

INTERNAL ENERGY DISTRIBUTION OF CH_3O (X^2E) FROM PHOTODISSOCIATION OF METHYL NITRATE

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The methoxy (CH_3O) radical has attracted a great deal of attention in the literature due to its unique spectroscopy, as well as its importance as a reactive intermediate in combustion and atmospheric chemistry. In this study, we employ CH_3O as a dynamical probe of the photodissociation dynamics of methyl nitrate, CH_3ONO_2 , at 193 nm. Rotationally-resolved spectra of the CH_3O photoproduct were recorded in the $A^2A_1 - X^2E$ system under both nascent and jet-cooled conditions using laser-induced fluorescence (LIF) spectroscopy. $\text{CH}_3\text{O } A^2A_1 - X^2E$ transitions could be simulated effectively using known spectroscopic constants at the lowest temperatures achieved under jet-cooled conditions. Spectra recorded at warmer temperatures are being used to refine reported spectroscopic constants. Under nascent conditions, transitions were observed from the vibrationless level of CH_3O (X^2E) as well as with C–O stretch vibrational excitation, and the vibrational branching ratio is determined. The rotational excitation of these vibrational bands was fit to a Boltzmann distribution to extract nascent rotational temperatures. The experimental data indicate that the CH_3O fragment is produced with minimal internal energy (1% of the available energy) following photodissociation of CH_3ONO_2 at 193 nm.