

STRUCTURE IN THE VISIBLE ABSORPTION BANDS OF JET-COOLED PHENYL PEROXY RADICALS

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The visible absorption bands of the phenyl peroxy radical in the gas phase have been investigated using cavity ring-down spectroscopy. Jet-cooling was used to reduce the spectral congestion. Structured spectra spanning the range from 17,500 - 19,000 cm^{-1} are reported for the first time. Analyses of these data have been guided by the results from time-dependent density functional calculations. The observed spectrum was found to be dominated by the bands of the $\tilde{B}^2A'' \leftarrow \tilde{X}^2A'$ transition. An analysis of the rotational contour for the origin band yielded a homogeneous linewidth of 2.2 cm^{-1} , corresponding to a decay rate of $4.1 \times 10^{11} \text{ s}^{-1}$. The results provide a rationale for the lack of structure in room temperature spectra that have been previously attributed to phenyl peroxy. They also indicate that the lower energy region of the spectrum may show resolvable structure at room temperature. If so, this would provide a more definitive signature for monitoring phenyl peroxy in kinetic measurements.