The $\widetilde{A}\leftarrow\widetilde{X}$ ABSORPTION SPECTRUM OF 2-NITROOXYBUTYL PEROXY RADICAL

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The nitrate radical is an important atmospheric oxidant in the nighttime sky. Nitrate radicals react by addition to alkenes, and in the presence of oxygen form nitrooxyalkyl peroxy radicals. The peroxy radical formed from the reaction of 2-butene, nitrate radical, and oxygen was detected by cavity ringdown spectroscopy (CRDS) via its $\widetilde{A}\leftarrow\widetilde{X}$ electronic absorption spectrum. The $\widetilde{A}\leftarrow\widetilde{X}$ electronic transition is a bound-bound transition with enough structure to distinguish between different peroxy radicals as well as different conformers of the same peroxy radical. Two conformers of the nitrooxybutyl peroxy radical have been observed; the absorption features are red shifted from the same absorption features of sec-butyl peroxy radical. Calculations on the structure of nitrooxyalkyl peroxy radicals and general trends of the position of the $\widetilde{A}\leftarrow\widetilde{X}$ absorption transitions have also been performed and compared to those of unsubstituted peroxy radicals.