Electronic Supplementary Material

Bifurcated Dissociative Photoionization Mechanism of Acetic Acid Anhydride Revealed by Imaging Photoelectron Photoion Coincidence Spectroscopy

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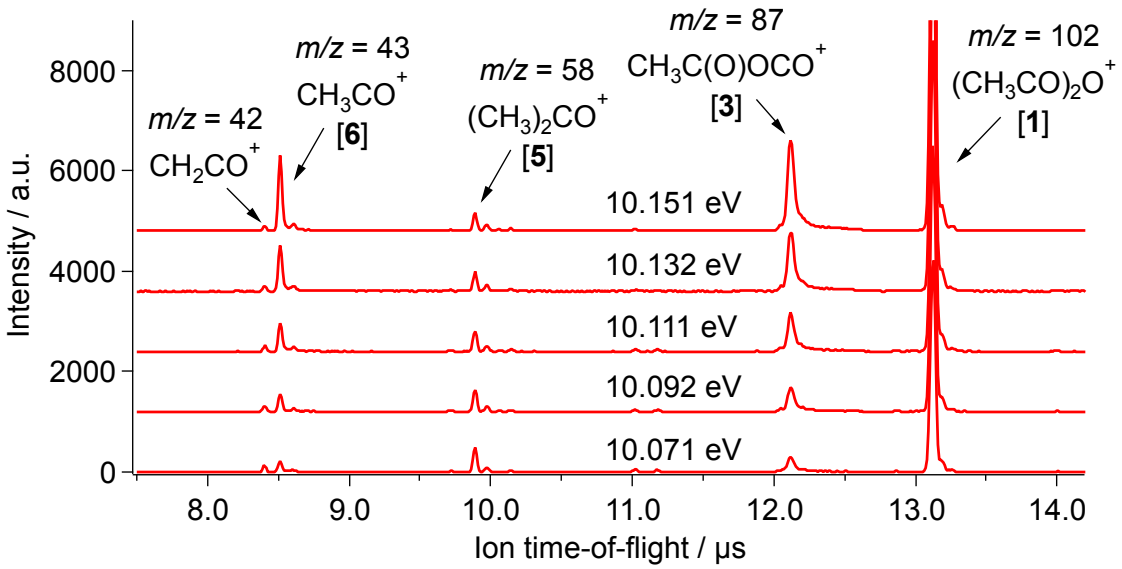

Figure S1. Sample coincidence time-of-flight mass spectra for Ac_2O. Threshold TOF mass spectra revealed the presence of trace amounts of acetone cations (*m/z* = 58) and its CH_4-loss fragment, the CH_2CO^+ ion (*m/z* = 42). To show the detection of this trace species, these time-of-flight spectra show coincidence with all electrons, rather than just the threshold PEPICO data used in the paper.

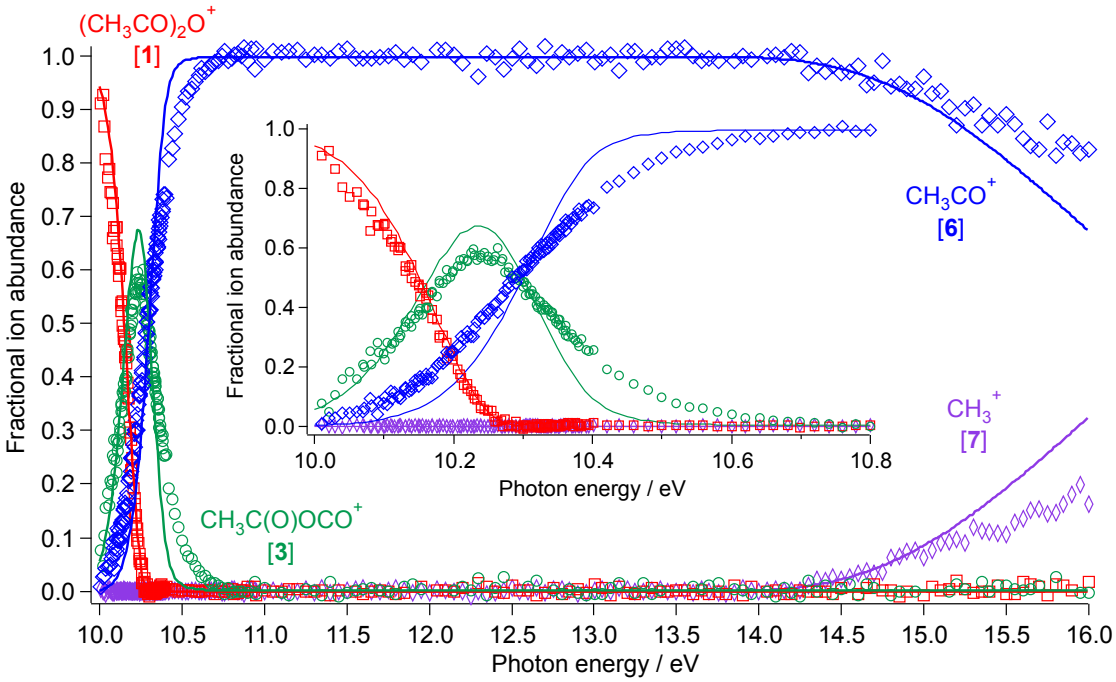

Figure S2. Breakdown diagram for Ac_2O in the 10 to 16 eV photon energy range. Open symbols are experimentally measured ion abundances and lines show the unsatisfactory fit of a statistical model using only sequential dissociation channels for the acetyl [**6**] and methyl [**7**] cations.

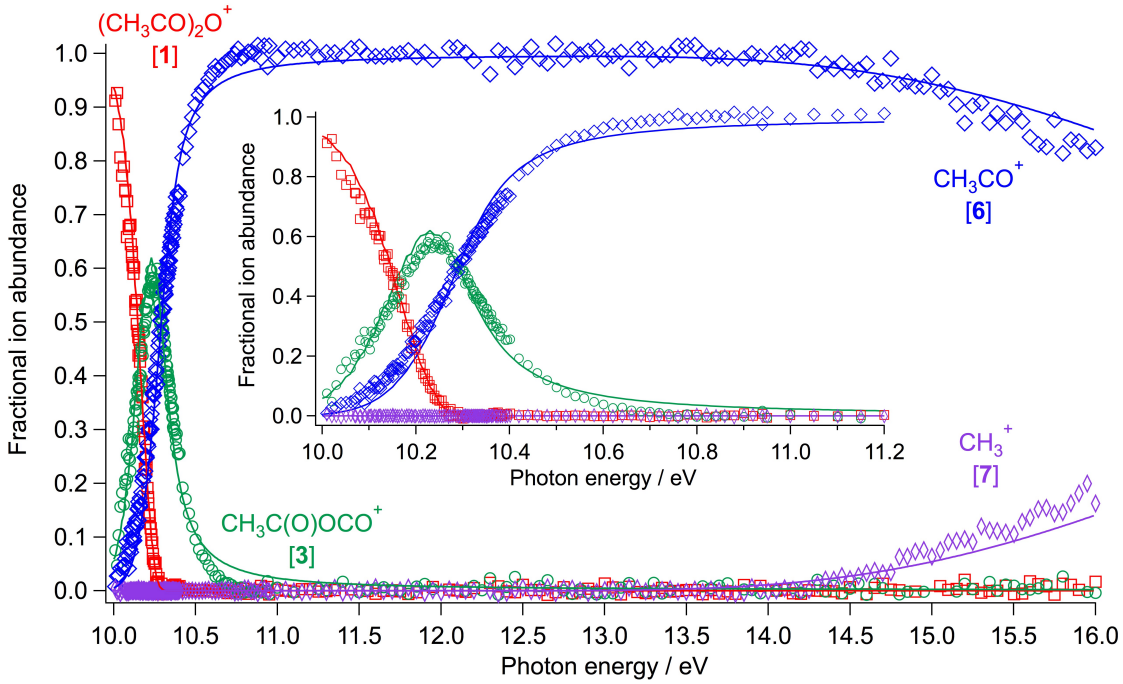

Figure S3. Breakdown diagram for Ac_2O in the 10 to 16 eV photon energy range. Open symbols are experimentally measured ion abundances and lines show the fit of the statistical modeling using only parallel dissociation channels for the acetyl [**6**] and methyl [**7**] cations, *i.e.* both of these product formed directly from the molecular ion. Although this model is not a very good fit to the experimental data, even this was only possible using an unreasonably tight TS for the formation of [**3**].