Electronic supplementary information for photoelectron photofragment coincidence spectroscopy of aromatic carboxylates: benzoate and p-coumarate

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1 Molecular structures



Figure S1: The structure of benzoic acid and p-coumaric acid.



Figure S2: The resonance structures of the carboxylate and phenolate forms of p-CA⁻.

2 Fragment mass spectra



Figure S3: The fragment mass spectrum resulting from two-body DPD of 11 keV $BzCO_2^-$ at 266 nm.



Figure S4: The two-body fragment mass spectrum of 11 keV p-CA⁻ recorded at 266 nm. The solid lines are the masses of CO₂ and HOC₆H₅CHCH resulting from two-body DPD, and the dashed lines are the reported masses of CO₂ and HOC₆H₅ produced via charge-symmetric three-body photodissociation. The peak at 81 a.m.u. is a result of false coincidences between two stable HOC₆H₄CHCHCO₂ radicals.

Figure S4 is the fragment mass spectrum of the products of p-CA⁻ at 266 nm (4.66 eV), where two neutrals are recorded in coincidence. The mass spectrum for p-CA⁻ is significantly wider than the mass spectrum recorded for benzoate. This may be indicative of the presence of another channel. One possibility are the three-body photodissociation channels, where both HOC₆H₅ + HCC⁻ + CO₂ or HOC₆H₄⁻ + HCCH + CO₂ are calculated to be energetically accessible as shown in Table 1 in the manuscript. In the current apparatus configuration, a two-photon process of three-body photodissociation and subsequent photodetachment is required to collect all three neutral fragments and a photoelectron. Therefore at the low laser powers used in the study the most likely products of three-body photodissociation are two neutral fragments and an undetected anionic fragment. For a concerted, charge symmetric, three-body photodissociation channel resulting in equal mass neutral fragments, the fragment mass spectrum and the KER spectrum for the three-body dissociation can be extracted from the two-body data. For a concerted, three-body mass-asymmetric photodissociation resulting in $HOC_6H_5 + HCC^- + CO_2$, it would be expected that the CO_2 would appear as mass $44 \times \frac{163}{94+44} = 52$ a.m.u. and OHC6H5 at mass $94 \times \frac{163}{94+44} = 111$ a.m.u. in the fragment mass spectrum. The mass spectrum in Figure S4 does indeed peak near 52 and 111 a.m.u. providing evidence for the presence of this channel. However, this is a crude approximation as the neutral fragments are different in mass, such that the undetected HCC⁻ would recoil significantly from the center-of-mass upon dissociation. It is likely this accounts for the observed broadening of the mass spectrum. No attempt is made to extract a KER spectrum for the three-body photodissociation, as the recoiling anion leaves a portion of the KER unaccounted for. Similar arguments cannot be made to predict the observed masses of HCCH + CO₂ produced via three-body photodissociation, where $HOC_6H_4^-$ is undetected, as in this case the anionic fragment is a terminal fragment in the molecular framework.