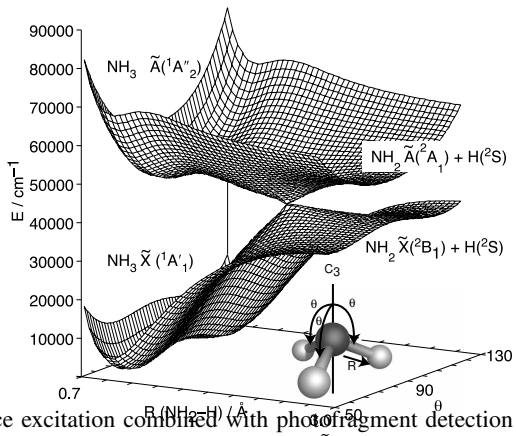
VIBRONIC STRUCTURE AND PHOTODISSOCIATION DYNAMICS OF THE $\tilde{A}$ STATE OF JET-COOLED AMMONIA

A. BACH, J. M. HUTCHISON, R. J. HOLIDAY, and F. F. CRIM, *Department of Chemistry,University of Wisconsin-Madison, Madison, WI 53706*.

Vibrationally mediated photodissociation action spectroscopy of jet-cooled ammonia provides information on the vibronic structure and photodissociaiton dynamics in the $\tilde{A}$ state. Initial vibrational excitation to selected rotation-inversion levels in the N–H stretching fundamental changes the Franck-Condon factors for the subsequent electronic transition markedly and allows assignment of sharp resonances to a progression in the degenerate bending mode (ν_4') including umbrella-bending combination states for the first time. We also identify broad, non-Lorentzian shaped resonances as transitions to the symmetric and antisymmetric stretching fundamentals. Our proposed assignment reveals an accidental degeneracy of the umbrella and bending modes with fundamental frequencies of 892±8 cm^{-1} and 906±30 cm^{-1}, respectively. The anharmonicities for the bend $x_{44} = 9 \pm 6$ and g_{44}=16±7 cm^{-1} are slightly larger than for the umbrella progression and the near degeneracy leads to a large off diagonal anharmonicity of $x_{24} = 56 \pm 13$ cm^{-1}.



Additional state selectivity in infrared-ultraviolet optical double resonance excitation combined with photofragment detection allows rovibronic analysis of the rapidly predissociating levels in the $\tilde{A}$ state of ammonia. The lifetime for NH_3 ($\tilde{A}$) excited to four quanta of bending motion is as short as 13±4 fs.