Electronic Supplementary Information for

"Dynamics of π^* -resonances in anionic clusters of *para*-toluquinone"

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Photodetachment yield spectra for pTQ⁻ and (pTQ)₃⁻

Photodetachment yield spectra for pTQ⁻ and $(pTQ)_3^-$, which plot total photoelectron signal with photon energy, are shown below. For pTQ⁻, the photoelectron yield for hv > 3.6 eV corresponds to the onset of the bright 3²[S] resonance. The MCP gate with was 50 ns for both spectra.



Global fit of the pTQ⁻ frequency-resolved spectrum

The global fit of the pTQ^- frequency-resolved spectrum, from which the detachment channel contributions were obtained, is shown below. There is excellent agreement between the experimental data and fit for all hv.



Angular distributions for the pTQ⁻ frequency-resolved spectrum

The photodetachment angular distributions associated with the frequency-resolved spectrum for pTQ⁻ are shown below. Angular anisotropy is quantified in terms of the conventional β_2 parameter, ranging $-1 \ge \beta_2 \ge 2$, where -1 and 2 correspond to electron ejection parallel and perpendicular with the laser polarization vector, respectively. $\beta_2 = 0$ corresponds to isotropic electron ejection. Overall, these β_2 are less pronounced than those for pBQ⁻ [see West et al., *J. Phys. Chem. A*, 2014, **118**, 11346]. For example, pBQ⁻ shows clear positive and negative β_2 parameters for PD and DA channels for hv < 3.3eV; corresponding β_2 for pTQ⁻ are ~0. We attribute the reduction of β_2 for pTQ⁻ to be a result of the reduced symmetry of pTQ⁻ (C_s compared with D_{2h} for pBQ). The negative β_2 region (-0.4) for hv >3.1 eV at an eKE consistent with PD confirms electron detachment occurs on a timescale fast compared with molecular rotation.



All individual pTQ⁻ frequency-resolved photoelectron spectra















All individual (pTQ)₃⁻ frequency-resolved photoelectron spectra











