OBSERVATION OF THE $\widetilde{A}$ - $\widetilde{X}$ TRANSITION OF ALLYL PEROXY RADICAL VIA CAVITY RINGDOWN SPECTROSCOPY

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Organic peroxy radicals are important chemical intermediates produced in combustion and by atmospheric oxidation of hydrocarbons. Peroxies containing the allyl functionality are particularly important as these are generated in large quantities by the OH-initiated oxidation of isoprene, the most abundant non-methane biogenic hydrocarbon. A structural diagnostic for the parent compound, the allyl peroxy radical, is therefore of great importance. We have recently measured the room temperature $\widetilde{A}$ - $\widetilde{X}$ electronic absorption spectrum of allyl peroxy via cavity ringdown spectroscopy. Photolysis of allyl bromide at 193 nm or 248 nm in the presence of O_2 results in observation of signals belonging to both allyl peroxy and HO_2 radicals, with the longer wavelength conditions being more favorable towards allyl peroxy formation. By comparing the experimental spectra with predictions from *ab initio* and density functional calculations, we have assigned the band origins and vibrational structure to conformers of allyl peroxy. Three of the five possible conformers (T_1G_2, G_1G_2, $G_1'G_2$) can be identified in the room temperature spectrum; the apparent absence of the remaining two conformers is rationalized on the basis of low Boltzmann factors and/or oscillator strengths. Computed OOCC torsional potentials are presented and their implications on the spectroscopy are discussed. This work represents an extension of recent progress in measuring $\widetilde{A}$ - $\widetilde{X}$ absorption spectra of alkyl peroxy radicals to unsaturated species.