

## INFRARED ABSORPTION OF CH<sub>3</sub>SONO 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<sub>3</sub>SSCH<sub>3</sub> and NO<sub>2</sub> in CO<sub>2</sub>. Irradiation of CH<sub>3</sub>SSCH<sub>3</sub> at 248 nm produces CH<sub>3</sub>S radicals that subsequently react with NO<sub>2</sub>. Under a total pressure of 100 Torr, we observed bands near 1560 cm<sup>-1</sup>, assignable to mainly the N=O stretching mode of CH<sub>3</sub>SONO, with a small contribution from CH<sub>3</sub>SNO<sub>2</sub>. Calculations with density-functional theory (B3LYP/aug-cc-pVTZ and B3P86/aug-cc-pVTZ) predicted the geometry, vibrational wavenumbers, and rotational parameters of CH<sub>3</sub>SONO and CH<sub>3</sub>SNO<sub>2</sub>. 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<sup>-1</sup> are assigned to NO<sub>2</sub> asymmetric and symmetric stretching modes of CH<sub>3</sub>SNO<sub>2</sub>, respectively; the former is overlapped with the N=O stretching mode of CH<sub>3</sub>SONO. An additional band near 1070 cm<sup>-1</sup> is assigned to the S=O stretching mode of CH<sub>3</sub>SO, reported previously as a secondary product in the reaction of CH<sub>3</sub>S + O<sub>2</sub>.<sup>a</sup> Reaction of CH<sub>3</sub>S + NO<sub>2</sub> at high pressure clearly yields CH<sub>3</sub>SONO, rather than CH<sub>3</sub>SNO<sub>2</sub>, as a major product.

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<sup>a</sup>L.-K. Chu and Y.-P. Lee, *J. Chem. Phys.* **133**, 184303 (2010).