PHOTODISSOCIATION OF VIBRATIONALLY EXCITED CH_3Cl: MODIFICATION OF THE DISSOCIATION DYNAMICS

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Vibrationally excited CH_3Cl is prepared by laser excitation in the fourth overtone C-H stretch band near 725 nm and photodissociated at fixed wavelengths near 240 nm which also probe either the H, Cl($^2P_{3/2}$), or Cl($^2P_{1/2}$) photofragments via (2+1) resonance enhanced multiphoton ionization (REMPI) in a time-of-flight mass spectrometer. Jet cooling of the CH_3Cl reveals two partially resolved bands in the overtone excitation spectrum which are assigned to [5,0,0] and [4,0,0] + $2\nu_2$. The product yields from the photolysis of vibrationally excited CH_3Cl show decided enhancement compared to photolysis of the ground state. Branching ratios of atomic products are also determined for photolysis of both excited and ground state CH_3Cl. The ratio of Cl($^2P_{1/2}$) to Cl($^2P_{3/2}$) is dramatically larger for photolysis of vibrationally excited vs. ground state CH_3Cl.