SUB-DOPPLER SPECTROSCOPY OF $ND_3H^+$ ION IN THE NH STRETCHING MODE

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Despite early successes with velocity modulation spectroscopy[a,b] of ammonium ($NH_4^+$ ) and perdeuteroammonium ($ND_4^+$) cation, corresponding studies of any of the mixed H/D isotopomers ($NH_mD_{4-m}^+$) have proven elusive. In this talk, we present first high resolution results on the lone NH stretch fundamental mode for the jet cooled $ND_3H^+$ ion, based on tunable IR difference frequency absorption spectroscopy in a slit jet, sub-Doppler resolution infrared spectrometer. Supersonically cooled $ND_3H^+$ ions are generated by modulated (50 KHz) discharges (650V, 500 mA) in $ND_3$ doped $H_2$/Ne slit jet expansions, monitored by time-gated, lock-in detection methods and with absorption sensitivities near the quantum shot noise limit. Jet cooled (30 K) $P$, $Q$, and $R$ branch rovibrational progressions in the $a$-type NH stretch band are observed and unambiguously assigned by four line ground state combination differences, with additional confirmation by nuclear spin statistical weights for the 3 identical D atoms (I = 1). Least squares fits to this parallel band yield precision rotational constants and an NH stretch vibrational band origin at 3316.8347(19) $cm^{-1}$. These high resolution spectroscopic results prove to be in generally excellent agreement with high level $ab$ initio theoretical predictions by Martin and Lee[c].

[a] Mark.W. Crofton, Takeshi. Oka, J. Chem. Phys. 86, 5983, (1987).
[b] E. Schafer, M. H. Begemann, C. S. Gudeman, R. J. Saykally, J. Chem. Phys. 79, 3159, (1983).
[c] Jan. M. L. Martin, Timothy J. Lee, Chem. Phys. Lett. 258, 129 (1996)