Hydrogen Tunneling with an Atypically Small KIE Measured in the Mediated Decomposition of the $Co(CH_3COOH)^+$ Complex

Supplemental Information

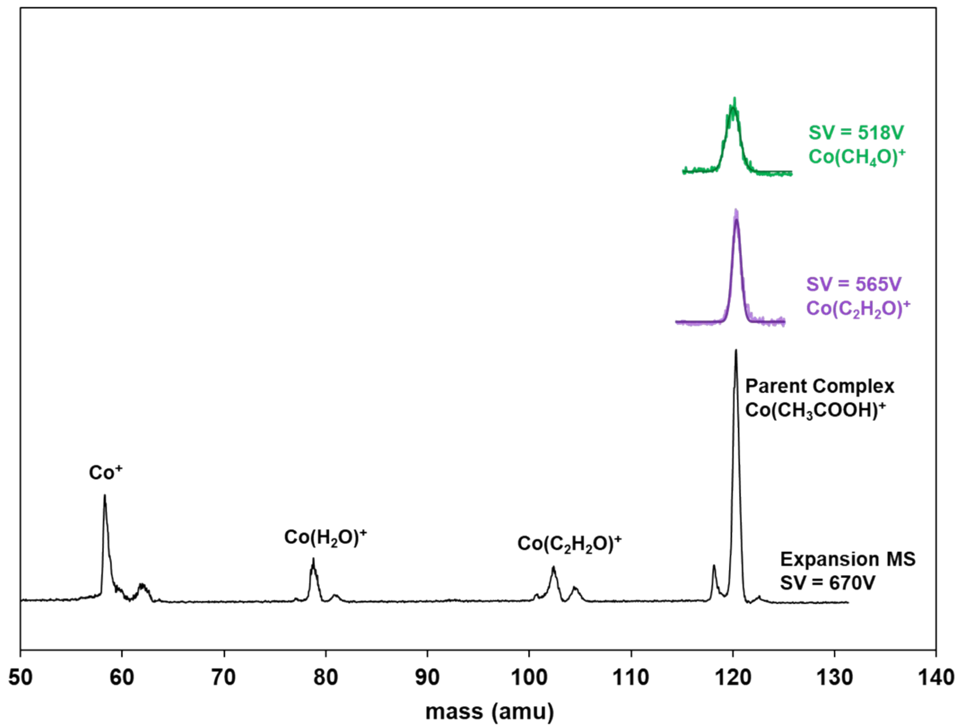

Figure SI-1. Typical mass spectrum showing the species created in the source. The sector voltage is tuned to transmit fragments to the detector. The fragments are the products of a chemical reaction, and these have the same arrival time to the detector as does the precursor.

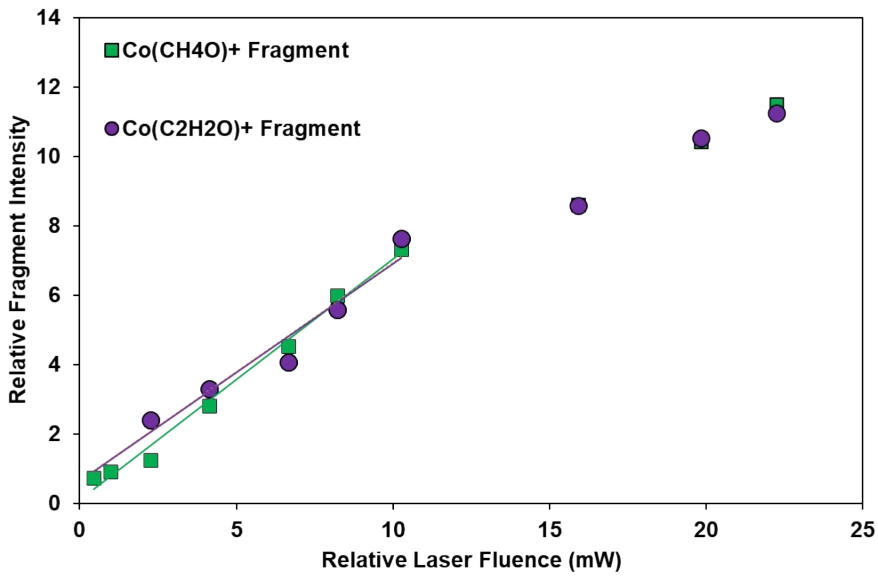

Figure SI-2. Relative fragment intensity is plotted vs relative dye laser photon fluence. The dye laser's reflection from an optic's surface is measured on a power meter while fragment intensity is measured. A linear relationship with a near zero intercept occurs at low fluence. The fragment signal saturates as the laser fluence increases.

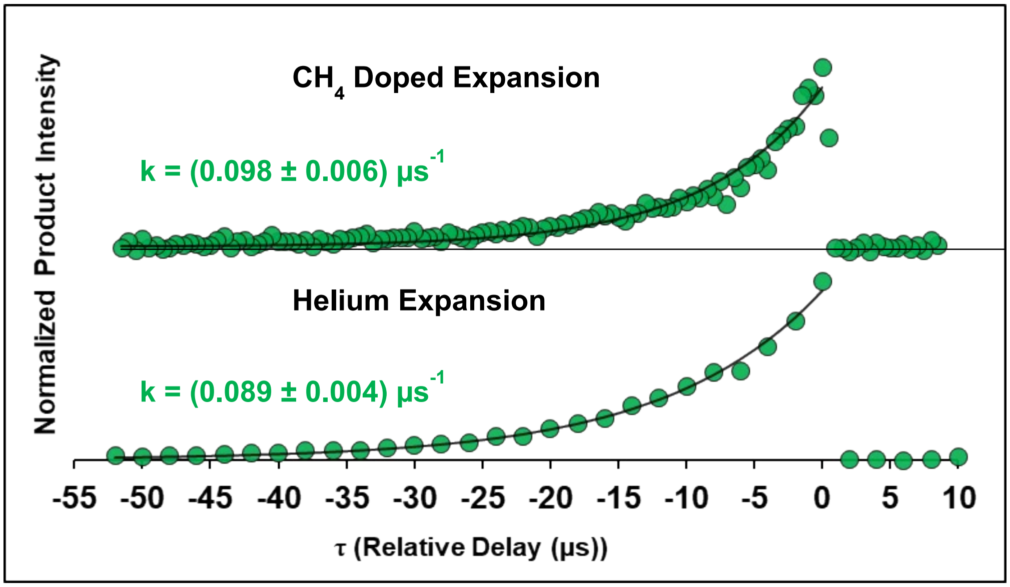

Figure SI-3. A comparison of the rate constants measured under two different expansion environments. The lower panel displays SPIDRR results when the precursor is seeded into a pure helium expansion and absorbs a 13950 cm^{-1} quantum of photon energy. The top panel shows the same measurement after doping a small quantity of CH_4 into the helium supply to more efficiently cool vibrational degrees of freedom within the precursor. The rate constants extracted from each exponential profile are the same within the error of the measurement. This suggests efficient cooling in the neat helium supersonic expansion.

Simon- change the y-axis to read "Normalized $Co(CH_4O)^+$ Intensity"

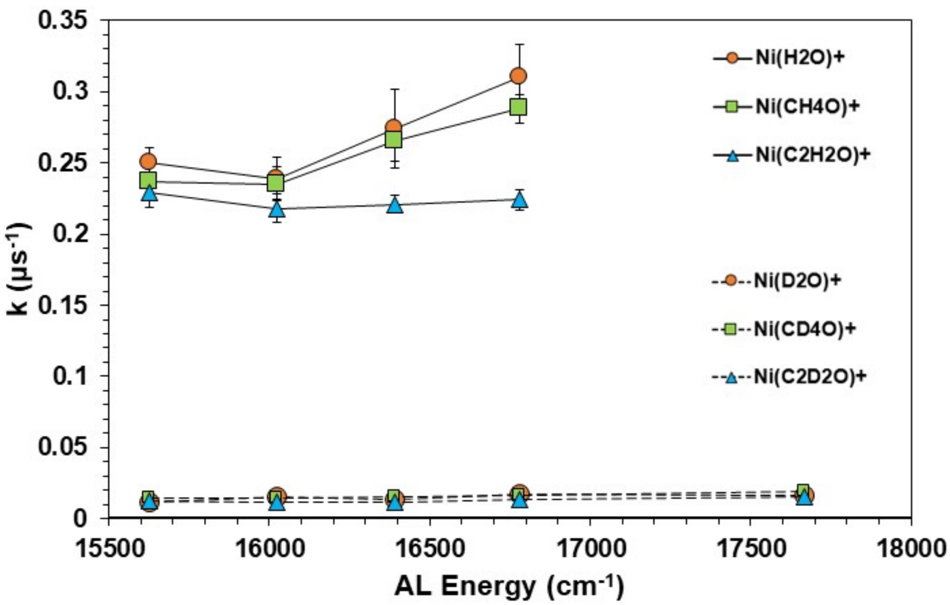

Figure SI-4. The k(E) dependence on AL photon energy in the $Ni(CH_3COOH)^+$ system. These are unpublished results measured in our lab using the SPIDRR technique. In this system, three products are measured with formation kinetics having a similar nearly linear k(E) dependence on AL photon energy.