THE CAVITY RING–DOWN ABSORPTION SPECTRUM OF THE $S_0 \to T_1$ and $S_0 \to S_1$ transition of Jet–Cooled aromatic thione compounds

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The cavity ring-down method has been applied to the measurement of the absorption of 4–H–1–benzopyrane–4–thione (BPT)^{*b*} and 4–H–pyrane–4–thione (PT) in a supersonic jet in the wavelength region of the weak $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$ transition.

In the case of jet–cooled BPT the absorption energies of vibronic states between 15800 and 16650 cm⁻¹ corroborate previous assignments in the $S_0 \rightarrow T_1$ phosphorescence excitation and resonance–enhanced multi–photon excitation spectra. The symmetry forbidden 0,0 transition, $S_{0,0} \rightarrow S_{1,0}$ at 16522 cm⁻¹, was found to be 7.5 times weaker than the absorption transition to the triplet origin, $S_{0,0} \rightarrow T_{1z,0}$. Relative phosphorescence quantum yields were estimated.

For the more volatile PT the CRD absorption spectrum of jet–cooled PT was compared to PT in a static cell. Through the hot band analysis ground state vibrations were assigned in comparison to ab initio force field calculations^c

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