CAVITY RINGDOWN SPECTROSCOPY AND KINETICS OF HO_2+HCHO: DETECTION OF THE ν_1 AND $\tilde{A}$-$\tilde{X}$ BANDS OF $HOCH_2OO$

MATTHEW K. SPRAGUE[a], MITCHIO OKUMURA, *California Institute of Technology, Division of Chemistry, MC 127-72, Pasadena, CA 91125*; and STANLEY P. SANDER, *Jet Propulsion Laboratory, California Institute of Technology, MS 183-901, Pasadena, CA 91109*.

The reactions of HO_2 with carbonyl compounds are believed to be a sink for carbonyl compounds in the upper troposphere and lower stratosphere. These reactions proceed through a hydrogen bound intermediate before isomerizing.[b] The reaction of HO_2 + formaldehyde (HCHO) serves as a prototype for this class of reactions, forming the isomerization product hydroxymethylperoxy ($HOCH_2OO$, HMP). Previous studies measured the spectrum and kinetics of HMP using either FTIR detection of the end products[c] or direct detection of HMP by the unstructured $\tilde{B}$-$\tilde{X}$ transition.[d,e] Despite these studies, considerable uncertainty exists in the rate constant of HMP formation (80%, 2σ).[f]

In this talk, we report the first detection of the ν_1 (OH stretch) and $\tilde{A}$-$\tilde{X}$ electronic spectra of the HMP radical. The OH stretch spectrum is broad and featureless, while the $\tilde{A}(0)$-$\tilde{X}(0)$ origin and combination band with the OOCO torsion $\tilde{A}(n_{OOCO}=1)$-$\tilde{X}(0)$ are rotationally resolved. Quantum chemistry calculations have been performed on both the $\tilde{A}$ and $\tilde{X}$ states as a function of the OOCO and HOCO dihedral angles to estimate the $\tilde{A}$-$\tilde{X}$ transition frequency and to assess the coupling between the two torsional modes. We also present kinetics data showing the rates of production and destruction of HMP.

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[a]Support from the NDSEG Fellowship, California Air Resources Board Contracts 03-333 and 07-730, and NASA Upper Atmosphere Research Program Grants NAG5-11657, NNG06GD88G and NNX09AE21G are gratefully acknowledged

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