

## ELECTRONIC SPECTROSCOPY OF THE CN-H<sub>2</sub>/D<sub>2</sub> VAN DER WAALS COMPLEX<sup>a</sup>

YALING CHEN, MICHAEL C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

A preliminary spectroscopic study of the CN-H<sub>2</sub>/D<sub>2</sub> van der Waals complex was reported recently<sup>a</sup>. A bound-free continuum spectrum was observed for the transition, while the system exhibited resolved rotational structure. Ground state dissociation energies of D<sub>0</sub><sup>0</sup>=38 (CN-H<sub>2</sub>) and 42 cm<sup>-1</sup> (CN-D<sub>2</sub>) were deduced from the onset of the B-X continuum and the A state predissociation dynamics. Anomalous isotope effects were noted for the dissociation energies and the rotational structures of the A-X bands (which were not assigned).

In recent work we have assigned the A-X bands and detected bound levels of CN(B)-H<sub>2</sub>/D<sub>2</sub>. Analyses of bands associated with the CN monomer 2-0 transition yielded ground state rotational constants of B<sup>0</sup>=0.245 (CN-H<sub>2</sub>) and 0.229 cm<sup>-1</sup> (CN-D<sub>2</sub>). The CN(X)-H<sub>2</sub> constant was much smaller than would be predicted using typical van der Waals radii. A similar discrepancy, but less pronounced, was present for CN(X)-D<sub>2</sub>. High-level ab initio calculations predict ground state constants of 0.518 (CN-H<sub>2</sub>) and 0.292 cm<sup>-1</sup> (CN-D<sub>2</sub>). However, these predictions were for J=0 complexes. Theoretical calculations show that the zero-point levels are mixed (via Coriolis coupling) to the first excited internal rotor states. This mixing can account for the small values for the rotational constants and the anomalous isotope effects (for both D<sub>0</sub> and B). The rotational structure is consistent with a collinear CN-H<sub>2</sub> equilibrium structure for the ground state.

Bound levels of CN(B)-H<sub>2</sub>/D<sub>2</sub> were observed by action spectroscopy. Excitation to the B state resulted in rapid CN(B)-H<sub>2</sub> → CN(A) + H<sub>2</sub> predissociation, so the B-X absorption was detected via A-X fluorescence. The B-X bands were homogeneously broadened and did not show rotational structure. Vibrational structure was evident in the CN-D<sub>2</sub> spectrum. The bound B-X bands cut-off at energies that exactly coincided with the onset of the bound-free continua. This observation validates our previous use of the thresholds to determine ground state dissociation energies.

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<sup>a</sup>Y. Chen and M. C. Heaven, *J. Chem. Phys.* 109, 5171 (1998)