

Rotationally resolved infrared absorption spectrum of N_4^+

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The rotationally resolved infrared band of the antisymmetric stretching vibration (ν_3) of N_4^+ has been recorded by tunable diode laser spectroscopy. A continuous supersonic expansion of pure nitrogen through a slit nozzle and electron impact ionization was employed. Forty-four *P* and *R* branch transitions with *J* up to 25 are observed. The band origin is at $\nu_0=2234.5084(4)$ cm^{-1} and the rotational constants are determined to be $B_0=0.112\,05(3)$ cm^{-1} and $B_1=0.111\,76(3)$ cm^{-1} . The infrared spectrum shows that N_4^+ has a linear ground state structure. © 1996 American Institute of Physics. [S0021-9606(96)01131-2]

INTRODUCTION

The N_4^+ molecular ion is an important species that is thought to play a significant role in stratospheric chemistry. For this reason, N_4^+ was investigated as a prototype for simple ion-molecule reactions by several groups.¹⁻⁶ *Ab initio*^{7,8} and matrix^{8,9} studies suggest that N_4^+ has a linear, centrosymmetric $^2\Sigma_u^+$ ground state structure, and from thermochemical¹⁰ and collision-induced dissociation¹¹ studies, a D_0 for the dissociation of N_4^+ into N_2^+ ($X\ ^2\Sigma_g^+$) and N_2 ($X\ ^1\Sigma_g^+$) of approximately 1 eV was found. Several groups have investigated the photodissociation processes of N_4^+ between 260 and 670 nm.¹²⁻¹⁵ It was concluded from these experiments that N_4^+ dissociates to N_2^+ and N_2 fragments in their ground state via the $^2\Sigma_g^+$ repulsive surface.

In spite of this information, the only infrared data on N_4^+ available up to now have been measured by isolating the ion in a 5 K Ne matrix.⁹ An absorption peak at $2237.6\ \text{cm}^{-1}$ was assigned to the infrared active antisymmetric stretching vibration of N_4^+ . By analyzing the infrared spectra of ^{15}N substituted species, it was concluded in agreement with earlier *ab initio* calculations^{7,8} that N_4^+ has a linear, centrosymmetric ground state structure. In this paper, we present the first infrared gas phase spectrum of N_4^+ which proves that this ion is indeed linear.

Since the initial experiments in 1983,¹⁶ it has been well demonstrated that a supersonic free expansion can be used to generate and spectroscopically characterize cold molecular radicals and ions. In addition to sensitive laser induced fluorescence and multiphoton ionization experiments, this technique has been also applied in recent years to the infrared and far infrared where direct absorption techniques are used. The main experimental problem in this wavelength range is to get an adequate absorption pathlength through the supersonic expansion. In the last few years, several techniques based on slit nozzles have been developed,¹⁷ using multipass optics to circumvent this problem, and employing either a corona discharge¹⁸⁻²¹ or laser photolysis²² for the production of ions. Recently, we reported a slit jet in combination with

an electron impact ionization arrangement,²³ and demonstrated that this device is well suited to detect electronic transitions of N_2^+ . In this article, the first observation of the N_4^+ $\nu_3(1\leftarrow 0)$ transition in the gas phase is presented. It shows that electron impact ionization can be used in combination with diode lasers for pure vibration-rotation spectroscopy as well.

EXPERIMENT

The vacuum apparatus (described in detail in Ref. 23) consists of two stainless-steel cross pieces connected by a spacer. A planar supersonic jet is crossed by a laser beam in the first chamber in which the ion source is also mounted. Simultaneously, the plasma can be sampled by a differentially pumped quadrupole mass spectrometer system that is mounted downstream in the second chamber. The main part of the vacuum system is evacuated by a roots blower backed by a two stage rotary pump.

The gas is expanded through a $32\ \text{mm}\times 50\ \mu\text{m}$ slit into the first vacuum chamber with subsequent ionization achieved by electron impact. The electrons are emitted from a 50 mm long tungsten wire typically carrying 4 A. This filament is mounted inside a slotted molybdenum tube which acts as a Wehnelt shield serving to direct the electrons towards the jet. The gas expansion region is protected from electric fields emanating from the filament and molybdenum tube by a slotted stainless-steel shield maintained at ground potential.

By applying a sinusoidal voltage between 0 and $-125\ \text{V}$ to the filament and the molybdenum tube, an effective production modulation can be achieved. We have applied this, rather than frequency modulation, in order to avoid etalon fringes that can arise from any reflection between laser diode and detector. Since the background emission caused by impact ionization was relatively low compared to the laser power and was further reduced by a filter in front of the detector, double modulation schemes as used in^{24,25} were not necessary.

Tunable infrared radiation was produced by a commercial lead-salt diode laser system. To measure the N_4^+ spectrum two different lead-salt diodes covering the frequency range 2228.6 to $2238.8\ \text{cm}^{-1}$ were used. By simultaneously recording a N_2O reference gas spectrum and marker etalons

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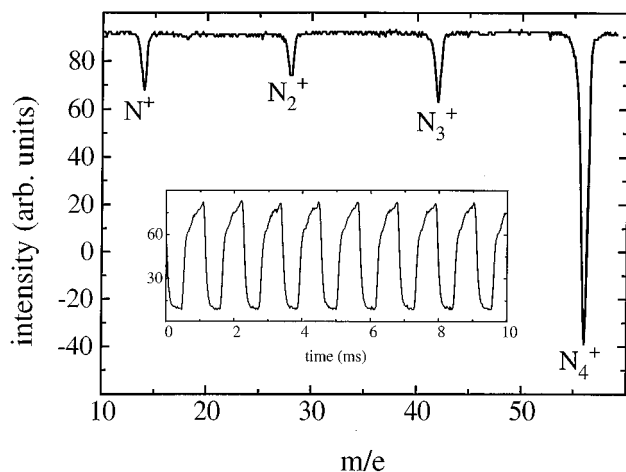


FIG. 1. The mass spectrum recorded after optimization of the N_4^+ production. The inset shows the time dependence of the N_4^+ mass signal when production modulation is applied.

an accuracy of about 0.002 cm^{-1} in the absolute calibration could be obtained. To increase the absorption pathlength in the plane of the expansion, a Perry arrangement giving 11 passes and a pathlength of $\approx 35 \text{ cm}$ was employed.²⁶ The laser beam was detected by focussing it onto an InSb detector and the signal was recorded phase sensitive using a lock-in amplifier.

To optimize the source for the production of a certain ion, a quadrupole mass spectrometer probe system is incorporated into the apparatus. The quadrupole is mounted in the second chamber inside a differentially pumped section. A nickel skimmer shields the mass spectrometer from the expansion and minimizes back reflection and scattering of the jet. Three electrostatic lenses after the skimmer serve to focus the ions into the quadrupole entrance.

RESULTS

Figure 1 shows a mass spectrum which was recorded after optimizing the slit-jet ion source for the production of N_4^+ . Pure nitrogen with a backing pressure of 2.5 bar was expanded through the slit nozzle and ionized by electron impact. The filament/nozzle distance was approximately 5 mm. Under these conditions, the N_4^+ was the dominant ion in the jet plasma. The production characteristics of N_4^+ are shown in the inset of Fig. 1 which shows a time resolved mass spectrum of N_4^+ when production modulation is applied. The mass spectrometer was tuned to N_4^+ and the current through the filament, the filament/nozzle distance, the modulation frequency and the voltage were adjusted for optimal N_4^+ mass signal. The best modulation frequency for the formation of N_4^+ was 874 Hz, which was still low enough for the expanding plasma to develop properly during each modulation cycle.

It is clear that N_2^+ and N_3^+ are also produced (Fig. 1) as well as N_6^+ (not shown). It turns out that N_3^+ is much harder to generate than N_2^+ and N_4^+ , whereas N_5^+ can hardly be

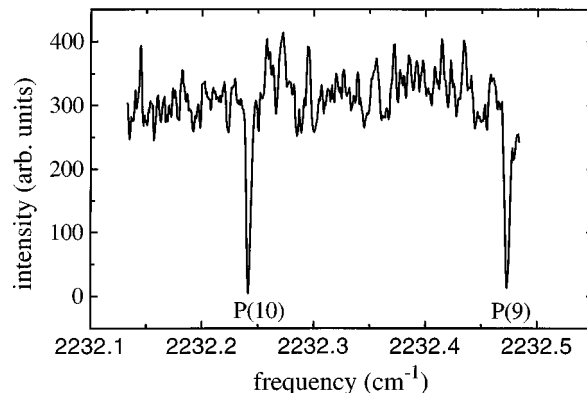


FIG. 2. The $P(9)$ and $P(10)$ transitions in the $N_4^+ \nu_3=1$ infrared absorption spectrum, observed with a slit nozzle expansion and electron impact ionization.

observed. This indicates that in the electron impact set-up the ionization channel involves N_2^+ , rather than recombinations of N^+ .

Figure 2 shows part of the absorption spectrum of N_4^+ . The signal to noise ratio of the strongest lines is about 10:1. In total, it was possible to record 44 rotational lines of N_4^+ . The spectrum shows the ordered structure anticipated for a $\Sigma-\Sigma$ type transition of a linear molecule, with P and R branch and an appropriate band gap. The observed frequencies and the assignment are given in Table I. Ground and excited state constants were evaluated by fitting the line positions to the expression $\nu_{\text{obs}} = \nu_0 + (B' + B'')m + (B' - B'' - D' + D'')m^2 - 2(D' + D'')m^3 - (D' - D'')m^4$, with $m = -J$ for the P branch and $J+1$ for the R branch.

The molecular constants determined in this manner are listed in Table II. From these the predicted transitions are calculated. The differences between observed and calculated frequencies are included in Table I. The resulting deviation is of the same order or smaller than the experimental uncertainty. The band origin is at $2234.5084(4) \text{ cm}^{-1}$ and the rotational constants are of the order of 0.112 cm^{-1} . The values for the distortion D constants in ground and upper state, derived from the fit are smaller than 10^{-7} cm^{-1} , but the uncertainties in these values are of the same order and have no physical meaning. For this reason, they are not listed in Table II.

DISCUSSION

The infrared spectrum shows a clear P and R branch and a band gap of 4 B. This proves that N_4^+ in the ground state is linear, which is in agreement with the conclusions of.⁷⁻⁹ Using the linear ground state geometry given in Ref. 7, a $B_e = 0.118 \text{ cm}^{-1}$ is calculated which is comparable to the experimentally determined ground state value, $B_0 = 0.11205(3) \text{ cm}^{-1}$. The ion seems to be quite rigid since no substantial distortion effects have been observed for levels up to $J=25$. This is in accord with its large binding energy of $\approx 1 \text{ eV}$.^{7,10,11} To get accurate distortion constants the rotational lines should be measured to much higher J levels than it was possible in the present work. The

TABLE I. Assigned rotational transitions (in cm⁻¹) for *P* and *R* branches of the ν_3 band of N₄⁺.

<i>J</i>	<i>P</i>	obs.-calc. (10 ⁻⁴)
1	2234.2849	5
2	2234.0601	5
3	2233.8330	-15
4	2233.6079	-7
5	2233.3818	-2
6	2233.1547	-5
7	2232.9267	-10
8	2232.6997	0
9	2232.4724	15
10	2232.2414	-2
11	2232.0124	5
12	2231.7808	-7
13	2231.5508	2
14	2231.3198	10
15	2231.0874	5
16	2230.8527	-12
17	2230.6198	-10
18	2230.3862	-7
19	2230.1538	12
20	2229.9179	5
21	2229.6827	7
22	2229.4454	-5
23	2229.2087	-2
24	2228.9721	5
25	2228.7334	-2

<i>J</i>	<i>R</i>	obs.-calc. (10 ⁻⁴)
0	2234.7328	10
1	2234.9555	7
2	2235.1777	5
3	2235.3993	2
4	2235.6206	2
5	2235.8411	2
6	2236.0577	-34
7	2236.2807	0
8	2236.5012	17
9	2236.7188	10
10	2236.9340	-15
11	2237.1521	-5
12	2237.3694	2
13	2237.5856	5
14	2237.8003	-2
15	2238.0162	7
16	2238.2294	-2
17	2238.4426	-7
18	2238.6568	5

$\nu_0 \approx 2234.5$ cm⁻¹ in the gas phase is about 3 cm⁻¹ to lower energy than the observed band in a neon matrix.⁹

It was not possible to measure reliably the line intensities due to power fluctuations during a scan, mode variations and slowly changing production circumstances. Furthermore,

TABLE II. Constants (in cm⁻¹) for the ground state and ν_3 excited level of N₄⁺. The values in brackets are two sigma confidence limits of the last digit.

State	ν_0	B_v
$\nu=0$		0.112 05(3)
$\nu_3=1$	2234.5084(4)	0.111 76(3)

the maximum scan range, without reoptimizing the diode mode was limited to 0.3 cm⁻¹, i.e., at most two rotational lines could be recorded simultaneously. For these reasons, the 4:5 spin statistical alternation for odd and even rotational lines, expected for a linear *and* centrosymmetric structure, could not be observed. However, from the observations of ¹⁵N substitution in the matrix study⁹ a centrosymmetric structure of N₄⁺ is indicated. Due to the unreliable line intensities it was not possible to estimate the rotational temperature. A value of T_{rot} between 30 and 150 K is expected.²³

In summary, the combination of a slit nozzle expansion employing electron impact ionization and a mass spectrometer is suited to study molecular ions in a free expansion by direct absorption spectroscopic techniques. The first high resolution gas phase spectrum of N₄⁺ has been measured, which shows that this ion is linear. These data provide line positions that may be used in laser based remote sensing of N₄⁺.

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