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THE INFRARED SPECTRUM AND THE MOLECULAR CONFIGURATION OF N_2O

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Abstract

Vibration spectrum. The three normal vibrations of N_2O are all active. The fundamental bands at 17.0μ, 7.78μ and 4.50μ, and the three harmonics have all been observed; also six combination bands at wave-lengths greater than 2μ. The 17.0μ fundamental and two combination bands involving this fundamental have strong zero branches, while the harmonic and two combination bands involving the harmonic transition have no zero branches. All other bands are doublets.

Rotational analysis. Three bands at 17.0μ, 7.78μ and 8.60μ have been resolved under high dispersion. All show rotation lines with continuously varying intensities (no alternation) and almost uniform spacing, the same for each band, viz. 0.84 cm^{-1}. The corresponding value of the moment of inertia, 59.4×10^{-40}, is practically equivalent to that computed from the doublet separations of the various bands.

Form of the molecule. The molecule is apparently linear but not symmetrical. The observations are not consistent with a triangular configuration, nor with the symmetrical linear configuration $N-O-N$, but they may be correlated precisely by means of the model $N\equiv N=O$.

THE infrared vibration spectrum of the N_2O molecule has been studied by Warburg and Leithauser[1], by E. v. Bahr[2], and more recently by Snow[3] but none of these observations were extended to wave-lengths sufficiently great to include all of the bands, nor was the available resolution adequate to reveal the rotational structure. Snow presented arguments based upon the physical properties of the gas which suggest that the molecule is linear in form, and believed that his results indicated the symmetrical arrangement N-O-N. Since the total number of electrons is the same as for CO_2 which is certainly linear and symmetrical[4] this would require that both in properties and spectrum the two gases should be very much alike. The observations indicate, however, a much richer spectrum for N_2O, with many more bands of appreciable intensity and without the restrictions as to combination frequencies which apply to CO_2.

The observations to be described below extend to about 20μ and include a number of bands not previously reported. The rotational structure is clearly resolved in several typical cases, and suggests at once a linear model, but certainly not a symmetrical one. The three fundamental frequencies are all active, as would have been expected for a triangular configuration of the atoms; they are however numerically inconsistent with the mechanical solu-

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[1] Warburg and Leithauser, Ber. D. phys. Ges. **1**, 148 (1908).

[2] E. v. Bahr, Verh. D. phys. Ges. **15**, 710 (1913).

[3] Snow, Proc. Roy. Soc. **A128**, 294 (1930).

[4] Martin and Barker, Phys. Rev. **37**, 1708 (1931).

tion for this case,[5] on the assumption of central force fields, yielding for the apex angle an imaginary value. It is quite apparent that the asymmetry must involve a difference in the distances from the oxygen atom to the two nitrogen atoms, rather than a departure from linearity. Such a situation seems probable only if the oxygen atom occurs at one end rather than at the middle of the group, the molecular form being $N\equiv N=0$.* In this case the vibration corresponding to ν_1, the inactive frequency for symmetrical molecules, would be represented in the absorption spectrum by fundamental and harmonic bands of the doublet type. The same would be true of ν_3, while ν_2 should exhibit zero branches in the fundamental and odd numbered harmonic bands, but none in even numbered harmonics. This follows immediately from the correspondence principle, and has been derived rigorously by Dennison.[6]

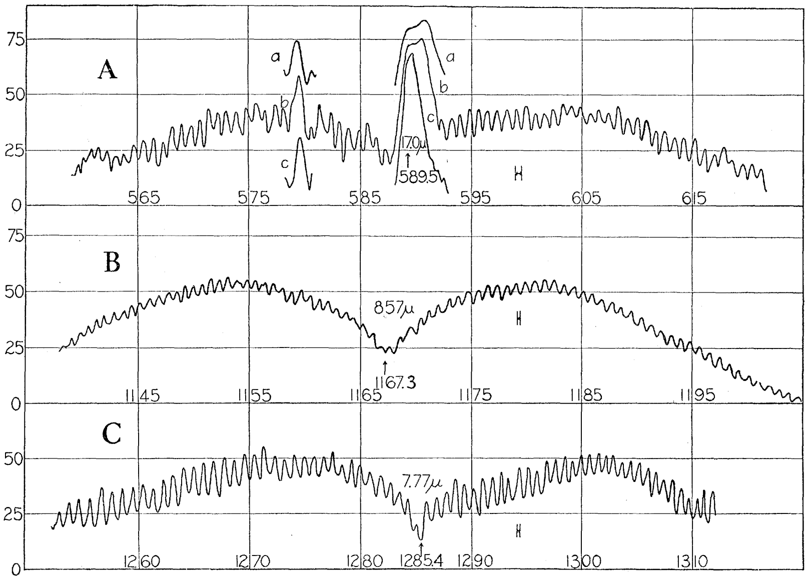

Fig. 1. Bands of N_2O showing rotational structure.

A. The fundamental ν_2, 26 cm cell, pressures 4, 16 and 30 cm.

B. The harmonic $2\nu_2$, 6 cm cell, 24 cm pressure.

C. The fundamental ν_1, 6 cm cell, 10 cm pressure.

THE OBSERVED FUNDAMENTAL BANDS

The lowest frequency fundamental band occurs at 17.0μ and arises from a change in electric moment perpendicular to the linear axis of the molecule, i.e. from the vibration ν_2. It has been resolved by means of a grating with a 7″×9″ surface ruled 1200 lines per inch, which was so effective that slits 0.6

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[5] Dennison, Phil. Mag. **1,** 203 (1926).

* During the course of the investigation our observations were submitted to Professor Dennison, and he first suggested this interpretation, which is apparently the only completely consistent one. We understand that the idea originated in a discussion between Dennison and Snow on the subject of the N_2O spectrum.

[6] Dennison, Rev. Mod. Phys. **3,** 280 (1931).

mm wide (including a frequency range of about 0.4 cm^{-1}) were adequate. The outline of this band is shown in Fig. 1A, upon a scale too small to indicate the individual readings which were taken at intervals of about 0.2 cm^{-1}. There is a strong zero branch at about 590 cm^{-1} with positive and negative branches consisting of lines appearing single at this resolution, which are spaced about 0.84 cm^{-1} apart. There is practically no convergence, as indicated in Table I, and the positions of the lines are well represented by the equation

TABLE I. *Observed frequencies for the fundamental ν_2 at 17.0μ, and residuals from the computed values.*

Positive branch			*Negative branch*	
wave numbers	residuals	*m*	wave numbers	residuals
		2	587.3	+.03
		3	6.4	+.10
592.4	−.04	4	5.6	+.06
3.3	−.10	5	4.9	−.08
4.0	+.05	6	3.9	+.07
4.9	−.01	7	3.1	+.03
5.7	+.04	8	2.4	−.09
6.5	+.07	9	1.4	+.07
7.4	+.01	10	0.6	+.03
8.3	−.05	11		
9.1	−.01	12		
600.0	−.07	13	78.1	+.03
0.8	−.03	14	7.4	−.11
1.6	+.01	15	6.5	−.05
2.4	+.07	16	5.7	−.09
3.3	+.01	17	4.8	−.03
4.1	+.04	18	3.9	+.04
4.9	+.09	19	3.0	+.11
5.7	+.13	20	2.2	+.07
6.5	+.17	21	1.4	+.03
7.4	+.12	22	0.6	.00
8.3	+.05	23	69.9	−.11
9.1	+.10	24	9.0	−.06
10.0	+.04	25	8.1	.00
0.8	+.10	26	7.3	−.04
1.7	+.04	27	6.5	−.08
2.5	+.08	28	5.6	.00
3.4	+.02	29	4.7	+.06
4.2	+.07	30	3.8	+.13
5.2	−.09	31	3.0	+.10
6.1	−.14	32	2.3	−.04
7.0	−.20	33	1.5	−.16
7.8	−.16	34		
8.6	−.11	35		
9.5	−.15	36		
20.4	−.20	37		
1.2	−.17	38		

$$\nu_2 = 589.01 \pm 0.839m + 0.0001m^2 \qquad (1)$$

m being merely an ordinal number, not equal to the quantum number *J*. The residuals in the table are differences between values from this equation and the observed frequencies; in only a few cases are they greater than 0.10 cm^{-1}, which is about the limit of accuracy in measurement. The maximum of the curve observed with 4 cm pressure in the cell, lies at 589.5 cm^{-1}, but this frequency would certainly be reduced somewhat if still less absorbing material were used.

In addition to the rotation lines there also appear secondary maxima at 590.6 and 579.6 which must be zero branches for the absorption due to molecules already possessing one or more quanta of vibrational energy. The former results in a curious broadening of the zero branch on its high frequency side as the amount of absorbing gas is increased, finally developing a double peak. Clearly this is not the result of a parabolic displacement of successive lines in the zero branch, since the convergence is so small. The proportion of molecules in the first excited state at ordinary temperatures is fairly large, in fact about 13.6 percent due to the low frequency and also to the fact that this state has a weight of two. For the first excited state the motion is isotropic in a plane normal to the molecular axis, and hence involves one quantum of rotational energy about this axis.[7] It may be represented by $1_{\pm 1}$, the normal state being 0_0, where the principal quantum number designates the vibrational state, and the subscript indicates angular momentum about the figure axis. From this state two transitions are possible, one to the double

TABLE II. *Observed frequencies for the fundamental ν_1 at 7.78μ, and residuals from the computed values.*

Positive branch			*Negative branch*	
wave numbers	residuals	*m*	wave numbers	residuals
1286.1	+.11	1	1284.5	+.03
7.0	+.03	2	3.8	−.11
7.9	−.03	3	2.9	−.05
8.7	−.02	4	2.0	+.00
9.5	+.01	5	1.1	+.05
90.3	+.04	6	2.0	+.09
1.2	−.06	7	79.4	+.02
2.0	−.04	8	8.6	−.04
2.8	−.04	9	7.7	.00
3.6	−.03	10	6.8	+.03
4.4	−.02	11	6.0	−.04
5.2	−.03	12	5.1	−.01
6.0	−.04	13	4.2	.00
6.9	−.15	14	3.4	−.07
7.6	−.06	15	2.5	−.06
8.4	−.07	16	1.5	+.03
9.2	−.09	17	0.6	+.05
1300.0	−.11	18	69.7	+.05
0.7	−.04	19	8.8	+.04
1.5	−.07	20	8.0	−.05
2.2	+.00	21	7.0	+.06
2.9	+.06	22	6.1	+.04
3.7	+.02	23	5.2	+.02
4.5	−.06	24	4.3	−.02
5.2	+.03	25	3.3	+.09
6.0	+.01	26	2.4	+.05
6.7	+.03	27	1.5	+.03
7.4	+.08	28	0.6	.00
8.2	+.01	29	59.7	−.03
8.9	+.05	30	8.7	+.03
9.7	−.02	31	7.8	−.02
10.4	+.02	32	6.9	−.04
1.0	+.14	33	5.8	+.10
1.8	+.07	34	4.9	+.04
		35	4.0	.00
		36	3.1	−.03

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[7] Dennison, Rev. Mod. Phys. **3**, 296 (1931), particularly Fig. 6.

level $2_{\pm 2}$, and one to the single level 2_0. These may be assigned the frequencies 590.6 and 579.6 respectively, corresponding to the two subsidiary zero branches. The rotation lines of these bands cannot be seen, of course, but they doubtless are responsible for slight displacements of observed maxima, making the residuals larger than they would otherwise be.

The band at 7.78μ, Fig. 1C was analysed with a 7″×9″ grating having 2400 lines per inch. The slit widths were 0.20 mm equivalent to about 0.27 cm^{-1}, and observations were made at intervals of 0.20 cm^{-1}. There is no zero branch, although a very weak line appears at the center, probably belonging to one of the bands originating in molecules already excited to the first vibration state of ν_2. The positive and negative branches have almost exactly the same spacing as in the lower frequency band, but there is some convergence toward smaller wave-lengths. The positions of the lines are given in Table II, together with the residuals (computed values minus observed values) obtained from the equation

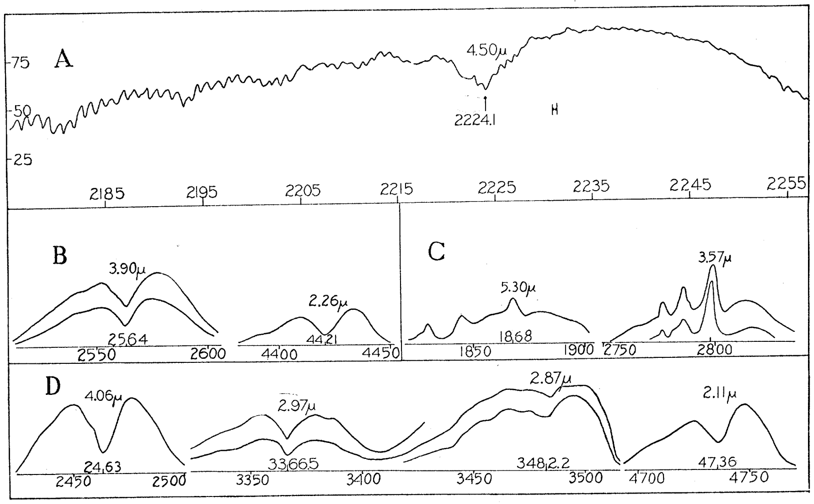

Fig. 2. Band envelopes.

A. The fundamental ν_3, partially resolved.

B. The harmonics $2\nu_1$ at 3.90μ and $2\nu_3$ at 2.26μ.

C. Combination bands $\nu_1+\nu_2$ at 5.30μ and $\nu_2+\nu_3$ at 3.57μ.

D. Combination bands $\nu_1+2\nu_2$ at 4.06μ, $2\nu_2+\nu_3$ at 2.97μ, $\nu_1+\nu_3$ at 2.87μ and $2\nu_1+\nu_3$ at 2.11μ.

$$\nu_1 = 1285.37 \pm 0.837m - 0.0017m^2. \qquad (2)$$

Although ν_1 and ν_2 are vibrations of essentially different character, the coefficients of the linear terms in both Eqs. (1) and (2) are practically equal, the corresponding difference in moment of inertia being no greater than would be expected as a result of deformations involved in the vibrations themselves. If the molecule had been in the form of a triangle with one atom at each vertex, thus constituting an asymmetrical rotator, the rotation lines would have been very irregular both in spacing and intensity: or, as a special case, the rotator might have been symmetrical, with moments of inertia $A=B=C/2$, but none of the bands would then exhibit a single strong zero branch as ν_2 does here, for no change in electric moment parallel to the symmetry axis could occur.

The third fundamental band lies at 4.50μ. It has been mapped with a grating having 7200 lines per inch and is shown in Fig 2A. The slit included 0.33 cm^{-1}. Although many trials were made to determine the optimum conditions for resolution, no clear cut rotation series could be obtained. From certain sections of the band it is evident that the line spacing is the same as in the other fundamentals, but the envelope shows a scalloped appearance for all gas pressures, indicating superposed bands of appreciable intensity. As before, these are probably due to absorption by molecules already vibrating in the lowest frequency mode. The interaction between ν_2 and ν_3 is apparently large, so that the maximum of the positive branch for the first upper stage band falls very near the center of the primary band, which is so obscured that an accurate determination os its position is impossible. The fact that the 7.8μ band is not so distorted indicates relatively less interaction between ν_1 and ν_2. The frequency indicated as the center, 2224.1 cm^{-1}, is that of the lowest point of this portion of the curve.

The relative intensities of the fundamentals ν_2 (17.0μ), ν_1 (7.8μ), and ν_3 (4.5μ) may be estimated as approximately 4:7:10.

THE HARMONIC AND COMBINATION BANDS

The harmonic of the 17.0μ band, located at 8.6μ, is shown in Fig. 1B, as mapped with the 2400 line grating. If the molecule were linear and symmetrical this transition would yield zero intensity of absorption;[6] if linear but unsymmetrical the component of the electric moment normal to the axis would still remain constant, but there would be a varying component along the axis, giving rise to a band with positive and negative branches but no zero branch. This is exactly as observed. The line spacing is about 0.84 cm^{-1} as before, and the intensity is about one fifth as great as that of the fundamental. The observed wave numbers shown in Table III are fairly well represented by the equation

$$\nu = 1167.31 \pm 0.835m + 0.0009m^2. \tag{3}$$

Beginning from the first excited state only one absorption band occurs in this region, instead of two as in the fundamental. It corresponds to the double transition $1_{\pm1} \rightarrow 3_{\pm1}$, but the suppression of the zero branch makes its position difficult to determine. The fact that the depressions between the lines are not nearly so marked as in the neighboring band at 7.8μ, indicates the disturbing effect of this superposition, which probably also explains the large residuals for small values of m.

Harmonics of the other two fundamentals are shown in Fig. 2B without high resolution. These are doublets, as would be expected. Six combination bands have been observed in the same manner. Of these two involve the fundamental transition in ν_2, and exhibit zero branches ($\lambda 5.3$ and $\lambda 3.57$, Fig. 2C)

TABLE III. *Observed frequencies for the harmonic $2\nu_2$ at 8.60μ, and residuals from the computed values.*

Positive branch wave numbers	residuals	m	*Negative branch* wave numbers	residuals
1167.8	+.34	1	1166.4	+.08
8.8	+.18	2	5.5	+.14
9.7	+.12	3	4.6	+.22
70.7	−.03	4	4.0	−.01
1.4	+.11	5	3.1	+.07
2.2	+.15	6	2.3	+.03
3.2	.00	7	1.6	−.06
4.0	+.05	8	0.7	−.01
4.9	−.01	9	59.9	−.03
5.8	−.05	10	9.1	−.05
6.7	−.05	11	8.3	−.05
7.5	−.04	12	7.4	+.02
8.4	−.09	13	6.6	+.01
9.2	−.03	14	5.8	−.01
80.0	+.04	15	5.0	.00
0.9	.00	16	4.2	−.02
1.8	−.04	17	3.3	+.08
2.7	−.06	18	2.6	−.04
3.6	−.11	19	1.8	−.03
4.4	−.03	20	1.0	−.03
5.3	−.13	21	0.2	−.02
6.1	−.04	22	49.5	−.05
7.0	−.06	23	8.7	−.11
7.9	−.03	24	8.0	−.18
8.7	+.03	25	7.1	−.09
9.6	+.03	26	6.3	−.09
90.5	+.02	27	5.4	+.02
1.4	+.03	28	4.7	−.09
2.3	+.03	29	4.0	+.02
3.2	+.04	30	3.1	−.03
4.1	−.05	31	2.2	+.09
4.9	+.05	32	1.5	+.01
5.8	+.04	33	0.7	+.04
6.7	+.04	34	0.0	−.04
7.6	+.04	35	39.2	.00
8.5	+.03	36		
9.3	+.13	37		
1200.3	+.06	38		
1.1	+.14	39		
2.1	+.05	40		
3.0	+.06	41		

while two others involve the first harmonic of ν_2 and are doublets (λ4.05 and λ2.97, Fig. 2D). The zero branch bands each show three maxima corresponding to transitions $0_0 \rightarrow 1_1$, $1_1 \rightarrow 2_0$, and $1_1 \rightarrow 2_2$ for the ν_2 component.

The positions and approximate intensities for all of the observed bands are assembled in Table IV, with the assigned interpretations indicated. From the equation given by Dennison* for the positions of the various vibration levels it is possible to determine in first approximation the anharmonic correction terms. Aside from a common constant the levels are given in frequency units by the expression

$$V_1\nu_1 + V_2\nu_2 + V_3\nu_3 + x_{11}V_1^2 + x_{22}(V_2^2 - \tfrac{1}{3}l^2) + x_{33}V_3^2 + x_{12}V_1V_2 + x_{13}V_1V_3 + x_{23}V_2V_3$$

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* Reference 6, p. 296. Although written for the linear symmetrical molecule, this equation is equally applicable to the unsymmetrical group of three colinear atoms, as may easily be seen.

TABLE IV. *Positions and relative intensities of observed bands.*

	λ	ν (obs.)	int.	ν^0	transition in V_2
ν_2	17.0	579.5	4	593.0	$1_1\rightarrow 2_2$
		589.0	40		$0_0\rightarrow 1_1$
		590.5	4		$1_1\rightarrow 2_0$
ν_1	7.78	1285.4	70	1288.7	
ν_3	4.50	2224.1	100	2237.9	
$2\nu_2$	8.60	1167.3	20		
$2\nu_1$	3.90	2564.2	16		
$2\nu_3$	2.26	4420.7	2		
$\nu_1+\nu_2$	5.30	1868.0	0.5		$0_0\rightarrow 1_1$
		1845	0.1		$1_1\rightarrow 2_2$
		1829	0.1		$1_1\rightarrow 2_0$
$\nu_1+2\nu_2$	4.06	2462.2	6		
$\nu_2+\nu_3$	3.57	2799.1	1.2		$0_0\rightarrow 1_1$
		2786	0.3		1_1+2_2
		2777	0.3		1_1+2_0
$2\nu_2+\nu_3$	2.97	3366.5	1.6		
$\nu_1+\nu_3$	2.87	3482.2	10		
$2\nu_1+\nu_3$	2.11	4736.0	0.8		

where l measures angular momentum about the axis, in units of $h/2\pi$. By taking differences between the appropriate expressions of this sort for different observed bands, sets of equations are obtained from which the values of the x's may be determined, and hence the frequencies ν^0 corresponding to infinitesimal amplitudes. Table V shows the values of these coefficients, with the transitions from which they are obtained. The values of ν^0 appear in Table IV, column 5. The above expression is, of course, a first approximation only: with our interpretation of the bands it gives consistent values whenever l is not greater than unity. It does not, however, fit very well the assignments $(2_2\rightarrow 1_1)\,V_2=590.5$ and $(1\rightarrow 0)\,V_1+(2_2\rightarrow 1_1)\,V_2=1845$.

TABLE V. *Anharmonic correction coefficients.*

coefficient	value	transitions employed
x_{11}	-3.3	$(0\rightarrow 2)\,V_1-(0\rightarrow 1)\,V_1$
x_{22}	-4.0	$(0_2\rightarrow 2_0)\,V_2-(0_0\rightarrow 1_1)\,V_2$
	-4.0	$(1_1\rightarrow 2_0)\,V_2$
	-1.25	$(1_1\rightarrow 2_2)\,V_2$
x_{33}	-13.8	$(0\rightarrow 2)\,V_3-(0\rightarrow 1)\,V_3$
x_{12}	-7.7	$(0\rightarrow 1)\,V_1+(0_0\rightarrow 1_1)\,V_2$
	-6.3	$(0\rightarrow 1)\,V_1+(0_0\rightarrow 2_0)\,V_2$
	-15.4	$(0\rightarrow 1)\,V_1+(1_1\rightarrow 2_2)\,V_2$
	-10.0	$(0\rightarrow 1)\,V_1+(1_1\rightarrow 2_0)\,V_2$
x_{13}	-27.3	$(0\rightarrow 1)\,V_1+(0\rightarrow 1)\,V_3$
	-26.1	$(0\rightarrow 2)\,V_1+(0\rightarrow 1)\,V_3$
x_{23}	-14.0	$(0_0\rightarrow 1_1)\,V_2+(0\rightarrow 1)\,V_3$
	-14.3	$(1_1\rightarrow 2_2)\,V_2+(0\rightarrow 1)\,V_3$
	-13.3	$(1_1\rightarrow 2_0)\,V_2+(0\rightarrow 1)\,V_3$
	-12.5	$(0_0\rightarrow 2_0)\,V_2+(0\rightarrow 1)\,V_3$

Form of the Molecule

The considerations bearing upon the question of geometric arrangement of the atoms in the molecule of N_2O may be summarized as follows: (1) The observed bands are of two types, one with an intense zero branch and one without, but in each case the rotation lines of the positive and negative branches form simple series with the same spacing. This excludes the possibility of a triangular configuration, which would result either in an asymmetrical rotator with very irregular lines, or in a symmetrical rotator with two different line spacings. (2) The moment of inertia as computed from the fine structure using the formula $B=h/4\pi^2I$, is 59.4×10^{-40}, which is of the same order of magnitude as the value obtained from the doublet differences of the band envelopes. This doublet difference is practically the same in all bands and averages 29 cm^{-1}, corresponding to $I=55\times10^{-40}$, a value somewhat smaller than the previous one because of slight broadening of the bands due to the large proportion of the molecules already excited vibrationally at room temperature. This numerical agreement also indicates the linear arrangement of atoms in the molecule. (3). The uniformly varying intensities in fine structure lines indicates that the molecule is not of the form N–O–N, since nuclear spin in the N atoms would then lead to alternating intensities, as in the bands of N_2. (4) The absence of any restriction upon vibrational transitions also excludes the possibility of the symmetrical arrangement. All combinations of ΔV_1, ΔV_2 and ΔV_3 appear, with zero branches only when ΔV_2 is odd. (5) The variation of specific heat with temperature is a further indication that the molecule is linear. Snow has kindly informed us that his computations using our three fundamental frequencies reproduce the specific heat curve very accurately.

A very rough comparison of the relative strengths of the two chemical bonds may be obtained by assuming infinitesimal harmonic vibrations as of mass points fastened together by two weightless springs, and vibrating along the line of centers. Let the force constants be K_1 and K_2 for the N–N and the N–O linkages respectively, the interaction between the two extreme atoms being neglected. From the character and the frequencies (ν_1 and ν_3) of the two normal vibrations, and the known masses of the atoms, it follows at once that $K_1=2.4\times10^6$ and $K_2=2.2\times10^6$ dynes/cm.

Raman Lines

The observed Raman spectrum of N_2O consists of a single line[8] at 1281 cm^{-1}, in fairly good agreement with our value for ν_1. For linear molecules ν_2 would not appear in the Raman scattering, due to the symmetry of the vibration.[9] Neither would ν_3 appear if the configuration were symmetrical. However, it should be observed, though possibly with low intensity, for the unsymmetrical arrangement indicated above.

[8] Dickinson, Dillon and Rasetti, Phys. Rev. **34,** 582 (1929).

[9] Placzek, Zeits. f. Physik **70,** 84 (1931).

PERMANENT ELECTRIC MOMENT

The electric moment of N_2O is apparently very small[10] which at first glance seems to favor the hypothesis of a symmetrical molecule. It is probably not zero, however. In the absence of definite information concerning the electron distribution and the interatomic distances, it is impossible to estimate precisely what value would be expected for an unsymmetrical linear configuration. It is clear, however, that the position of the electrical center for the positive nuclei is very sensitive to changes in the relative distances from central to extreme atoms, and it might happen to fall very close to the corresponding center for the electron shell. Hence our model is not necessarily inconsistent with the observed dipole value.

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[10] Braunmuhl, Phys. Zeits. **28,** 141 (1927).