OBSERVATION OF THE $\widetilde{A}$ - $\widetilde{X}$ ABSORPTION SPECTRA OF CYCLOPENTYL AND CYCLOHEXYL PEROXY RADICALS BY CAVITY RINGDOWN SPECTROSCOPY

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Alkyl peroxy radicals are important intermediates in combustion chemistry. These molecules, formed from the addition of oxygen to organic radicals, are also pivotal species in atmospheric oxidation of organic compounds. Previous spectroscopic studies have monitored the intense $\widetilde{B}$ - $\widetilde{X}$ transition; however, this system cannot be used to exact detailed structural information due to predissociation in the $\widetilde{B}$ state. On the other hand, the weak $\widetilde{A}$ - $\widetilde{X}$ manifold has been used to selectively distinguish between isomers and conformers of a number of straight and branched aliphatic peroxy radicals. This research, mediated by cavity ringdown spectroscopy (CRDS) is now extended to include cyclic chain systems, beginning with cyclopentyl and cyclohexyl peroxy radicals.

In this work, we present a full vibrational analysis of the $\widetilde{A}$ - $\widetilde{X}$ CRDS spectra of cyclopentyl, cyclohexyl, and cyclohexyl-d_{11} peroxy radicals. For cyclohexyl peroxy, the spectrum obtained is consistent with calculated predictions for both axial and equatorial *gauche* conformers; for cyclopentyl peroxy, a single *gauche* conformer is observed. Contrary to our expectations, we see no clear evidence for the *cis*- conformers for either peroxy. Shapes of the electronic origin bands are well reproduced by hot band simulations, and Franck-Condon simulations facilitate assignment of the numerous active COO bending vibrations observed for cyclohexyl peroxy. Mode mixing appears to have important consequences on the spectrum in the O-O stretch region.