THE ROTATIONAL AND ROTATION-VIBRATIONAL
RAMAN SPECTRA OF $^{14}N_2$, $^{14}N^{15}N$ AND $^{15}N_2$

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Abstract. The pure rotational and rotation-vibrational Raman spectra of $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ have been photographed using a previously described instrument. The analyses of the bands yield for each molecule v_0, B_0, B_1-B_0 and D. From the values of B_0 and B_0-B_1 the internuclear distances r_e are calculated independently for each species. Within the experimental accuracy the distances are identical as required by the Born-Oppenheimer approximation. The mean value for r_e is $1.097701 \pm \pm 0.000004$ Å.

1. Introduction

The nitrogen molecules $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ do not exhibit any microwave or infrared spectra. A determination of the molecular constants in the electronic ground state may then be obtained by Raman spectroscopy or by electronic spectroscopy. The molecular constants in question are defined by the expressions

$$E_v = \omega \left(v + \tfrac{1}{2}\right) + X \left(v + \tfrac{1}{2}\right)^2 + Y \left(v + \tfrac{1}{2}\right)^3 + \cdots \tag{1}$$

$$B_v = B_e - \alpha \left(v + \tfrac{1}{2}\right) + \gamma \left(v + \tfrac{1}{2}\right)^2 + \cdots \tag{2}$$

$$D_v = D_e - \beta \left(v + \tfrac{1}{2}\right) + \cdots. \tag{3}$$

In principle all these parameters are obtainable from electronic spectroscopy whereas Raman spectroscopy yields $v_0 \,(=E_1-E_0)$, B_0, B_0-B_1, D_0 and D_0-D_1 from the observable bands, i.e. the pure rotational band and the fundamental band. The constants obtained from Raman spectroscopy are, however, more accurately determined than those from the electronic spectra.

Nitrogen $^{14}N_2$ was investigated by means of Raman spectroscopy in 1954 by Stoicheff [1]. This work gave rather precise values for B_0 and D_0 and a value for the unresolved Q-branch for the fundamental band.

Butcher *et al.* [2] have measured very precise values for B_0 and D_0 from the pure rotational Raman spectrum. The constant B_0-B_1 has not yet been measured in Raman which prevents a determination of the equilibrium distance r_e from pure Raman data. In ultraviolet $^{14}N_2$ has been measured by Lofthus [3], Wilkinson [4], and Vanderslice *et al.* [5]. In Table X a comparison is given between the results obtained by these authors and those obtained in this work for the $^{14}N_2$ molecule.

Compared to $^{14}N_2$ very little spectroscopic work has so far been carried out on $^{14}N^{15}N$ and $^{15}N_2$. In the ultraviolet region Mahon-Smith and Carroll [6] and Bleekrode [7] have measured some transitions in the $^{15}N_2$ molecule, but no rotational con-

stants are reported. So far no Raman work on $^{14}N^{15}N$ and $^{15}N_2$ has been published.

It seemed, therefore, worth-while to measure the pure rotational and the rotation-vibrational Raman spectra of $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$ in order to obtain for each molecule ν_0, B_0, B_1-B_0, and D. From each set of constants the internuclear distance r_e may then be calculated and a valuable check on the experimental accuracy achieved because the Born-Oppenheimer approximation requires these distances to be equal.

2. Experimental

The sample of natural nitrogen, from which the $^{14}N_2$ spectra were obtained, was delivered by 'Dansk Ilt og Brint Fabrik' (purity 99.9995%). The $^{14}N^{15}N$ sample from 'Prochem' consists of 98% $^{14}N^{15}N$, 1.5% $^{14}N_2$ and 0.5% $^{15}N_2$. The $^{15}N_2$ spectra were photographed from a 95% $^{15}N_2$ sample supplied by 'Stohler'. All samples were used without further purifications, and the observed spectra shows no sign of non-isotopic impurities. Even after several days of radiation there was no sign of damage of the samples.

The Raman spectra were obtained using the instrument described earlier [8]. The experimental technique has been modified on the following three points:

First, it was found that the intensity of the Rayleigh scattering relative to the Raman scattering is so favourable that it is possible to photograph the Stokes and anti-Stokes part of the pure rotational spectrum in one exposure. An example is shown in Figure 1.
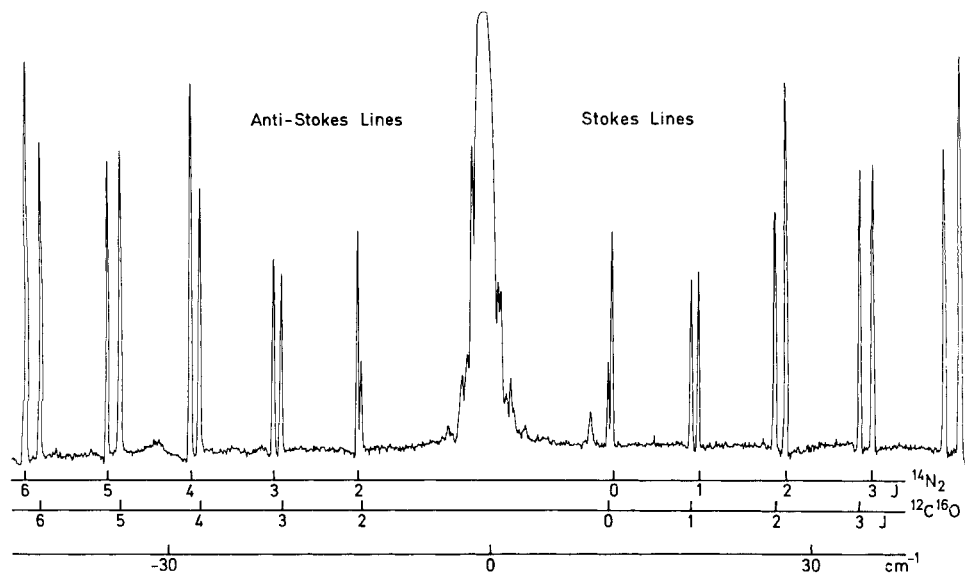

Fig. 1.   Microphotometer trace of the central part of the pure rotational Raman spectrum of a mixture of $^{14}N_2$ and $^{12}C^{16}O$. Excitation 5145 Å; gaspressure $^{14}N_2$ 30 torr and $^{12}C^{16}O$ 150 torr; slitwidth 0.15 cm^{-1}; exposure time 90 min; platefactor 2.07 cm^{-1} mm^{-1}; plate Kodak IIa-D. The J numbering of the lower levels is indicated.

Second, the processing of the Kodak IIa-D plates, which were used throughout, was carried out according to the method proposed by Gollnow and Hagemann [9]. In this procedure Kodak Tropical Developer is used together with a saturated sodium sulphate stop-bath and the Kodak Acid Fixing with hardener. This method seems to minimize the distortion of the spectral lines due to stretching effects in the gelatine layer during the processing period. The positions of the lines on the plates were measured as described in [8].

Third, it was intended to perform the calibration as described in [8], but it was found that the precision of the frequencies of the Th-lines [10] was insufficient compared to the high accuracy obtained for the line positions. Therefore, as far as possible the pure rotational Raman spectrum of CO was chosen as a basis of the calibration. The rotational constants for CO are known to a very high degree of accuracy from infrared spectroscopy [11].

In all cases the frequencies of the calibration lines were fitted to a fourth order polynomial

$$v = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + a_4 x^4 \qquad (4)$$

by a least squares procedure. In (4) v is the frequency of the calibration line at the position x on the plate. The Raman frequencies were determined by inserting the Raman line positions in (4).

The calibration was performed in three different ways:

(1) The sample of $^{14}N_2$ and $^{15}N_2$ were mixed with CO gas. In the pure rotational spectra originating from these samples the CO spectrum acts as an internal standard.

(2) The pure rotational spectra of $^{14}N^{15}N$ and CO coincide within the resolution available. A separate CO spectrum was in this case used to calculate the frequencies of the Th-lines by inserting the positions of the Th-lines in the polynomial obtained from the CO-spectrum. The calibration of the $^{14}N^{15}N$ Raman spectrum was then performed using only those Th-frequencies from the list of Giacchetti et al. [10] which agree with those calculated. This method was also used in a few cases for $^{14}N_2$ and $^{15}N_2$ spectra. The agreement between the frequencies obtained by the two calibration procedures was within the experimental accuracy.

(3) The third method [12] is to construct a set of curves giving the constants of the calibration polynomial (4) as a function of the grating angle. Points on these curves are obtained from pure rotational Raman spectra of CO excited by different wavelength The use of the Th-spectrum is in this case restricted to a determination of the zero and first-order polynomial constants a_0 and a_1, whereas a_2, a_3 and a_4 are constrained to values obtained from the curves.

The pure rotational Raman spectra were obtained either from samples at atmospheric pressure using few minutes exposure time or from samples consisting of 30 torr nitrogen and 150 torr CO using few hours exposure time. This proportion yields Raman spectra of equal intensity of the two molecules as shown in Figure 1. The low pressure of CO was chosen to avoid pressure-broadening. The spectra were excited by 4880 Å and 5145 Å radiation. The grating was used in the 12th order for both exciting

lines. The spectal slitwidth was kept constant at 0.15 cm^{-1}. For each molecule three to five spectra were recorded.

To obtain the rotation-vibrational spectra, samples at atmospheric pressure were excited by 4880 Å radiation and exposed for 20 hours. The grating was used in the 11.

TABLE I

Wave numbers of the rotational Raman lines of $^{14}N_2$

J	$|v|_{obs}$	est. dev.	obs. — calc.
0	11.9344	0.0020	—0.0028
1	19.8941	0.0010	—0.0008
2	27.8517	0.0010	—0.0002
3	35.8084	0.0010	0.0004
4	43.7629	0.0010	0.0001
5	51.7163	0.0010	0.0003
6	59.6658	0.0010	—0.0017
7	67.6162	0.0010	—0.0007
8	75.5643	0.0010	0.0003
9	83.5061	0.0010	—0.0023
10	91.4513	0.0010	0.0014
11	99.3881	0.0010	—0.0001
12	107.3242	0.0010	0.0011
13	115.2546	0.0010	0.0004
14	123.1839	0.0010	0.0025
15	131.1061	0.0020	0.0019
16	139.0205	0.0010	—0.0020
17	146.9378	0.0030	0.0019
18	154.8418	0.0020	—0.0025

TABLE II

Wave numbers of the rotational Raman lines of $^{14}N^{15}N$

J	$|v|_{obs}$	est. dev.	obs. — calc.
0	11.5397	0.0030	—0.0017
1	19.2377	0.0020	0.0025
2	26.9281	0.0010	—0.0003
3	34.6191	0.0020	—0.0016
4	42.3122	0.0010	0.0004
5	50.0010	0.0010	—0.0005
6	57.6905	0.0010	0.0010
7	65.3763	0.0010	0.0008
8	73.0588	0.0010	—0.0006
9	80.7402	0.0010	—0.0006
10	88.4194	0.0010	—0.0002
11	96.0952	0.0010	—0.0001
12	103.7676	0.0010	—0.0002
13	111.4380	0.0020	0.0012
14	119.1036	0.0030	0.0015
15	126.7638	0.0050	0.0004
16	134.4102	0.0150	—0.0102
17	142.0755	0.0200	0.0027

order and the spectral slitwidth was 0.15 cm^{-1}. Two spectra were photographed of each molecule. A microphotometer trace of the central part of the $^{14}N_2$ vibrational band is shown in Figure 2.

TABLE III

Wave numbers of the rotational Raman lines of $^{15}N_2$

| J	$|\nu|_{obs}$	est. dev.	obs. — calc.
0	11.1482	0.0020	0.0028
1	18.5775	0.0010	0.0022
2	26.0012	0.0010	—0.0034
3	33.4333	0.0010	0.0003
4	40.8616	0.0010	0.0012
5	48.2849	0.0020	—0.0014
6	55.7109	0.0010	0.0001
7	63.1317	0.0010	—0.0016
8	70.5537	0.0020	—0.0001
9	77.9723	0.0010	0.0003
10	85.3884	0.0010	0.0007
11	92.8005	0.0020	0.0000
12	100.2109	0.0020	0.0006
13	107.6130	0.0020	—0.0038
14	115.0242	0.0020	0.0044
15	122.4210	0.0020	0.0021
16	129.8120	0.0030	—0.0021
17	137.2016	0.0050	—0.0034
18	144.5872	0.0040	—0.0042
19	151.9637	0.0150	—0.0094
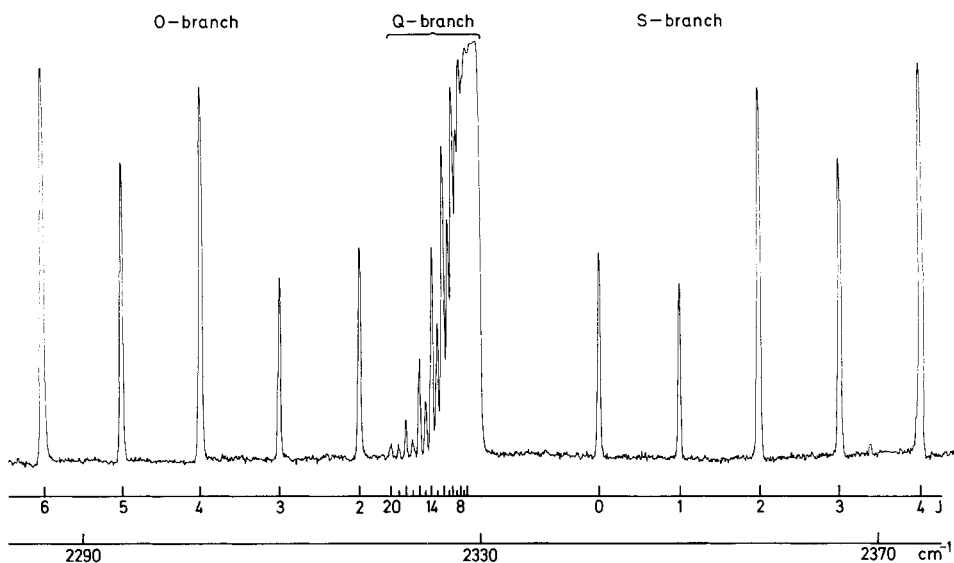
Fig. 2. Microphotometer trace of the central part of the rotation-vibrational Raman spectrum of $^{14}N_2$. Exitation 4880 Å; gaspressure 1 atm; slitwidth 0.15 cm^{-1}; exposure time 20 h; platefactor 2.22 cm^{-1} mm; plate Kodak IIa-D. The J numbering of the lower levels is indicated.

TABLE IV

Wave numbers of the lines of the fundamental vibrational
Raman band of $^{14}N_2$

assign.	ν_{obs}	est. dev.	obs. — calc.
$O(17)$	2194.6277	0.0300	−0.0021
$O(16)$	2203.0725	0.0300	−0.0025
$O(15)$	2211.4874	0.0200	−0.0023
$O(14)$	2219.8725	0.0050	−0.0011
$O(13)$	2228.2280	0.0030	0.0016
$O(12)$	2236.5464	0.0010	−0.0015
$O(11)$	2244.8366	0.0010	−0.0012
$O(10)$	2253.0963	0.0010	0.0005
$O(9)$	2261.3203	0.0010	−0.0013
$O(8)$	2269.5158	0.0020	0.0008
$O(7)$	2277.6737	0.0020	−0.0020
$O(6)$	2285.8056	0.0010	0.0022
$O(5)$	2293.8986	0.0010	0.0008
$O(4)$	2301.9561	0.0020	−0.0026
$O(3)$	2309.9851	0.0010	−0.0007
$O(2)$	2317.9750	0.0020	−0.0038
$Q(20)$	2322.6143	0.0050	−0.0010
$Q(19)$	2323.3062	0.0100	−0.0045
$Q(18)$	2323.9741	0.0030	0.0028
$Q(17)$	2324.5984	0.0030	0.0012
$Q(16)$	2325.1906	0.0030	0.0024
$Q(15)$	2325.7484	0.0030	0.0039
$Q(14)$	2326.2697	0.0030	0.0036
$Q(13)$	2326.7647	0.0060	0.0119
$Q(12)$	2327.2095	0.0030	0.0047
$Q(11)$	2327.6334	0.0100	0.0113
$Q(10)$	2328.0115	0.0030	0.0070
$Q(9)$	2328.3511	0.0050	−0.0011
$Q(8)$	2328.6691	0.0050	0.0040
$S(0)$	2341.7515	0.0030	0.0010
$S(1)$	2349.6061	0.0010	0.0017
$S(2)$	2357.4243	0.0010	0.0014
$S(3)$	2365.2059	0.0010	0.0002
$S(4)$	2372.9518	0.0010	−0.0006
$S(5)$	2380.6621	0.0010	−0.0008
$S(6)$	2388.3376	0.0010	0.0008
$S(7)$	2395.9739	0.0010	0.0000
$S(8)$	2403.5720	0.0010	−0.0019
$S(9)$	2411.1352	0.0010	−0.0013
$S(10)$	2418.6610	0.0010	−0.0004
$S(11)$	2426.1495	0.0010	0.0010
$S(12)$	2433.5964	0.0010	−0.0009
$S(13)$	2441.0080	0.0020	0.0003
$S(14)$	2448.3801	0.0050	0.0008
$S(15)$	2455.7083	0.0200	−0.0036
$S(16)$	2463.0068	0.0300	0.0015
$S(17)$	2470.2647	0.0500	0.0057

TABLE V

Wave numbers of the lines of the fundamental vibrational
Raman band of $^{14}N^{15}N$

assign.	ν_{obs}	est. dev.	obs. — calc.
$O(16)$	2168.7475	0.0200	−0.0015
$O(15)$	2176.8732	0.0100	−0.0041
$O(14)$	2184.9751	0.0010	−0.0013
$O(13)$	2193.0453	0.0010	−0.0006
$O(12)$	2201.0848	0.0010	−0.0009
$O(11)$	2209.0979	0.0010	0.0024
$O(10)$	2217.0788	0.0010	0.0038
$O(9)$	2225.0270	0.0010	0.0030
$O(8)$	2232.9422	0.0010	0.0001
$O(7)$	2240.8311	0.0010	0.0019
$O(6)$	2248.6836	0.0010	−0.0013
$O(5)$	2256.5080	0.0010	−0.0011
$O(4)$	2264.2996	0.0010	−0.0018
$O(3)$	2272.0599	0.0010	−0.0017
$O(2)$	2279.7860	0.0010	−0.0035
$Q(21)$	2283.7061	0.0100	0.0004
$Q(20)$	2284.3809	0.0150	−0.0181
$Q(19)$	2285.0459	0.0100	−0.0134
$Q(18)$	2285.6819	0.0020	−0.0047
$Q(17)$	2286.2823	0.0100	0.0014
$Q(16)$	2286.8376	0.0030	−0.0046
$Q(15)$	2287.3656	0.0020	−0.0048
$Q(14)$	2287.8662	0.0020	0.0005
$Q(13)$	2288.3295	0.0030	0.0016
$Q(12)$	2288.7647	0.0030	0.0076
$Q(11)$	2289.1601	0.0040	0.0068
$Q(10)$	2289.5309	0.0100	0.0144
$S(0)$	2302.7725	0.0020	−0.0037
$S(1)$	2310.3701	0.0010	−0.0019
$S(2)$	2317.9371	0.0020	0.0030
$S(3)$	2325.4579	0.0020	−0.0044
$S(4)$	2332.9554	0.0010	−0.0009
$S(5)$	2340.4177	0.0010	0.0018
$S(6)$	2347.8416	0.0010	0.0009
$S(7)$	2355.2333	0.0010	0.0027
$S(8)$	2362.5867	0.0010	0.0014
$S(9)$	2369.9043	0.0010	−0.0001
$S(10)$	2377.1886	0.0010	0.0007
$S(11)$	2384.4340	0.0020	−0.0013
$S(12)$	2391.6458	0.0010	−0.0006
$S(13)$	2398.8147	0.0200	−0.0064
$S(14)$	2405.9521	0.0200	−0.0068
$S(15)$	2413.0519	0.0200	−0.0078
$S(16)$	2420.1171	0.0200	−0.0061
$S(17)$	2427.1511	0.0300	0.0020

TABLE VI

Wave numbers of the lines of the fundamental vibrational
Raman band of $^{15}N_2$

assign.	ν_{obs}	est. dev.	obs. — calc.
$O(19)$	2110.1105	0.0300	−0.0088
$O(18)$	2118.0303	0.0200	−0.0130
$O(17)$	2125.9381	0.0100	−0.0022
$O(16)$	2133.8109	0.0020	0.0010
$O(15)$	2141.6510	0.0010	−0.0009
$O(14)$	2149.4660	0.0010	−0.0002
$O(13)$	2157.2505	0.0010	−0.0018
$O(12)$	2165.0120	0.0010	0.0018
$O(11)$	2172.7404	0.0010	0.0008
$O(10)$	2180.4405	0.0010	0.0004
$O(9)$	2188.1121	0.0010	0.0005
$O(8)$	2195.7576	0.0020	0.0037
$O(7)$	2203.3647	0.0010	−0.0019
$O(6)$	2210.9527	0.0020	0.0031
$O(5)$	2218.5021	0.0010	−0.0004
$O(4)$	2226.0226	0.0020	−0.0027
$O(3)$	2233.5163	0.0010	−0.0012
$Q(23)$	2243.4750	0.0150	−0.0015
$Q(22)$	2244.1920	0.0150	−0.0052
$Q(21)$	2244.8842	0.0030	−0.0023
$Q(20)$	2245.5431	0.0030	−0.0015
$Q(19)$	2246.1690	0.0050	−0.0023
$Q(18)$	2246.7689	0.0060	0.0023
$Q(17)$	2247.3336	0.0030	0.0029
$Q(16)$	2247.8716	0.0060	0.0083
$Q(15)$	2248.3728	0.0060	0.0081
$Q(13)$	2249.2803	0.0030	0.0069
$Q(11)$	2250.0629	0.0030	0.0061
$S(0)$	2263.1696	0.0080	−0.0072
$S(1)$	2270.5137	0.0010	0.0008
$S(2)$	2277.8121	0.0050	−0.0051
$S(3)$	2285.0877	0.0020	−0.0015
$S(4)$	2292.3289	0.0010	0.0001
$S(5)$	2299.5357	0.0020	−0.0001
$S(6)$	2306.7104	0.0010	0.0006
$S(7)$	2313.8485	0.0020	−0.0022
$S(8)$	2320.9610	0.0020	0.0028
$S(9)$	2328.0325	0.0010	0.0004
$S(10)$	2335.0718	0.0010	−0.0002
$S(11)$	2342.0745	0.0030	−0.0034
$S(12)$	2349.0493	0.0010	−0.0000
$S(13)$	2355.9854	0.0010	−0.0008
$S(15)$	2369.7632	0.0100	0.0081
$S(16)$	2376.5858	0.0050	−0.0009
$S(17)$	2383.3830	0.0050	0.0004
$S(18)$	2390.1482	0.0100	0.0054
$S(19)$	2396.8679	0.0050	0.0010
$S(21)$	2410.2048	0.0050	−0.0011

The final sets of rotational Raman frequencies are given in Tables I, II, and III for $^{14}N_2$, $^{14}N^{15}N$ and $^{15}N_2$, respectively, as meanvalues of the averaged Stokes and anti-Stokes frequencies from each plate. To each individual line an estimated deviation is assigned. This deviation is judged from the appearance of the line on the plate taking into account that the positions of faint lines and overexposed lines are less accurately determined than medium exposed lines. Furthermore, it is considered that lines situated near to the plate-edge are distorted due to stretching effects in the gelatine layer [9].

The final sets of rotation-vibrational frequencies and estimated deviations are listed in Tables IV, V and VI. They are established as described above except for the averaging of Stokes and anti-Stokes frequencies.

3. Analysis

The energy expressions used in the analysis of the spectra are

$$E = B_0 J_0 (J_0 + 1) - DJ^2 (J_0 + 1)^2 \tag{5}$$

for the vibrational ground state $(v=0)$ and

$$E = v_0 + B_1 J_1 (J_1 + 1) - DJ_1^2 (J_1 + 1)^2 \tag{6}$$

for the fundamental state $(v=1)$. The dependence of D on v is neglected, because ΔD is beyond the experimental accuracy.

A calculation of the spin statistical weights $g_{ns}(J)$, shows that for $^{14}N_2$ the lines with even J are twice as intense as lines with odd J whereas for $^{15}N_2$ lines with odd J are three times more intense as those with even J. For $^{14}N^{15}N$ no intensity alternation occurs. The observed spectra show intensity variations which agree with this statement.

The observed frequencies were fitted to the energy expressions and the Raman

TABLE VII

Molecular constants in cm^{-1}

		B_0	$D \times 10^6$	v_0	$B_0 - B_1$
$^{14}N_2$	Rot.	*1.989 574 ± 12*	*5.76 ± 3*		
	Rot.-Vib. unconstrained	1.989 707 ± 12	5.71 ± 5	*2329.9168 ± 3*	*0.017 384 ± 3*
	Rot.-Vib. constrained	(1.989 574)	(5.76)	2329.9156 ± 7	0.017 357 ± 6
$^{14}N^{15}N$	Rot.	*1.923 596 ± 9*	*5.38 ± 3*		
	Rot.-Vib. unconstrained	1.923 848 ± 18	5.42 ± 7	*2291.3324 ± 4*	*0.016 508 ± 2*
	Rot.-Vib. constrained	(1.923 596)	(5.38)	2291.3296 ± 13	0.016 482 ± 12
$^{15}N_2$	Rot.	*1.857 624 ± 16*	*5.08 ± 5*		
	Rot.-Vib. unconstrained	1.857 677 ± 9	5.06 ± 3	*2252.1249 ± 3*	*0.015 667 − 2*
	Rot.-Vib. constrained	(1.857 624)	(5.08)	2252.1243 ± 3	0.015 664 ± 2

Preferred values are in italics.
Deviations are standard deviations quoted in units of the last decimal.

selection rule $\Delta J = 0,\ \pm 2$ by a weighted least squares procedure. The reciprocal of the square of the estimated deviations were used as weighting factors [13]. The analyses of the vibrational bands have in addition been carried out by constraining B_0 and D to the values obtained from the pure rotational analyses. The results of the analyses are given in Table VII. In Tables I to VI only the difference between the observed and the calculated frequencies are given. The columns 'obs. −calc.' in the Tables IV, V and VI have been obtained using the constants from the unconstrained analysis.

4. Discussion

The deviations quoted in Table VII refers only to the internal consistency. Sources contributing to these deviations are the distortion of the spectral lines on the plates and the limited precision of the comparator measurement. The distortion due to processing may amount to $\pm 1\ \mu$ within the central part of the plate but may exeed $20\ \mu$ near to the edge [9]. The precision of the compator is better than $\pm 0.5\ \mu$. The accuracy setting on the spectral lines may vary from less than $\pm 1\ \mu$ for medium exposed, symmetrical lines to several μ's for overexposed or faint lines.

The frequency determination is, however, also affected by systematic shifts. An overall shift, different from plate to plate, is recognized by the fact that corresponding Stokes and anti-Stokes shifts differ by a constant amount except when calibration is performed by the use of an internal standard. The shift may originate in the uncertainty in filling out the entrance slit in exactly the same manner for the Raman spectrum and for the calibration spectrum. Clearly the ν_0 determination in the vibrational bands is affected by a similar shift. By experience it is found that the absolute frequency determination is not better than $\pm 0.01\ \mathrm{cm}^{-1}$.

The rotational constant B_0 given in Table VII shows a systematic shift between the two types of spectra, whereas the D values are in excellent agreement. The B_0's obtained from the pure rotational spectra have to be preferred because of the calibration by the internal standard. The reason for the shift between the B_0's is believed to be an inaccurate determination of the constant a_1 when the third calibration procedure is used. Work is in progress to determine better polynomial constants. In this connection it has to be noticed that using Th-calibration as described in [8] for the pure rotational spectra, the analyses yield even worse values, for instance for $^{14}N_2$: $B_0 = 1.989\,785 \pm \pm 20 \times 10^{-6}\ \mathrm{cm}^{-1}$.

The main information obtained from the analyses of the vibrational bands is the $B_0 - B_1$ value. A comparison between values obtained from the constrained and unconstrained analyses shows that $B_0 - B_1$ is almost independent of the choice between the two procedures. $B_0 - B_1$ is related to α through (2) giving

$$\alpha = B_0 - B_1 + 2\gamma. \tag{7}$$

Inserting $\gamma = -4.6 \times 10^{-5}\ \mathrm{cm}^{-1}$ as determined by Lofthus [3] and neglecting that γ is different for the isotopic molecules, α is obtained for each molecule. The results given in Table VIII for α have been obtained using $B_0 - B_1$ from both the constrained and the

unconstrained analysis. From the theoretical expressions given by H. H. Nielsen [14] it is possible to deduce that α is proportional to $\mu^{-3/2}$. Using this relation the consistency of the constants may be elucidated. The values of $\alpha \cdot \mu^{3/2}$ are also given in Table VIII. It is seen that the results from the unconstrained analyses give slightly better consistency. Therefore, these values are adopted for further calculations.

TABLE VIII

Values of α

	unconstrained		constrained	
	α	$\alpha \cdot \mu^{3/2}$	α	$\alpha \cdot \mu^{3/2}$
$^{14}N_2$	*0.017292 ± 3*	0.32036 ± 6	0.017265 ± 6	0.31986 ± 10
$^{14}N^{15}N$	*0.016416 ± 2*	0.31994 ± 4	0.016390 ± 12	0.31944 ± 23
$^{15}N_2$	*0.015575 ± 2*	0.31991 ± 4	0.015572 ± 2	0.31985 ± 4

Preferred values are in italics.
Deviations are standard deviations quoted in units of the las decimal.

To get an idea of the confidence of the D values, $\omega(^{14}N_2)$ as given by Lofthus [3] may be inserted in the relation [14]

$$D = 4\, B_e^3 / \omega^2 \qquad (8)$$

to yield $D(^{14}N_2)$. Using that D for isotopic molecules are proportional to μ^{-2} [14], D values for $^{14}N^{15}N$ and $^{15}N_2$ are obtained. The results are: $D(^{14}N_2) = 5.74 \times 10^{-6}$ cm^{-1}; $D(^{14}N^{15}N) = 5.36 \times 10^{-6}$ cm^{-1}; $D(^{15}N_2) = 5.00 \times 10^{-6}$ cm^{-1}; agreeing well with the values given in Table VII.

The values of B_e given in Table IX were calculated from (2) using the α-values from Table VIII and $\gamma = -4.6 \times 10^{-5}$ cm^{-1} as determined by Lofthus [3]. From B_e the equilibrium distances r_e were calculated using the fundamental constants given by Taylor *et al.* [15]. The results for r_e are also given in Table IX.

TABLE IX

The equilibrium constants B_e(cm^{-1}) and r_e(Å)

	B_e	r_e
$^{14}N_2$	1.998232 ± 12	1.097700 ± 7
$^{14}N^{15}N$	1.931816 ± 9	1.097702 ± 4
$^{15}N_2$	1.865424 ± 16	1.097700 ± 8

Deviations are standard deviations quoted in units of the last decimal.

Within the experimental accuracy r_e is the same for the three molecules as required by the Born-Oppenheimer approximation. The experimental accuracy is just insufficient to detect any deviation from the Born-Oppenheimer approximation, as de-

TABLE X

Molecular constants for $^{14}N_2$

		B_0	$D \times 10^6$	α	ν_0	r_e(Å)
Raman:	Stoicheff [1]	1.98973 ± 30	6.1 ± 5		2329.66 ± 20 [a]	1.09758 ± 10
	Butcher et al. [2]	1.989506 ± 27	5.48 ± 6			
	This work	1.989574 ± 12	5.76 ± 3	0.017292 ± 3	2329.92 ± 2	1.097700 ± 7
Ultraviolet:	Lofthus [3]	(1.9897)	6	0.01709 ± 30	(2329.66)	1.09755 ± 10
	Wilkinson [4]	1.9898 ± 5	6.4	0.01781	(2329.66)	1.0976
	Vanderslice [5]	1.9896	5.80			

Error limits are quoted in units of the last decimal.
Values in parentheses are transferred from Stoicheff [1] and used in a constrained analysis. [a] Q branch maximum.

scribed by Watson [16]. The equilibrium bond length for nitrogen may then be given as the meanvalue of the three independently determined r_e values:

$$r_e = 1.097701 \pm 0.000004 \text{ Å}.$$

The $^{14}N_2$ molecule has been investigated by many workers. Some of the results given in the literature are summarized in Table X. In those cases where error limits are given, the agreement with the results obtained in the present work are within 2 or 3 times the sum of the deviations. In those cases where no error limits are given, the agreement with the results in the present work is reasonable, with the possible exception of the α value found by Wilkinson [4].

As mentioned in the introduction no values of the constants of $^{14}N^{15}N$ and $^{15}N_2$ are given in the literature.

Acknowledgements

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