A THEORETICAL CHARACTERIZATION OF ELECTRONIC STATES OF CH_2IOO AND CH_2OO RADICALS RELEVANT TO THE NEAR IR REGION

RICHARD DAWES, PHALGUN LOLUR, *Department of Chemistry, Missouri University of Science and Technology, Rolla, MO, USA*; MENG HUANG, NEAL KLINE, TERRY A. MILLER, *Department of Chemistry and Biochemistry, The Ohio State University, Columbus, OH, USA*.

Criegee intermediates (R_1R_2COO or CIs) arise from ozonolysis of biogenic and anthropogenic alkenes, which is an important process in the atmosphere. Recent breakthroughs in producing them in the gas phase have resulted in a flurry of experimental and theoretical studies. Producing the simplest CI (CH_2OO) in the lab via photolysis of CH_2I_2 in the presence of O_2 yields both CH_2OO and CH_2IOO with pressure dependent branching.

As discussed in the preceding talk, both species might be expected to have electronic transitions in the near IR (NIR). Here we discuss electronic structure calculations used to characterize the electronic states of both systems in the relevant energy range. Using explicitly-correlated multireference configuration interaction (MRCI-F12) and coupled-cluster (UCCSD(T)-F12b) calculations we were first able to exclude CH_2OO as the carrier of the observed NIR spectrum. Next, by computing frequencies and relaxed full torsional scans for the $\tilde{A}$ and $\tilde{X}$ states, we were able to aid in analysis and assignment of the NIR spectrum attributed to CH_2IOO.