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Velocity modulation infrared laser spectroscopy of negative ions: The (011)–(001) band of azide (N_3^-)

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We have measured 43 transitions centered at 1972 cm^{-1} in the (011)–(001) bending hot band of the azide ion (N_3^-) using diode laser velocity modulation spectroscopy of an NH_3/N_2O discharge. The data, ranging from $P(32)$ to $R(40)$, were fit to a standard l-type doubling Hamiltonian through quartic terms. The l splittings in the spectrum were unusually large compared with similar molecules. Intensity measurements indicate that the vibrational and rotational degrees of freedom are equilibrated, unlike the case for isoelectronic NCO^-. Additional lines of the ν_3 fundamental have also been measured, which further refine the values of the ground state parameters.

INTRODUCTION

Although the chemically important azide ion (N_3^-) has interested vibrational spectroscopists since 1934,[1] its high resolution spectrum has been detected only very recently.[2] The detection of azide and other molecular anions in the gas phase[3] has been facilitated by experimental measurements of gas phase ion kinetics, the availability of increasingly accurate *ab initio* predictions, and the development of the ion selective velocity modulation technique. In our laboratory, this progress has been essential to our study of the isovalent series N_3^- (antisymmetric stretch),[2] NCO^- (CN stretch and three hot bands),[4] and NCS^- (CN stretch and two hot bands).[5] In continuing this study, we have measured and analyzed the ν_3 bending hot band of N_3^- and estimated the vibrational and rotational temperatures of azide in the positive column plasma.

A review of previous experimental and theoretical studies of N_3^- is presented in our previous paper.[2] The measurement of azide as the dominant product of the reaction of NH_2^- with N_2O by Bierbaum *et al.*[6] was particularly useful to us in determining optimal discharge conditions for N_3^- production. In addition, it was known that detectable amounts of NH_2^- ($\simeq 10^{11}/cm^3$) are formed in ammonia discharges,[7] and that the sputtering of metal films on the cell walls often enhances negative ion concentrations.[8] This information, aided by Botschwina's *ab initio* calculations,[9] led to the detection of ν_3 of N_3^-. Subsequently, analogous reactions were used to produce NCO^- and NCS^-.

In the previous paper,[2] 25 lines had been tentatively assigned to the R branch of the (011)–(001) bending hot band of N_3^-. Here, we report a complete analysis of the band which yields some surprising results. First, the large difference in l-type doubling constants between upper and lower states gives the spectrum a much different appearance from those of its isoelectronic counterparts: N_2O, CO_2, and NCO^-. A possible perturbation of the upper state, accounting for this difference in l-type doubling constants, is discussed below. In addition, although the formation processes and discharge environments of N_3^- and NCO^- are expected to be similar, NCO^- is found to be unusually highly excited in the bending mode, relative to rotational and other vibrational degrees of freedom,[4] while no such excitation is observed for N_3^-.

EXPERIMENTAL

The experimental design is described in our previous paper.[2] Briefly, infrared radiation from a Laser Analytics diode laser is passed through a 1 m long 1 cm diameter discharge cell containing a 400 mA positive column discharge driven at 25 kHz. Ion transitions are detected by their Doppler modulated absorption signals. The symmetries of the lines detected in this study were opposite those of positive ion lines, indicating absorption by a negative ion. The only change in the experiment was a substitution of the Hg:Cd:Te detector with a liquid nitrogen cooled Infrared Associates In:Sb detector optimized at 5.5 μ. This replacement increased the signal-to-noise ratio up to threefold for low power laser modes, where we were previously detector noise limited.

The water cooled discharge was operated with a 1.7 Torr NH_3/300 mTorr N_2O gas mixture, with the voltage maintained just above the breakdown value (1 kV at 400 W). Sputtering of a copper film on the cell walls was crucial, increasing the N_3^- ion density by at least a factor of 10. The chemical explanation for this enhancement remains unestablished.

Frequencies were measured to ± 0.003 cm^{-1} by using OCS,[10] CO,[11] H_2O,[11] and allene[12] as reference gases and an oil bath stabilized Ge étalon for relative calibration. Approximate relative intensities were obtained by using étalon fringe intensities to calibrate the laser power. Because of the difficulty of reproducing discharge conditions, intensities used in comparing different regions of the spectrum were measured in rapid succession.

ASSIGNMENT AND ANALYSIS

The most difficult aspect of assigning the hot band was recognizing its overall structure, particularly given the incomplete coverage of the diode laser. In both the P and R branches the line positions of a Π–Π band are given by

$$\nu(m) \pm \tfrac{1}{2}\Delta, \qquad (1)$$

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where the *l*-splitting term is

$$\Delta = (q' - q'')m^2 + (q' + q'')m ; \qquad (2)$$

in these expressions $m = J'' + 1$ for an R branch line and $m = -J''$ for a P branch line, and the $\nu(m)$ are the frequencies that would be expected for a Σ–Σ band. Typical Π–Π bands, where q'–q'' is small, consist of a series of doublets in which the splitting increase is roughly linear in J for both the P and R branches. In N_3^-, where q'–$q'' = 0.23\, q''$, the quadratic term in Eq. (2) dominates even at relatively low J yielding a much different appearance of the spectrum. Figure 1 shows the l splittings as a function of m for both N_3^- and for a "normal" Π–Π band, the (011)–(010) band of CO_2.[13] As can be seen, the N_3^- splittings in the R branch quickly become large, while the splittings in the P branch remain unresolvable until $P(14)$. A similar pattern was observed for DNN^+.[14]

The nuclear spin statistics for centrosymmetric N_3^- were essential for verifying this splitting structure. Because nitrogen atom has a nuclear spin of one, states with + parity have twice the degeneracy of those with − parity. This causes the intensity order of the doublets to switch with each J as shown in Fig. 2. The order also switches when Δ changes sign. Besides verifying the unusual splitting patterns, the spin statistics also confirmed the rotational assignment. The rotational assignment was established by making α_2 small and negative, as in the case of isoelectronic CO_2 [13] and N_2O.[15] Assuming the l-type doubling constant is positive (i.e., the Π^+ states lie lower in energy than the Π^- states), as is true for all linear triatomic molecules where the bending vibration is the lowest excited vibrational state,[16] the observed intensity alternation is in agreement with this assignment.

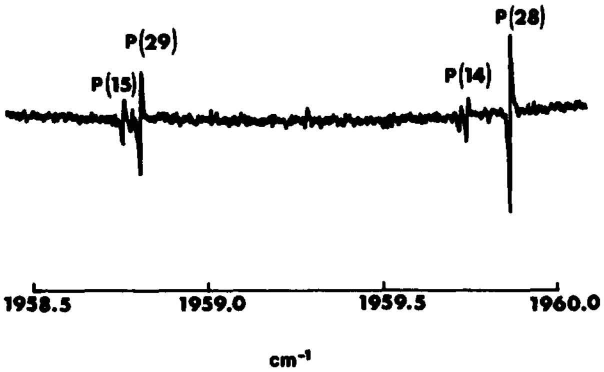

FIG. 2. Velocity modulation spectrum of the P branch region showing the intensity alternation in the hot band doublets as well as in the ν_3 fundamental.

The 43 observed hot band transitions were fit to the Hamiltonian

$$H = E(\nu) + B(\nu)[J(J+1) - l^2]$$
$$- D(\nu)[J(J+1) - l^2]^2 \pm \tfrac{1}{2}q(\nu)J(J+1) . \qquad (3)$$

The measured transition frequencies and their residuals are shown in Table I and the molecular constants obtained are presented in Table III. The standard deviation of the fit ($0.0044\ cm^{-1}$) is somewhat larger than the estimated measurement accuracy ($0.003\ cm^{-1}$). Table III also presents values for α_2 and χ_{23} which agree well with expectations based on similar linear triatomics.

In the process of collecting the data six additional lines of the ν_3 fundamental band have been measured, slightly improving the accuracy of the constants. The measurements and results of this fit are summarized in Tables II and III, respectively. The standard deviation of this fit was 0.0032 cm^{-1}, consistent with the measurement uncertainty.

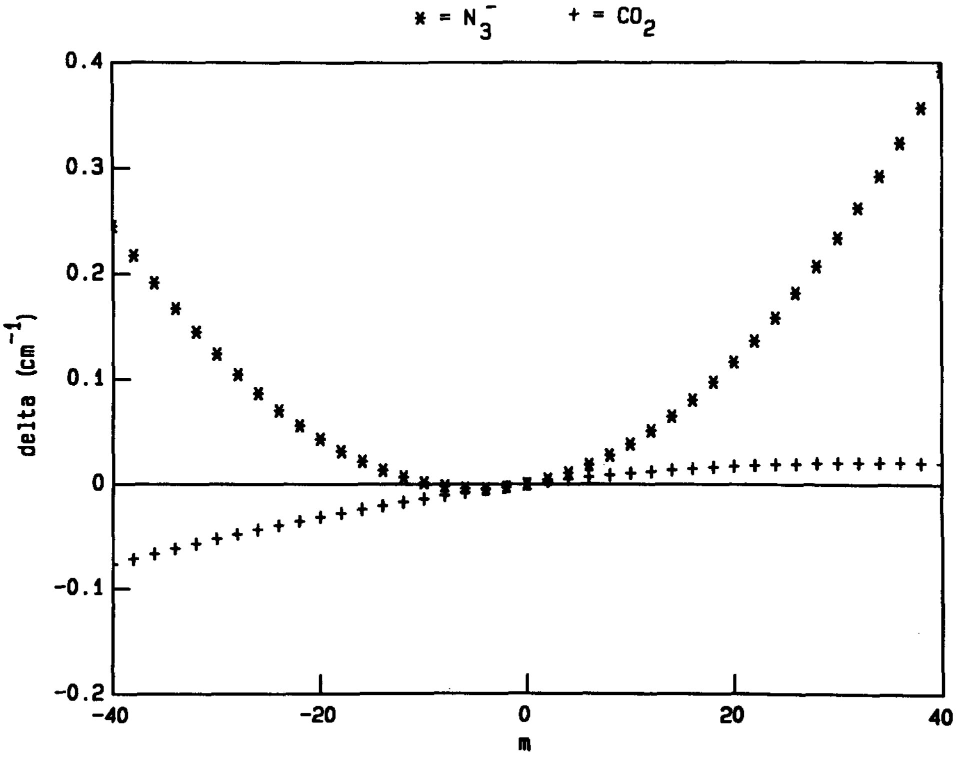

FIG. 1. Calculated l splittings for the (011)–(010) bands of N_3^- and CO_2, from constants in Table III and Ref. 13.

TABLE I. Frequencies (cm^{-1}) and residuals ($10^{-3}\,\mathrm{cm}^{-1}$) for the (011)–(010) bending hot band. The sign refers to the sign of the *l*-type doubling term in the Hamiltonian. A ± sign indicates an unresolved doublet, fit as the average of its two components.

Line	Freq.	Res.
P(32) −	1941.428	−1.7
P(32) +	1941.571	−3.6
P(28) −	1945.702	6.5
P(28) +	1945.801	0.9
P(24) +	1949.923	3.1
P(20) +	1953.936	3.6
P(19) −	1954.875	−6.6
P(19) +	1954.920	1.4
P(18) +	1955.900	2.1
P(16) −	1957.806	−8.6
P(16) +	1957.837	0.9
P(15) −	1958.773	−4.7
P(15) +	1958.798	3.1
P(14) −	1959.731	−2.5
P(14) +	1959.749	2.2
P(9) ±	1964.405	2.5
P(8) ±	1965.316	2.6
P(6) ±	1967.111	−2.8
P(4) ±	1968.884	−1.3
R(7) −	1978.894	2.1
R(7) +	1978.924	4.7
R(8) −	1979.678	0.9
R(8) +	1979.716	6.3
R(9) −	1980.448	−6.8
R(13) −	1983.490	−1.2
R(13) +	1983.562	6.1
R(14) −	1984.225	−6.7
R(14) +	1984.306	2.0
R(15) −	1984.961	−3.8
R(18) −	1987.112	−7.5
R(18) +	1987.227	0.9
R(19) −	1987.821	−1.9
R(19) +	1987.943	3.8
R(20) −	1988.514	−5.0
R(20) +	1988.648	2.8
R(22) −	1989.886	−3.0
R(22) +	1990.040	3.6
R(24) −	1991.233	3.4
R(24) +	1991.404	4.2
R(28) +	1994.043	−0.8
R(39) +	2000.750	−4.3
R(41) −	2001.466	6.2
R(40) +	2001.321	−3.3

TABLE II. Frequencies (cm^{-1}) and residuals ($10^{-3}\,\mathrm{cm}^{-1}$) for the ν_3 fundamental (asymmetric stretch).

Line	Freq.	Res.
P(45)	1941.012	0.7
P(44)	1942.172	−4.6
P(42)	1944.488	1.4
P(41)	1945.632	0.8
P(40)	1946.765	−3.8
P(37)	1950.142	2.1
P(34)	1953.449	0.9
P(33)	1954.539	2.2
P(32)	1955.622	3.6
P(30)	1957.758	−2.6
P(29)	1958.822	0.9
P(28)	1959.876	1.4
P(24)	1964.022	4.6
P(23)	1965.038	2.6
P(19)	1969.034	−1.9
P(16)	1971.958	−3.2
P(13)	1974.821	−0.9
P(11)	1976.686	−7.1
P(7)	1980.346	−2.9
P(3)	1983.890	1.0
P(2)	1984.757	1.0
R(1)	1988.153	2.0
R(3)	1989.801	−4.0
R(5)	1991.429	−0.7
R(8)	1993.810	−2.3
R(14)	1998.382	1.6
R(16)	1999.850	5.4
R(17)	2000.566	0.2
R(18)	2001.282	2.4
R(24)	2005.415	5.9
R(28)	2008.015	−0.8
R(29)	2008.647	−2.2
R(30)	2009.278	2.8
R(31)	2009.896	2.0
R(36)	2012.876	−2.2
R(39)	2014.579	−2.1
R(40)	2015.128	−6.2
R(46)	2018.298	−1.4
R(47)	2018.802	0.5
R(57)	2023.426	2.7

The intensity measurements were used to calculate the rotational and vibrational temperatures of N_3^- in the plasma. The rotational temperature of the ground state was determined by measuring nine lines ranging from $R(8)$ to $R(60)$ in rapid succession. By fitting the results to a Boltzmann distribution, we obtained a rotational temperature of 800 K ± 25%. The vibrational temperature was calculated by comparing intensity ratios of fundamental lines and hot band lines that were measured in the same scan. The vibrational temperature was calculated with the assumption that $T_{\mathrm{rot}} = 800$ K in both the ground and (010) states, and that $\nu_2 = 640\,\mathrm{cm}^{-1}$,[17] its value for N_3^- trapped in a KI lattice. the value obtained for T_{vib} was 700 ± 150 K. Since the intensity ratios from lines measured in the same scan are quite accurate, the largest error in the calculation is caused by the large uncertainty in T_{rot}. Fortunately, varying T_{rot} from 500 to 1000 K in the calculation caused a change in T_{vib} of only ± 100 K, indicating that the vibrational and rotational degrees of freedom are, in fact, roughly equilibrated, unlike the case of NCO^- ($T_{\mathrm{vib}} = 2000$ K).

DISCUSSION

Most of the constants for the (011)–(010) hot band agree with expectations; χ_{23} and α_2 are close to their values in similar molecules, while $B(010)$–$B(011)$ is only 3% smaller than $B(000)$–$B(001)$. The *l*-type doubling constant for the lower state (q'') is approximately $2.8\,B_e^2/\nu_2$; the value usually quoted for a "normal" linear triatomic molecule is $2.6\,B_e^2/\nu_2$,[16] but this is expected to vary considerably with the particular Coriolis coupling scheme of an individual molecule.

The only constant that is significantly different from expectations is q', the *l*-type doubling constant for the (011) state. It is considerably larger than q'', causing the unusual splitting patterns discussed previously. This deviation is likely a result of Coriolis coupling. The symmetry of the

TABLE III. Molecular constants (cm^{-1}) and correlation matrices from the least-squares fit. All uncertanties are 2σ.

Constant	$\nu_3 + \nu_2 - \nu_2$	ν_3
ν	1972.337 9(32)	1986.468 0(19)
B''	0.426 593(80)	0.426 201(44)
B'	0.422 965(74)	0.422 569(44)
$D'' \times 10^7$	2.09(58)	1.78(15)
$D' \times 10^7$	1.75(52)	1.71(14)
$q'' \times 10^4$	8.18(70)	
$q' \times 10^4$	10.17(68)	

Derived constants

$\alpha_2 \times 10^3$	− 0.392(91)
$\alpha_3 \times 10^3$	3.6322(40)
χ_{23}	− 14.1301(37)

Correlation matrix: $\nu_3 + \nu_2 - \nu_2$

ν	B''	B'	D''	D'	q''	q'
1.00						
0.281	1.00					
0.154	0.988	1.00				
0.365	0.889	0.849	1.00			
0.284	0.897	0.874	0.993	1.00		
0.0563	− 0.0807	− 0.0861	− 0.0237	− 0.0232	1.00	
0.0645	− 0.0715	− 0.0784	− 0.0127	− 0.0127	0.998	1.00

Correlation matrix: ν_3

ν	B''	B'	D''	D'
1.00				
0.175	1.00			
0.111	0.996	1.00		
0.220	0.916	0.898	1.00	
0.170	0.925	0.914	0.996	1.00

(011) state in the $D_{\infty h}$ point group is $\Sigma_u^+ \times \Pi_u = \Pi_g$. This is the symmetry of the rotations of the molecule about the x and y axes (z axis = molecular axis), therefore the (011) state can only Coriolis couple with vibrational states of the totally symmetric representation, Σ_g^+. The (011) state lies at $E_0(\nu_2) + E_0(\nu_3) = \chi_{23}$, where the energies are referenced to the zero-point vibrational energy. Using our accurate gas phase measurements of ν_3 and χ_{23} and the KI lattice value for ν_2,[17] $E_0(\nu_2 + \nu_3) \simeq 2612$ cm^{-1}. The Coriolis interaction of this state with $2\nu_1$, a Σ_g^+ mode predicted by Botschwina[9] at $E_0(2\nu_1) = 2581$ cm^{-1}, should be strong, and the $2\nu_1$ mode can interact strongly with only Π^+ states. However, repulsion of the Π^+ states by a lower energy $2\nu_1$ mode would result in q' being less than q'', but the opposite result is actually found. It is probable that either the *ab initio* calculations underestimate $2\nu_1$ (ν_3 is underestimated by 36 cm^{-1}) or the condensed phase value of ν_2 is an overestimate due to lattice shifts, and $2\nu_1$ actually lies higher in energy than $\nu_2 + \nu_3$.

There is additional evidence for a perturbation affecting the Π^+ levels of the (011) state. From Table I it can be seen that the largest residuals of the fit are found for the Π^+–Π^+ band. In Table I these transitions are labeled with a minus sign, the sign of the l-type doubling term in the Hamiltonian, since the Π^+ levels are lower in energy. In fact, if the two bands are fit separately to a linear molecule Hamiltonian including centrifugal distortion, the Π^-–Π^- band has a standard deviation of 0.0019 cm^{-1}, while the Π^+–Π^+ band has a standard deviation of 0.0042 cm^{-1}. Unfortunately, these anomalies are very close in magnitude to the measurement uncertainty, and lack of complete spectral coverage precludes a systematic analysis of the residuals.

The vibrational temperatures observed for the isovalent series N_3^-, NCO^-, and NCS^- in the discharge plasmas are interesting to compare. The three ions are formed by the similar reactions,

$$NH_2^- + N_2O \rightarrow N_3^- + H_2O, \tag{4a}$$

$$NH_2^- + CO_2 \rightarrow NCO^- + H_2O, \tag{4b}$$

$$NH_2^- + CS_2 \rightarrow NCS^- + H_2S, \tag{4c}$$

and the reaction mechanisms are postulated to be virtually identical.[6] In NCO^-, the bending mode was exceptionally highly excited, with an effective vibrational temperature of 2000 K ($T_{rot} = 700$ K). However, for NCS^- and N_3^- the rotations and all the vibrational degrees of freedom observed were roughly equilibrated at about 600–800 K. This was especially surprising for N_3^-, because its vibrational frequencies, formation mechanism, mass, and discharge environment are nearly identical to those of NCO^-.

Other highly vibrationally excited ions have been observed in plasmas as well, notably CF^+,[18] CCl^+,[19] C_2^-,[20] and HCS^+.[21] HCS^+, like NCO^-, was excited spcifically in the bending mode. It would be interesting to carry out experimental and theoretical investigations addressing the roles of transition states that result in ion formation in excited states, of discharge excitation mechanisms that may resonantly excite certain ions, and of the relaxation processes that are sufficiently slow to maintain such observed disequilibrium among the various degrees of freedom.

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[1] A. Langseth, J. R. Nielsen, and J. O. Sørenson, Z. Phys. Chem. B **27**, 100 (1934).

[2] M. Polak, M. Gruebele, and R. J. Saykally, J. Am. Chem. Soc. **109**, 2884 (1987).

[3] J. C. Owrutsky, N. H. Rosenbaum, L. M. Tack, M. Gruebele, M. Polak, and R. J. Saykally, Philos. Trans. R. Soc. London Ser. A **324**, 97 (1987).

[4] M. Gruebele, M. Polak, and R. J. Saykally, J. Chem. Phys. **86**, 6631 (1987).

[5] M. Polak, M. Gruebele, and R. J. Saykally, J. Chem. Phys. **87**, 3352 (1987).

[6] V. M. Bierbaum, C. H. DePuy, and R. H. Shapiro, J. Am. Chem. Soc. **99**, 5800 (1977); V. M. Bierbaum, J. J. Grabowski, and C. H. DePuy, J. Phys. Chem. **88**, 1389 (1984).

[7] L. M. Tack, N. H. Rosenbaum, J. C. Owrutsky, and R. J. Saykally, J. Chem. Phys. **85**, 4222 (1986).

[8] D.-J. Liu and T. Oka, J. Chem. Phys. **84**, 2426 (1986).

[9] P. Botschwina, J. Chem. Phys. **85**, 4591 (1986).

[10] N. Hunt, S. C. Foster, J. W. C. Johns, and A. R. W. McKeller, J. Mol. Spectrosc. **111**, 42 (1985).

[11] G. Guelachvili and K. N. Rao, *Handbook of Infrared Standards* (Academic, Orlando, 1986).

[12] J. Plíva and C. A. Martin, J. Mol. Spectrosc. **91**, 218 (1982).

[13] G. Guelachvili, J. Mol. Spectrosc. **79**, 72 (1980).

[14] D. J. Nesbitt, H. Petek, C. S. Gudeman, C. B. Moore, and R. J. Saykally, J. Chem. Phys. **81**, 5281 (1984).

[15] C. Amiot and G. Guelachvili, J. Mol. Spectrosc. **59**, 171 (1976).

[16] C. H. Townes and A. L.Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975), pp. 31–35.

[17] R. T. Lamoureux and D. A. Dows, Spectrochim. Acta Part A **31**, 1945 (1975).

[18] M. Gruebele, M. Polak, and R. J. Saykally, Chem. Phys. Lett. **125**, 165 (1986).

[19] M. Gruebele, M. Polak, G. A. Blake, and R. J. Saykally, J. Chem. Phys. **85**, 6276 (1986).

[20] B. D. Rehfuss, D.-J. Liu, M.-F. Jagod, W. C. Ho, M. W. Crofton, and T. Oka, J. Chem. Phys. (to be published).

[21] N. H. Rosenbaum, Ph.D. thesis, University of California at Berkeley, 1986.