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Millimeter-Wave Rotational Spectrum of NO in the $^2\pi_{\frac{3}{2}}$ State[*]

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The $J=\frac{3}{2}\rightarrow\frac{5}{2}$ rotational transition of NO in the $^2\pi_{\frac{3}{2}}$ electronic state has been measured in the 1.17 mm wave region. Theory applied to these measurements combined with previous measurements on transitions of the ground $^2\pi_{\frac{1}{2}}$ state lead to the following values for the characteristic constants of $N^{14}O^{16}$: The rotational constant, $B_0=50\,848.42$ Mc/sec, and the spin orbit coupling constant $A=122.1$ cm^{-1}. The N^{14} nuclear magnetic couplings $a=83.82$ Mc/sec, $b=68.49$ Mc/sec, $c=-86.34$ Mc/sec, and the N^{14} nuclear quadrupole couplings $eQq_1=-2$ Mc/sec, $eQq_2=22$ Mc/sec. The Λ-doubling constants $p_\Lambda=175.15$ Mc/sec, $q_\Lambda=1.15$ Mc/sec.

INTRODUCTION

NITRIC oxide is a particularly interesting molecule for the spectroscopist. It is the only stable diatomic molecule which has an odd number of electrons and an electronic orbital momentum. Furthermore, it is unique in having an excited electronic state ($^2\pi_{\frac{3}{2}}$) so near (123 cm^{-1}) to the ground electronic state ($^2\pi_{\frac{1}{2}}$) that it is appreciably populated at room temperature. Despite the fact that it is only a diatomic molecule, its microwave spectrum is extremely complicated by the interaction of closely spaced electronic states, by the coupling of the molecular rotational and electronic moments, and by the two kinds of nuclear interactions —magnetic dipole and electric quadrupole. It thus provides a suitable model for testing theory for study of various coupling mechanisms between angular momentum vectors. Although it is the only stable molecule of its class, there are many unstable free radicals such as CH, OH, and SiH which have π electronic ground states and to which similar theory applies. So far as we know, rotational transitions have not been observed in such unstable free radicals although transitions between Λ doublets of OH in particular rotational states have been observed in the microwave region.[1]

Rotational transitions of NO in the ground $^2\pi_{\frac{1}{2}}$ state have been studied rather thoroughly in the microwave region, but until now it has not been possible to detect the weaker lines of the $^2\pi_{\frac{3}{2}}$ state, the lowest frequencies of which fall above 250 000 Mc/sec (1.2 mm). Microwave measurements of the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition of the $^2\pi_{\frac{1}{2}}$ state were made by Burrus and Gordy.[2] Later, more detailed studies, including measurements on the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ and $\frac{3}{2}\rightarrow\frac{5}{2}$ transitions in the $^2\pi_{\frac{1}{2}}$ state, were made by Gallagher and Johnson.[3] The Zeeman effect of the $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition has been studied by Mizushima, Cox, and Gordy[4] and the Stark effect by Burrus and Graybeal.[5] Before the detection of the rotational spectrum Beringer and Castle[6] observed the paramagnetic resonance of NO in the $^2\pi_{\frac{3}{2}}$ state.

EXPERIMENTAL METHODS

For generation and detection of the microwave power in the 1.17 mm wave region the harmonic generator and millimeter wave detector of the type developed earlier in this laboratory were employed.[7] In the harmonic generator a specially treated silicon crystal kindly supplied us by R. S. Ohl, of Bell Telephone Laboratories, was used. The absorption cell consisted of a three-meter-long section of coin silver *K*-band rectangular waveguide (inside dimensions: 0.420 in. × 0.170 in.). In the $^2\pi_{\frac{3}{2}}$ state NO is paramagnetic. Thus it was possible to increase the sensitivity of the spectrometer by a detecting system which depends on magnetic modulation of the absorption lines, such as was first employed[8] for detection of the fine structure of the millimeter wave spectrum of O_2. Magnetic modulation of several gauss at 400 cps was achieved through a solenoid placed around the wave-guide absorption cell. A phase-sensitive, lock-in amplifier controlled by the modulating voltage was used to detect the signal, which was then recorded with an Esterline-Angus pen-and-ink recorder. Figure 1 shows the six stronger components displayed in this way. After the lines were found on the recorder, it was possible to observe and measure the stronger components with a video-sweep spectrometer employing a cathode-ray scope. The frequencies were measured at the fundamental klystron driver frequency with a frequency standard monitored by Station WWV. The complete multiplet for the $J=\frac{3}{2}\rightarrow\frac{5}{2}$ transition consists of six doublets. It did not prove possible to measure the three weaker doublets, two of which are

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[1] Dousmanis, Sanders, and Townes, Phys. Rev. **100**, 1735 (1955).

[2] C. A. Burrus and W. Gordy, Phys. Rev. **92**, 1437 (1953).

[3] J. J. Gallagher and C. M. Johnson, Phys. Rev. **103**, 1727 (1956).

[4] Mizushima, Cox, and Gordy, Phys. Rev. **98**, 1034 (1955).

[5] C. A. Burrus and J. D. Graybeal, Phys. Rev. **109**, 1553 (1958).

[6] R. Beringer and J. G. Castle, Jr., Phys. Rev. **78**, 581 (1950).

[7] W. C. King and W. Gordy, Phys. Rev. **93**, 407 (1954).

[8] Burkhalter, Anderson, Smith, and Gordy, Phys. Rev. **77**, 152 (1950); **79**, 651 (1950).

only 12% and the third 0.5% of the strength of the strongest one.

THEORY EMPLOYED

The rotational spectrum of NO in the $^2\pi_{\frac{3}{2}}$ state differs in a number of ways from that in the $^2\pi_{\frac{1}{2}}$ state. For the $^2\pi_{\frac{1}{2}}$ state there is a $J=\frac{1}{2}\rightarrow\frac{3}{2}$ transition which falls in the 2-mm wave region. For the $^2\pi_{\frac{3}{2}}$ state the lowest value for J (which represents the sum of the electronic and the end-over-end rotational motion) is $\frac{3}{2}$, and the lowest rotational frequency corresponds to the $J=\frac{3}{2}\rightarrow\frac{5}{2}$ transition, which occurs at 1.17-mm wavelength, near the second rotational transition for the $^2\pi_{\frac{1}{2}}$ state. The Zeeman effect and the magnetic hyperfine structure are much more pronounced for the $^2\pi_{\frac{3}{2}}$ state because the electronic orbital and the spin magnetic moments add, to give a magnetic moment of 2 Bohr magnetons, whereas for the $^2\pi_{\frac{1}{2}}$ state they cancel, to make the molecule nonmagnetic except for small uncoupling effects. A third significant difference is that the Λ doubling of the rotational levels, caused by l uncoupling, is much smaller for the $^2\pi_{\frac{3}{2}}$ state. The $^2\pi_{\frac{3}{2}}$ state is much closer to Hund's case (a)—total electronic momentum strongly coupled to the internuclear axis—than is the $^2\pi_{\frac{1}{2}}$ state.

The interactions of the rotational and electronic motions of NO cause some admixing of the $^2\pi_{\frac{1}{2}}$ and $^2\pi_{\frac{3}{2}}$ states (spin uncoupling) and a displacement of the rotational levels. A slight admixing of $^2\pi$ and $^2\Sigma$ states (l uncoupling) breaks down the Λ degeneracy and leads to a doublet splitting of each rotational level (Λ doubling). These effects have been calculated by Hill and Van Vleck[9] and by Mulliken and Christy.[10] Effects of centrifugal distortion have been calculated by Almy and Horsfall.[11] Later refinements in the theory have been made by Dousmanis, Sanders, and Townes.[1] The theory of the nuclear magnetic hyperfine interactions for NO has been developed by Frosch and Foley[12] and reexamined by Dousmanis.[13] The theory for the nuclear quadrupole interactions has been developed by Mizushima[14] and corrected and extended by Lin and Mizushima.[15] The various terms in the theory of the NO spectrum are discussed briefly in the paper by Gallagher and Johnson.[3] The formulas applied here are essentially those used by Gallagher and Johnson with some modifications made from consideration of the theoretical papers mentioned.

Exclusive of hyperfine structure arising from nuclear interactions, the characteristic rotational energy of NO can be expressed as

$$E_{\text{rot.}}=E_0\pm\tfrac{1}{2}E_\Lambda. \qquad (1)$$

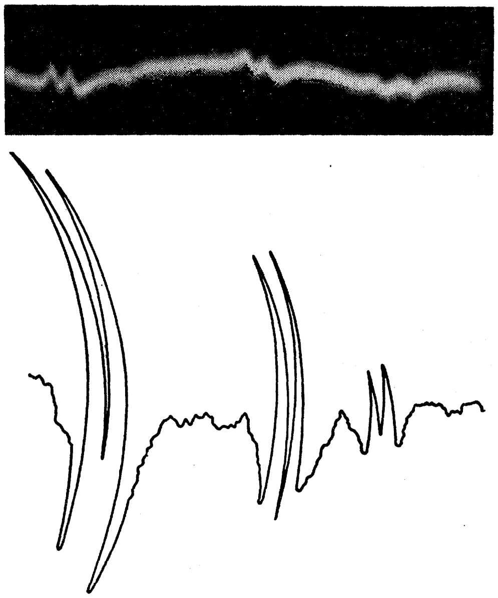

FIG. 1. Components in the $J=\frac{3}{2}\rightarrow\frac{5}{2}$ transition of $N^{14}O^{16}$ in the $^2\pi_{\frac{3}{2}}$ state. Upper figure is cathode-ray scope presentation, lower is tracing on Esterline-Angus recorder.

Here E_0 represents the rotational energy including displacement of the levels by spin uncoupling (effects of admixing of $^2\pi_{\frac{1}{2}}$ and $^2\pi_{\frac{3}{2}}$ states) but not the Λ-doubling (l-uncoupling effects), which is represented by E_Λ.

For the $^2\pi_{\frac{1}{2}}$ state

$$E_0=\left\{B_0-\frac{B_0-\beta}{\lambda-2}+\frac{2B_0+\alpha+\gamma}{(\lambda-2)^3}-\gamma+\frac{3}{2}D_0+\frac{\alpha B_0{}^s}{E}-\frac{\alpha B_0[1-1/(\lambda-2)]}{E}\right\}(J+\tfrac{1}{2})^2-\left\{D_0-\frac{B_0}{(\lambda-2)^3}\right\}(J+\tfrac{1}{2})^4,$$

and

$$E_\Lambda=-2p_\Lambda(J+\tfrac{1}{2})+\frac{4q_\Lambda}{\lambda-2}(J-\tfrac{1}{2})(J+\tfrac{1}{2})(J+\tfrac{3}{2})+\frac{2p_\Lambda}{(\lambda-2)^2}(J-\tfrac{1}{2})(J+\tfrac{1}{2})(J+\tfrac{3}{2})+\frac{p_\Lambda-2q_\Lambda}{2E}\left(\lambda B_0-\frac{B_0{}^s(p_\Lambda-2q_\Lambda)}{q_\Lambda}\right)(J+\tfrac{1}{2}).$$

For the $^2\pi_{\frac{3}{2}}$ state

$$E_0=\left\{B_0+\frac{B_0-\beta}{\lambda-2}-\frac{2B_0+\alpha+\gamma}{(\lambda-2)^3}-\gamma+\frac{1}{2}D_0\right\}(J+\tfrac{1}{2})^2-\left\{D_0+\frac{B_0}{(\lambda-2)^3}\right\}(J+\tfrac{1}{2})^4,$$

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[9] E. Hill and J. H. Van Vleck, Phys. Rev. 32, 250 (1928).
[10] R. S. Mulliken and A. Christy, Phys. Rev. 38, 87 (1931).
[11] G. M. Almy and R. B. Horsfall, Phys. Rev. 51, 491 (1937).
[12] R. A. Frosch and H. M. Foley, Phys. Rev. 88, 1337 (1952).
[13] G. C. Dousmanis, Phys. Rev. 97, 967 (1955).
[14] M. Mizushima, Phys. Rev. 94, 569 (1954).
[15] C. C. Lin and M. Mizushima, Phys. Rev. 100, 1726 (1955).

and

$$E_\Lambda = -\frac{4q_\Lambda}{\lambda-2}(J-\tfrac{1}{2})(J+\tfrac{1}{2})(J+\tfrac{3}{2}) - \frac{2p_\Lambda}{(\lambda-2)^2}(J-\tfrac{1}{2})(J+\tfrac{1}{2})(J+\tfrac{3}{2}) - \frac{(p_\Lambda-2q_\Lambda)\lambda B_0}{2E}(J+\tfrac{1}{2}).$$

In these expressions J is the quantum number for the total angular momentum exclusive of nuclear momentum, B_0 and D_0 are the usual spectral constants, $\lambda = A/B_0$ where A is the spin orbit coupling constant, p_Λ and q_Λ are λ-doubling constants and

$$\alpha = \sum \frac{|(\pi|AL_{x'}|\Sigma)|^2}{E},$$

$$\beta = \sum \frac{|(\pi|AL_{x'}|\Sigma)(\Sigma|BL_{x'}|\pi)|}{E},$$

$$\gamma = \sum \frac{|(\pi|BL_{x'}|\Sigma)|^2}{E},$$

E = energy difference between Σ and π states.

To the rotational energy expressed by Eq. (1) must be added the nuclear magnetic and electric quadrupole effects which can be expressed by

$$E_{\mathrm{hyp.}} = P(\mathbf{I}\cdot\mathbf{J} + R[\tfrac{3}{4}C(C+1-I(I+1)J(J+1)] \pm\tfrac{1}{2}P_\Lambda(\mathbf{I}\cdot\mathbf{J}) \pm\tfrac{1}{2}R_\Lambda[\tfrac{3}{4}C(C+1)-I(I+1)J(J+1)],$$

where

$$C = F(F+1)-J(J+1)-I(I+1).$$

For the $^2\pi_{\frac{1}{2}}$ state

$$P = \frac{a-\frac{1}{2}(b+c)}{2J(J+1)} + \frac{b(J-\frac{1}{2})(J+\frac{3}{2})}{(\lambda-2)J(J+1)} + \frac{(a+b+c)(J-\frac{1}{2})(J+\frac{3}{2})}{(\lambda-2)^2J(J+1)},$$

$$R = \frac{-eQq_1[1-6/(\lambda-2)^2]}{8I(2I-1)J(J+1)},$$

$$P_\Lambda = -\frac{d(J+\frac{1}{2})}{J(J+1)} + \frac{d(J-\frac{1}{2})(J+\frac{1}{2})(J+\frac{3}{2})}{(\lambda-2)^2J(J+1)},$$

$$R_\Lambda = +\frac{3eQq_2(J+\frac{1}{2})}{8(\lambda-2)I(2I-1)J(J+1)}.$$

For the $^2\pi_{\frac{3}{2}}$ state

$$P = \frac{3[a+\frac{1}{2}(b+c)]}{2J(J+1)} - \frac{b(J-\frac{1}{2})(J+\frac{3}{2})}{(\lambda-2)J(J+1)} - \frac{(a+b+c)(J-\frac{1}{2})(J+\frac{3}{2})}{(\lambda-2)^2J(J+1)},$$

$$R = \frac{3eQq_1}{I(2I-1)J(J+1)(2J-1)(2J+3)} - \frac{eQq_1[1-6/(\lambda-2)^2]}{8I(2I-1)J(J+1)},$$

$$P_\Lambda = -\frac{d(J-\frac{1}{2})(J+\frac{1}{2})(J+\frac{3}{2})}{(\lambda-2)^2J(J+1)},$$

$$R_\Lambda = -\frac{3eQq_2(J+\frac{1}{2})}{8(\lambda-2)I(2I-1)J(J+1)}.$$

In these expressions a, b, c, and d represent nuclear magnetic coupling constants defined by

$$a = 2g_I\mu_0\mu_n(1/r_1^3)_{\mathrm{Av}},$$

$$b = 2g_I\mu_0\mu_n\left[\frac{8\pi|\psi(0)|^2}{3} - \left(\frac{3\cos^2\chi-1}{2r_1^3}\right)_{\mathrm{Av}}\right],$$

$$c = 3g_I\mu_0\mu_n[(3\cos^2\chi-1)/r_1^3]_{\mathrm{Av}},$$

$$d = g_I\mu_0\mu_n[3\sin^2\chi/r_1^3]_{\mathrm{Av}},$$

where g_I is the g factor of N^{14}, μ_0 is the Bohr magneton, μ_n the nuclear magneton, r_1 is the distance of the interacting electron from the N^{14} nucleus, χ is the angle between r_1 and the bond axis and $|\psi(0)|^2$ is the electron-spin density at the N^{14} nucleus. The nuclear quadrupole constants are eQq_1 and eQq_2, where e is the electronic charge, Q is the quadrupole moment of the N^{14} nucleus, and

$$q_1 = \left\langle\frac{3\cos^2\chi-1}{r_1^3}\right\rangle_{\mathrm{Av}},$$

$$q_2 = 3\left\langle\frac{x_1^2-y_1^2}{r_1^5}\right\rangle_{\mathrm{Av}},$$

where the average is taken over all coupling electrons.

ANALYSIS OF DATA

Our procedure for analysis of data was as follows. Using the above formulas for the hyperfine structure, we sought to fit the hyperfine structure of the measured rotational transitions of $N^{14}O^{16}$ in both the $^2\pi_{\frac{3}{2}}$ and $^2\pi_{\frac{1}{2}}$ states. By choosing the mean value of each Λ doublet as the hypothetical frequency unperturbed by l uncoupling, we avoided at this time any consideration of Λ doubling. We allowed for changes of the various hyperfine constants, but in such a way that the combinations of constants in the $^2\pi_{\frac{1}{2}}$ formulas retain the values they have in the work of Gallagher and Johnson.[3] For this reason the formula agrees well with the observed transitions of the $^2\pi_{\frac{1}{2}}$ state. From this procedure we obtained new values for the hyperfine constants and calculated the various hyperfine levels. This then allowed us to calculate the hypothetical rotational

TABLE I. Molecular constants for nitric oxide.[a]

	Present work	Gallagher and Johnson[b]	
B_{eff}	51 571.61 (for $\pi\frac{3}{2}$)	51 553.91 (for $\pi\frac{3}{2}$)	
D_{eff}	...	0.319 (for $\pi\frac{3}{2}$)	
B_0	50 848.42	50 838.56	
D_0	...	0.177	
r_0	1.153_8 A	1.153_9 A	
A	122.1_4 cm^{-1}		123.8[c] cm^{-1}
a	83.82	83.40	
b	68.49	68.91	
c	−86.34	−87.60	
$a+\frac{1}{2}(b+c)$	74.89_5		74.05[d]
eQq_1	−2	−1.75	
eQq_2	22	9.3	
q_Λ	1.15	1.15	
p_Λ	175.15	175.15	
$a-\frac{1}{2}(b+c)$	...	92.74_5	
d	...	112.60	
α	...	+3217	
β	...	+176.15	
γ	...	+1.15	

[a] Calculated by using the following constants $E=43\,966.0$ cm^{-1}, $B_0{}^s=1.987$ cm^{-1} [G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950) p. 558]. Units are in Mc/sec unless otherwise stated.

[b] See reference 3.

[c] H. Margenau and A. Henry, Phys. Rev. **78**, 587 (1950).

[d] From Beringer, Rawson, and Henry, Phys. Rev. **94**, 343 (1954).

frequency, unperturbed by nuclear interaction and l-uncoupling.

Next, we used a combination of the $^2\pi_{\frac{1}{2}}$ and $^2\pi_{\frac{3}{2}}$ formulas for E_0, given above, for calculating new values of B_0 and A. In this calculation we used the same values of α, β, γ, and D_0 as those obtained by Gallagher and Johnson. With the new values for B_0 and A we calculated the Λ-doubling terms and the nuclear coupling constants. We could not improve on the values of p_Λ and q_Λ obtained by Gallagher and Johnson. However, the nuclear quadrupole coupling constant eQq_2 obtained agrees better with that from the analysis by Lin and Mizushima[15] than does that of Gallagher and Johnson. The value for eQq_2 given by Lin and Mizushima, 22 Mc/sec, which we concur with, is more than double that given by Gallagher and Johnson, 9.3 Mc/sec. As Lin and Mizushima pointed out, q_2 can be calculated more accurately than can q_1, and hence eQq_2 gives a means of obtaining a better value for the nuclear quadrupole moment, Q, of N^{14}.

The various constants which we obtained are given in Table I, with those of Gallagher and Johnson listed for comparison. In Table II are given comparisons of the observed frequencies with those calculated from the constants given in Table I.

TABLE II. Microwave spectrum of nitric oxide $^2\pi_{\frac{3}{2}}$ state.

Transition	Measured frequency (Mc/sec)	Calculated frequency (Mc/sec)	Calculated frequency intensity
π^+ band			
$F=\frac{5}{2}\rightarrow\frac{7}{2}$	257 822.06±0.3	257 822.05	100
$F=\frac{3}{2}\rightarrow\frac{5}{2}$	257 852.87	257 852.99	63
$F=\frac{1}{2}\rightarrow\frac{3}{2}$	257 867.67	257 867.62	37.5
$F=\frac{5}{2}\rightarrow\frac{5}{2}$	...	257 780.80	12
$F=\frac{3}{2}\rightarrow\frac{3}{2}$	...	257 822.64	12
$F=\frac{5}{2}\rightarrow\frac{3}{2}$	...	257 750.50	0.5
π^- band			
$F=\frac{5}{2}\rightarrow\frac{7}{2}$	257 825.02±0.3	257 825.00	100
$F=\frac{3}{2}\rightarrow\frac{5}{2}$	257 855.36	257 855.30	63
$F=\frac{1}{2}\rightarrow\frac{3}{2}$	257 870.35	257 870.27	37.5
$F=\frac{5}{2}\rightarrow\frac{5}{2}$	...	257 782.65	12
$F=\frac{3}{2}\rightarrow\frac{3}{2}$	...	257 826.08	12
$F=\frac{5}{2}\rightarrow\frac{3}{2}$	...	257 753.40	0.5

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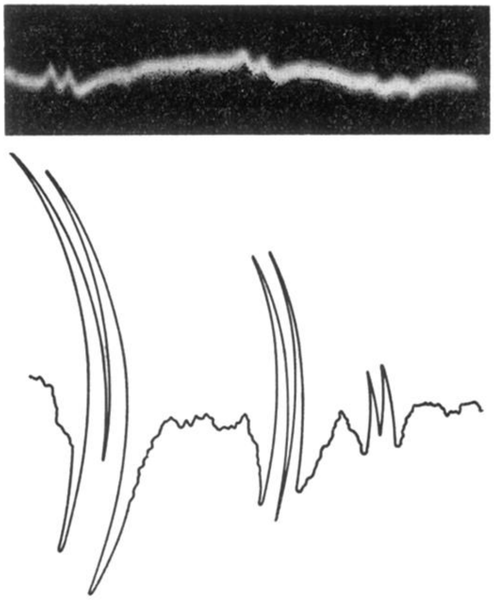

FIG. 1. Components in the $J=\frac{3}{2}\rightarrow\frac{5}{2}$ transition of $N^{14}O^{16}$ in the $^2\pi_{\frac{3}{2}}$ state. Upper figure is cathode-ray scope presentation, lower is tracing on Esterline-Angus recorder.