INFRARED ABSORPTION OF CH_3SO_2 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 CH_3SO_2 radical, produced upon irradiation of a flowing mixture of CH_3I and SO_2 in CO_2 at 248 nm. Two transient bands with origins at 1280 and 1076 cm^{-1} were observed and assigned to the SO_2-antisymmetric and SO_2-symmetric stretching modes of CH_3SO_2, 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 CH_3SO_2 and CH_3OSO. Based on predicted rotational parameters, the simulated absorption band of SO_2-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 CH_3SO_2I. The reaction kinetics of $CH_3 + SO_2 = CH_3SO_2$ and $CH_3SO_2 + I = CH_3SO_2I$ based on the rise and decay of absorption bands of CH_3SO_2 and CH_3SO_2I agree satisfactorily with previous reports.