INFRARED ACTION SPECTROSCOPY AND VIBRATIONAL PREDISSOCIATION DYNAMICS OF OH–N_2

SHAWN M. HOPMAN, BETHANY V. POND, MARK D. MARSHALL,[a] and MARSHA I. LESTER, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323*.

A sensitive IR pump - UV probe technique has been used to obtain the infrared action spectrum of OH–N_2 complexes and probe their subsequent decay dynamics. An optical parametric oscillator operating in the OH overtone region near 1.4 μm prepares OH–N_2 with two quanta of OH stretch ($2\nu_{\mathrm{OH}}$). The OH (v = 1) fragments resulting from vibrational predissociation are then detected by laser-induced fluorescence on the OH A-X 0-1 transition. Scanning the IR pump laser has revealed the pure OH overtone band of OH–N_2 at 6973.5 cm^{-1}, which is shifted 2.3 cm^{-1} to higher energy of the OH Q(3/2) line. The rotational band structure is indicative of a parallel transition for a linear OH–N_2 complex having a projection P = 3/2 of the total angular momentum along the intermolecular axis. The nonzero projection originates from the electronic angular momentum of OH. Several combination bands involving the simultaneous excitation of OH stretching and geared bending modes have also been identified 32.9, 38.9, and 70.6 cm^{-1} to higher energy of the pure overtone band. The rotational structures of these bands are characteristic of transitions to P = 1/2, 5/2, and 3/2 states with vibrational angular momentum from fundamental and overtone geared bending excitation. In addition, the rate of appearance of the OH fragments yields the lifetime for OH–N_2 ($2\nu_{\mathrm{OH}}$) of 30 $\pm$ 4 ns, while the OH product state distribution indicates that vibrational predissociation proceeds by a vibration-to-vibration energy transfer mechanism. The experimental measurements for OH–N_2 will be compared with previous results for closely related systems.

[a]Permanant address: Department of Chemistry, Amherst College, Amherst, MA 01002-5000