ION-DIP INFRARED SPECTROSCOPY OF CRIEGEE INTERMEDIATES

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In the troposphere, alkene ozonolysis produces carbonyl oxide intermediates, known as Criegee intermediates, which can undergo unimolecular decay to generate hydroxyl (OH) radicals, an important atmospheric oxidant. This study focuses on the *syn* conformer of the methyl-substituted Criegee intermediate (*syn*-CH_3CHOO) that decays via 1,4 hydrogen transfer from the methyl group to the terminal oxygen, followed by O-O bond fission to yield OH radical products. IR excitation of jet-cooled *syn*-CH_3CHOO in the overtone CH stretch ($2\nu_{CH}$) region facilitates this process, leading to rapid dissociation to OH + vinoxy radicals within 10 ns.[a] Here, we demonstrate ion-dip infrared spectroscopy of *syn*-CH_3CHOO by combining IR activation in the $2\nu_{CH}$ region with VUV photoionization (10.5 eV, preferentially probing the *syn* conformer)[b] and time-of-flight mass spectrometry detection (m/z 60). The resultant ground state depletion spectrum is recorded and compared with that previously obtained by IR action spectroscopy with detection of OH products using laser-induced fluorescence.[c] The ion-dip infrared spectrum reproduces the two main features at 5987 and 6081 cm^{-1}, but with notable changes that are being explored. In addition, the experimental results are compared with anharmonic frequency calculations at various levels of theory, which predict a single strong absorption in the $2\nu_{CH}$ region. Further calculations of vibrational couplings are needed to interpret the experimental observations.

[a] Y. Fang, F. Liu, V. P. Barber, S. J. Klippenstein, A. B. McCoy and M. I. Lester, *J. Chem. Phys.* **145**, 234308 (2016).

[b] C. A. Taatjes, O. Welz, A. J. Eskola, J. D. Savee, A. M. Scheer, D. E. Shallcross, B. Rotavera, E. P. F. Lee, J. M. Dyke, D. K. W. Mok, D. L. Osborn and C. J. Percival, *Science* **340**, 177-180 (2013).

[c] F. Liu, J. M. Beames, A. S. Petit, A. B. McCoy and M. I. Lester, *Science* **345**, 1596-1598 (2014).