

## CAVITY RINGDOWN SPECTROSCOPY AND KINETICS OF HO<sub>2</sub>+HCHO: DETECTION OF THE $\nu_1$ AND $\tilde{A}-\tilde{X}$ BANDS OF HOCH<sub>2</sub>OO

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The reactions of HO<sub>2</sub> 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.<sup>b</sup> The reaction of HO<sub>2</sub> + formaldehyde (HCHO) serves as a prototype for this class of reactions, forming the isomerization product hydroxymethylperoxy (HOCH<sub>2</sub>OO, HMP). Previous studies measured the spectrum and kinetics of HMP using either FTIR detection of the end products<sup>c</sup> or direct detection of HMP by the unstructured  $\tilde{B}-\tilde{X}$  transition.<sup>d,e</sup> Despite these studies, considerable uncertainty exists in the rate constant of HMP formation (80%,  $2\sigma$ ).<sup>f</sup>

In this talk, we report the first detection of the  $\nu_1$  (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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<sup>b</sup>I. Hermans, J. F. Muller, T. L. Nguyen, P. A. Jacobs, and J. Peeters. *J. Phys. Chem. A* **2005**, *109*, 4303.

<sup>c</sup>F. Su, J. G. Calvert, and J. H. Shaw *J. Phys. Chem.* **1979**, *83*, 3185.

<sup>d</sup>B. Veyret, R. Lesclaux, M. T. Rayez, J. C. Rayez, R. A. Cox, and G. K. Moortgat *J. Phys. Chem.* **1989**, *93*, 2368.

<sup>e</sup>J. P. Burrows, G. K. Moortgat, G. S. Tyndall, R. A. Cox, M. E. Jenkin, G. D. Hayman, and B. Veyret *J. Phys. Chem.* **1989**, *93*, 2375

<sup>f</sup>S. P. Sander, B. J. Finlayson-Pitts, D. M. Golden, R. E. Huie, C. E. Kolb, M. J. Kurylo, M. J. Molina, *et al.* *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 16*, Jet Propulsion Laboratory, 2009