CAVITY RINGDOWN SPECTROSCOPY OF THE NITRATE AND PEROXY RADICALS

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ABSTRACT

The chemistry of the Earth's atmosphere consists of complex networks of reactions. Photooxidation of volatile organic compounds (VOCs) in the atmosphere initiates free radical formation. These radicals attack other VOCs to form pollutants and secondary organic aerosols. Quantitative understanding of the radicals and reactions is needed for accurate modeling of the atmosphere. Many species are difficult to study due to low concentrations and short lifetimes. Spectroscopic methods in the ultraviolet and visible regions either do not have the sensitivity or the specificity to characterize these reactions. The work here examines the chemistry and physics of atmospheric radicals by using the sensitive and fast spectroscopic technique cavity ringdown spectroscopy (CRDS), to detect transient species in the near-infrared (NIR) region.

The nitrate radical NO_3 is a major nighttime oxidant in the troposphere. It is also a classic example of the breakdown of the Born-Oppenheimer approximation. The radical was first observed a century ago in atmospheric measurements. The structures of the three lowest electronic state however are still not well understood. Difficulties arise from the non-adiabatic Jahn Teller and Pseudo-Jahn-Teller effects. In Chapter 3, we examine the electronic-dipole forbidden $\tilde{A} \leftarrow \tilde{X}$ transition of NO_3 in the NIR to elucidate the $\tilde{A}$ state of NO_3. In Chapter 4, we examine the role of NO_3 in atmospheric reactions by detecting the peroxy radical intermediate of the oxidation of 2-butene by NO_3.

The chlorine atom Cl is highly reactive and has been historically considered a coastal or marine layer oxidant. Studies now indicate that Cl atoms can play significant roles in urban mainland chemistry. Isoprene and 2-methyl-3-buten-2-ol (MBO232) are two important biogenic VOC

emissions. Isoprene alone is responsible for emissions of 500 Tg C y^{-1}. The peroxy radical intermediates of the oxidation of isoprene and MBO232 by Cl have never been detected using absorption spectroscopy. Chapter 5 includes the first preliminary CRD spectra of the $\tilde{A} \leftarrow \tilde{X}$ transition of Cl-isoprenyl and Cl-MBO232 peroxy radials in the NIR. We also outline kinetic experiments to measure the rates of reaction between the Cl-substituted peroxy radicals and nitric oxide (NO) and hydroperoxy radical (HO_2) under high and low NO_x conditions in the troposphere.

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