

## UV SPECTRUM AND PHOTOCHEMISTRY OF THE SIMPLEST CRIEGEE INTERMEDIATE CH<sub>2</sub>OO

JOSEPH M. BEAMES, FANG LIU, LU LU, and MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323.*

In the troposphere, ozonolysis of ethene as well as other terminal alkenes, such as isoprene, results in formation of the simplest Criegee intermediate, CH<sub>2</sub>OO, which gives rise to many products of atmospheric significance. In the laboratory, CH<sub>2</sub>OO is prepared in a quartz capillary tube reactor using a new synthetic route<sup>a</sup> based on 248 nm photolysis of CH<sub>2</sub>I<sub>2</sub> and subsequent reaction with O<sub>2</sub>. The CH<sub>2</sub>OO and other products undergo supersonic expansion, and are detected using fixed frequency VUV ionization (118 nm) with mass (m/z=46) and isomer selectivity. Spectroscopic studies of CH<sub>2</sub>OO are carried out by UV laser excitation on the B <sup>1</sup>A'-X <sup>1</sup>A' transition prior to photoionization, which results in significant depletion of the ion signal (approaching 100%) near the peak of a broad absorption profile centered at 335 nm.<sup>b</sup> The large depletion and broad absorption are indicative of rapid dissociation, consistent with the repulsive B <sup>1</sup>A' state potential in the O-O coordinate that has been computed theoretically. The experimental spectrum is in very good agreement with the absorption spectrum calculated using the one-dimensional reflection principle. The atmospheric lifetime of CH<sub>2</sub>OO due to solar photolysis at midday is estimated to be ~ 1 s. These findings provide a UV spectral signature of the strong π\*-π transition associated with the four π electrons on the carbonyl oxide group in CH<sub>2</sub>OO. Extensions of this work to methyl substituted Criegee intermediates reveal similar absorption features arising from the COO π -system .

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<sup>a</sup>O. Welz, J. D. Savee, D. L. Osborn, S. S. Vasu, C. J. Percival, D. E. Shallcross, and C. A. Taatjes, *Science* **335**, 204 (2012).

<sup>b</sup>J. M. Beames, F. Liu, L. Lu, and M. I. Lester, *J. Am. Chem. Soc.* **134**, 20045 (2012).