

Spectroscopy of the simplest Criegee intermediate CH₂OO: Simulation of the first bands in its electronic and photoelectron spectra

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CH₂OO, the simplest Criegee intermediate, are isoelectronic with ozone. They both play very important roles in atmospheric chemistry. However, CH₂OO is much more reactive and there were no direct gas-phase studies until very recently when its photoionization efficiency spectrum was recorded and kinetics studies were made of some reactions of CH₂OO with a number of molecules of atmospheric importance, using photoionization mass spectrometry to monitor CH₂OO.

In order to encourage more direct studies on CH₂OO and other Criegee intermediates, the electronic and photoelectron spectra of CH₂OO have been simulated using high level electronic structure calculations and Franck-Condon factor calculations. Adiabatic and vertical excitation energies of CH₂OO were calculated with TDDFT, EOM-CCSD, and CASSCF methods. DFT, QCISD and CASSCF calculations were also performed on neutral and low-lying ionic states, with single energy calculations being carried out at higher levels to obtain more reliable ionization energies. The results show that the most intense band in the electronic spectrum of CH₂OO corresponds to the $\tilde{B}^1A' \leftarrow \tilde{X}^1A'$ absorption. It is a broad band in the region 250-450 nm showing extensive structure in vibrational modes involving O-O stretching and C-O-O bending. Evidence is presented to show that the electronic absorption spectrum of CH₂OO has probably been recorded in earlier work, albeit at low resolution. The results suggested that CH₂OO were prepared and observed in earlier work from the CH₂I + O₂ reaction and that the assignment of the observed spectrum solely to CH₂IOO was not correct.

The low ionization energy region of the photoelectron spectrum of CH₂OO consists of two overlapping vibrationally structured bands corresponding to one-electron ionizations from the highest two occupied molecular orbitals of the neutral molecule. In each case, the adiabatic component is the most intense and the adiabatic ionization energies of these bands are expected to be very close, at 9.971 and 9.974 eV at the highest level of theory used.