Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Dissociative Photodetachment vs. Photodissociation of Aromatic Carboxylates: The Benzoate and Naphthoate Anions

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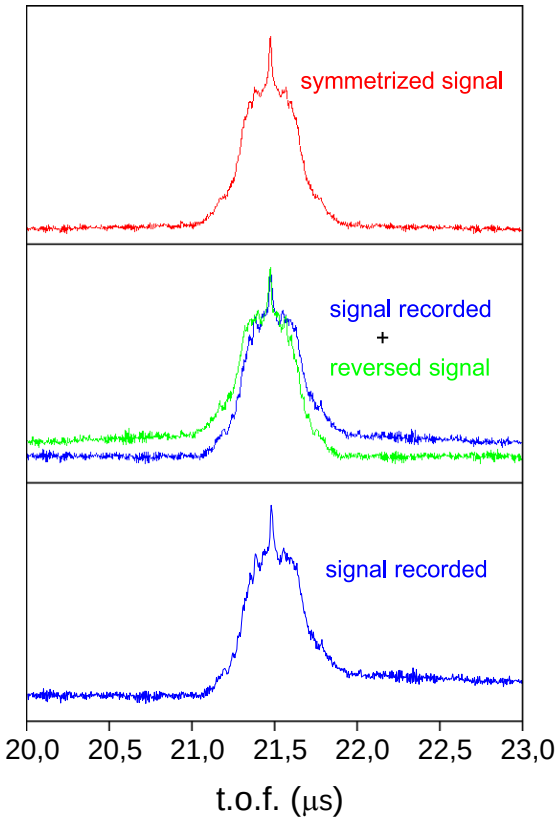

Figure SI-1: Symmetrization procedure of the TOF signals.

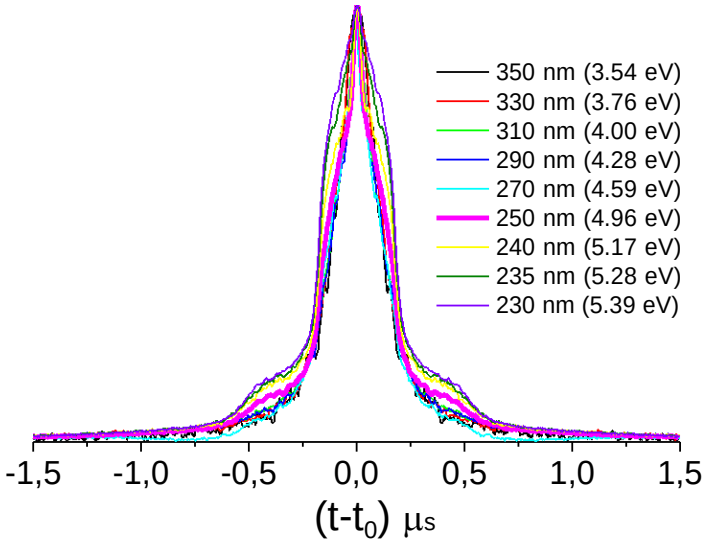

Figure SI-2: Time of Flight profiles of the neutral species obtained after excitation at different photon energies the $NpCO_2^-$ anion. At energies above 4.96 eV (250 nm) there is a clear change in the shape of the signal, with a continuous growing of wings to both sides of the fastest fragments (CO_2) component, indicating a change in the fragmentation mechanism.

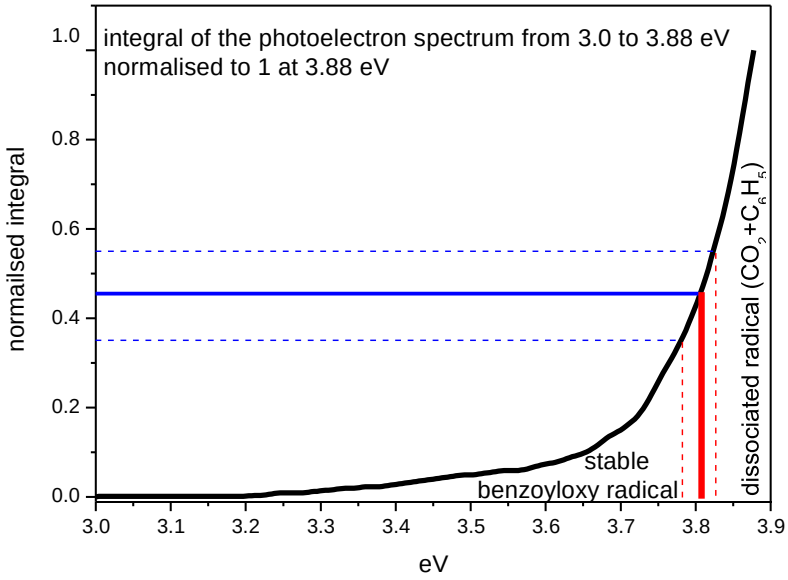

Figure SI-3: Determination of the fragmentation energy barrier of the $BzCO_2^{\bullet}$ radical. The black curve is the integral of the electron binding energy derived from Woo et al[8] normalized at the lowest energy where we measured (3.88eV) the fragmentation yield. The high energy population is dissociating and the lowest one is stable. Assuming a fragmentation yield of 45% sets the barrier at 3.8 eV, which is 0.55 eV above the ADE of the $BzCO_2^-$ anion.

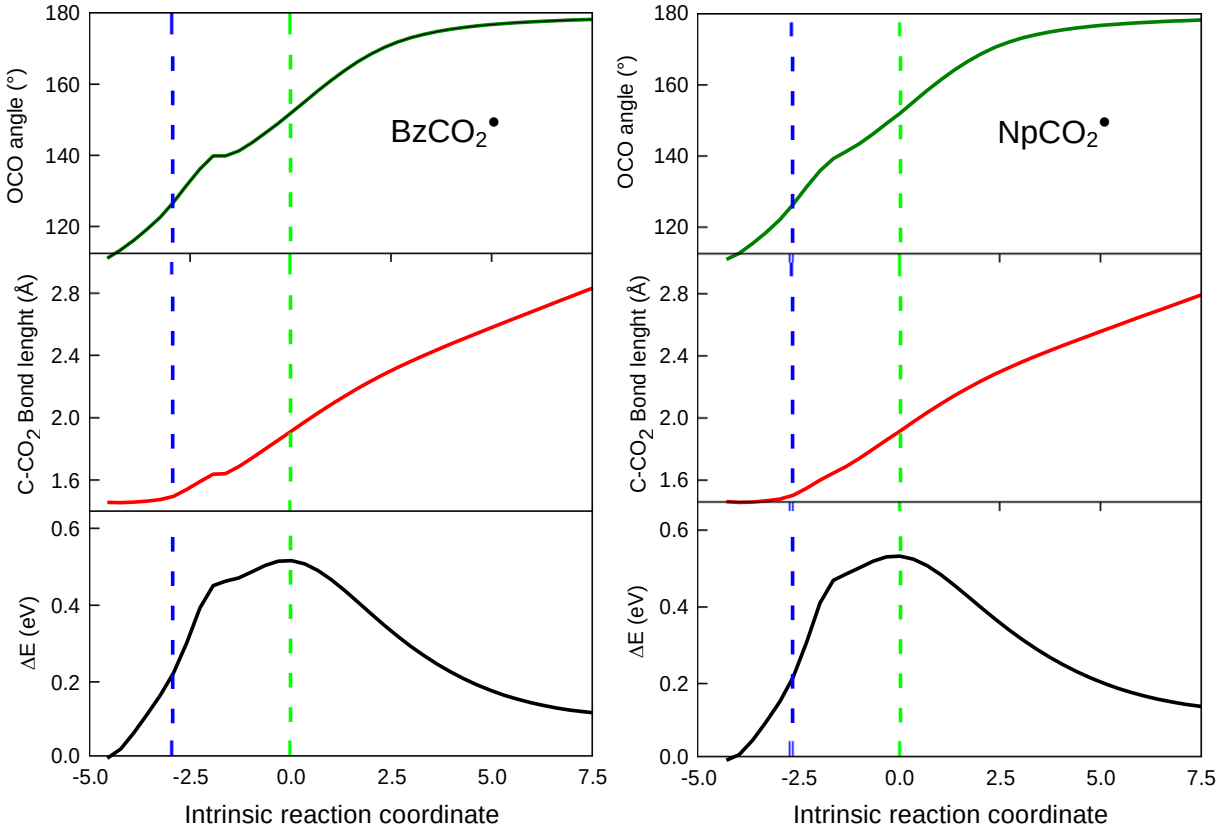

Figure SI-4: Energy (lower panel), C-CO_2 bond distance (middle panel) and OCO angle (upper pane) along the MEP for the decarboxylation of $BzCO_2^{\bullet}$ (left) and $NpCO_2^{\bullet}$ (right) radicals, calculated at the DFT-CAM-B3LYP/cc-pVDZ level. (**---**) indicates the TS position and (**---**) indicates a point at the beginning of the MEP close to the reactant geometry at which only the OCO angle has changed substantially.

Table SI-1: Adiabatic electronic transition energies of 2-Naphthoate calculated at the TD/DFT - B3LYP/cc-pVTZ level. The first state with reasonable oscillator strength is the third one at 3.2eV.

Energy (eV)	Os.Strength
2.7	4×10^{-6}
2.9	2×10^{-5}
3.2	6×10^{-3}
3.4	4×10^{-6}
3.6	3×10^{-5}
3.9	4×10^{-3}
4.1	2×10^{-2}