HIGH RESOLUTION CAVITY RINGDOWN SPECTROSCOPY OF JET-COOLED DEUTERATED METHYL PEROXY (CD_3O_2) IN THE NEAR IR.

SHENGHAI WU, PATRICK RUPPER, PATRICK DUPRÉ and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus OH 43210.*

Alkyl peroxy radicals play a key role as intermediates in the oxidation of hydrocarbons in atmospheric as well as combustion chemistry, and a detailed knowledge about gas phase reactions involving such reactive species is of great importance. Methyl peroxy is the simplest alkyl peroxy radical and is therefore the starting point for the spectroscopic characterization of this class of molecules. Cavity ringdown spectroscopy at room-temperature showed that their near-IR $\tilde{\mathrm{A}} - \tilde{\mathrm{X}}$ electronic transition is a sensitive, species-specific diagnostic for the radicals.

Spectra of such peroxy radicals under jet-cooled conditions would be of great value since congestion caused by the overlap of different rotational lines and different conformers obscures much detail at ambient temperature. In this work, the $\tilde{\mathrm{A}}\,^2\mathrm{A}'$ - $\tilde{\mathrm{X}}\,^2\mathrm{A}''$ vibrationless transition of CD_3O_2 at 1.36 μm was studied via cavity ringdown spectroscopy. Albeit this is a weak transition, it was possible to observe the spectrum under jet-cooled conditions (T_{rot} ~15 K) by combining a narrow-bandwidth laser source with a supersonic slit-jet expansion and discharge. High spectral resolution in the near-IR is obtained by using stimulated Raman shifting of the pulsed amplified output of a cw Ti:Sa ring laser. Rotational and spin-rotational structure have been resolved in the spectra. The resolved structure has been fully assigned and analyzed (transitions with N up to 10 and K up to 4), resulting in the determination of ground and excited states' rotational constants, spin-rotational constants, and the $\tilde{\mathrm{A}} - \tilde{\mathrm{X}}$ electronic excitation energy.