Statistical vibrational autodetachment and radiative cooling rates of *para*-benzoquinone radical anions

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We report measurements of the statistical vibrational autodetachment (VAD, also called thermionic emission) and radiative cooling rates of isolated *para*-benzoquinone (pBQ, $C_6H_4O_2$) radical anions using the cryogenic electrostatic ion storage ring facility DESIREE [1]. The results are interpreted using master equation simulations with rate coefficients calculated using statistical detailed balance theory. The VAD rate is determined by measuring the time-dependent yield of neutral pBQ due to spontaneous electron emission from a highly-excited ensemble of anions formed in an electron-attachment ion source. Competition with radiative cooling quenches the VAD rate after a critical time of $\tau_c = 11.00(5)$ ms. Master equation simulations which reproduce the VAD yield provide an estimate of the initial effective vibrational temperature of the ions of 1100(20) K, and provide insight into the anion formation scenario. A second measurement of the radiative cooling rate of pBQ$^-$ stored for up to 0.5 s was achieved using time-dependent photodetachment action spectroscopy across the $^2A_u \leftarrow {}^2B_{2g}$ and $^2B_{2u} \leftarrow {}^2B_{2g}$ transitions. The rate at which hot-band contributions fade from the action spectrum is quantified by non-negative matrix factorisation. This is found to be commensurate with the average vibrational energy extracted from the simulations, with $1/e$ lifetimes of 0.16(3) s and 0.1602(7) s, respectively. Implications for astrochemistry are discussed.

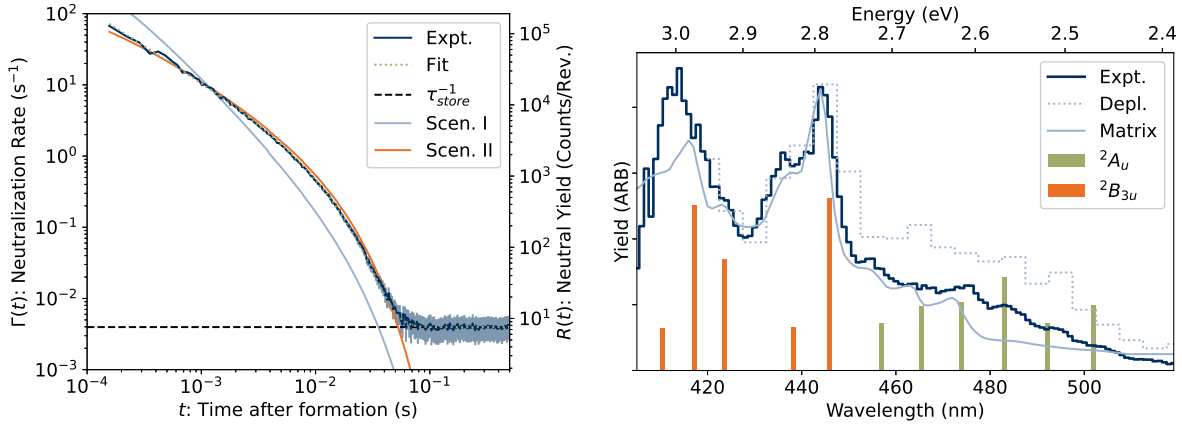

Figure 1: Left: Neutral yield from pBQ$^-$ formed in an electron attachment ion source. Right: Action spectrum of pBQ$^-$ integrated over 0.5–5 s storage time.

[1] M. H. Stockett *et al.* Phys. Chem. Chem. Phys. **24** 12002 (2022).