INFRARED ABSORPTION SPECTRUM OF THE SIMPLEST CRIEGEE INTERMEDIATE CH_2OO

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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 CH_2OO, produced from $CH_2I + O_2$ in a flow reactor, using a step-scan Fourier-transform spectrometer coupled with a mulitpass absorption cell. CH_2I was produced on photolysis of CH_2I_2 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 CH_2-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 CH_2OO. The observed vibrational frequencies are more consistent with a zwitterion rather than a diradical structure of CH_2OO. The direct IR detection of CH_2OO should prove useful for kinetic and mechanistic investigations of the Criegee mechanism.