

INFRARED ABSORPTION SPECTRUM OF THE SIMPLEST CRIEGEE INTERMEDIATE CH₂OO

YU-TE SU, YU-HSUAN HUANG, HENRYK WITEK, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan*; YUAN-PERN LEE, *Department of Applied Chemistry and Institute of Molecular Science, National Chiao Tung University, Hsinchu 30010, Taiwan and Institute of Atomic and Molecular Sciences, Academia Sinica, Taipei 10617, Taiwan*.

The Criegee intermediates are carbonyl oxides postulated to play key roles in the reactions of ozone with unsaturated hydrocarbons; these reactions constitute an important mechanism for the removal of unsaturated hydrocarbons and for the production of OH in the atmosphere. Here we report the transient infrared (IR) absorption spectrum of the simplest Criegee intermediate CH₂OO, produced from CH₂I + O₂ in a flow reactor, using a step-scan Fourier-transform spectrometer coupled with a multipass absorption cell. CH₂I was produced on photolysis of CH₂I₂ with laser light at 248 nm. The five bands observed near 1435, 1286, 1241, 908, and 848 cm⁻¹ provide definitive identification of this intermediate on comparison of anharmonic vibrational wavenumbers and relative IR intensities predicted using quadratic force field obtained with the NEVPT2 method implemented in the MOLPRO quantum chemistry package using the CASSCF(8,8) reference wave function. Observed rotational contours also agree with those simulated based on rotational constants predicted with the B3LYP method. Observation of the out-of-plane CH₂-wagging (ν_8) mode near 848 cm⁻¹ with a characteristic *c*-type structure showing a prominent Q-branch further supports the assignment of the observed features to a planar CH₂OO. The observed vibrational frequencies are more consistent with a zwitterion rather than a diradical structure of CH₂OO. The direct IR detection of CH₂OO should prove useful for kinetic and mechanistic investigations of the Criegee mechanism.