

THE \tilde{A} - \tilde{X} ELECTRONIC TRANSITIONS OF THE CH₂BrOO AND CH₂ClOO RADICALS IN THE NEAR INFRARED REGION

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Moderate resolution cavity ring-down spectroscopy (CRDS) is used to obtain the \tilde{A} - \tilde{X} electronic transition of the CH₂BrOO and CH₂ClOO radicals in the near-infrared region at room temperature. The CH₂BrOO radical was generated by 248nm excimer laser photolysis of a gas mixture of CH₂Br₂, O₂ and inert gas. The CH₂ClOO radical was generated similarly except for using CH₂ClI as the precursor. In both spectra, the first strong transition is located near 6800 cm⁻¹, and is assigned as the origin band. Several transitions are observed in the region between the origin and 9000 cm⁻¹. A strong vibrational transition is observed around 800 cm⁻¹ to the blue of the origin and attributed to the OO stretch which is characteristic of the peroxy radical spectra. Our analysis of the vibrational structure is conducted using frequencies and Franck-Condon factors based on electronic structure calculations. Rotational structure analyses with ab-initio calculated rotational constants and dipole moments show good agreement with the contour of the origin band. Numerous transitions around the origin band in the CH₂BrOO radical spectrum can be explained by excitation from low-lying torsional levels in the \tilde{X} state that are populated at room temperature.