Fourier transform spectroscopy of the ν_3 band of the N_3 radical

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We have analyzed the ν_3 antisymmetric stretching fundamental of the N_3 radical. Azide radicals N_3 were generated in a multipass cell by the reaction of Cl atoms and HN_3 and detected in absorption using a Fourier transform spectrometer. Improved constants for the 000 vibrational level of $\tilde{X}\,^2\Pi_g$ are reported along with observations of the 001 level. The frequency of the ν_3 fundamental at 1645 cm^{-1} was found to be somewhat lower than expected.

INTRODUCTION

Although diatomic nitrogen N_2 is one of the most extensively analyzed molecular species, the triatomic analog N_3 has been only rarely studied. The azide radical N_3 was first observed by Thrush[1] in 1956 following flash photolysis of HN_3. The bands observed by Thrush at 2700 Å were subsequently analyzed at high resolution by Douglas and Jones[2] and assigned to the $\tilde{A}\,^2\Sigma_u^+ - \tilde{X}\,^2\Pi_g$ transition of N_3. This was the only previous rotational analysis of the azide radical. Recently, the photoelectron spectrum of N_3 was observed.[3]

Since the completion of this study, Tian *et al.*[4] observed the ν_2, ν_3, and $\nu_1 + \nu_3$ vibrations of N_3 in an N_2/Ar matrix. Very recently, Pahnke *et al.*[5] observed transitions in the ν_3 band of N_3 by laser magnetic resonance spectroscopy using results from this work.

There are remarkably few theoretical papers on N_3, unlike the azide anion where very precise *ab initio* calculation[6] gave an accurate prediction of the vibrational frequencies, assisting in the observation of the ν_3 fundamental of N_3^-.[7] Two calculations[8,9] on N_3 predict it to be linear and symmetric, but these are at a fairly low level of theory and a more sophisticated calculation predicts a linear asymmetric structure.[10] The *ab initio* calculations by Tian *et al.*[4] predict a linear symmetric structure as does a state-of-the-art calculation by Adamowicz.[11] The present work is consistent with a linear symmetric structure, but the existence of a low barrier to $D_{\infty h}$ symmetry cannot be ruled out conclusively.

Several kinetic studies of the production and destruction of N_3 have been made. These include the early studies by Clark and Clyne[12,13] of ClN_3 and N_3, as well as more recent studies by Yamasaki *et al.*[14] of the reaction of N_3 with nitrogen atoms and with itself. Coombe and co-workers[15–17] have studied the chemiluminescent reactions of azide radicals, and have shown[17] that the reaction between N and N_3 might power a chemical laser.

EXPERIMENTAL

Absorption spectra of N_3 in a long path length cell were recorded using a Bomen DA3.002 Fourier transform spectrometer. The experimental apparatus has been described in detail elsewhere,[18] so it will be discussed only briefly here. The light source was a high temperature incandescent graphite rod and a CaF_2 beam splitter was used. A liquid helium cooled copper doped germanium detector, with a liquid nitrogen cooled sapphire filter to block below 7 μm and a 4.5 μm long pass filter, was used to record the signal. The filters reduced the optical bandwidth and thus improved the signal-to-noise ratio for the system.

The absorption cell has a mirror spacing of 1.6 m and an effective path length of about 100 m was obtained by multipassing the beam 62 times. There are three inlet ports, each equipped with a microwave discharge to provide atomic reactants. The first of these, which also contains an inlet for a stable reactant gas, is 10 cm from the first mirror. The other inlets are spaced at 55 cm intervals down the tube. The reaction products are quickly pumped out by a mechanical vacuum pump–booster pump combination.

While it has been shown[19] that N_3 can be generated by thermal decomposition of NaN_3, this method is not suitable for the apparatus used. Instead, hydrogen abstraction from HN_3 by chlorine atoms was used:

$$Cl + HN_3 \rightarrow N_3 + HCl.$$

This reaction proceeds readily ($k \sim 1 \times 10^{-11}$ cm^3/molecule s),[20] but the maximum N_3 concentration is limited by the reactions

$$Cl + N_3 \rightarrow NCl + N_2,$$

$$Cl_2 + N_3 \rightarrow \text{products}.$$

It was found that the highest N_3 concentration was obtained with a large excess of HN_3.

Hydrogen azide was produced by the reaction of sodium azide with molten stearic acid[21] and was continuously flowed into the absorption cell. An HN_3 pressure of 30–40 Torr was maintained in the reaction flask. This provided a steady partial pressure of a few millitorr in the absorption cell. Chlorine atoms were added to the cell through the three discharge ports. The flow consisted of about 0.02% Cl_2 in helium at a total pressure in the cell of 220 mTorr. Reducing the pumping rate by closing a gate valve on the exhaust did not significantly change the N_3 concentration in the cell.

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RESULTS

No definite observation of vibrational transitions of the N_3 radical had been reported in either the gas phase or rare gas matrices when this work was initiated. Very recently, Beaman *et al.*[22] have observed N_3 using laser induced fluorescence. They obtained two weak bands in their resolved emission experiments which they attributed to emission from the excited $\tilde{A}\,^2\Sigma_u^+$ 000 vibrational level to the 100 and 020 levels of the $X\,^2\Pi_g$ ground state. From this they obtained $\nu_1 = 1320\ \text{cm}^{-1}$ and $\nu_2 = 457\ \text{cm}^{-1}$. Emission to the 001 level is forbidden as this mode has σ_u^+ symmetry. A band at 2140 cm^{-1} observed following photolysis of HN_3 in an argon matrix was tentatively assigned to the ν_3 mode of N_3 by Becker *et al.*[23] Other estimates were obtained by comparison with similar molecules. The most suitable species is the isoelectronic NCO radical for which the ν_3 mode has been observed directly by laser magnetic resonance[24] and also by laser induced fluorescence,[25] the former providing the best value for the vibrational frequency, 1921 cm^{-1}. Following these estimates, we initially searched for N_3 in the 1850–2150 cm^{-1} region using a liquid nitrogen cooled indium–antimonide detector, for which the low frequency detection limit is 1850 cm^{-1}. No lines due to N_3 were observed in this region.

An estimate of the ν_3 frequency for N_3 can also be made by comparison with the negative ion N_3^-, for which ν_3 has recently been determined[7] to be 1986 cm^{-1}. The value given by the same group[26] for NCO^- is 2124 cm^{-1}, suggesting an increase of 203 cm^{-1} for the vibrational frequency on formation of the negative ion from the corresponding neutral. This provided a new estimate for the antisymmetric stretching frequency of N_3 of 1783 cm^{-1}, so the region from 1650 to 1850 cm^{-1} was searched using a Cu:Ge detector. A series of doublets spaced by about 0.8 cm^{-1} was found: this was the expected pattern for N_3. The UV absorption results of Douglas and Jones[2] showed that the ground state has $^2\Pi_g$ symmetry with a spin–orbit splitting of $-71.3\ \text{cm}^{-1}$ and a rotational constant of 0.43 cm^{-1}. Thus, for a transition between two Hund's case (a) $^2\Pi$ states, four strong branches are expected (R_1, P_1, R_2, P_2); an R and a P branch for each spin component. In any branch, the spacing between adjacent lines should be about 0.86 cm^{-1}, and the spacing between corresponding lines [$R_1(J)$, $R_2(J)$ or $P_1(J)$, $P_2(J)$] in the two spin components should be small because of the small vibrational dependence of the spin–orbit constant. Only the R branches were observed initially, but another scan covering the 1600–1700 cm^{-1} region showed that the spectrum consisted of the expected two P and two R branches with an origin of 1645 cm^{-1}. This can clearly be seen in the low resolution spectrum, Fig. 1.

When the resolution was increased to the instrumental limit of 0.004 cm^{-1}, each line was found to be split into two components at J of about 17.5. The two components have a 2:1 intensity ratio, which alternates with J as can be seen in Fig. 2. This intensity alternation arises from the two equivalent nitrogen nuclei each of spin $I = 1$ and confirms the assignment of the transition to the N_3 radical.

After optimizing the N_3 concentration, a final spectrum was recorded in which 83 scans were co-added in 7 h of integration. The spectrum obtained is shown in Fig. 1. The strong lines gave about 10% absorption and have a signal-to-noise ratio of about 20 to 1. This permits determination of the line positions with a precision of 0.0002 cm^{-1} given the linewidth of 0.004 cm^{-1}. The lines were calibrated by admitting OCS to the cell and measuring its absorption immediately following the completion of the N_3 spectrum. A total of 28 OCS lines were compared with the published spectrum of Wells *et al.*[27] The average deviation was 0.000 27 cm^{-1}, giving a correction factor of 1.000 000 16 which was applied to the N_3 spectrum.

ANALYSIS

Assignment of the spectrum was relatively easy because all but one, $P_2(1.5)$, of the first lines were present in the spectrum. In addition, the previous UV work[2] gave the spin–orbit splitting and also provided ground state combination differences. The lambda-doubling levels can also be assigned readily. The two equivalent nitrogen nuclei are bosons which requires that when $J - \frac{1}{2}$ is even in the $\tilde{X}\,^2\Pi_g$ 000 level the more intense component must be of e parity and the weaker one of f parity.

The observed P and R branch lines, together with the four weak Q branch lines, were fitted to the standard $\hat{N}^2$ Hamiltonian for a $^2\Pi$ state of Brown *et al.*[28] Explicit matrix elements are given by Amiot *et al.*[29] The levels with partially resolved lambda doubling presented some problems in the analysis due to the 2:1 intensity ratio between the lines. Those lines where the weaker component was a partially resolved shoulder were assigned to the stronger transition. When the splitting was completely unresolved, the line was assigned to a 2:1 weighted average of the two components. Using this method, almost all the strong lines could be fitted to the experimental precision of 0.0002 cm^{-1}, with only a few lines near J of 15.5 weighted at 0.0005 cm^{-1}. The weak lines at low and high J were also assigned reduced weights

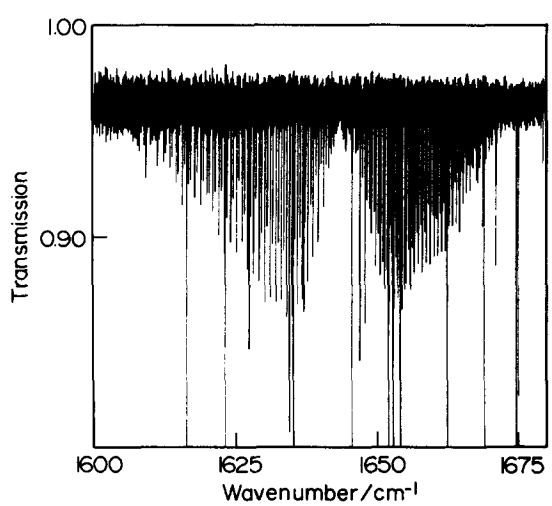

FIG. 1. The ν_3 band of N_3 showing the doubled P and R branches. Several strong water lines are also present, H_2O is present as an impurity from the HN_3 source. The maximum absorption is about 10% for the $^2\Pi_{3/2}$ lines and somewhat less for $^2\Pi_{1/2}$.

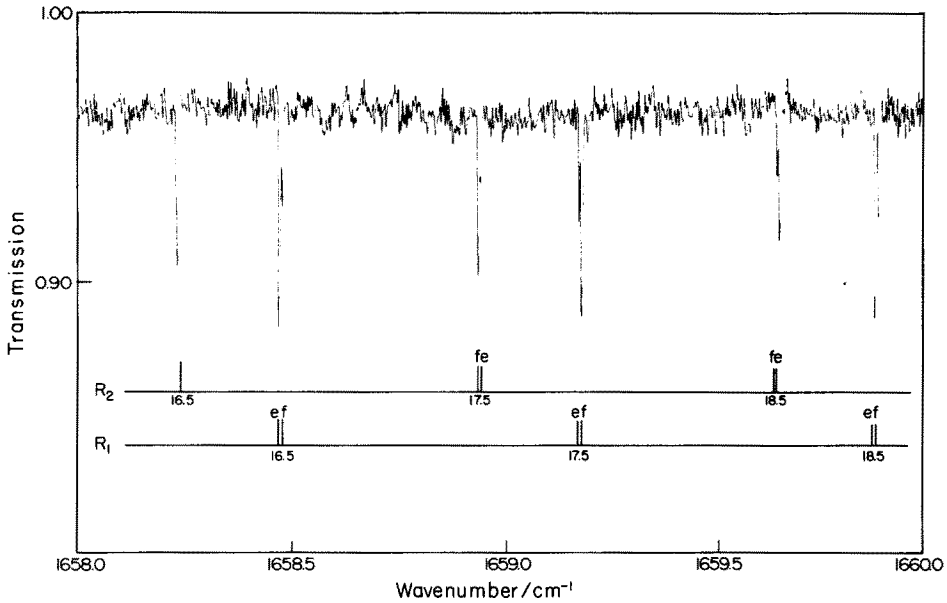

FIG. 2. A section of the R branch of the ν_3 band of N_3. There are two branches, R_1 ($^2\Pi_{3/2}$) and R_2 ($^2\Pi_{1/2}$), and each splits into two because of the lambda-doubling interaction. The splitting, which is just becoming apparent at this point, clearly shows the 2:1 spin statistics caused by two equivalent nitrogen atoms.

according to their estimated precision. The vibrational spectrum provides no direct information on the size of the spin–orbit splitting, so in the final fit the $\tilde{A}\,^2\Sigma_u^+$–$\tilde{X}\,^2\Pi_g$ data of Douglas and Jones[2] were fitted simultaneously. The unblended optical lines were given a precision of 0.01 cm^{-1}.

A total of 176 vibration–rotation lines listed in Table I, together with 240 optical lines,[2] were fitted to a total of 16 parameters. The final constants are given in Table II. The spin–rotation constants in the Π states were constrained to zero and the centrifugal distortion of the spin–orbit constant A_D was varied because these parameters cannot be simultaneously determined.[30] All four lambda-doubling parameters were obtained, although there was a high correlation between p_0 and p_1, as well as q_0 and q_1. No higher order terms were needed as the lambda-doubling splittings were fairly small, and only moderately high rotational levels were probed. Usually in a $^2\Pi$ vibrational transition, significant lambda doubling is seen only in the $^2\Pi_{1/2}$ subband; however, in this case, the splitting was about the same in both components. This is due to the large change in q between $v = 0$ and $v = 1$, while p only changes slightly. The P and R branch splittings involve only the difference of the lambda-doubling, hence the observed splittings are dominated by the contributions from Δq.

The revised constants for the $\tilde{A}\,^2\Sigma_u^+$ state are listed in Table III. The changes from those of Douglas and Jones[2] are fairly small and arise mainly from changes in the correlation of the parameters and the use of a least squares routine to fit the data.

DISCUSSION

The constants determined for $v = 0$ of the ground state are consistent with the previous values of Douglas and Jones,[2] but considerably more precise. Assuming equal N–N bond lengths, the new rotational constant gives $r_0 = 1.181\ 15$ Å. This is slightly shorter than the value for N_3^-, $r_0 = 1.188\ 40$ Å,[7] consistent with the removal of a nonbonding electron from N_3^-. The original theoretical calculation of Archibald and Sabin[9] gave 1.177 Å for $D_{\infty h}$ symmetry, in good agreement but they found a $C_{\infty v}$ structure to have lower energy. Along with their matrix isolation studies of N_3, Tian *et al.*[4] also carried out *ab initio* calculations. While their results were only at the SCF level they did obtain a $D_{\infty h}$ structure, with a bond length of 1.1538 Å, somewhat shorter than the experimental value.

Adamowicz has carried out some very high quality calculations[11] on N_3 using the 6-311G* basis set. He found N_3 to have $D_{\infty h}$ symmetry and derived an N–N bond length (using correlated wave functions) at the full fourth order many body perturbation level [MBPT(4)] of 1.186 and 1.181 Å with the coupled cluster (CCSD) method. These r_e bond lengths are in excellent agreement with the r_0 bond length of 1.181 15 Å derived from our experiments.

The experimental vibrational frequency of Tian *et al.*,[4] 1657.5 cm^{-1} for ν_3, is slightly larger than the gas phase value of 1644.6784 cm^{-1}. This indicates a matrix shift of 13 cm^{-1}, a reasonable value, and similar to the observed shift for N_3^- of 17 cm^{-1} obtained in the same spectra.

The value for the ν_3 fundamental of 1644.6784 cm^{-1} was significantly lower than expected. A similarly low asymmetric stretching frequency has also been observed in the isoelectronic species BO_2[31,32] and CO_2^+.[33,34] Kawaguchi *et al.*[31] explained the low value for ν_3 in BO_2 by a vibronic interaction between the $\tilde{A}\,^2\Pi_u$ and $\tilde{X}\,^2\Pi_g$ electronic states involving the ν_3 mode. A $^2\Pi_u$ state lying about 37 000 cm^{-1} above the ground state was tentatively identified by Douglas and Jones.[2] This separation is about twice as large in N_3 as in BO_2 so the effect on ν_3 was much larger in the case of BO_2. It seems reasonable that this effect is also occurring in N_3. An analysis of the $^2\Pi_u$ excited state or the observation of higher excited levels involving the ν_3 vibration in the ground state would be needed to confirm this.

The dominant feature of the lambda-doubling parameters is the large change in q between $v = 0$ and $v = 1$. The

TABLE I. Observed transitions in the ν_3 band of N_3 (in cm^{-1}).

	$P_1(J)$		$P_2(J)$		$R_1(J)$		$R_2(J)$	
J	ν	$10^4\,\Delta\nu$	ν	$10^4\,\Delta\nu$	ν	$10^4\,\Delta\nu$	ν	$10^4\,\Delta\nu$
0.5							1645.7669	−3
1.5			...		1646.9788	−2	1646.6133	−2
2.5	1642.7123	2	1642.2958	4	1647.8061	−2	1647.4502	0
3.5	1641.8328	1	1641.4052	4	1648.6250	−0	1648.2786	−1
4.5	1640.9443	−3	1640.5063	2	1649.4348	−1	1649.0976	1
5.5	1640.0477	−1	1639.5982	2	1650.2362	−1	1649.9081	−2
6.5	1639.1423	−0	1638.6815	−1	1651.0286	−0	1650.7094	−0
7.5	1638.2283	0	1637.7556	−2	1651.8128	0	1651.5020	−3
8.5	1637.3056	1	1636.8221	2	1652.5874	−2	1652.2858	1
9.5	1636.3741	−0	1635.8783	−1	1653.3544	−0	1653.0608	2
10.5	1635.4340	1	1634.9268	−2	1654.1116	−0	1653.8265	1
11.5	1634.4854	1	1633.9658	−0	1654.8614	−0	1654.5832	1
12.5*e*	}1633.5276	0	}1632.9969	−1	1655.6003	4	}1655.3318	5
12.5*f*					...			
13.5*e*	}1632.5620	0	}1632.0180	−0	...		}1656.0697	−1
13.5*f*					1656.3341	−6		
14.5*e*	}1631.5868	1	}1631.0321	2	1657.0539	2	}1656.8005	0
14.5*f*					...			
15.5*e*	...		}1630.0349	−4	...		...	
15.5*f*	1630.6045	−3			1657.7725	1	1657.5201	3
16.5*e*	1629.6108	8	1629.0325	−5	1658.4726	2	1658.2352	−1
16.5*f*	...		...		1658.4786	2	...	
17.5*e*	...		...		1659.1685	−0	...	
17.5*f*	1628.6127	−0	1628.0160	0	1659.1755	0	1658.9340	−1
18.5*e*	1627.5994	1	1626.9986	0	1659.8560	0	1659.6278	−0
18.5*f*	...		1626.9936	−1	1659.8639	−1	1659.6336	0
19.5*e*	1626.5810	1	1625.9685	2	1660.5347	2	1660.3126	1
19.5*f*	1626.5863	1	1625.9628	1	1660.5439	1	1660.3197	2
20.5*e*	1625.5540	2	1624.9291	−2	1661.2043	−1	1660.9878	−3
20.5*f*	1625.5600	−0	1624.9229	1	1661.2146	−3	1660.9963	0
21.5*e*	1624.5186	6	1623.8815	−2	1661.8655	1	1661.6548	2
21.5*f*	1624.5256	2	1623.8744	2	1661.8774	1	1661.6646	4
22.5*e*	1623.4735	−1	1622.8250	−5	1662.5175	−1	1662.3122	−0
22.5*f*	1623.4826	6	1622.8167	−2	1662.5307	−4	1662.3230	−2
23.5*e*	1622.4201	−4	1621.7611	5	1663.1609	−1	1662.9605	−1
23.5*f*	1622.4298	−2	1621.7510	2	1663.1760	−1	1662.9732	−2
24.5*e*	1621.3587	1	1620.6868	−2	1663.7956	1	1663.5994	−7
24.5*f*	1621.3688	−8	1620.6762	3	1663.8126	2	1663.6148	3
25.5*e*	1620.2879	−2	1619.6052	4	1664.4210	−2	1664.2301	−3
25.5*f*	1620.3008	2	1619.5923	−1	1664.4402	2	1664.2461	−5
26.5*e*	1619.2085	−3	1618.5141	1	1665.0382	1	1664.8524	7
26.5*f*	1619.2227	−1	1618.4997	−4	1665.0590	1	1664.8701	2
27.5*e*	1618.1215	5	1617.4141	−5	1665.6462	1	1665.4639	0
27.5*f*	1618.1367	1	1617.3990	−0	1665.6692	0	1665.4842	0
28.5*e*	1617.0246	3	1616.3062	−4	1666.2453	−0	1666.0669	−1
28.5*f*	1617.0419	−0	1616.2894	1	1666.2710	3	1666.0894	−2
29.5*e*	1615.9185	−6	1615.1890	−10	1666.8358	1	1666.6612	2
29.5*f*	1615.9385	−0	1615.1706	−1	1666.8632	−2	1666.6859	−2
30.5*e*	1614.8048	−4	1614.0643	−5	1667.4172	1	1667.2462	3
30.5*f*	1614.8284	18	1614.0434	−0	1667.4472	−3	1667.2734	−1
31.5*e*	1613.6825	1	1612.9309	−2	1667.9901	4	1667.8220	2
31.5*f*	1613.7067	5	1612.9079	3	1668.0228	−1	1667.8527	6
32.5*e*	1612.5506	−6	1611.7895	8	1668.5536	1	1668.4214	−2
32.5*f*	1612.5775	3	...		1668.5888	−6	...	
33.5*e*	1611.4109	−2	...		1669.1090	6	...	
33.5*f*	1611.4402	5	1610.6106	10	1669.1468	−5	1668.9475	14
34.5*e*	1610.2625	1	1609.4778	−6	1669.6545	2	1669.5324	−14
34.5*f*	1610.2946	10	...		1669.6955	−9	...	
35.5*e*	...		...		...		...	
35.5*f*	1609.1394	4	1608.2777	8	1670.2371	3	1670.0352	12
36.5*e*	1607.9388	−2	1607.1340	1	1670.7194	−1	1670.6098	−4
36.5*f*	...		...		...		...	
37.5*e*	...		...		...		...	
37.5*f*	1606.8042	−0	1605.9093	−0	1671.2907	−7	1671.0879	25
$Q_1(1.5)$	1644.8570	6						
$Q_1(2.5)$	1644.8343	−4						
$Q_1(3.5)$	1644.8058	15						
$Q_2(0.5)$	1644.4771	−20						

TABLE II. Molecular constants for the ν_3 band of N_3 (in cm^{-1}).

Constant	000	001
ν_3		1644.678 32(4)
A	−71.272 9(18)	−70.890 9(18)
$10^6 A_D$	−8.84(95)	2.99(94)
B	0.431 449 5(13)	0.427 064 5(13)
$10^7 D$	1.886(10)	1.885(10)
$10^3 p$	1.357(73)	1.561(72)
$10^4 q$	−0.613(28)	−1.392(27)

[a]Numbers in parentheses represent one standard deviation error estimates in the last significant figure.

lambda doubling is usually considered to arise from interaction with other electronic states, in this case the excited $^2\Sigma_g^+$ and $^2\Sigma_g^-$ states; however, no states of this symmetry are known for N_3. Brown[35] has shown that in addition to the electronic contribution there can also be a large vibrational contribution to q in the Π states of polyatomic molecules. The expression given by Brown[35] reduces to the following for a molecule of $D_{\infty h}$ symmetry, when the bending mode is not excited:

$$q = \frac{B^2\epsilon}{\omega_2}\left\{\left(v_3+\frac{1}{2}\right)\frac{16\omega_2^2\omega_3}{(\omega_3^2-\omega_2^2)^2} - \frac{4\omega_2^2(\omega_3^2+\omega_2^2)}{(\omega_3^2-\omega_2^2)^2}+1\right\}+q_{el}.$$

The electronic contribution q_{el} can be estimated as pB/A, which is an order of magnitude smaller than the experimental value as can be seen in Table IV. Douglas and Jones[2] give $\epsilon\omega_2 = -94.38\ cm^{-1}$ and Beaman *et al.*[22] give $\omega_2 = 457\ cm^{-1}$, and the remaining constants are taken from this work. The calculated values are given in Table IV. The agreement for both 000 and 001 is quite good although the change between 000 and 001 is somewhat smaller than the experimental result.

The transition strength for the ν_3 mode of N_3 has not been measured or calculated; however, N_3^- has a calculated integrated molar absorption strength of 66 000 $cm^2\ mol^{-1}$. A similar intensity for N_3 would imply a density of about 10^{12} molecule cm^{-3}.

Only ν_3 fundamental band lines were observed in the spectrum. Given the value for ν_2 of 457 cm^{-1} and assuming a Boltzmann distribution at 300 K, the population in the 010 level should be about 10% of that in 000, implying a signal-to-noise ratio of perhaps 2 for the bending hot band. The region around the fundamental was examined carefully, but no extra branches were found. It seems that a slightly higher signal-to-noise level is necessary to obtain the hot band lines.

TABLE III. Molecular constants for the $\tilde{A}\ ^2\Sigma_u^+$ state of N_3 (in cm^{-1}).

T_0	36 738.749 7(18)[a]
B_0	0.432 645 3(64)
$10^7 D_0$	1.897(43)

[a]Values in parentheses represent one standard deviation error estimates in the last significant figure.

TABLE IV. Contributions to the q lambda-doubling parameter in the $\tilde{X}\ ^2\Pi_g$ state of N_3 (in cm^{-1}).

Vibrational level	Experimental value	Electronic contribution	Vibrational contribution	Calculated total
000	-6.1×10^{-5}	-0.8×10^{-5}	-6.9×10^{-5}	-7.7×10^{-5}
001	-13.9×10^{-5}	-0.9×10^{-5}	-10.2×10^{-5}	-11.1×10^{-5}

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