Direct detection and kinetics of NO_3 and Cl-substituted alkylperoxy radicals using cavity ringdown spectroscopy

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Peroxy radicals dominate atmospheric chemistry as important reaction intermediates in the oxidation of volatile organic compounds. Biogenic alkene emissions such as isoprene and 2-methyl-3-buten-2-ol (MBO-232) react rapidly with free radicals to form β-substituted alkylperoxy radicals. We have directly detected the A-X electronic transition spectrum of NO_3- and Cl-substituted atmospherically-relevant alkyl peroxy radicals from 7000-8500 cm^{-1} using cavity ringdown spectroscopy. Spectra of peroxy radicals formed by NO_3 and Cl radical-initiated oxidation of 2-butene, 3-methyl-1-butene, and MBO-232 are presented here with preliminary kinetic results. Kinetic rate constants of peroxy radical self-reactions and peroxy radical reactions with HO_2 and NO will be obtained by directly observing the near-infrared absorption spectrum of the peroxy radical intermediate. The preliminary Cl-substituted isoprenyl peroxy radical A-X electronic transition spectrum has also been obtained.