Hydrogen and Halogen Oxide Radical Spectroscopy in the Laboratory and the Atmosphere: Applications to Studies of Stratospheric Ozone Depletion

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Research in atmospheric chemistry attempts to understand the complex system of interactions that affect the overall production and loss of the key molecule, ozone. A key element in this process is the measurement of reaction rates and abundances of short-lived species in both laboratory studies and the atmosphere. High resolution spectroscopy plays an important role in both of these endeavors. In this talk we discuss several recent applications from our group’s work as applied to species in the hydrogen oxide and halogen oxide radical families.

In the first of these studies, rate coefficients were measured for the recombination reaction, \( \text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HO}_2\text{NO}_2 + \text{M} \), over the temperature range 210-298 K. Reactions were initiated by laser photolysis at 308 nm and reactants were probed using cw long-path two-color absorption for \( \text{HO}_2 \) and \( \text{NO}_2 \). RF-modulated DFB lasers in a Herriott-cell configuration probed \( \text{HO}_2 \) radicals in both the \( ^2A' \leftrightarrow ^2A'' \) transition at 1.4 \( \mu \text{m} \) as well as the first vibrational overtone in the \( \text{OH} \) stretch at 1.5 \( \mu \text{m} \).

The kinetics of the formation and destruction of \( \text{CIOOCI} \), a key intermediate in the catalytic destruction of ozone in the polar stratosphere, have been studied using both pulsed photolysis and flow tube methods. In the pulsed photolysis experiments, the recombination of \( \text{CIO} \) radicals has been studied over the temperature range 180-250 K. \( \text{CIO} \) and \( \text{CIOOCI} \) were monitored simultaneously using long-path differential absorption between 210-280 nm. The discharge-flow/mass spectrometry method has been used to study the reactions of \( \text{Cl} \), \( \text{Br} \) and \( \text{NO} \) with \( \text{CIOOCI} \) using a high-pressure pre-reactor for the \textit{in situ} synthesis of \( \text{CIOOCI} \).

Finally, results shall be presented on three years of atmospheric measurements of the \( \text{OH} \) radical at Table Mountain, California, using a new, compact high-resolution interferometer (FTUVS) which probes several lines in the \( \text{A} \leftrightarrow \text{X} \) progression at 308 nm in solar absorption mode. Applications to the measurement of other trace atmospheric species will be discussed.

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