THE PHOTODISSOCIATION DYNAMICS OF METHYL NITRATE

CRAIG MURRAY, ERIKA L. DERRO, MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104*; and MARK D. MARSHALL, *Department of Chemistry, Amherst College, Amherst, MA 01002*.

Interest in the photodissociation mechanism of alkyl nitrates ($RONO_2$, where R = CH_3, C_2H_5, etc.) stems from recent experimental measurements in the troposphere indicating that they are an important component of "missing NO_y". In this study, the photodissociation dynamics of methyl nitrate, CH_3ONO_2, at 193 nm have been investigated by examining the products from the primary channel, namely, CH_3O and NO_2. Laser-induced fluorescence (LIF) spectroscopy was employed to probe the nascent internal energy distribution of the CH_3O radical, a small fraction of which was found to be produced with one quantum of C−O stretch excitation. The stretch-excited methoxy was observed to be formed with a significantly greater degree of rotational excitation than the vibrational ground state. Furthermore, dispersed fluorescence measurements reveal that the NO_2 fragment is produced electronically excited with internal energies out to the NO + O dissociation limit, indicating that the initial excitation is strongly localized on the NO_2 moiety. Comparisons will be drawn with the analogous photodissociation of nitric acid, $HONO_2$.