

# Supporting Information for

## Exploitation of Synchrotron Radiation Photoionization Mass Spectrometry in the Analysis of Complex Organics in Interstellar Model Ices

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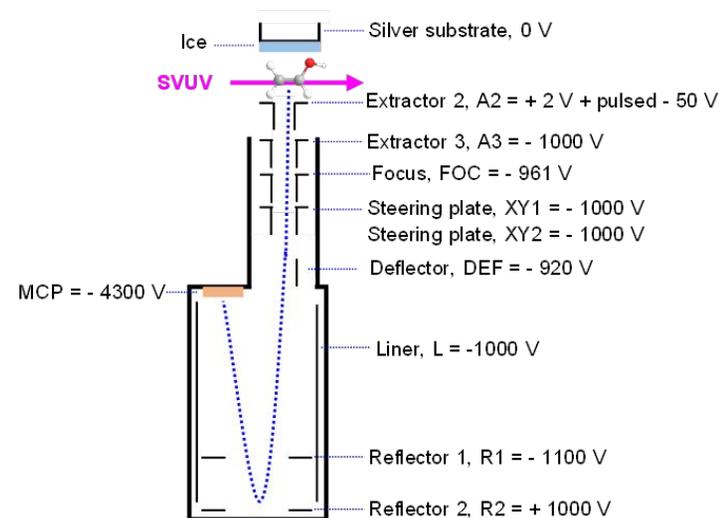
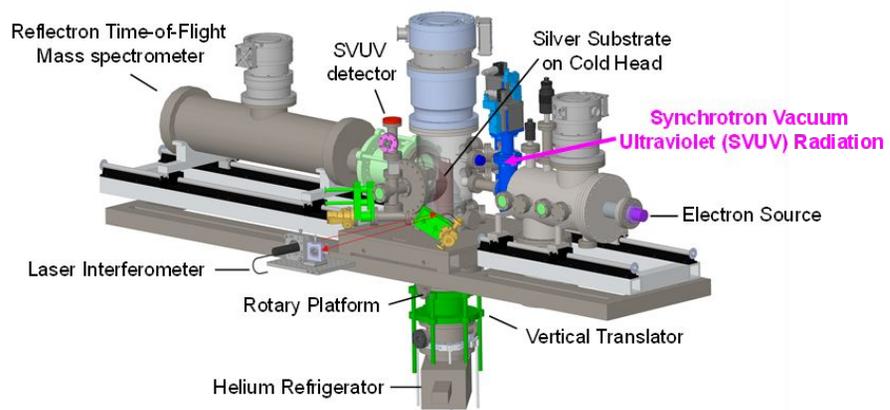
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## **SIMION simulation**

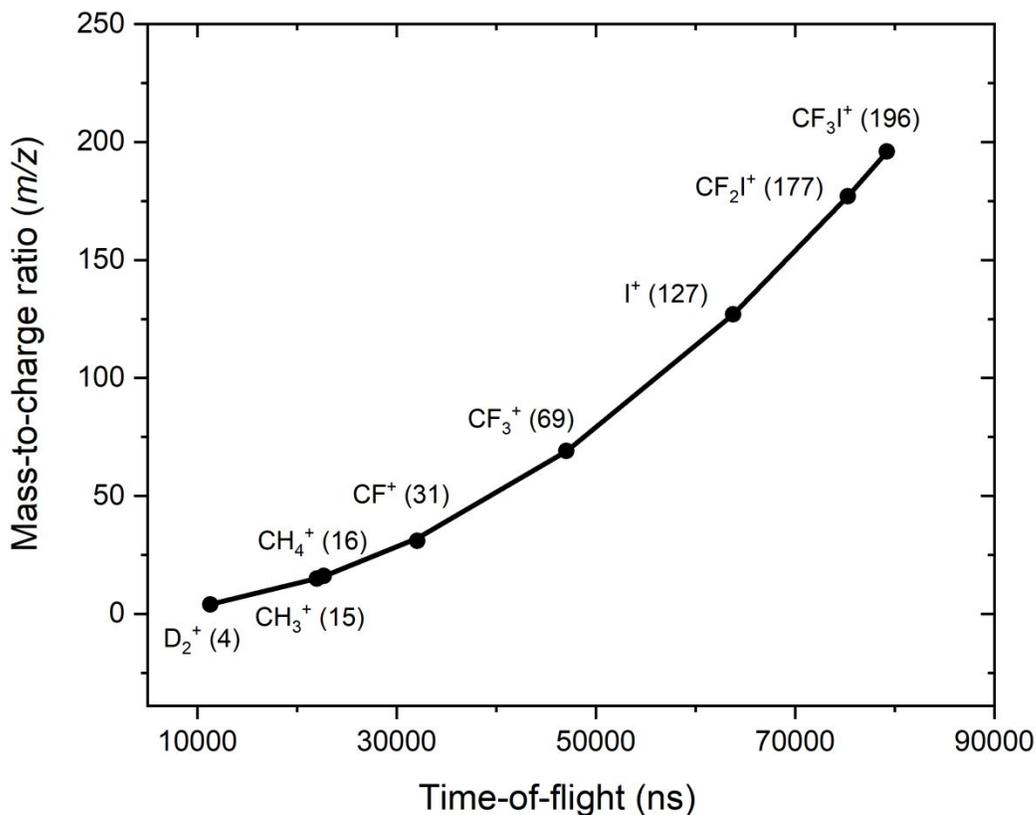
SIMION 7.0 was used to model the reflectron time-of-flight mass spectrometer (ReTOF-MS) and predict approximate voltages and timings. The computational model was constructed using a 0.025 inch grid. The ion source, ion acceleration optics, reflectron and detector were individually modeled in their own environment. This reduces errors from unphysical sources, such as discontinuous electric fields, while maintaining computational efficiency. These regions of the mass spectrometer are all separated by grids or floating voltage flight tubes. The geometry of the various components of the mass spectrometer are based on schematics provided by Jordan TOF Products, Inc. The ion source region included a model of the gridded extraction electrode and upper 5 cm of the cold head assembly including the analog ice deposition wafer, wafer clamps, wedged copper plates that cover the cold head above and below the wafer, and the uppermost portion of the cold head itself. The acceleration optics included a gridded entry electrode, einzel lens, deflector plates, and floating voltage exit flight tube. The dual stage reflectron model included a beveled edge geometry on the interior openings of all electrodes, and included grids at the entrance and exit of the first stage. The detector was composed only of an entrance grid and an electrically charged target with the size of the active area of the microchannel plate.

To simulate the initial position of ions produced by photoionization, ions are generated in a cuboid shape of  $1 \times 1 \times 12 \text{ mm}^3$ . The 12 mm axis is collinear with the vacuum ultraviolet (VUV) light, which passes about 3 mm above the surface of the wafer. Ions initially have a 200 K distribution of translational energy. Ion extraction at 20 kHz with continuous photoionization was modeled by maintaining a small retarding voltage on the extraction electrode for at least 47  $\mu\text{s}$  before applying an extraction voltage pulse for the final few  $\mu\text{s}$  of the 50  $\mu\text{s}$  cycle.

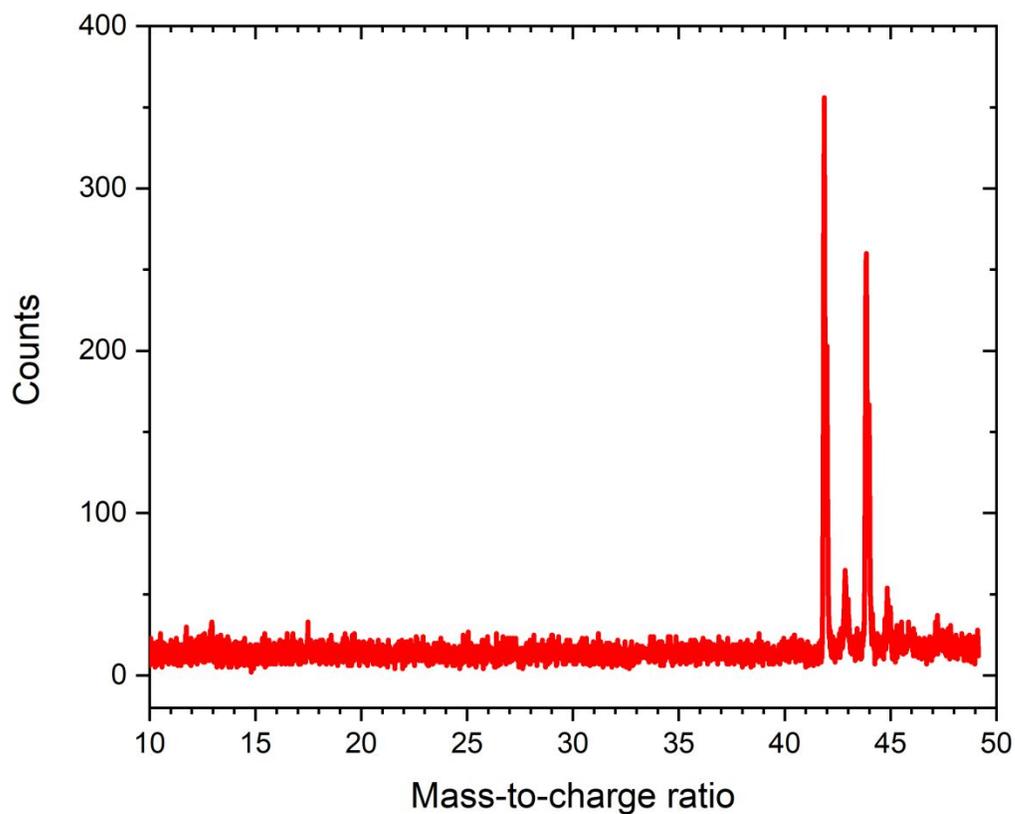
Electrode voltages were optimized while observing the behavior of singly charged ions weighing 42 amu. Ion optics used for steering, mainly the einzel lens and deflector, were adjusted to improve the ion transmission. The remaining electrodes were adjusted with the goal of increasing mass resolving power while maintaining peak ion transmission. In addition to predicting electrode voltages, the pulsed nature of the model allowed a calculation of effective duty cycle. The ions that contribute to a well resolved peak in the mass spectrum are those that are produced a few  $\mu\text{s}$  before ion extraction. Of all ions produced, 6% are extracted, and of those 54% impact the detector.



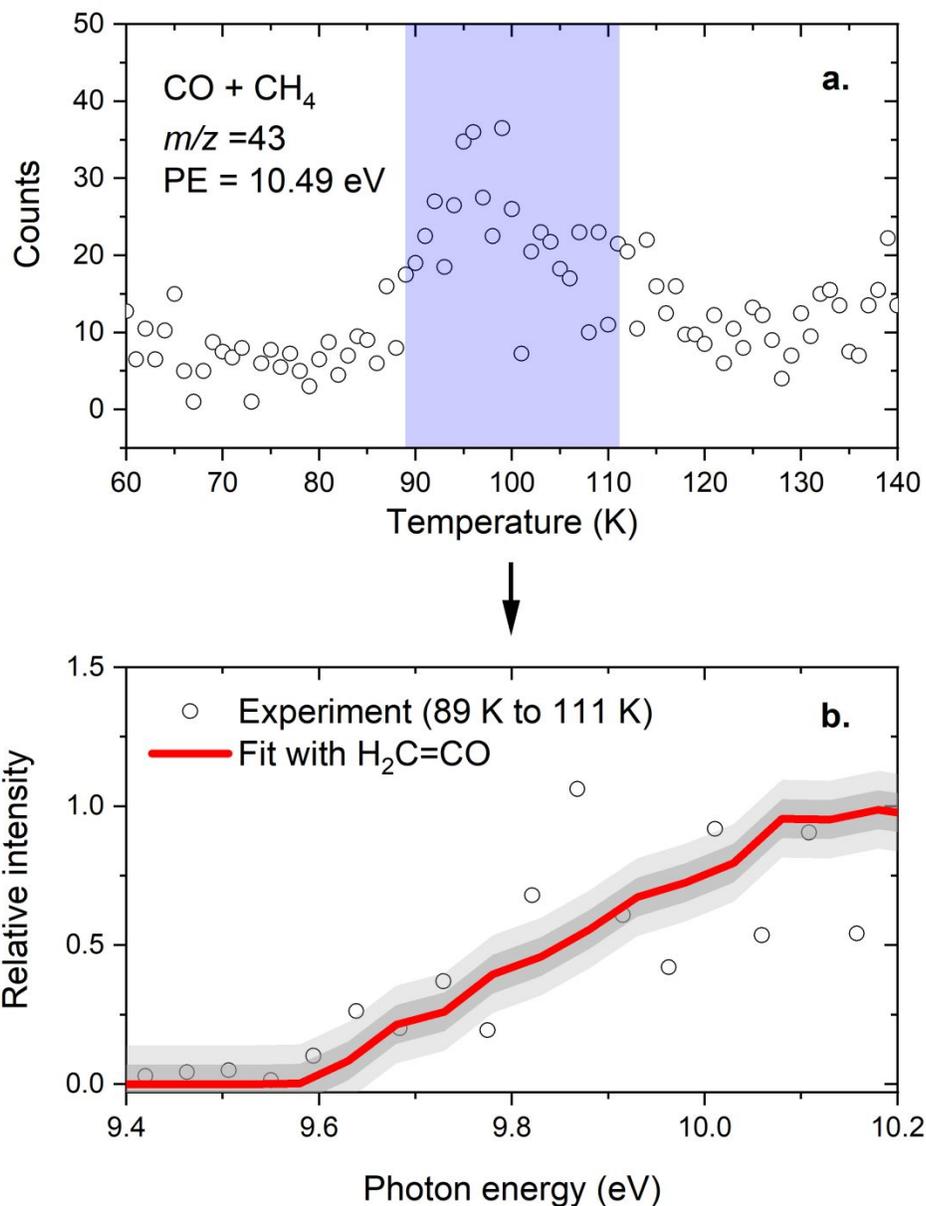
**Figure S1.** Schematics of the experimental setup (left) and reflectron time-of-flight mass spectrometer along with its voltage settings (right).



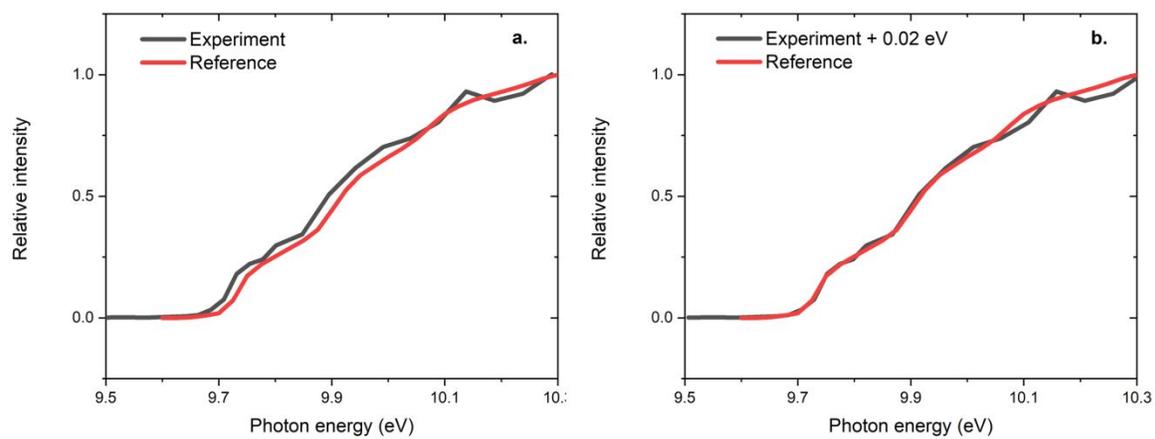
**Figure S2.** Relation curve between the mass-to-charge ratio and time-of-flight of ions calibrated using the synchrotron vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (SVUV-PI-ReTOF-MS) of deuterium (D<sub>2</sub>), methane (CH<sub>4</sub>), and trifluoroiodomethane (CF<sub>3</sub>I). The photoionization energy was set as 11 eV, along with its high harmonics, which induced mass fragmentation of CH<sub>4</sub> and CF<sub>3</sub>I. The curve was achieved by fitting polynomials up to the second order, *i.e.*  $m/z = 3.1304 \times 10^{-8} \times (\text{TOF})^2 - 8.0393 \times 10^{-6} \times \text{TOF} + 6.8426 \times 10^{-2}$ .



**Figure S3.** Integrated mass spectrum of the detected species during the TPD phase of the energetic electron processed carbon monoxide (CO) – methane (CH<sub>4</sub>) ice at the photoionization energy of 10.49 eV.



**Figure S4.** SVUV-PI-ReTOF-MS data at  $m/z = 43$ . **a:**  $m/z = 43$  signal detected during the Temperature Programmed Desorption (TPD) phase of the processed carbon monoxide (CO) – methane (CH<sub>4</sub>) ice at the photon energy of 10.49 eV. **b:** photoionization efficiency (PIE) curve for the species linked to  $m/z = 43$  (open cycles) recorded from 89 K to 111 K (light-blue shaded region in panel **a**). The red line shows the fit of the PIE curve of ketene (H<sub>2</sub>C=CO) to the experimental  $m/z = 43$  data. The dark- and light-gray shaded regions represent the 1 $\sigma$  and 2 $\sigma$  uncertainties in the fit, respectively.



**Figure S5.** Comparison of the experimental photoionization efficiency (PIE) curve for propene ( $C_3H_6$ ) with the reference PIE curve taken from *J. Chem. Phys.* 119, 8356 (2003). **a:** raw experimental data versus the reference PIE curve. **b:** experimental data shifted by 0.02 eV versus the reference PIE curve.

**Table S1.** List of experiments.

#	Precursors	Electron dose	Photoionization Energy (eV)
1	CH <sub>4</sub> + CO	30 nA, 60 min	10.49
2	CH <sub>4</sub> + CO	30 nA, 60 min	9.00 to 10.49
3	CH <sub>4</sub> + CO	0 nA, blank	10.49

**Table S2.** Data used to calculate the average irradiation dose per molecule.

Initial kinetic energy of the electrons, $E_{init}$ (keV)	5	
Ice	CH <sub>4</sub> + CO	
Irradiation current, $I$ (nA)	$30 \pm 2$	
Total number of electrons	$(6.7 \pm 0.7) \times 10^{14}$	
Average penetration depth, $l_{ave}$ (nm) <sup>a</sup>	$370 \pm 40$	
Average kinetic energy of backscattered electrons, $E_{bs}$ (keV) <sup>a</sup>	$3.26 \pm 0.33$	
Fraction of backscattered electrons, $f_{bs}$ <sup>a</sup>	$0.34 \pm 0.03$	
Irradiated area, $A$ (cm <sup>2</sup> )	$1.0 \pm 0.1$	
Dose (eV/molecule)	CO	$4.7 \pm 0.8$
	CH <sub>4</sub>	$2.7 \pm 0.4$

**Note:**

<sup>a</sup> Parameters obtained using the CASINO software v2.42.