

the orbitals, particularly $z\sigma_g$, should be considerably modified (especially as regards extent of $s-p$ mixing) by the clustering of other atoms around the carbons, so that r_0 values calculated on the basis of a diatomic carbon molecule are no longer entirely appropriate.

When a table similar to Table I and an

equation similar to Eq. (2) are written down for N_2 and N_2^+ , one finds relations similar to those for carbon: bonding to other atoms seems to shorten the $N=N$ and $N-N$ bond distances as compared with those for N_2 itself. The equation for N_2 and N_2^+ is

$$r_0 = 1.49 + 0.03(N_y - N_x) - 0.10(N_w - N_v). \quad (3)$$

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The Infra-Red Spectrum and Molecular Constants of Nitric Oxide

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The infra-red spectrum of nitric oxide has been re-measured under high dispersion with the result that the fundamental at 5.3μ has been almost completely resolved. The absorption in this region comprises two superposed bands arising from a ${}^2\Pi_{1/2, 3/2}$ electronic ground state. In the P , and R branches a great many of the lines split up into doublets, the components of which belong to these two bands, respectively. The lines were found to fit the following two empirical formulas:

$$\begin{aligned} \nu_{\Omega=1/2} &= 1877.36 + 3.34 J - 0.019 J^2 \text{ cm}^{-1} \\ &\text{where } J=0, \pm 3/2, 5/2, \dots, \\ \nu_{\Omega=3/2} &= 1877.00 + 3.42 J - 0.019 J^2 \text{ cm}^{-1} \\ &\text{where } J=0, \pm 5/2, 7/2, \dots \end{aligned}$$

An experimental curve in percent absorption against frequency in cm^{-1} is compared with a theoretical intensity plot of the bands. From the new data some of the constants have been re-calculated, and compared with the results of the electronic band spectra. $I_0 = 1.63 \times 10^{-30} \text{ g cm}^2$, $r_0 = 1.15 \times 10^{-8} \text{ cm}$, $\nu_0 = 1891.3 \text{ cm}^{-1}$.

I. INTRODUCTION

AMONG the diatomic molecules having infra-red spectra nitric oxide is of special interest. Because of its electronic configuration, which gives it a ground state of ${}^2\Pi_{1/2, 3/2}$, the molecule has resultant angular momentum of $(1/2)\hbar$ and $(3/2)\hbar$ around its nuclear axis. It becomes, therefore, the only one of the diatomic molecules to exhibit a Q branch in the infra-red.

Warburg and Leithauser¹ in 1908, the first to investigate the spectrum, succeeded in showing that the contour of the fundamental at 5.3μ was a doublet. Later, in 1929–1930, Snow, Rawlins, and Rideal² resolved both the fundamental at 5.3μ and the first harmonic at 2.7μ into rotational structure by means of a grating spectrometer.

This spectrum has been re-investigated using an instrument of somewhat better resolving power. Several details of interest were observed and are reported here. Some of the constants are calculated from our data and compared with values given in the earlier work, and with those determined from the electronic band spectrum.³

II. APPARATUS

The nitric oxide was prepared according to the method outlined by Snow, Rawlins, and Rideal.² A large spherical bulb was filled to atmospheric pressure by passing gas through the bulb until all the air had been displaced by the gas. The nitric oxide was allowed to generate and flow until the colorlessness of the gas in the storage tank attested to its purity. For the 5.3μ region a cell 2 cm long fitted with rocksalt windows was used; for the 2.7μ region the cells used were from 10–30 cm long. Each cell was

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¹ Warburg and Leithauser, *Ber. D. Chem. Ges.* **1**, 145 (1908).

² C. P. Snow, F. I. G. Rawlins and E. K. Rideal, *Proc. Roy. Soc.* **124**, 453 (1929); C. P. Snow, F. I. G. Rawlins and E. K. Rideal, *Proc. Roy. Soc.* **126**, 355 (1929).

³ M. Guillery, *Zeits. f. Physik* **42**, 121 (1927); F. A. Jenkins, H. A. Barton and R. S. Mulliken, *Phys. Rev.* **30**, 150 (1927); R. S. Mulliken, *Phys. Rev.* **32**, 186 (1928).

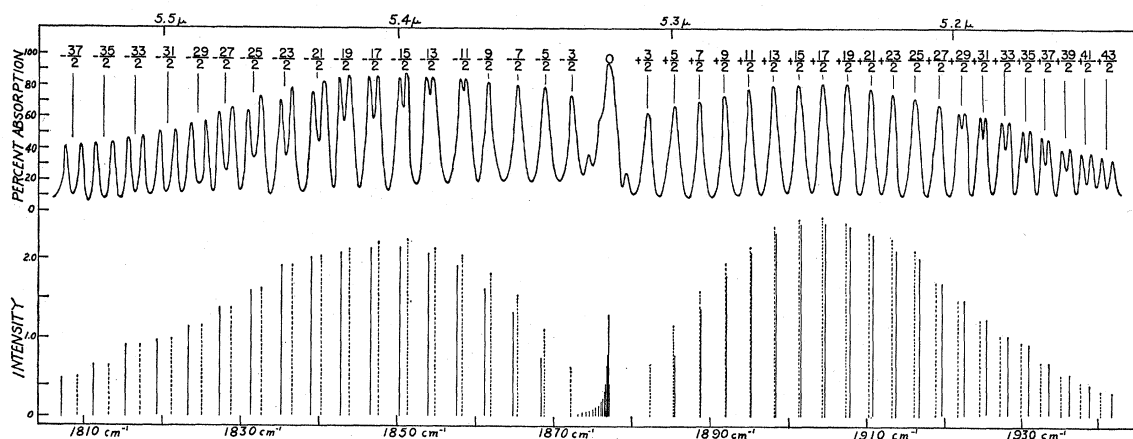


FIG. 1. The upper curve shows the observed absorption of NO at 5.3μ ; the lower diagram gives theoretically predicted band spectrum of NO.

filled to atmospheric pressure from the storage tank.

Both regions in which absorption occurs—but more especially the harmonic region—overlap those of atmospheric absorption by water vapor. To make measurements in these regions it was found necessary to dry the spectrometer box thoroughly. This was accomplished by distributing P_2O_5 in photographic trays throughout the spectrometer box and sealing it securely. One such charge would last about a week indicating that the box was quite airtight. No falsification by water vapor was now apparent even in the middle of the 2.7μ water band.

The instrument with which these measurements were made was of the conventional prism-grating type and has been described in previous papers from this laboratory. The 5.3μ band was measured with the aid of the 3600 line-per-inch grating in the first order while the harmonic at 2.7μ was measured using the 4800 line-per-inch grating in first order. Both gratings were ruled by Professor R. W. Wood at Johns Hopkins University.

III. EXPERIMENTAL RESULTS

The 5.3μ region

Figure 1 shows our observations on the fundamental vibration-rotation band of nitric oxide plotted with ordinates in percent absorption against abscissae of frequency in cm^{-1} and wave-length in μ . This curve differs from the one

by Snow, Rawlins, and Rideal in several respects. The rotation lines are much more completely resolved, and the curve shows the existence of the two transitions ${}^2\Pi_{3/2} - {}^2\Pi_{3/2}'$, and ${}^2\Pi_{1/2} - {}^2\Pi_{1/2}'$ as two bands, whose Q branches are very nearly coincident. That two bands exist is evident from the fact that in both the P and the R branches the lines split up into pairs beginning a few lines from the center. The splitting appears to increase with the rotational quantum number. The lines in the P branch begin splitting up with the fifth line from the Q branch, while in the R branch the splitting does not occur until the fourteenth line. The closest pair which was resolved has a spacing of 0.6 cm^{-1} . The Q branch is much better resolved than in the earlier work and appears to be more intense. The slit widths used in this region included a spectral region of about 0.6 cm^{-1} and observations were made at intervals of 0.45 cm^{-1} .

The 2.7μ region

No curve for the harmonic is given in this paper. This region was very carefully measured and yields a band which appears to have a Q branch at 3740.2 cm^{-1} . The band has a very irregular structure and does not at all resemble the fundamental nor indeed a band due to a diatomic molecule. It does, however, in many respects corroborate the curve shown by Snow, Rawlins, and Rideal and the line spacing is about the same as that estimated from the curve given by them. This spacing is about

7.0 cm⁻¹ and not at all in agreement with the spacing in the fundamental. It is hoped that this band may be measured again in the near future under better conditions.

IV. DISCUSSION OF RESULTS

The energy of a diatomic molecule having angular momentum around the nuclear axis is given by Kronig⁴ as

$$W_{v, J} = W^0 - B_0\alpha + h\nu_0(v + \frac{1}{2}) \{1 - k(J + \frac{1}{2})^2 + \Gamma\} + B_0[(J + \frac{1}{2})^2 + \Gamma] \{1 - \gamma^2[(J + \frac{1}{2})^2 + \Gamma]\} - B_0\beta(v + \frac{1}{2})^2, \quad (1)$$

where $\alpha = (7/4)c_3 + (7/8)c_3^2 + (3/4)c_4$;
 $k = (3/2)\gamma^2(1 + 2c_3)$;
 $\Gamma = S(S+1) - 2\Omega\Sigma$;
 $\beta = (3 + 15c_3 + 15/c_3^2 + 3c_4)$.

The frequencies of the rotation lines in the bands may be obtained from this energy relation and are:

$$\nu_{\Omega=\frac{1}{2}} = [\nu_0 - (3/2)\nu_0k - 2B_0\beta/h] + [2B_0/h - 2\nu_0k - 6B_0\gamma^2/h]J - \nu_0kJ^2 - 4B_0\gamma^2J^3/h$$

where $J=0, \pm 3/2, 5/2, 7/2, \dots$, etc. (2)

arising from the transition ²Π_{1/2} - ²Π_{1/2}' with $\Omega = \frac{1}{2}$, $\Sigma = -\frac{1}{2}$, $S = \frac{1}{2}$; and

$$\nu_{\Omega=\frac{3}{2}} = [\nu_0 + (1/2)\nu_0k - 2B_0\beta/h] + [2B_0/h - 2\nu_0k + 2B_0\gamma^2/h]J - \nu_0kJ^2 - 4B_0\gamma^2J^3/h$$

where $J=0, \pm 5/2, 7/2, \dots$, etc. (3)

arising from the transition ²Π_{3/2} - ²Π_{3/2}' with $\Omega = \frac{3}{2}$, $\Sigma = \frac{1}{2}$, $S = \frac{1}{2}$.

These equations are of the form $\nu = a \pm bJ - cJ^2 \pm dJ^3$. It has been found possible to fit the lines in the two bands to the following formulas:

$$\nu_{\Omega=\frac{1}{2}} = 1877.36 + 3.34J - 0.019J^2;$$

where $J=0, \pm 3/2, 5/2, \dots$, etc. (4)

and

$$\nu_{\Omega=\frac{3}{2}} = 1877.00 + 3.42J - 0.019J^2;$$

where $J=0, \pm 5/2, 7/2, \dots$, etc. (5)

The cube term in J was omitted because its value was known with too little accuracy to have any meaning. Table I shows the observed

line positions in cm⁻¹ and the line positions as computed from the empirical equations (4) and (5). In most cases the error between the observed and calculated positions is of the order of 0.3 cm⁻¹.

In Fig. 1, lower diagram, the rotation lines in the transitions ²Π_{1/2} - ²Π_{1/2}' and ²Π_{3/2} - ²Π_{3/2}' are plotted with calculated intensities as ordinates and as abscissa the same scale of frequency in cm⁻¹ as was used in Fig. 1, upper curve. The intensities were computed from the relations given by Dennison.⁵ The ²Π_{1/2} - ²Π_{1/2}' transition is represented by the dotted lines, while the solid lines represent the ²Π_{3/2} - ²Π_{3/2}' transition. The individual lines in the Q branch of the first transition and the Q branch of the latter transi-

TABLE I. Observed and calculated frequencies (cm⁻¹) of the lines in the fundamental of NO.

2J	ν (CALC)	$\Omega = \frac{1}{2}$ ν (OBS)	$\Delta\nu$	ν (CALC)	$\Omega = 3/2$ ν (OBS)	$\Delta\nu$
+43	1940.4	1940.1	-0.3	1941.8	1942.1	+0.3
+41	1937.9	1938.2	+ .3	1939.1	1939.6	+ .5
+39	1935.7	1935.6	- .1	1936.5	1936.6	+ .1
+37	1933.1	1932.8	- .3	1933.8	1933.7	- .1
+35	1930.0	1930.2	+ .2	1931.0	1931.4	+ .4
+33	1927.3	1927.5	+ .2	1928.3	1928.6	+ .3
+31	1924.6	1924.6	.0	1925.5	1925.4	- .1
+29	1921.8	1922.0	+ .2	1922.6	1922.7	+ .1
+27	1919.0	1919.8	+ .8	1919.7	1919.8	+ .1
+25	1916.1	1916.3	+ .2	1916.8	1916.3	- .5
+23	1913.3	1913.4	+ .1	1913.8	1913.4	- .4
+21	1910.3	1910.6	+ .3	1910.8	1910.6	- .2
+19	1907.4	1907.6	+ .2	1907.8	1907.6	- .2
+17	1904.4	1904.5	+ .1	1904.7	1904.5	- .2
+15	1901.3	1901.5	+ .2	1901.6	1901.5	- .1
+13	1898.3	1898.2	- .1	1898.4	1898.2	- .2
+11	1895.2	1895.1	- .1	1895.3	1895.1	- .2
+ 9	1892.0	1891.7	- .3	1892.0	1891.7	- .3
+ 7	1888.8	1888.6	- .2	1888.7	1888.6	- .1
+ 5	1885.8	1885.5	- .3	1885.4	1885.5	+ .1
+ 3	1882.3	1882.1	- .2			
0	1877.36			1877.00		
- 3	1872.3	1872.2	- .1			
- 5	1868.9	1869.0	- .1	1868.3	1869.0	+ .7
- 7	1865.4	1865.4	.0	1864.8	1865.4	+ .6
- 9	1862.0	1861.6	- .4	1861.2	1861.6	+ .4
-11	1858.4	1858.7	+ .3	1857.7	1858.1	+ .4
-13	1854.9	1854.7	- .2	1854.0	1853.7	- .3
-15	1851.2	1851.2	.0	1850.3	1850.2	- .1
-17	1847.6	1847.4	- .2	1846.6	1846.1	- .5
-19	1843.9	1843.8	- .1	1842.8	1842.5	- .3
-21	1840.2	1840.4	+ .2	1839.0	1839.1	+ .1
-23	1836.4	1836.3	- .1	1835.2	1835.0	- .2
-25	1832.6	1832.3	- .3	1831.3	1830.8	- .5
-27	1828.8	1828.9	+ .1	1827.4	1827.2	- .2
-29	1824.9	1824.5	- .4	1823.4	1823.5	+ .1
-31	1821.0	1821.4	+ .4	1819.2	1819.4	+ .2
-33	1817.1	1817.2	+ .1	1815.4	1815.4	.0
-35	1813.1	1813.3	+ .2	1811.3	1811.2	- .1
-37	1809.1	1808.7	- .4	1807.2	1807.3	+ .1

⁴ R. del Kronig, *Band Spectra* (Macmillan, Cambridge Series, 1930), p. 31.

⁵ D. M. Dennison, *Rev. Mod. Phys.* **3**, 315 (1931).

tion are so nearly equal in position that on this scale it is impossible to distinguish them. The corresponding lines from each Q branch have therefore been added and the Q branch shown is the line for line sum of the two Q branches. The intensities in the experimental curve are only relative and can be compared with the lines in the theoretical curve only in general characteristics. The two curves agree very well except that in the experimental curve the Q branch appears to be too intense as compared with the lines of maximum intensity in the P and R branches. Also the resolution was not complete, as only about one-half of the lines could be separated into doublets.

From Eqs. (2) and (3) it is evident that the theory predicts that the constant term of $\nu_{\Omega=3/2}$ should be greater than the constant term of $\nu_{\Omega=1}$. It was not found possible to make the observed lines fit a set of equations in which this was the case but a very good fit was obtained by letting the reverse be true. A possible explanation of this inconsistency may be that ν_0 for the ${}^2\Pi_{3/2}$ state is greater than ν_0 for the ${}^2\Pi_{1/2}$ state by just this amount. It seems not unlikely that the two values may differ by small amounts. Some evidence of this is also presented by Jenkins, Barton, and Mulliken in their work.

The constants I_0 , r_0 , may be computed from Eqs. (2), (3), (4) and (5) by identifying the constant first term in (2) and (3) with the empirical constant of (4) and (5); and by identifying the theoretical coefficients of J and J^2 in (2) and (3) with the empirical coefficients of J and J^2 in (4) and (5).

The Q branch of the harmonic as obtained from our unpublished curve lies at 3740.2 cm^{-1} .

TABLE II. *Assembled values of some of the constants for NO.*

CONSTANT	NIELSEN- GORDY	JENKINS- BARTON- MULLIKEN	SNOW- RAWLINS- RIDEAL	JEVONS ¹
$I_0 \times 10^{-39} \text{ g cm}^2$	1.63	1.63	1.64	
$r_0 \times 10^{-8} \text{ cm}$	1.15	1.15	1.15	1.146
$\nu_0 \text{ cm}^{-1}$	1891.3	1892	1895.2	1906.5

¹ W. Jevons, *Report on Band Spectra of Diatomic Molecules* (Univ. Press Cambridge, 1932).

We may then set $[2\nu_0 - 6B_0\beta/h - 3\nu_0k] = 3740.2 \text{ cm}^{-1}$ and, using this together with the previously mentioned data, calculate ν_0 . These values are compared with values for the same constants obtained by other investigators in Table II.

I_0 and r_0 agree very well in all cases because they are determined from the fundamental band only. ν_0 from our data agrees with the value given by Jenkins, Barton, and Mulliken rather than with the other values given in Table II. The reason for disagreement here is that ν_0 determined from the positions of both the fundamental and harmonic, depends on how these band centers are chosen. We believe the value 1877 cm^{-1} for the fundamental to be correct. It differs from Snow, Rawlins, and Rideal's value by 5.9 cm^{-1} . There is, however, some doubt about the position of the center of the harmonic. Therefore we feel that accurate values of such constants as ν_0 , $\nu\nu_0$, c_3 and c_4 from infra-red data cannot be determined until the question of the position of the harmonic is settled.

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