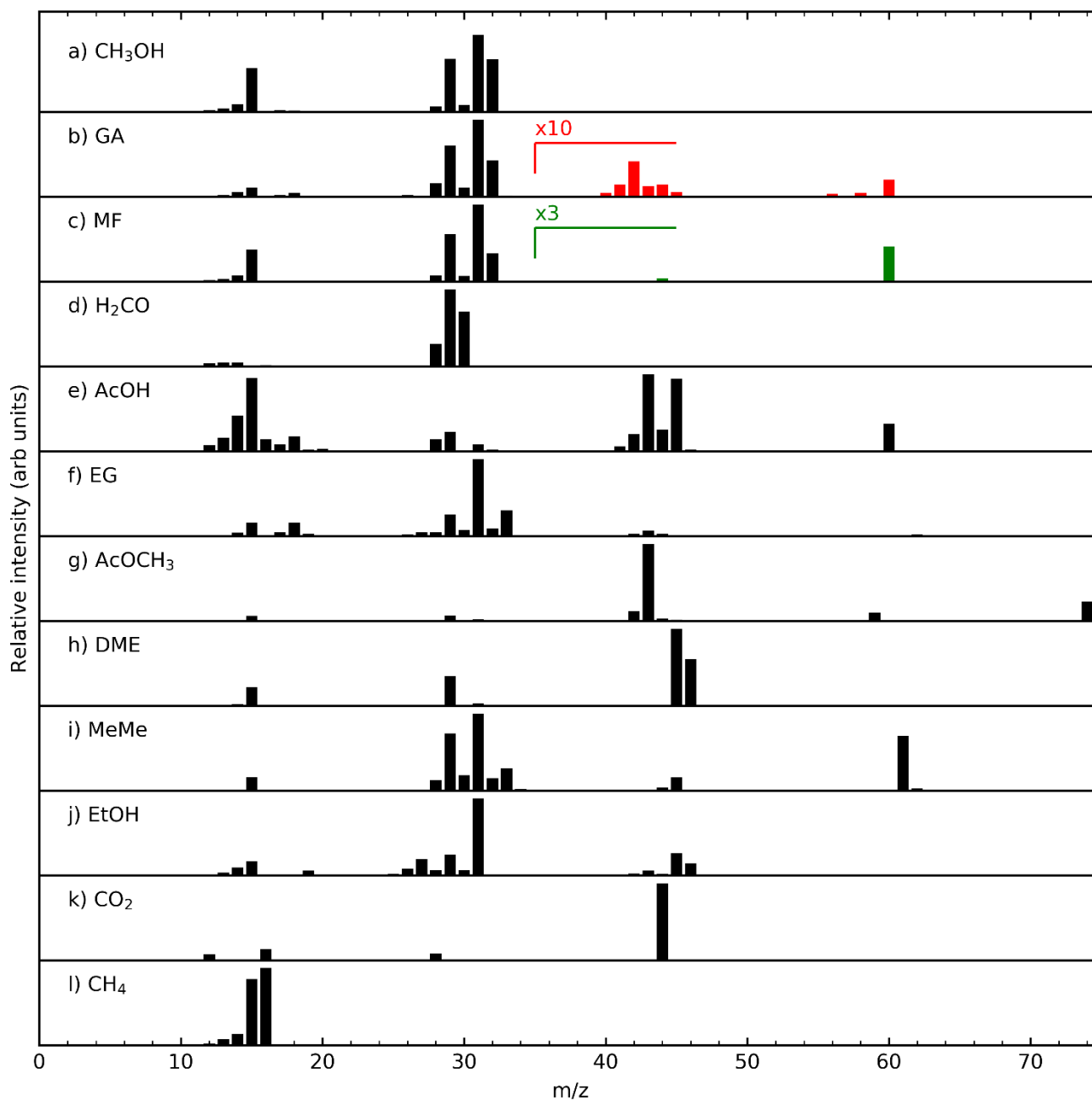
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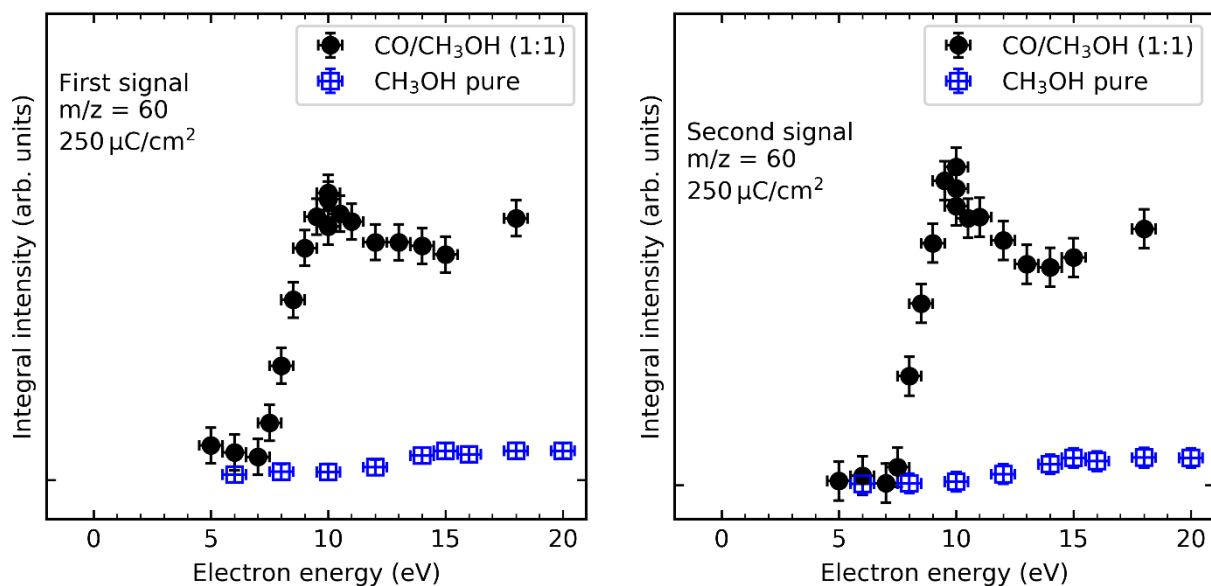
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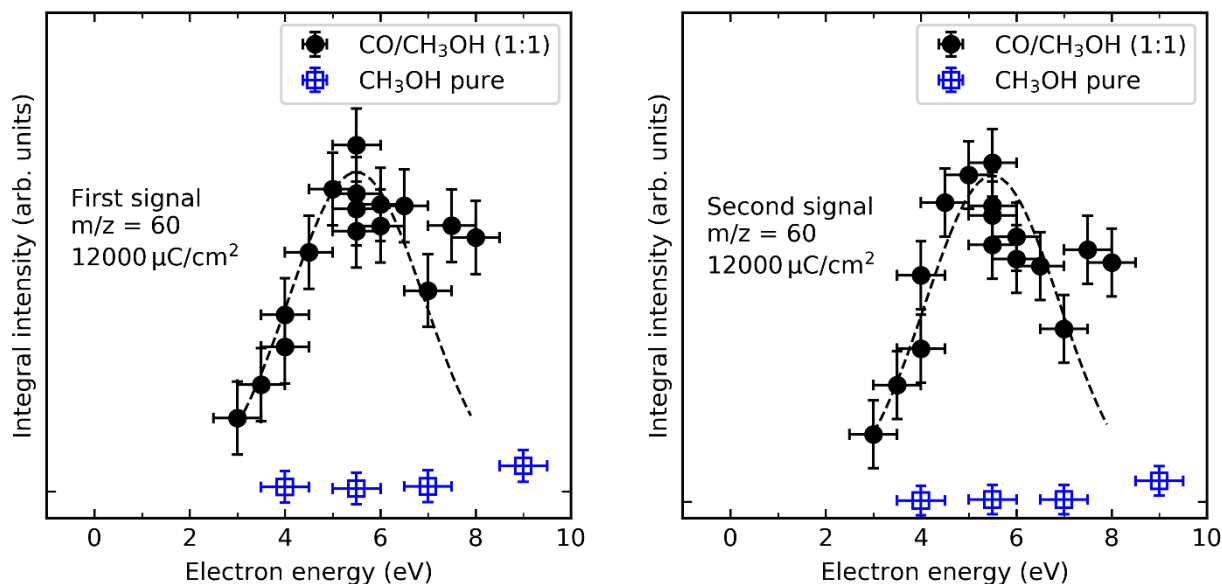
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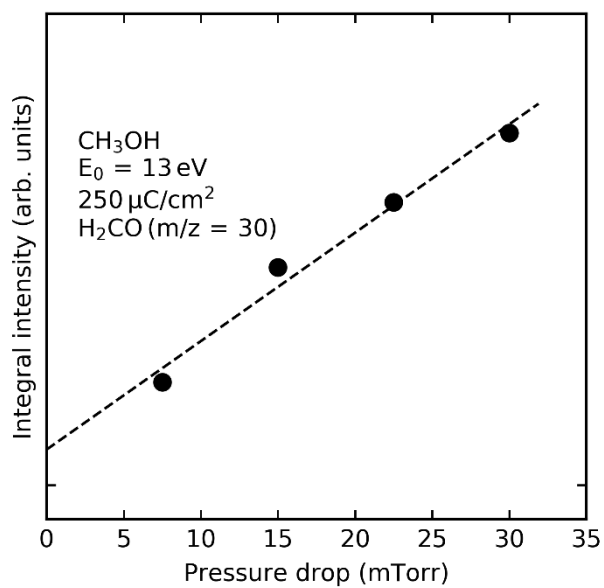
**Fig. S1.** Mass spectra of (a)  $\text{CH}_3\text{OH}$ , (b) glycolaldehyde (GA), (c) methyl formate (MF), (d)  $\text{H}_2\text{CO}$ , (e) acetic acid ( $\text{AcOH}$ ), (f) ethylene glycol (EG), (g) methyl acetate ( $\text{AcOCH}_3$ ), (h) dimethyl ether (DME), (i) methoxymethanol (MeMe), (j) ethanol ( $\text{EtOH}$ ), (k) carbon dioxide ( $\text{CO}_2$ ), (l) and methane ( $\text{CH}_4$ ). Spectra (a)–(f) and (j)–(l) were recorded upon leaking the pure compounds into the vacuum chamber whereas spectra (g)–(h) have been retrieved from NIST,<sup>1</sup> and spectrum (i) from Johnson and Stanley.<sup>2</sup> Note that relative intensities for  $m/z \geq 35$  in the mass spectra of glycolaldehyde and methyl formate have been scaled by the denoted factors.



**Fig. S2.** Integral intensities of the first and second  $m/z = 60$  desorption signal obtained by TDS after irradiation of  $\text{CH}_3\text{OH}$  (blue) and  $\text{CO}/\text{CH}_3\text{OH}$  (1:1) (black) multilayers with  $250 \mu\text{C}/\text{cm}^2$ . Integral intensities obtained from pure  $\text{CH}_3\text{OH}$  were scaled by a factor of  $1/2.3$  to correct for the higher amount of  $\text{CH}_3\text{OH}$  in these samples. Error bars denote the estimated uncertainties of energy spread and peak area. Tick marks on the vertical axis mark an integral intensity of zero.



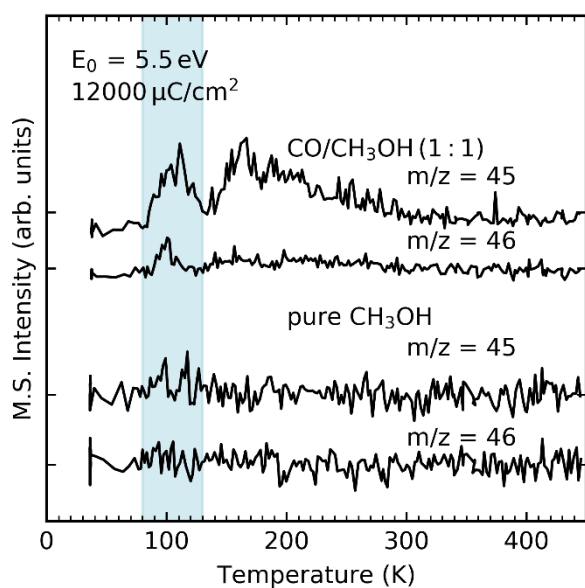
**Fig. S3.** Integral intensities of the first and second  $m/z = 60$  desorption signal obtained by TDS after irradiation of  $\text{CH}_3\text{OH}$  (blue) and  $\text{CO}/\text{CH}_3\text{OH}$  (1:1) (black) multilayers with  $12000 \mu\text{C}/\text{cm}^2$ . Peak areas obtained from pure  $\text{CH}_3\text{OH}$  were scaled by a factor of  $1/2.3$  to correct for the higher amount of  $\text{CH}_3\text{OH}$  in these samples. Error bars denote the estimated uncertainties of energy spread and peak area. Tick marks on the vertical axis mark an integral intensity of zero. The Gaussian serves as a guide to the eye.



**Fig. S4.** Integral intensity of the  $m/z = 30$  desorption signal of  $\text{H}_2\text{CO}$  obtained by adding the integrated ESD and TDS integrals after irradiation at 13 eV with  $250 \mu\text{C}/\text{cm}^2$ , for increasing amount of deposited  $\text{CH}_3\text{OH}$ , as deduced from the pressure drop in the gas handling manifold. Tick marks on the vertical axis mark an integral intensity of zero.

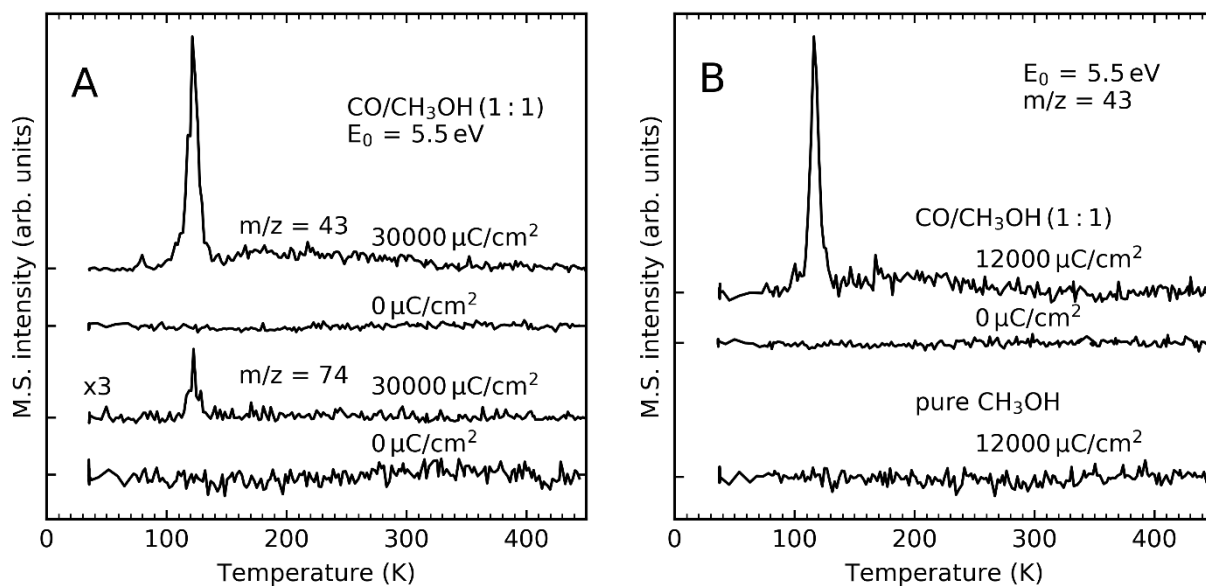
## Discussion of the formation of dimethyl ether and methyl acetate

After irradiation of the CO/CH<sub>3</sub>OH (1:1) mixture with 12000  $\mu\text{C}/\text{cm}^2$  at 5.5 eV, two signals at 110 K and 160 K can be observed in the  $m/z = 45$  curve of the TDS which are not present after irradiation of pure CH<sub>3</sub>OH. The signal at 110 K shows a corresponding signal in the  $m/z = 46$  curve and was thus assigned to dimethyl ether. The desorption temperature is in agreement with that found in a previous study.<sup>3</sup> The signal at 160 K was assigned to methoxymethanol as it coincides with the  $m/z = 33$  and 61 signals (compare with Fig. 14).



**Fig. S5** Thermal desorption spectra of pure CH<sub>3</sub>OH and of a CO/CH<sub>3</sub>OH (1:1) film after irradiation with 12000  $\mu\text{C}/\text{cm}^2$  at 5.5 eV. The signal at 110 K (blue), which is ascribed to dimethyl ether, is only observed after irradiation of the mixed film but not after irradiation of pure CH<sub>3</sub>OH. The signal at 160 K is due to methoxymethanol (compare with Fig. 14). Scaling is the same for all curves. Tick marks on the vertical axis indicate the vertical offset.

In addition, we observed another signal after irradiation of the CO/CH<sub>3</sub>OH (1:1) mixture at 120 K in the  $m/z = 43$  curve (Fig. S6). This signal might be assigned to methyl acetate as has been verified by a small signal in the  $m/z = 74$  curve which is the molecular ion of methyl acetate. The molecular ion at  $m/z = 74$ , however, was only observed after a higher electron exposure of 30000  $\mu\text{C}/\text{cm}^2$  due to the small intensity of this ion in the mass spectrum of methyl acetate (see Fig. S1). The desorption temperature also agrees roughly with that reported by Zahidi et al.<sup>4</sup> for pure methyl acetate films. Methyl acetate can be formed by recombination between CH<sub>3</sub>OCO• and CH<sub>3</sub>•, or by disproportionation between two CH<sub>3</sub>OCO• radicals yielding methyl acetate and CO<sub>2</sub> which suggest that CH<sub>3</sub>OCO• has a sufficiently long lifetime to react with other radicals before it decays into CO<sub>2</sub> and CH<sub>3</sub>•.



**Fig S6** (Panel A) Thermal desorption spectrum of a mixed multilayer CO/CH<sub>3</sub>OH (1:1) without irradiation (denoted as 0 μC/cm<sup>2</sup>) and after irradiation with 30000 μC/cm<sup>2</sup> at 5.5 eV. The signals at ~120 K in the *m/z* = 43 and 74 curves are assigned to methyl acetate. (Panel B) Methyl acetate is only observed after irradiation of CO/CH<sub>3</sub>OH (1:1) mixtures but not after irradiation of pure CH<sub>3</sub>OH. Scaling is the same for all curves unless a scaling factor is denoted. Tick marks on the vertical axis indicate the vertical offset.

## Relative molecular abundances

The relative molecular abundance of a specific product was determined by comparing the areas under its ESD and TDS signals with that of CH<sub>3</sub>OH in a non-irradiated sample. This comparison is based on the different cross sections for formation of the observed fragments inside the ionizer of the mass spectrometer, which are also known as partial ionization cross sections. Fragments monitored during ESD and TDS have been chosen on the basis of characteristic mass-to-charge ratios as deduced from the mass spectra of the products (Fig. S1). The *m/z* = 31 signal was selected for CH<sub>3</sub>OH, the *m/z* = 30 signal for H<sub>2</sub>CO, and the *m/z* = 60 signal for methyl formate. Uncertainties of the integral intensities were determined by the standard deviation of product yields at E<sub>0</sub> = 5.5 and 10 eV for the energy dependences monitored for higher and lower electron exposures, respectively. ESD was observed for H<sub>2</sub>CO but not for methyl formate. Thus, the relative yields of methyl formate were derived from the TDS signal areas alone. The yields of H<sub>2</sub>CO, on the other hand, were derived by adding the ESD and TDS signal areas. The ESD signal of H<sub>2</sub>CO was corrected for desorption of CO whose isotopologue C<sup>18</sup>O overlaps with the *m/z* = 30 signal of H<sub>2</sub>CO. This was achieved by subtracting the *m/z* = 28 ESD signal of CO multiplied with the natural abundance of the oxygen-18 isotope, which is 0.002. The uncertainty of the combined ESD and TDS intensities were derived from the individual uncertainties by using standard error propagation. For a number of compounds, experimental values for ionization cross sections have not been reported. Therefore, total ionization cross sections were calculated by the Binary Encounter-Bethe (BEB) model.<sup>5,6</sup> The necessary orbital properties

were obtained by calculation with the GAMESS software package.<sup>7,8</sup> This resulted in 5.26 Å<sup>2</sup> for CH<sub>3</sub>OH, 8.08 Å<sup>2</sup> for methyl formate and 3.98 Å<sup>2</sup> for H<sub>2</sub>CO. The formation cross sections of specific fragments, i.e., the partial ionization cross sections, were then obtained by multiplying the absolute total ionization cross section with the relative intensity of the respective ion, as deduced from the mass spectrum, divided by the sum of intensities over all ions. In order to account for possible differences in detection efficiencies and quadrupole transmission factors, mass spectra were recorded with the same mass spectrometer used for subsequent experiments, even though only negligible deviations from literature spectra<sup>1</sup> were observed. Following this procedure, the formation cross sections of specific ions at 70 eV were calculated to be 1.57 Å<sup>2</sup> for the  $m/z = 31$  fragment of CH<sub>3</sub>OH, 0.43 Å<sup>2</sup> for the  $m/z = 60$  ion of methyl formate, and 1.3 Å<sup>2</sup> for the  $m/z = 30$  ion of H<sub>2</sub>CO.

The results reveal that after irradiation of CO/CH<sub>3</sub>OH (1:1) with 250 μC/cm<sup>2</sup> at 15 eV, the yield of H<sub>2</sub>CO is 2.2% and that of methyl formate 1.13% with respect to the initial amount of CH<sub>3</sub>OH. After irradiation with 250 μC/cm<sup>2</sup> at 10 eV, the yields of H<sub>2</sub>CO and methyl formate are 0.9% and 1.43%, respectively. After irradiation with 12000 μC/cm<sup>2</sup> at 5.5 eV, the yields of H<sub>2</sub>CO and methyl formate are 2.0% and 2.6%, respectively.

## References

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