INFRARED ABSORPTION OF CH_3SONO DETECTED WITH TIME-RESOLVED FOURIER-TRANSFORM SPECTROSCOPY

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A step-scan Fourier-transform spectrometer coupled with a 6.4-m multipass absorption cell was employed to detect time-resolved infrared absorption spectra of reaction intermediates produced upon UV irradiation of a flowing mixture of CH_3SSCH_3 and NO_2 in CO_2. Irradiation of CH_3SSCH_3 at 248 nm produces CH_3S radicals that subsequently react with NO_2. Under a total pressure of 100 Torr, we observed bands near 1560 cm^{-1}, assignable to mainly the N=O stretching mode of CH_3SONO, with a small contribution from CH_3SNO_2. Calculations with density-functional theory (B3LYP/aug-cc-pVTZ and B3P86/aug-cc-pVTZ) predicted the geometry, vibrational wavenumbers, and rotational parameters of CH_3SONO and CH_3SNO_2. Based on these predicted rotational parameters, the simulated absorption band agrees satisfactorily with experimental results. Under a total pressure of 16 Torr, bands near 1560 and 1260 cm^{-1} are assigned to NO_2 asymmetric and symmetric stretching modes of CH_3SNO_2, respectively; the former is overlapped with the N=O stretching mode of CH_3SONO. An additional band near 1070 cm^{-1} is assigned to the S=O stretching mode of CH_3SO, reported previously as a secondary product in the reaction of $CH_3S + O_2$.[a] Reaction of $CH_3S + NO_2$ at high pressure clearly yields CH_3SONO, rather than CH_3SNO_2, as a major product.

[a] L.-K. Chu and Y.-P. Lee, *J. Chem. Phys.* 133, 184303 (2010).