NEAR IR CAVITY RINGDOWN SPECTROSCOPY OF CHLORO-ALKYL PEROXYL RADICALS

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Chloro-alkyl peroxyl radicals are intermediates of alkene oxidation in the marine boundary layer, and serve as models for hydroxy-alkyl peroxyl radicals. Cavity ringdown spectra of the electronic $\widetilde{A}$ - $\widetilde{X}$ transition of chloro-ethyl, -propyl, -butyl and -butenyl peroxyl radicals will be reported. The spectra observed have more complex structure than the spectra of alkyl peroxyl radicals. DFT calculations predict multiple confomers of the radicals with the energies within 2 kcal/mol. These spectra reveal the subtle substituent effects on the $\widetilde{A}$ - $\widetilde{X}$ transition of the O-O chromophore. An integrated cross-section for chloro-ethyl peroxyl is estimated from the known rate of self-reaction.