

# The infrared spectrum of the $\text{N}_2\text{H}^+$ –He ion-neutral complex

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Rotationally resolved, vibrational predissociation spectra of the  $\text{HN}_2^+$ –He complex have been recorded in the region of the N–H stretch ( $3100$ – $3200\text{ cm}^{-1}$ ). The complex appears to be linear. Fitting of the measured lines to the pseudodiatomic expression  $\nu = \nu_0 + (B'_\nu + B''_\nu)m + (B'_\nu - B''_\nu - D'_\nu + D''_\nu)m^2 - 2(D'_\nu + D''_\nu)m^3 - (D'_\nu - D''_\nu)m^4$  yields the following constants:  $\nu_0 = 3158.419 \pm 0.009\text{ cm}^{-1}$ ,  $B'' = 0.3517 \pm 0.0005\text{ cm}^{-1}$ ,  $D'' = (5.8 \pm 0.5) \times 10^6\text{ cm}^{-1}$ ,  $B' = 0.3579 \pm 0.0005\text{ cm}^{-1}$ ,  $D' = (3.9 \pm 0.6) \times 10^6\text{ cm}^{-1}$ . The data support a proton bound He– $\text{HNN}^+$  structure, with a  $1.72\text{ \AA}$  vibrationally averaged intermolecular bondlength, and an approximate intermolecular stretching frequency of  $150\text{ cm}^{-1}$ . © 1995 American Institute of Physics.

The last 10–15 years have witnessed dramatic progress in the understanding of intermolecular interactions in *neutral* van der Waals molecules through the application of high resolution techniques in almost all parts of the electromagnetic spectrum.<sup>1–4</sup> Corresponding efforts directed toward the elucidation of intermolecular bonding in ionic complexes have been somewhat less advanced, often being frustrated by low species densities and the presence in any cool plasma environment of a plethora of possible absorbers. For some species these difficulties have been surmounted through the fruitful combination of laser spectroscopy and mass spectrometry.<sup>5,6</sup> The method most often used involves mass selecting the species before exciting a predissociative transition through resonant excitation with a tunable IR, visible or UV light source. Photofragment ions resulting from resonant excitation may be efficiently detected, with the molecular absorption spectrum being mirrored in a photocurrent vs wavelength plot. In essence the method is analogous to the bolometer optothermal method used so successfully to characterize neutral van der Waals and hydrogen bonded species,<sup>7</sup> though having the advantage of size selectivity. We have instituted the scheme in a tandem mass spectrometer and have used it to characterize a variety of weakly bound ion-neutral complexes ( $\text{N}_2^+$ – $\text{He}_n^8$ ,  $\text{N}_2^+$ – $\text{Ne}_n^9$ ,  $\text{N}_2\text{O}$ – $\text{Ar}^+^{10}$ ) through their absorptions in the visible and UV spectral regions. In the current work infrared absorptions of the  $\text{HN}_2^+$ –He complex have been investigated in the  $3100$ – $3200\text{ cm}^{-1}$  range (N–H stretch band). The spectra exhibit full rovibrational resolution and furnish an unprecedented view of ion-neutral interaction near the potential minimum. As the proton affinity of  $\text{N}_2$  considerably exceeds the one of He ( $118.2\text{ kcal/mol}$  vs  $42.5\text{ kcal/mol}^{11}$ ), expectations are that the complex should consist essentially of a He atom bound to an  $\text{HN}_2^+$  core, a linear  $\text{NNH}^+$ –He structure allowing the most favorable incipient chemical interaction between the He and the proton.

The tandem mass spectrometer apparatus and cooled cluster ion source have been described previously.<sup>12,13</sup> The  $\text{N}_2\text{H}^+$ –He complexes are created by crossing a pulsed expansion of  $\text{N}_2$ ,  $\text{H}_2$ , and He (1:1:100 ratio, 6 bar stagnation pressure) with electrons emanating from twin filaments positioned close to the nozzle orifice. The complexes are mass selected with a quadrupole mass filter, and are deflected

through  $90^\circ$  before being injected into an octopole ion guide where they are intercepted by the IR beam. Photofragment ions are detected by a Daly scintillation detector, with the resulting current measured by a boxcar integrator. Tunable light in the  $3\text{ }\mu\text{m}$  region with  $0.02\text{ cm}^{-1}$  bandwidth was generated using a Nd:YAG pumped optical parametric oscillator system (Continuum Mirage 3000 B). Line positions were calibrated by simultaneously recording an  $\text{NH}_3$  optoacoustic spectrum, and by sending the output of the OPO system master oscillator into an etalon. The ions possessed  $7.0\text{ eV}$  of kinetic energy in the octopole necessitating a  $+0.065\text{ cm}^{-1}$  Doppler correction to the measured wave numbers.

A search in the N–H stretch spectral region ( $3000$ – $3200\text{ cm}^{-1}$ ) while monitoring the  $\text{N}_2\text{H}^+$  ion current revealed a comparatively strong band, red shifted by around  $75\text{ cm}^{-1}$  from the free  $\text{N}_2\text{H}^+\nu_1$  transition ( $3233.96\text{ cm}^{-1}$ <sup>14</sup>). This band is shown in Fig. 1 with rotational line positions listed in Table I. The spectrum has the structure expected for a linear molecule  $\Sigma$ – $\Sigma$  transition and thus the rotational lines were fitted to the pseudodiatomic formula:

$$\nu = \nu_0 + (B'_\nu + B''_\nu)m + (B'_\nu - B''_\nu - D'_\nu + D''_\nu)m^2 - 2(D'_\nu + D''_\nu)m^3 - (D'_\nu - D''_\nu)m^4,$$

where  $m = -J$  for the *P* branch and  $m = J + 1$  for the *R* branch lines. Constants from the fit are listed in Table II. Neglecting zero point vibrations and assuming for the moment that  $\text{HN}_2^+$  does not distort when complexed with He ( $r_{\text{N–N}} = 1.097\text{ \AA}$  and  $r_{\text{N–H}} = 1.035\text{ \AA}$ <sup>15</sup>), one can use the  $B''$  value from Table II to estimate a H–He separation of  $1.72\text{ \AA}$  for the linear  $\text{NNH}^+$ –He structure, although due to a rather soft intermolecular bond and low reduced mass for the stretching motion the equilibrium intermolecular separation may be somewhat less. While the rotational constants are also consistent with a physically reasonable bond distance for the alternative He– $\text{NNH}^+$  structure ( $r_{\text{N–He}} = 2.64\text{ \AA}$  compared to  $2.72\text{ \AA}$  for  $\text{He}\cdots\text{N}_2^+$ <sup>16</sup>) inductive stabilization will be maximized when the He is situated near the proton. A rather large red shift in the N–H stretch frequency from the free molecule value ( $\approx 75\text{ cm}^{-1}$ ) also suggests that the He is adjacent to the proton.

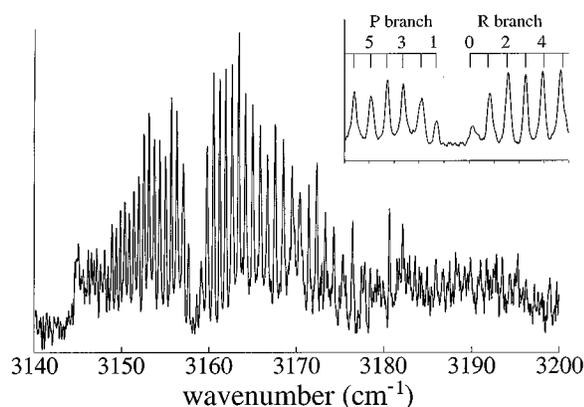


FIG. 1. Vibrational predissociation spectrum of the  $\text{N}_2\text{H}^+-\text{He}$   $\nu_1$  band. The spectrum was recorded by mass selecting the parent complex prior to exposure with tunable IR radiation ( $0.02\text{ cm}^{-1}$  bandwidth) in the  $3100\text{ cm}^{-1}$  region. Photoabsorption is inferred through detection of  $\text{N}_2\text{H}^+$  photofragments. The dependence of the intermolecular bondlength on the N–H stretch vibration is underscored by the prominent *P* branch head near  $3145\text{ cm}^{-1}$ . Rotational lines to higher energy of the main band presumably arise from hot band transitions in complexes with intermolecular energy.

The intermolecular bondlength decreases upon excitation of the N–H stretch (by approximately  $0.036\text{ \AA}$ ), which, along with the  $75\text{ cm}^{-1}$  red shift in the  $\nu_1$  vibration and smaller upper state *D* value, suggest a somewhat stronger intermolecular interaction in the upper vibrational level. The reason for vibrational enhancement of the intermolecular bond strength is not immediately apparent, but may be re-

TABLE I. Rotational line wave numbers ( $\text{cm}^{-1}$ ) for the  $\nu_1$  band of  $\text{HN}_2^+-\text{He}$ . Differences (last two significant figures) between the measured wave numbers and those calculated by inserting the fitted constants (Table II) into the pseudodiatomic expression (see text) follow the slash.

| <i>J</i> | <i>P</i> ( <i>J</i> ) | <i>R</i> ( <i>J</i> ) |
|----------|-----------------------|-----------------------|
| 0        |                       | 3159.21/01            |
| 1        | 3157.77/–01           | 3159.94/01            |
| 2        | 3157.11/02            | 3160.70/04            |
| 3        | 3156.42/01            | 3161.43/00            |
| 4        | 3155.76/02            | 3162.18/–01           |
| 5        | 3155.11/01            | 3162.94/–02           |
| 6        | 3154.45/–01           | 3163.76/01            |
| 7        | 3153.82/–01           | 3164.54/–02           |
| 8        | 3153.21/–01           | 3165.37/00            |
| 9        | 3152.62/–01           | 3166.20/00            |
| 10       | 3152.02/–02           | 3167.04/00            |
| 11       | 3151.46/–02           | 3167.85/–04           |
| 12       | 3150.92/–01           | 3168.74/–02           |
| 13       | 3150.41/01            | 3169.67/01            |
| 14       | 3149.90/01            | 3170.54/–01           |
| 15       | 3149.41/02            | 3171.50/03            |
| 16       | 3148.93/01            | 3172.41/01            |
| 17       | 3148.49/02            | 3173.36/01            |
| 18       | 3148.04/00            | 3174.29/–03           |
| 19       | 3147.64/02            | 3175.34/03            |
| 20       | 3147.23/00            | 3176.34/03            |
| 21       | 3146.84/–02           | 3177.37/04            |
| 22       | 3146.56/04            | 3178.33/–05           |
| 23       | 3146.16/–06           | 3179.44/–01           |
| 24       | 3145.94/01            |                       |
| 25       | 3145.67/00            |                       |

TABLE II. Fitted constants for the  $\nu_1$  band of  $\text{HN}_2^+-\text{He}$ . Constants were obtained by fitting rotational line positions given in Table I to the pseudodiatomic expression:  $\nu = \nu_0 + (B'_v + B''_v)m + (B'_v - B''_v - D'_v + D''_v)m^2 - 2(D'_v + D''_v)m^3 - (D'_v - D''_v)m^4$ . The standard error in the last two digits is given in brackets.

| Constant           | Value ( $\text{cm}^{-1}$ ) |
|--------------------|----------------------------|
| $\nu_0$            | 3158.419 (09)              |
| $B''$              | 0.3517 (05)                |
| $D''(\times 10^6)$ | 5.8 (0.5)                  |
| $B'$               | 0.3579 (05)                |
| $D'(\times 10^6)$  | 3.9 (0.6)                  |

lated to the anharmonicity in the N–H stretch motion, whereby excitation of the N–H vibration leads to the proton spending less time near the  $\text{N}_2$  molecule, allowing it to interact more effectively with the He atom.

The strength of the  $\text{He}\cdots\text{HN}_2^+$  intermolecular bond near the equilibrium can be assessed by inserting the rotational and centrifugal constants (Table II) into the relationship<sup>17</sup>  $\nu_s = \sqrt{(4B_e^3/D)}(1 - B_e/B_{\text{HN}_2})$ , ( $B_{\text{HN}_2} = 1.554\text{ cm}^{-1}$ <sup>15</sup>). If this is done, one arrives at an harmonic intermolecular stretch vibrational frequency in the  $145\text{--}160\text{ cm}^{-1}$  range. Thus the  $\text{He}\cdots\text{HN}_2^+$  bond appears to be somewhat stronger than for example the  $\text{He}\cdots\text{N}_2^+$  one, where  $D_0$  lies between  $100$  and  $130\text{ cm}^{-1}$ ,<sup>8</sup> and the first stretching vibrational spacing has been calculated to be  $55\text{ cm}^{-1}$ .<sup>16</sup> Finally, we remark that measurements of individual rotational lines at reduced power show that linewidths are of the order of  $0.1\text{ cm}^{-1}$ , around 5 times the bandwidth of the light source ( $0.02\text{ cm}^{-1}$ ), implying an approximate 50 ps lifetime for the optically prepared level.

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<sup>1</sup>D. J. Nesbitt, *Chem. Rev.* **88**, 843 (1988).

<sup>2</sup>R. J. Miller, *Science* **240**, 420 (1988).

<sup>3</sup>M. J. Elrod and R. J. Saykally, *Chem. Rev.* **94**, 1957 (1994).

<sup>4</sup>See contributions to *Structure and Dynamics of Weakly Bound Molecular Complexes*, edited by A. Weber (Reidel, Dordrecht, 1987).

<sup>5</sup>M. W. Crofton, J. M. Price, and Y. T. Lee, in *Clusters of Atoms and Molecules II*, edited by H. Haberland (Springer Verlag, Berlin, 1994).

<sup>6</sup>E. J. Bieske and J. P. Maier, *Chem. Rev.* **93**, 2603 (1993).

<sup>7</sup>T. E. Gough, R. E. Miller, and G. Scoles, *Appl. Phys. Lett.* **30**, 338 (1977).

<sup>8</sup>E. J. Bieske, A. M. Soliva, A. Friedmann, and J. P. Maier, *J. Chem. Phys.* **96**, 28 (1992).

<sup>9</sup>E. J. Bieske, A. M. Soliva, A. Friedmann, and J. P. Maier, *J. Chem. Phys.* **100**, 4156 (1994).

<sup>10</sup>E. J. Bieske, A. M. Soliva, A. Friedmann, and J. P. Maier, *J. Chem. Phys.* **96**, 7535 (1992).

<sup>11</sup>S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, and W. G. Mallard, *J. Phys. Chem. Ref. Dat.* **17** (1988).

<sup>12</sup>E. J. Bieske, A. M. Soliva, and J. P. Maier, *J. Chem. Phys.* **94**, 4749 (1991).

<sup>13</sup>E. J. Bieske, *Faraday Trans.* (in press).

<sup>14</sup>C. S. Gudeman, M. H. Begemann, J. Pfaff, and R. J. Saykally, *J. Chem. Phys.* **78**, 5837 (1983).

<sup>15</sup>S. C. Foster and A. R. W. McKellar, *J. Chem. Phys.* **81**, 3424 (1984).

<sup>16</sup>S. Miller, J. Tennyson, B. Follmeg, P. Rosmus, and H. Werner, *J. Chem. Phys.* **89**, 2178 (1988).

<sup>17</sup>D. C. Millen, *Can. J. Chem.* **63**, 1477 (1985).