INFRAVERD ABSORPTION OF CH₃SO₂ 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 the reaction intermediate CH₃SO₂ radical, produced upon irradiation of a flowing mixture of CH₃I and SO₂ in CO₂ at 248 nm. Two transient bands with origins at 1280 and 1076 cm⁻¹ were observed and assigned to the SO₂-antisymmetric and SO₂-symmetric stretching modes of CH₃SO₂, respectively. Calculations with density-functional theory (B3LYP/aug-cc-pVTZ and B3P86/aug-cc-pVTZ) predicted the geometry, vibrational wave numbers, and rotational parameters of CH₃SO₂ and CH₃OSO. Based on predicted rotational parameters, the simulated absorption band of SO₂-antisymmetric stretch which is dominated by the b-type rotational structure agrees satisfactorily with experimental results. In addition, a band near 1159 cm⁻¹ was observed at a later period and was attributed to CH₃SO₂I. The reaction kinetics of CH₃ + SO₂ = CH₃SO₂ and CH₃SO₂ + I = CH₃SO₂I based on the rise and decay of absorption bands of CH₃SO₂ and CH₃SO₂I agree satisfactorily with previous reports.