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LETTER TO THE EDITOR

N_4^+ Structure and Distortion

Thomas Speck, Thomas Ruchti, Harold Linnartz, and John P. Maier

Institut für Physikalische Chemie, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

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Recently the rotationally resolved infrared band of the antisymmetric stretching vibration (ν_3) of N_4^+ was recorded, using a tunable diode laser for the detection (*1*). The N_4^+ ion was generated in a nitrogen plasma formed by electron impact in a supersonic slit jet expansion (*2*). The band origin was determined to be at 2234.5084(4) cm^{-1}. The spectrum consisted of a *P* and an *R* branch, separated by a band gap of 4B, proving that this ion is linear. No distortional effects could be observed. Although it is likely that the molecule is centrosymmetric, as was suggested by isotopic substitutions in matrix experiments (*3*), this could not be confirmed in the gas phase experiment. The rotational levels for the $^2\Sigma_u$ ground state are expected to exhibit a 5 to 4 spin weight for odd and even rotational levels, respectively, for a linear and centrosymmetric structure (*4*). Fluctuations in the laser power as well as in the N_4^+ production and the limited scanning range of the diodes precluded the observation of this alternation in the jet experiment.

Additional results on N_4^+ are presented here. Higher *J* levels, up to J = 35, both in the *P* branch (5 transitions) and in the *R* branch (11 transitions), have been observed (Table 1), using another diode and better controlling the production conditions. The experimental technique was the same as that described in (*1*). Due to mode gaps in the scanning range of the diode some rotational transitions were not discernible. The constants listed in Table 2 are obtained by fitting the new line positions together with the former data set (*1*) to the standard expression for a $\Sigma-\Sigma$ type transition. The deviations between observed and calculated values are listed in Table 1. The B' and B'' values agree with those presented in (*1*), but now also statistically significant distortion constants D' and D'' are obtained. These values are small ($<10^{-7}$), suggesting that the ion is rather strongly bound, which is in agreement with the result of dissociation studies that yield a D_0 of approximately 110 kJ/mol (*6*). Whereas N_2–N_2 is only bound in the van der Waals sense, in the case of N_4^+ electrostatic forces are involved. It is for this reason that N_4^+ is expected to play a key role in atmospheric chemistry via reactions such as $N_2 + N_4^+ + M \rightarrow N_4^+ + M$ (*M* being a third body collision partner). From the mass spectra recorded simultaneously with a quadrupole mass spectrometer that is incorporated in the vacuum system, it is clear that N^+ recombinations play only a minor role. Consequently, N_4^+ may be used as an infrared probe for molecular nitrogen.

In contrast to the earlier studies, it also turned out to be possible to determine the relative intensities of some of the rotational lines. These were measured for the *P*(2) to *P*(11) transitions while the production was kept constant during the scan by simultaneously monitoring the N_4^+ intensity in

TABLE 1
New Vibration–Rotation Transitions (in cm^{-1}) for the Antisymmetric Stretch (ν_3) of N_4^+

	P-Branch		R-Branch	
J″	ν	obs.-calc. (10^{-4})	ν	obs.-calc. (10^{-4})
19			2238.8668	-3
25			2240.1252	-21
26	2228.4977	5	2240.3343	-9
27	2228.2604	19	2240.5420	-4
28	2228.0206	12	2240.7490	-1
29	2227.7802	5	2240.9556	5
30	2227.5381	-14	2240.3652	0
31				
32			2240.5692	-2
33			2240.7717	-12
34			2240.9778	20
35			2240.1781	0

Note. The obs.−calc. values are obtained from the constants listed in Table 2.

TABLE 2
Constants (in cm^{-1}) for the Ground State and ν_3 Excited Level of N_4^+

State	ν_0	B_ν	D_ν
v = 0		0.11207(1)	0.72(8).10^{-7}
v = 1	2234.5087(3)	0.11178(1)	0.71(7).10^{-7}

Note. The values in brackets are two sigma confidence limits of the last digit. The overall accuracy of the fit increased slightly compared to (*1*).

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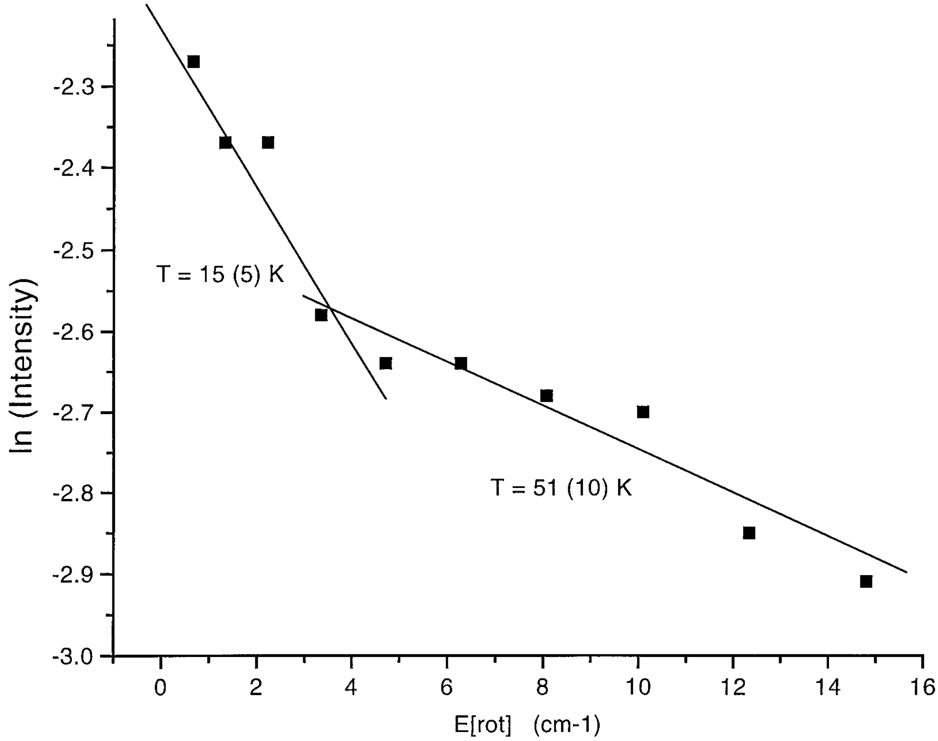

FIG. 1. Boltzmann plot for the power and spin weight corrected $P(2)$ to $P(11)$ transitions of N_4^+, indicating a rotational temperature of 15(5) K for the lower and 51(10) K for the higher rotational levels.

the mass spectrometer (*2*). To compare line intensities the signals have to be both power normalized and Boltzmann corrected. The latter procedure is complicated by the effect that in the jet expansion the lower rotational levels cool more effectively than the higher ones. The expansion is characterized by two different temperature regimes (Fig. 1). In the N_4^+ plasma it is found that the lower rotational levels have $T_{rot} = (15 \pm 5)$ K and the levels with $J > 4$ have $T_{rot} = (51 \pm 10)$ K. These values are of the same order as was found previously for other expansion cooled plasmas (see, e.g., (*7, 8*)). The error arises mainly from small fluctuations in N_4^+ production. The relative intensity ratios listed in Table 3 are obtained after correcting the power-normalized intensities for Boltzmann temperatures of 15 and 51 K. Indeed, within the error margins a J_{odd}/J_{even} ratio of 5:4 is obtained. For the lower J values this alternation is not as clear as for the higher ones.

TABLE 3
Relative Intensity Ratios of 10 Adjacent *P* Rotational Lines after Power Normalization and Boltzmann Correction, Assuming $T_{rot} = 15$ K for $J \leq 4$ and 51 K for Higher Levels

P(2)	P(3)	P(4)	P(5)	P(6)
0.92(9)	1.11(8)	0.92(9)	1.01(5)	0.77(5)

P(7)	P(8)	P(9)	P(10)	P(11)
1.00(10)	0.81(9)	1.04(8)	0.76(8)	0.95(6)

In addition to the infrared isotopic studies in a neon matrix (*3*), this proves that the molecule is not only linear but also centrosymmetric. This conclusion is in agreement with *ab initio* calculations (*4*) and a combined ESR/*ab initio* study (*5*). In these articles it is concluded that the collinear geometry lies lower in energy than the regular trapezoid or T-shaped structure. Using the labeling convention N1–N2–N2–N1, the calculated values for *R*12 and *R*22 yield B_e's ranging from 0.118 (*4*) to 0.113 cm^{-1} (*5*), which are comparable to the B_0 value (0.11207(1) cm^{-1}) obtained here.

It is expected that the low temperatures in the jet also allow the formation of weakly bound ionic complexes. High resolution studies of such complexes are scarce. Most of the available information arises from vibrational predissociation experiments which, however, have achieved rotational resolution only for a limited number of systems (*10*). Both $Ar–HN_2^+$ and $N_2–HN_2^+$ have been observed mass spectroscopically in the present apparatus, using a mixture of Ar, N_2, and H_2. The signals for $Ar–HN_2^+$ and $N_2–HN_2^+$ are about a factor 4 to 6 weaker than the typical signals found for N_4^+, which means that the density should be high enough for direct absorption measurements.

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