

# Spectroscopic and theoretical characterization of linear centrosymmetric $\text{N}\equiv\text{N}\cdot\cdot\text{H}^+\cdot\cdot\text{N}\equiv\text{N}$

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The first high resolution infrared spectrum of the ionic complex  $\text{N}_2\cdot\cdot\text{H}^+\cdot\cdot\text{N}_2$  and its deuterated derivative is reported. The spectra were obtained in direct absorption in a supersonic slit nozzle plasma. The observed rovibrational transitions were assigned to the  $\nu_3$  antisymmetric NN stretching vibration and the spectrum is consistent with a linear centrosymmetric equilibrium structure. The band origin is found at  $2352.2364(6)\text{ cm}^{-1}$  and the ground state rotational constant is determined as  $B''=0.081\,809(14)\text{ cm}^{-1}$ . The assignment is supported by *ab initio* calculations including electron correlation effects. The best estimate for the equilibrium structure is  $R_e(\text{NN})=1.095\text{ \AA}$  and  $r_e(\text{N}\cdot\cdot\text{H})=1.277\text{ \AA}$ . The transition moment of the  $\nu_3$  band of  $\text{N}_2\cdot\cdot\text{H}^+\cdot\cdot\text{N}_2$  is predicted to be 0.21 D, an order of magnitude larger than for the NN stretching vibration of  $\text{HN}_2^+$ . The equilibrium dissociation energy  $D_e$  for fragmentation into  $\text{N}_2$  and  $\text{HN}_2^+$  is calculated to be  $\sim 5900\text{ cm}^{-1}$ .  
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## INTRODUCTION

Proton bound complexes are involved in a variety of chemical processes, but high resolution spectra of such species are still scarce. Only for  $\text{Ar}\cdot\cdot\text{H}_3^+$  (Ref. 1) and  $\text{Ar}\cdot\cdot\text{HCO}^+$  (Ref. 2) detailed submillimeter and microwave studies have been reported. While lower resolution predissociation infrared spectra could be obtained for a variety of ionic complexes,<sup>3</sup> IR spectra with a resolution better than  $0.002\text{ cm}^{-1}$  are currently available only for  $\text{Ar}\cdot\cdot\text{HN}_2^+$  (Ref. 4) and  $\text{Ar}\cdot\cdot\text{HCO}^+$ .<sup>5</sup> These were investigated by direct absorption techniques in a supersonic slit nozzle plasma. Such an approach meets the principal conditions required for the formation and detection of relatively weakly bound ionic complexes and is used here for the investigation of the protonated molecular nitrogen dimer,  $(\text{N}_2)_2\text{H}^+$ . This proton bound complex was found earlier in a mass spectrometric investigation of the equilibrium reaction  $\text{N}_2\text{H}^+ + \text{N}_2 \rightleftharpoons (\text{N}_2)_2\text{H}^+$  ( $\Delta H_{298\text{ K}}^0 = -16.0\text{ kcal/mol}$ ).<sup>6</sup> It may be considered as a prototype of cluster ions of the form  $\text{Mol}-\text{H}^+-\text{Mol}$ , of which  $\text{H}_2\text{O}-\text{H}^+-\text{OH}_2$  is a particularly important one.

Early *ab initio* calculations predicted a linear equilibrium structure for  $\text{N}_2\cdot\cdot\text{H}^+\cdot\cdot\text{N}_2$ , but could not conclude whether the structure is centrosymmetric or not.<sup>6-8</sup> This problem has been solved by carrying out state-of-the-art *ab initio* calculations that are reported here. These confirm the

assignment of the observed spectra and provide additional information currently not accessible to experiment, like predictions of the equilibrium bond lengths, the transition moment of the  $\nu_3$  band, the harmonic wave number of the lowest bending vibration and the equilibrium dissociation energy.

## METHODS

The details of the experimental set-up have been described previously.<sup>9</sup> The spectrometer consists of a commercial tunable diode laser system sampling a supersonic plasma that is generated by electron impact ionization of an Ar: $\text{N}_2:\text{H}_2(\text{D}_2)$  expansion (90:5:5 mixing ratio at a stagnation pressure of 800 mbar) through a  $32\text{ mm}\times 50\text{ }\mu\text{m}$  slit. The production is optimized by monitoring the plasma with a quadrupole mass spectrometer. A Perry multi-pass arrangement increases the total absorption length to  $\sim 50\text{ cm}$ . The laser radiation is focused onto an InSb detector and is phase-sensitively detected by production modulation, typically at 10 kHz. An additional 5% band pass filter in front of the detector is used to suppress background radiation of the plasma. The spectra are calibrated by simultaneously recording marker etalons and  $\text{CO}_2$  reference gas spectra. The absolute accuracy is estimated to be  $\sim 0.004\text{ cm}^{-1}$ , which is about a factor two less than achieved usually with the set-up. This is due to strong atmospheric  $\text{CO}_2$  absorptions in the 2320 to 2380  $\text{cm}^{-1}$  region,<sup>10</sup> even when the path of the infrared beam is purged by nitrogen gas.

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The theoretical part of this work deals with the results of high-level *ab initio* calculations which were mainly carried out by the coupled cluster variants CCSD-T<sup>11</sup> and CCSD(T).<sup>12</sup> They include the effects of connected triple substitutions in an economical noniterative way following a converged coupled cluster calculation with single and double excitation operators, CCSD.<sup>13</sup> Large basis sets of 250 and 419 contracted Gaussian-type orbitals (cGTOs) were employed. These correspond to Dunning's cc-pVQZ and cc-pV5Z sets,<sup>14</sup> respectively. Since core–valence correlation effects are not very important in  $\text{N}_2$  and  $\text{HN}_2^+$ , only the 20 valence electrons were correlated. Throughout, the MOLPRO suite of programs<sup>15</sup> was used in the calculations.

## RESULTS AND DISCUSSION

In total 39 vibration–rotation lines around  $2352.2\text{ cm}^{-1}$  were observed that are assigned to the  $\nu_3$  antisymmetric NN stretch of  $\text{N}_2\cdot\cdot\text{H}^+\cdot\cdot\text{N}_2$ . The spectrum shows the ordered structure of a  $\Sigma-\Sigma$  transition of a linear molecule, with *P* and *R* branches and a band gap of approximately  $4B$ . In Fig. 1 a typical spectrum of adjacent *R*-branch transitions is shown. The line positions and rotational assignments are given in Table I. The accurate determination of some transitions was hampered by strong laboratory  $\text{CO}_2$  absorptions and these line positions are not included in the Table. For the

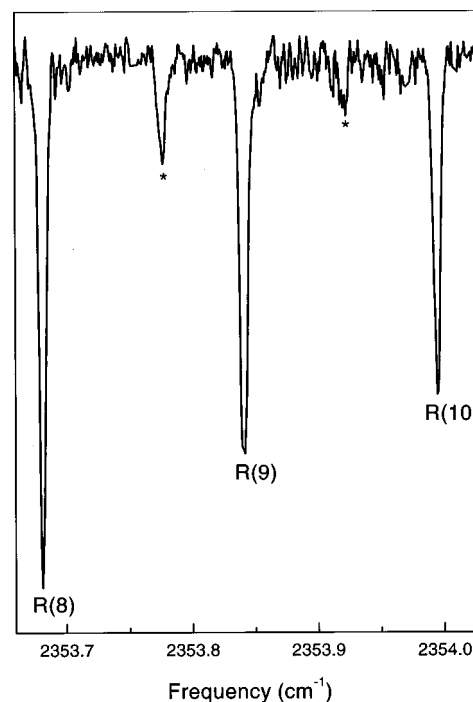


FIG. 1. Adjacent *R*-branch transitions of the  $\nu_3$  band of  $\text{N}_2\cdot\cdot\text{H}^+\cdot\cdot\text{N}_2$  observed in a continuous slit nozzle plasma. The lines indicated by \* are most likely due to hot band transitions.

TABLE I. Observed frequencies (in  $\text{cm}^{-1}$ ) of rotational transitions involving the  $\nu_3$  NN antisymmetric stretch of  $\text{N}_2\cdot\cdot\text{H}^+\cdot\cdot\text{N}_2$  and  $\text{N}_2\cdot\cdot\text{D}^+\cdot\cdot\text{N}_2$  and the derived spectroscopic constants ( $1\sigma$  deviations in brackets).

<i>J</i>	$\text{N}_2\cdot\cdot\text{H}^+\cdot\cdot\text{N}_2$				$\text{N}_2\cdot\cdot\text{D}^+\cdot\cdot\text{N}_2$			
	<i>P</i> -branch	$o-c^a$ ( $10^{-4}$ )	<i>R</i> -branch	$o-c^a$ ( $10^{-4}$ )	<i>P</i> -branch	$o-c^a$ ( $10^{-4}$ )	<i>R</i> -branch	$o-c^a$ ( $10^{-4}$ )
0			2352.3966	−27				
1	2352.0699	−29	2352.5586	−29			2357.7045	−40
2	2351.9039	−45	2352.7207	−22	2357.0585	48	2357.8682	−14
3	2351.7407	−27			2357.8857	−17	2358.0285	−13
4	2351.5745	−31			2356.7202	1	2358.1888	0
5			2353.2013	−15	2356.5523	5	2358.3466	−3
6	2351.2412	−26	2353.3628	14	2356.3838	14	2358.5056	17
7	2351.0768	10	2353.5224	33	2356.2150	30		
8	2350.9065	−6	2350.6783	21				
9	2350.7391	15	2353.8356	31				
10	2350.5703	29	2353.9918	37			2359.1176	−41
11	2350.3969	4	2354.1455	25	2355.5236	35	2359.2709	−26
12					2355.3470	24	2359.4219	−25
13	2350.0542	17			2355.1667	−13	2359.5750	8
14	2349.8812	18			2354.9862	−42	2359.7300	70
15	2349.7086	30	2354.7554	2	2354.8100	−18		
16	2349.5349	38	2354.9064	0				
17	2349.3581	23	2355.0571	2				
18	2349.1808	10	2355.2069	2			2360.3146	...
19	2349.0027	−4	2355.3536	−22				
20	2348.8259	3	2355.5020	−21	2353.9365	...	2360.5920	...
21	2348.6468	−6	2355.6517	1	2353.7646	...	2360.7447	...
22					2353.5866	...	2360.8759	...
23	2348.2855	−34			2353.4035	...	2361.0143	...
24	2348.1075	−10			2353.2162	...		
25	2347.9260	−14						
$\nu_0$			2352.2364(6)				2357.3832(10)	
$B''$			0.081 809(14)				0.082110(35)	
$B'$			0.081 444(13)				0.081596(35)	

<sup>a</sup>Observed–calculated.

TABLE II. Calculated equilibrium structures, total energies, equilibrium dissociation energies and rotational constants for  $\text{N}\equiv\text{N}\cdot\cdot\text{H}^+\cdot\cdot\text{N}\equiv\text{N}$ .

Method	Basis	$R_e(\text{NN})(\text{\AA})$	$r_e(\text{N}\cdot\cdot\text{H})(\text{\AA})$	$V_e(E_h)$	$D_e(\text{cm}^{-1})^a$	$B_e(\text{cm}^{-1})$
SCF	cc-pVQZ	1.0596/1.0633	1.0896/1.5896	-218.201968	4166	0.07960
MP2	cc-pVQZ	1.1078	1.2738	-219.004511	6445	0.08251
MP2	cc-pV5Z	1.1071	1.2747	-219.026979	6321	0.08248
CCSD	cc-pVQZ	1.0899	1.2742	-218.991647	5643	0.08345
CCSD	cc-pV5Z	1.0890	1.2749	-219.008745	5534	0.08344
CCSD-T	cc-pVQZ	1.0971	1.2757	-219.032796	6027	0.08294
CCSD-T	cc-pV5Z	1.0963	1.2765	-219.050972	5911	0.08291
CCSD(T)	cc-pVQZ	1.0974	1.2757	-219.033638	6028	0.08292
CCSD(T)	cc-pV5Z	1.0966	1.2765	-219.051797	5911	0.08290

<sup>a</sup>With respect to  $\text{N}_2\text{H}^+$  and  $\text{N}_2$  in the equilibrium configurations of the individual methods.

same reason absolute intensities were not obtained, prohibiting the observation of an intensity alternation due to spin statistics. The results have been analyzed assuming a conventional linear molecule energy level expression for the ground and excited states, with the rotational energy levels expressed as an expansion in  $J(J+1)$ . The resulting parameter set is listed in Table I. The overall rms error of the fit is better than  $0.002\text{ cm}^{-1}$ . The band origin is found at  $2352.2364(6)\text{ cm}^{-1}$  and the ground state rotational constant is  $0.081809(14)\text{ cm}^{-1}$ . Upon  $\nu_3$  vibrational excitation this value decreases by  $\sim 0.5\%$ . Inclusion of centrifugal distortion constants does not appreciably improve the fit and yields rather inaccurate values for  $D''$  and  $D'$ .

In the vicinity of the  $\nu_3$  band origin a second,  $\sim 5$ – $10$  times weaker, band system appears (see Fig. 1). In total nine transitions were observed that exhibit similar chemical behavior and have similar spacings between adjacent lines as the main band system.<sup>16</sup> It is unlikely that the lines are due to multi-mode conditions of the laser because the etalon pattern was regular. As vibrational temperatures in the jet expansion are estimated from  $T_{\text{rot}} (\approx 15\text{ K})^{17}$  to be of the order  $150$ – $200\text{ K}$  and the harmonic wave number of the lowest bending vibration is calculated to be  $141\text{ cm}^{-1}$  [CCSD(T)/cc-pVQZ], these transitions may be due to a hot band.

The vibrational assignment to the  $\nu_3$  antisymmetric stretch is supported by the present *ab initio* calculations. Ad-

ditional evidence comes from the rather small vibrational shift observed for the deuterium substituted derivative. In total 32 transitions were observed for  $\text{N}_2\cdot\cdot\text{D}^+\cdot\cdot\text{N}_2$ . Due to laboratory  $\text{CO}_2$  absorptions some transitions could not be detected, including the band origin region. As a consequence the rotational assignment may be off by  $\pm 1\text{ J}$ . The resulting fit is rather inaccurate when transitions with  $J > 19$  are included. Perturbations in the vibrationally excited state may thus be involved. However, due to the excessive consumption of  $\text{D}_2$  in the continuous jet expansion a more accurate characterization was not possible. Therefore a reduced data set, excluding the higher  $J$ -levels, was used for the fit. This results in the constants listed in Table I. The isotopic shift of  $5.14\text{ cm}^{-1}$  to higher energy appears to be somewhat peculiar and must be the result of vibrational anharmonicity. However, such effects are not uncommon in hydrogen bonded ions.<sup>18,19</sup>

Calculated equilibrium structures obtained by five different methods and two basis sets are listed in Table II. An asymmetric linear equilibrium structure is obtained at the Hartree–Fock level, just as for  $\text{ClHCl}^-$ .<sup>19</sup> The centrosymmetric structure with  $R_e = 1.061\text{ \AA}$  and  $r_e = 1.274\text{ \AA}$  corresponds to a saddle point on the potential energy surface and lies higher in energy than the equivalent asymmetric minima by  $354\text{ cm}^{-1}$  (cc-pVQZ basis). Upon inclusion of electron correlation the equilibrium structure becomes centrosymmetric. As expected, CCSD-T and CCSD(T) yield almost identical results. Compared with analogous calculations for the nitrogen molecule, the NN distances are only slightly shortened by  $0.0028\text{ \AA}$  [CCSD(T)/cc-pV5Z]. Consequently, a similar error in the calculations as for  $\text{N}_2$  is expected, resulting in  $R_e = 1.0949(2)\text{ \AA}$  for  $\text{N}_2\cdot\cdot\text{H}^+\cdot\cdot\text{N}_2$ , where an estimate of the uncertainty is given in parentheses. Compared to  $\text{HN}_2^+$ , the NH equilibrium separation is elongated by as much as  $0.243\text{ \AA}$  [CCSD(T)/cc-pV5Z]. All methods accounting for electron correlation yield very similar values for the NH distance.

The equilibrium dissociation energy  $D_e$  for dissociation into the fragments  $\text{N}_2$  and  $\text{HN}_2^+$  is predicted to be  $5911\text{ cm}^{-1}$  [CCSD(T)/cc-pV5Z]. This value is expected to have an uncertainty of less than  $100\text{ cm}^{-1}$ . The same value is obtained by CCSD-T. The inclusion of connected triple substitutions increases  $D_e$  by  $377\text{ cm}^{-1}$ . MP2 overestimates the electron correlation effects by about  $400\text{ cm}^{-1}$ . Due to the strongly anharmonic nature of the potential energy surface with re-

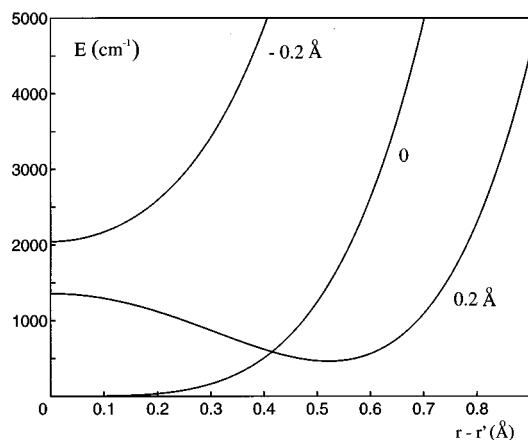


FIG. 2. CCSD(T)/cc-pVQZ potentials for antisymmetric proton stretching motion at a different N–N separation (0 corresponds to equilibrium), with  $R_e(\text{N}\equiv\text{N})$  kept fixed at its equilibrium value.

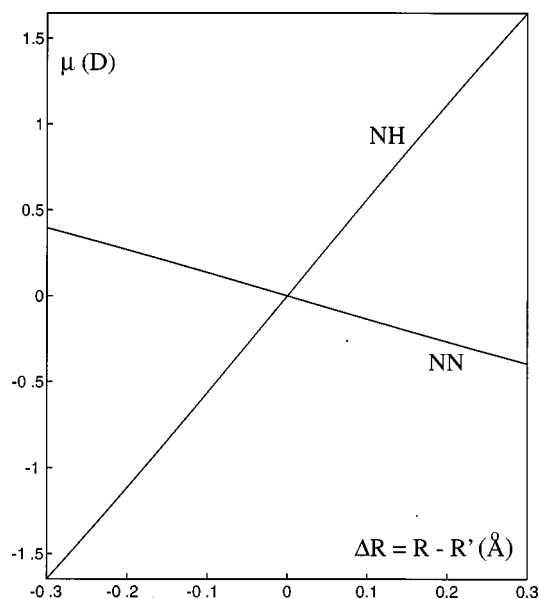


FIG. 3. Variation of the electric dipole moment [CCSD(T)/cc-pVQZ] with the NN and NH antisymmetric stretching coordinates.

spect to proton motion (Fig. 2), an accurate calculation of the corresponding  $D_0$  value is a demanding task, which is outside the scope of the present work.

The antisymmetric NN stretching vibration is only loosely coupled to the remaining vibrations and is quite well described in the harmonic approximation. CCSD(T) calculations with the cc-pVQZ basis set yield  $\omega_3 = 2383 \text{ cm}^{-1}$ . Analogous calculations for the nitrogen molecule overestimate  $\omega_e$  by  $3 \text{ cm}^{-1}$  and a similar error is expected for the ionic complex. This gives a value of  $2386 \text{ cm}^{-1}$  for  $\omega_3$ . The difference  $\omega_e - \nu$  for  $\text{N}_2$  is known from experiment to be  $29 \text{ cm}^{-1}$ .<sup>20</sup> The corresponding anharmonicity contribution to the NN stretching vibrational wave number of  $\text{HN}_2^+$  has been calculated to be  $37 \text{ cm}^{-1}$ .<sup>21</sup> It is not unreasonable to expect an anharmonicity contribution of comparable size for the symmetric and antisymmetric NN stretching vibrations in the complex  $\text{N}_2\cdot\text{H}^+\cdot\text{N}_2$ . Indeed, the difference between the calculated  $\omega_3$  value and the experimental  $\nu_3$  band origin from this work is  $34 \text{ cm}^{-1}$ , intermediate between the values for  $\text{N}_2$  and  $\text{HN}_2^+$ . The present calculations thus confirm the assignment of the observed infrared transitions to the  $\nu_3$  antisymmetric NN stretching vibration of  $\text{N}_2\cdot\text{H}^+\cdot\text{N}_2$ .

As is shown in Fig. 3, the variation of the electric dipole moment with the antisymmetric NN stretching coordinate is almost linear over a considerable range. Consequently, the

familiar double-harmonic approximation should work well in the prediction of the vibrational transition moment  $\mu_3$ . CCSD(T) calculations with the cc-pVQZ basis predict  $\mu_3 = 0.21 \text{ D}$ . This is much larger than a value of  $0.016 \text{ D}$  obtained for the NN stretching vibration of  $\text{HN}_2^+$  from analogous calculations.

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- <sup>1</sup> S. Bailleux, M. Bogey, H. Bolvin *et al.*, *J. Mol. Spectrosc.* **190**, 85 (1997).
- <sup>2</sup> Y. Ohshima, Y. Sumiyoshi, and Y. Endo, *J. Chem. Phys.* **106**, 2977 (1997).
- <sup>3</sup> E. J. Bieske and J. P. Maier, *Chem. Rev.* **93**, 2603 (1993), and references therein.
- <sup>4</sup> T. Speck, H. Linnartz, and J. P. Maier, *J. Chem. Phys.* **107**, 8706 (1997).
- <sup>5</sup> H. Linnartz, T. Speck, and J. P. Maier, *Chem. Phys. Lett.* **288**, 504 (1998).
- <sup>6</sup> P. Kebarle, *Annu. Rev. Phys. Chem.* **28**, 445 (1977); K. Hiraoka, P. P. S. Saluja, and P. Kebarle, *Can. J. Chem.* **57**, 2159 (1979).
- <sup>7</sup> S. Yamabe and K. Hirao, *J. Am. Chem. Soc.* **103**, 2176 (1981).
- <sup>8</sup> S. Ikuta, *Chem. Phys. Lett.* **77**, 369 (1981); *J. Comput. Chem.* **6**, 116 (1985).
- <sup>9</sup> T. Ruchti, A. Rohrbacher, T. Speck, J. P. Connelly, E. J. Bieske, and J. P. Maier, *Chem. Phys.* **209**, 169 (1996).
- <sup>10</sup> G. Guelachvili and K. N. Rao, *Handbook of Infrared Standards* (Academic, New York, 1986).
- <sup>11</sup> M. J. O. Deegan and P. J. Knowles, *Chem. Phys. Lett.* **227**, 321 (1994).
- <sup>12</sup> K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **157**, 479 (1989).
- <sup>13</sup> G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.* **76**, 1910 (1982).
- <sup>14</sup> T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989).
- <sup>15</sup> MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, C. Hampel, T. Leininger, R. Lindh, A. W. Lloyd, W. Meyer, M. E. Mura, A. Nicklass, P. Palmieri, K. Peterson, R. Pitzer, R. Pulay, G. Rauhut, M. Schütz, H. Stoll, A. J. Stone, and T. Thorsteinsson.
- <sup>16</sup> A list with frequencies is available on request.
- <sup>17</sup> T. Speck, T. Ruchti, H. Linnartz, and J. P. Maier, *J. Mol. Spectrosc.* **185**, 425 (1997).
- <sup>18</sup> P. Botschwina, in *Proceedings of the NATO Advanced Study Institute on Structure/Reactivity and Thermochemistry of Ions* (Kluwer, Dordrecht, 1986), pp. 261–270.
- <sup>19</sup> P. Botschwina, P. Sebald, and R. Burmeister, *J. Chem. Phys.* **88**, 5246 (1988).
- <sup>20</sup> K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- <sup>21</sup> S. Schmatz and M. Mladenovic, *Ber. Bunsenges. Phys. Chem.* **101**, 372 (1997).