

Lifetime Determination of the NO $A^2\Sigma^+$ State*

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A coincidence of the Te I emission line at 2147.25 Å with the $Q_1(21/2)$ and the $Q_{P_{21}}(21/2)$ absorption lines of the (1, 0) band of the NO γ system is used to perform a Hanle-effect measurement on the $v'=1$, $N'=10$ level of the NO $A^2\Sigma^+$ state. A linear least squares fit to the pressure-broadened data yields an intercept of 3.37 ± 0.36 G for the zero-pressure linewidth and a slope of 12.7 ± 2.4 mG/mtorr. By measuring the zero-field polarization of the resolved fluorescence lines, the ratio of the hyperfine splitting to the rotational spin splitting is estimated to be less than or equal to 1:5, and the angular momentum coupling scheme is found to conform closely to Hund's case ($b_{\beta J}$). An optical radio-frequency double resonance study provides further confirmation. Using g values appropriate to Hund's case ($b_{\beta J}$), the radiative lifetime is determined to be 178 ± 19 nsec. These results are in excellent agreement with the previous Hanle-effect measurements by German, Zare, and Crosley on the $v'=1$, $N'=13$ level.

I. INTRODUCTION

Within the last decade, advances in electronic instrumentation have permitted direct lifetime measurements to be carried out on a number of diatomic molecules. However, since the accuracy of these measurements seldom approaches their precision, it is difficult to evaluate the extent to which they are free from large systematic errors. The lifetime measurements of the nitric oxide γ bands are a case in point. Table I summarizes all previous direct lifetime measurements of the $A^2\Sigma^+$ state of NO. Unfortunately, even results published within the past year differ by almost a factor of two, well outside their error estimates.

The Hanle effect, traditionally used to measure the radiative lifetime of atoms,¹ has the advantage of being relatively free from major systematic errors. Although the measurements must be extrapolated to zero pressure, it is not necessary to know the absolute number density. A disadvantage of this technique is that the Hanle effect does not measure the lifetime τ directly, but rather the product $g\tau$ where g is the Landé factor of the excited state.

For atoms, g values can often be calculated from a limited knowledge of the atomic excited state. When this is so, Hanle-effect measurements can provide a determination of the atomic radiative lifetime to an accuracy of better than 10%. For molecules, on the other hand, g values can seldom be accurately calculated because the excited state may satisfy various angular momentum coupling schemes. For example, in the $A^2\Sigma^+$ state of NO, the rotational angular momentum \mathbf{N} , the electron spin \mathbf{S} , and the nuclear spin \mathbf{I} may couple in two different ways depending on the relative strength of the spin rotation ($\mathbf{N} \cdot \mathbf{S}$) and the hyperfine ($\mathbf{I} \cdot \mathbf{S}$) interactions.² In Hund's case ($b_{\beta J}$), \mathbf{N} , and \mathbf{S} form the resultant \mathbf{J} , which couples to \mathbf{I} to form the total angular momentum \mathbf{F} ; in Hund's case ($b_{\beta S}$), \mathbf{I} and \mathbf{S} form the resultant \mathbf{G} , which couples to \mathbf{N} to form the total angular momentum \mathbf{F} . In general,

for a fixed value of \mathbf{N} and \mathbf{F} , the g value calculated from Hund's case ($b_{\beta J}$) is quite different from that calculated from Hund's case ($b_{\beta S}$).

Recently, German, Zare, and Crosley³ (GZC), using a coincidence with the Cd II 2144-Å line, reported a measurement of $g\tau$ for the $v'=1$, $N'=13$ level of the NO $A^2\Sigma^+$ state. They offered arguments in support of case ($b_{\beta J}$) coupling, and using a g value calculated with that scheme, they obtained a lifetime in fair agreement with the previous direct measurement of Jeunehomme⁴ (see Table I).

Since then, Poland and Broida⁵ have studied the fluorescence from the $v'=1$, $N'=13$ level of the NO $A^2\Sigma^+$ state with the same atomic line coincidence. They measured the polarization of the rotationally resolved fluorescence from the (1, 5) band, and they found the degree of polarization had the same sign as predicted by theoretical calculations⁶ but was smaller in magnitude. This disagreement might be evidence that the $A^2\Sigma^+$ state does not follow Hund's case ($b_{\beta J}$) coupling, and hence, that the lifetime determination of GZC is in error.

In order to test the lifetime determined by GZC, we have (1) carried out a Hanle-effect study of the $v'=1$, $N'=10$ level using the 2147.25-Å Te I line as an excitation source, (2) made measurements of the degree of polarization on the rotationally resolved fluorescence from the $v'=1$, $N'=10$ level, and (3) repeated Poland and Broida's polarization measurements on the $v'=1$, $N'=13$ level. We find that for both the $v'=1$, $N'=10$ and $v'=1$, $N'=13$ levels, our polarization measurements verify case ($b_{\beta J}$) coupling. With g values calculated from case ($b_{\beta J}$), our determination of $(g\tau)_{N=10}$ yields a lifetime in excellent agreement with the previous determination of GZC.

In addition, we observe an optical radio-frequency double resonance (ORFDOR) signal. In our experiment we could not resolve the hyperfine components of the ORFDOR signal. However, its average g value is 0.11 ± 0.02 , in good agreement with the mean of the

TABLE I. Radiative lifetime determinations of the $A^2\Sigma^+$ state of NO.

Molecular level	Investigator (year)	Method (excitation source)	Lifetime (nsec)
$v'=0$, many N'	Jeunehomme and Duncan ^a (1964)	Fluorescence decay (pulsed discharge)	449±54
$v'=1$, many N'			410±55
$v'=2$, many N'			448±33
$v'=0$, many N'	Jeunehomme ^d (1966)	Fluorescence decay (pulsed white light)	196.5±3
$v'=0$, many N'	Fink and Welge ^b (1968)	Phase-shift (modulated electron beam)	425±50
$v'=1$, many N'			400±20
$v'=0$, many N'	Hesser ^c (1968)	Phase-shift (modulated electron beam)	215±30
$v'=0$, many N'	Copeland ^d (1970)	Delayed coincidence (pulsed discharge)	108±6
$v'=1$, many N'			106±7
$v'=2$, many N'			95±8
$v'=1$, 1, many N'	Bubert and Froben ^e (1971)	Fluorescence decay (pulsed electron beam)	215±22
$v'=1$, $N'=13$	German, Zare, and Crosley ³ (1971)	Hanle effect (atomic line)	181±22
$v'=1$, $N'=10$	This work	Hanle effect (atomic line)	178±19

^a M. Jeunehomme and A. B. F. Duncan, *J. Chem. Phys.* **41**, 1692 (1964).

^b E. H. Fink and K. H. Welge, *Zeit. Naturforsch.* **239**, 358 (1968).

^c J. E. Hesser, *J. Chem. Phys.* **48**, 2518 (1968).

^d G. E. Copeland, R. T. Thompson, and R. G. Fowler, *Bull. Am. Phys. Soc.* **15**, 429 (1970); G. E. Copeland, *J. Chem. Phys.* **56**, 689 (1972).

^e H. Bubert and F. W. Froben, *Chem. Phys. Letters* **8**, 242 (1971).

hyperfine g values calculated for $N'=10$ from Hund's case ($b_{\beta J}$).

Based on our Hanle-effect measurement and on the verification of Hund's case ($b_{\beta J}$) coupling from the polarization and ORFDOR measurements, we conclude that the $v'=1$, $N'=10$ level of the NO $A^2\Sigma^+$ state has a lifetime of 178 ± 19 nsec.

II. EXPERIMENTAL

A. Hanle Effect and Double Resonance Measurements

Molecular Hanle-effect studies have previously been carried out using various sources of excitation, including white light, lasers, molecular lamps, and atomic lines.⁷ The last alternative, when feasible, often has an advantage of populating a single vibrational-rotational level. However, the occurrence of coincidences of atomic emission lines with molecular absorption lines has not been extensively investigated.⁸ Recently, one of us made a systematic study of atomic line coincidences with the NO γ bands.⁹ In the course of that investigation, the Te I 2147.25-Å line¹⁰ was found to populate only the $v'=1$, $N'=10$ level of the NO $A^2\Sigma^+$ state.

The experimental apparatus for measuring the Hanle effect has been described previously by GZC. The Te lamp excitation source is an electrodeless microwave discharge. The cylindrical quartz lamp (9 mm o.d., 40 mm long) is operated in a hot air stream at a temperature of about 350°C. Tellurium lamps are prepared by distilling tellurium metal into lamp blanks under vacuum. The tellurium lamp is more stable if the quartz tubing is cleaned by the following procedure.

The quartz tubing is first washed in dilute HF and then attached to a vacuum manifold. After being heated red hot with a hand torch, the lamp blank is filled with argon at a few torr pressure, and a microwave discharge is struck. During this stage, the tellurium metal is distilled throughout the discharge region with the needed additional heat supplied by a hand torch. A few flushings with argon are necessary. After this cleaning procedure, the blank is pumped out and refilled with argon at a final pressure of a few torr and tipped off.

The Te I line overlaps the unresolved $Q_1(21/2)$ and $Q_{P_{21}}(21/2)$ lines, as shown in Fig. 1. The resulting fluorescence spectrum of the (1, 5) band is shown in Fig. 2. Figure 2 also gives the sign of the degree of polarization for each of the eight resolved lines. The $Q_1+Q_{P_{21}}$ line, in addition to being the most intense, also gives the strongest Hanle signal. Consequently, for the Hanle studies we isolate this line with a $\frac{1}{2}$ -M Jarrel-Ash spectrometer used in second-order. This excludes mercury resonance fluorescence which cannot otherwise be removed (see GZC).

In the Hanle studies, the NO is contained in a 4 in. pyrex cross having four $1\frac{1}{2}$ in. diameter quartz windows attached by Torrseal epoxy to its ends. The NO is admitted to the cell through a stopcock and fill tube attached to the main body. All NO pressure measurements are made by means of a McLeod gauge.

With the following exceptions, the apparatus used in the double resonance experiment is the same as that used by German and Zare¹¹ in their studies of the hydroxyl radical. Polacoat UV-105 polarizers, specially

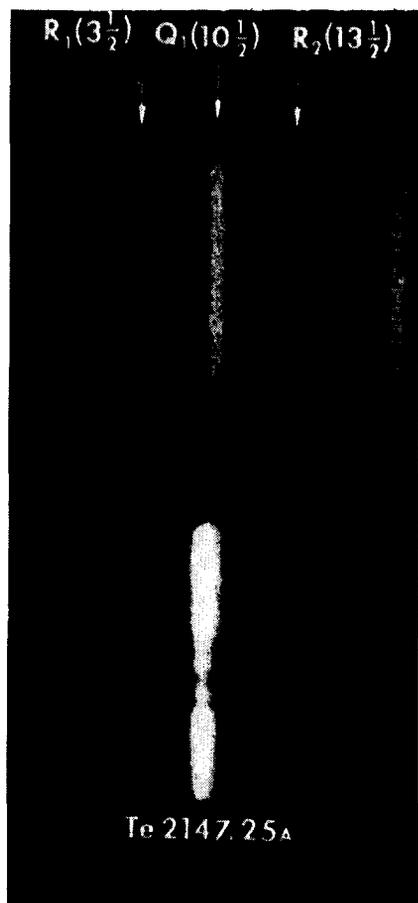


FIG. 1. Coincidence of the Te I 2147.25-Å line with the $Q_1(10\frac{1}{2})$ line of the (1, 0) NO γ band. An enlargement of a high resolution plate is shown. The Te I line and the (1, 0) band were photographed in emission. A slit mask is used to separate the exposures; the plate was not moved during the exposures. Careful measurement of this plate indicates that the line centers are separated by 0.2 cm^{-1} .

selected for high transmission, are used to provide π -polarized light for excitation and detection. A standard right angle geometry is employed. In order to reduce the reflected light, the NO cell used in the Hanle studies was altered so that (1) the exit window in the excitation direction was at approximately Brewster's angle for 2650-Å light; (2) this exit window was

moved back about 4 in. from the center of the cell; and (3) the inside of the cell was coated with a colloidal graphite suspension in ethanol (Aquadag). Because of the reduction in reflected light, a Corning 7-54 filter is used as a rejection filter in front of the photomultiplier, in place of the narrow-band interference filter. The rf power is coupled into the NO cell using ten 2 in. diameter turns of $\frac{1}{8}$ in. o.d. copper tubing. It is estimated that this configuration provides a few rf Gauss at 1–5 MHz. For higher rf frequencies impedance matching requires that the number of turns in the coil be reduced.

B. Polarization Measurements

The NO fluorescence is characterized by its degree of polarization P , customarily defined as

$$P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp}), \quad (1)$$

where the fluorescent intensity is viewed at right angles to the direction of excitation. In Eq. (1), I_{\parallel} and I_{\perp} are the intensities polarized parallel and perpendicular to the polarization vector of the excitation beam. In our experiment it is convenient to use an unpolarized light beam as the excitation source because the transmission of linear polarizers decreases sharply below 2500 Å. The observed degree of polarization using natural (unpolarized) light, P_n , is defined as

$$P_n = (I_{\parallel}^n - I_{\perp}^n) / (I_{\parallel}^n + I_{\perp}^n), \quad (2)$$

where I_{\parallel}^n and I_{\perp}^n are the intensity components polarized parallel and perpendicular to an axis perpendicular to the plane containing the excitation and observation directions. Accordingly, P_n and P are related by¹²

$$P_n = P / (2 - P). \quad (3)$$

The NO fluorescence, viewed at right angles to the excitation beam, is rotationally resolved by a $\frac{3}{4}$ -M SPEX spectrometer operated in second order (1–2 Å resolution). Quartz lenses are used to focus the excitation light on the center of the cell and to focus the fluorescence on the entrance slit of the spectrometer. In order to approach closely the right angle geometry required for these measurements, the excitation beam is carefully collimated. For Te excitation, a cylindrical

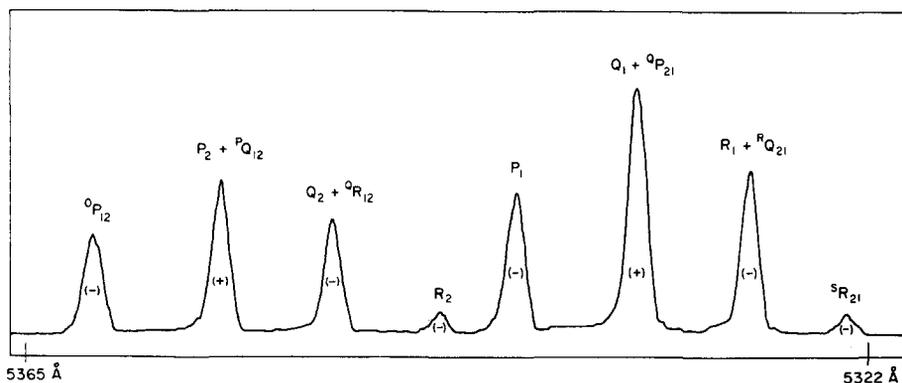


FIG. 2. Fluorescence spectrum (second-order) of the (1, 5) band of the NO γ system. The signs in parentheses indicate whether the sign of the degree of polarization is positive or negative.

quartz cell is employed with the excitation along the cylinder axis. In this setup, no interference from reflected light was observed. However, for Cd excitation, the cell modified for the double resonance study had to be used. The polarization of each light source was measured and found to be unpolarized within the errors of measurement.

A Polacoat UV-105 polarizer is employed to measure the degree of polarization. At 2650 Å, it transmits 32% of I_{\parallel} and 2% of I_{\perp} . A correction factor is applied to take account of this leakage. A quartz scrambler¹³ is placed 2 in. in front of the spectrometer entrance slit and removes the effects of grating polarization. In order to reduce collisional depolarization and rotational energy transfer, the NO pressure must be minimized. For $N'=10$ fluorescence, a pressure of 50 mtorr of NO provides sufficient signal-to-noise; for the $N'=13$ fluorescence, a 100 mtorr of NO is required. Because the Hanle linewidth is large compared to the earth's magnetic field (see Sec. III), it is not necessary to perform these polarization measurements under field-free conditions.

The spectrometer is centered on each of the resolved fluorescent lines, and I_{\parallel} and I_{\perp} are alternately measured by rotating the position of the polarizer. Each measurement is made over a period of 2-3 min and is checked for reproducibility.

III. RESULTS AND DISCUSSION

A. Determination of $(g\tau)_{N=10}$

The lineshapes of the Hanle signals are fit by a non-linear least squares program to Eqs. (1) and (2) of GZC. In the absence of pressure broadening, the linewidth Γ , defined as the half-width at half-maximum for a Lorentzian signal, is related to the lifetime τ and the magnetic moment $g\mu_0$ by

$$\Gamma = \hbar/2\mu_0 g\tau. \quad (4)$$

From a simple pressure broadening model, an effective coherence time T is defined by

$$T^{-1} = \tau^{-1} + Rn, \quad (5)$$

where n is the number density and R is the bimolecular rate constant for the destruction of alignment. Figure 3 is a plot of the Hanle linewidth as a function of NO pressure. A linear least squares fit to this data yields an intercept $\Gamma = 3.37 \pm 0.36$ G and a slope of 12.7 ± 2.4 mG/mtorr. The quoted errors are three standard deviations.

As an initial check on the validity of these results, a comparison can be made to the previously determined value $\Gamma = 4.25 \pm 0.45$ G for the $v'=1$, $N'=13$ levels of the NO $A^2\Sigma^+$ state. Since the lifetimes of the $v'=10$ and $N'=13$ levels are expected to be identical, the linewidths of the two Hanle signals should be inversely proportional to their g values. The ratio of the linewidths is found to be $\Gamma_{13}/\Gamma_{10} = 1.26$. Table II lists the

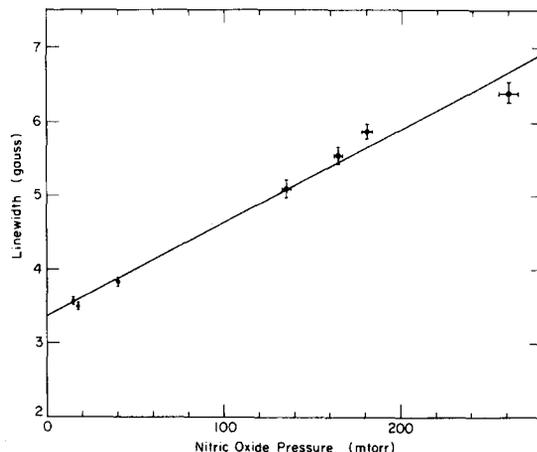


FIG. 3. The Hanle linewidth as a function of NO pressure.

g values for the $N'=10$ and $N'=13$ levels calculated using Hund's case (b), case ($b_{\beta J}$), and case ($b_{\beta S}$). In Table II, the ratio of the linewidths agrees with the value of g_{10}/g_{13} , regardless of the coupling scheme chosen. Therefore this test merely serves to establish the consistency of the two Hanle measurements and does not indicate which coupling scheme is appropriate.

B. ORFDOR Measurement of the g Value

The most obvious way to extract the lifetime from the Hanle linewidth is to determine the g values directly. Accordingly, we have carried out an optical radio-frequency double resonance study of the $v'=1$, $N'=10$ level excited by the Ter line. The ORFDOR signal obtained at 3 MHz is shown in Fig. 4. The observed signal is very broad, with a width of about 20 G. The center of the signal yields a rough g value of 0.11 ± 0.02 . This measurement gives only the magnitude of the g value and not its sign.

In the $N'=10$ level, there are six hyperfine levels with F values ranging from 8.5 to 11.5. For Hund's case ($b_{\beta J}$) we calculate that these g values cluster about ± 0.094 and differ from one another by at most 20%, as shown in Table II. However, for Hund's case ($b_{\beta S}$), there is a much wider spread in the g values, and their magnitude is in general less than in case ($b_{\beta J}$). The excellent agreement of the experimentally determined average g value with the mean of the g values calculated from Hund's case ($b_{\beta J}$) strongly suggests that the angular momentum coupling scheme is close to case ($b_{\beta J}$).

Because of the breadth of the double resonance signal, it is not possible to resolve the ORFDOR signals of the hyperfine components. An attempt to observe ORFDOR signals at higher rf frequencies where they might be resolved was unsuccessful.

Hund's case ($b_{\beta J}$) and case ($b_{\beta S}$) are idealized limiting forms of the angular momentum coupling in the molecular excited state, and the actual coupling scheme is expected to be intermediate between these extremes. Whether the nuclear spin I couples more strongly to

TABLE II. g Values^a in the $A^2\Sigma^+$ state of NO.

A. $N'=10$				B. $N'=13$			
Hund's case	$J(b_{\beta J})$ $G(b_{\beta S})$	F	g value	Hund's case	$J(b_{\beta J})$ $G(b_{\beta S})$	F	g value
b			± 0.095	b			± 0.074
$b_{\beta J}$	10.5	11.5	+0.087	$b_{\beta J}$	13.5	14.5	+0.069
	10.5	10.5	+0.094		13.5	13.5	+0.074
	10.5	9.5	+0.104		13.5	12.5	+0.080
	9.5	10.5	-0.089		12.5	13.5	-0.069
	9.5	9.5	-0.094		12.5	12.5	-0.074
	9.5	8.5	-0.105		12.5	11.5	-0.080
$b_{\beta S}$	1.5	11.5	+0.086	$b_{\beta S}$	1.5	14.5	+0.069
	1.5	10.5	+0.040		1.5	13.5	+0.030
	1.5	9.5	-0.021		1.5	12.5	-0.019
	1.5	8.5	-0.105		1.5	11.5	-0.080
	0.5	10.5	-0.031		0.5	13.5	-0.025
	0.5	9.5	+0.031		0.5	12.5	+0.025

^a For case (b) coupling ($I=0$),

$$g_J = \pm g_s \{ [J(J+1) + S(S+1) - N(N+1)] / 2J(J+1) \} = \pm (N + \frac{1}{2})^{-1};$$

for case $b_{\beta J}$ coupling,

$$g_F = g_J \{ [F(F+1) + J(J+1) - I(I+1)] / 2F(F+1) \};$$

and for case $b_{\beta S}$ coupling,

$$g_F = \pm g_s \{ [G(G+1) + S(S+1) - N(N+1)] / 2G(G+1) \}$$

$$\times \{ [F(F+1) + G(G+1) - N(N+1)] / 2F(F+1) \}$$

where g_s is the g value of the free electron, taken here to be 2.

J or more strongly to S depends on the ratio of the spin-rotation splitting, $\gamma \mathbf{N} \cdot \mathbf{S}$, to the hyperfine splitting, approximately $b \mathbf{I} \cdot \mathbf{S}$. Normally in $^2\Sigma$ states, the rho-type doubling constant γ is much larger than the hyperfine parameters, here represented by b , and the coupling scheme is well characterized by Hund's case ($b_{\beta J}$).² However, the $A^2\Sigma^+$ state of NO is a σns molecular Rydberg state.¹⁴ Because the outermost electron is well removed from the molecular core, splittings caused by spin-rotation or hyperfine interactions are expected to be small. Indeed, the rho-type doubling constant has eluded detection by optical means until recently. In 1970 Engleman and Rouse¹⁵ photographed in absorption the NO γ bands at high resolution following the flash photolysis of nitrosyl chloride. For the (1, 6), (1, 7), and (1, 8) bands, they found γ to be -1.3×10^{-3} , -0.9×10^{-3} , and -2.1×10^{-3} cm⁻¹. The average value for γ based on all these bands is about -1.5×10^{-3} cm⁻¹ = -45 MHz, but Engleman and Rouse state that " γ has very large errors attached to it, and no significance can be given to the computed values." Although the single ORFDOR measurement shows the coupling scheme is close to case ($b_{\beta J}$), it does not establish the ratio of the spin-rotation splitting, $\gamma(N' + \frac{1}{2})$, to the hyperfine splitting, b , for the $v'=1$, $N'=10$ state.

C. Polarization Measurements

An alternative procedure for determining the intermediate coupling scheme of $v'=1$, $N'=10$ level is to measure the degree of polarization of the rotationally

resolved fluorescence lines. The fluorescence intensity I^{af} for absorption of plane polarized light ϵ_a and re-emission of plane polarized light ϵ_f is proportional to

$$\sum_{JF M_F} \sum_{J'F' M_{F'}} | \langle N I J F M_F | \mu_a | N' I' J' F' M_{F'} \rangle \times \langle N' I' J' F' M_{F'} | \mu_f | N'' I'' J'' F'' M_{F''} \rangle |^2, \quad (6)$$

where the wavefunctions are expressed in terms of case ($b_{\beta J}$) quantum numbers, and μ is the dipole moment operator. From these expressions, the degree of polarization for pure case ($b_{\beta J}$) coupling is readily calculated by summing over all possible absorption and fluorescence routes which contribute to the intensity of a resolved fluorescent line. We also assume that the spectral profile of the lamp is flat over all the absorption paths. This last assumption may not be satisfied

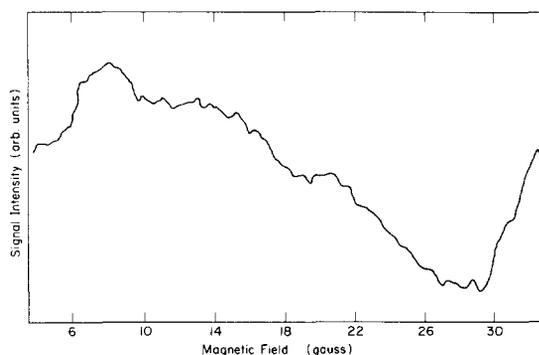


FIG. 4. Double resonance signal at 3 MHz.

TABLE III. Measured and calculated values of the degree of polarization P_n of the fluorescence in the NO γ (1, 5) band. In the calculations, the value of γ is estimated from optical work to be -45 MHz.

Fluorescence from the $v'=1, N'=10$ level						
	R_1+RQ_{21}	Q_1+QP_{21}	P_1	Q_2+QR_{12}	P_2+PQ_{12}	OP_{12}
Measured	$-13.3\pm 2\%$	$+30.5\pm 2\%$	$-12.0\pm 2\%$	$-12.1\pm 2\%$	$+25.4\pm 2\%$	$-10.8\pm 2\%$
Calculated						
$b=0$ MHz	-14.8%	$+30.0\%$	-12.1%	-13.7%	$+25.8\%$	-12.1%
25	-14.4	$+29.7$	-12.1	-13.6	$+25.8$	-12.1
50	-13.9	$+29.4$	-12.0	-13.1	$+25.6$	-12.0
75	-13.3	$+28.9$	-11.9	-12.4	$+25.3$	-11.9
100	-12.6	$+28.5$	-11.8	-11.5	$+24.8$	-11.8
125	-11.8	$+27.0$	-11.8	-10.5	$+24.3$	-11.8
200	-9.4	$+26.4$	-11.4	-6.9	$+22.2$	-11.4
400	-5.1	$+23.6$	-16.8	0.0	$+17.9$	-10.8
Fluorescence from the $v'=1, N'=13$ level						
	R_1+RQ_{21}	Q_1+QP_{21}	P_1+R_2	Q_2+QR_{12}	P_2+PQ_{12}	
Measured	$+21.0\pm 2\%$	$-13.7\pm 2\%$	$-7.0\pm 3\%$	$+27.0\pm 2\%$	$-13.2\pm 2\%$	
Calculated						
$b=0$ MHz	$+20.7\%$	-14.7%	-8.2%	$+28.1\%$	-13.9%	
25	$+20.4$	-14.7	-8.2	$+28.0$	-13.8	
50	$+20.0$	-14.4	-8.2	$+27.7$	-13.7	
75	$+19.6$	-14.1	-8.2	$+27.4$	-13.6	
100	$+19.1$	-13.6	-8.2	$+27.0$	-13.4	
125	$+18.5$	-13.2	-8.3	$+26.5$	-13.1	
150	$+18.0$	-12.6	-8.3	$+25.9$	-12.8	
175	$+17.3$	-12.1	-8.3	$+25.3$	-12.4	
200	$+16.7$	-11.6	-8.3	$+24.6$	-12.1	

in these experiments, but the polarizations are rather insensitive to the details of the absorption profile. In intermediate coupling, the excited state wavefunction may be expressed as a linear combination of case ($b_{\beta J}$) wavefunctions

$$\psi_{\text{int}}(F'M_F') = \sum_{J'} a_{J'} |N'IJ'F'M_F'\rangle, \quad (7)$$

where the $a_{J'}$ are the elements of a unitary matrix that diagonalizes the ${}^2\Sigma^+$ Hamiltonian.

A computer program¹⁶ has been written to calculate the degree of polarization for arbitrary values of γ and b . In Table III we present the measured and calculated values of P_n for the (1, 5) band of the NO fluorescence spectrum, assuming a value of $\gamma = -45$ MHz. Inspection of Table III shows that P_n changes slowly with b for $b \leq 100$ MHz. At $b = 100$ MHz, the hyperfine splitting is only one-fifth of the spin-rotation splitting, $\gamma(N'+\frac{1}{2})$. The experimentally determined values of P_n for both $v'=1, N'=10$ and $v'=1, N'=13$ are fit satisfactorily with $b \leq 100$ MHz. Thus we conclude from these polarization measurements that the excited state coupling scheme for the $v'=1, N'=10$ and $v'=1, N'=13$ levels is excellently approximated by Hund's case ($b_{\beta J}$).

Subsequent to this study, Bergeman and Zare¹⁷ reported a zero-field optical double resonance determination of the fine and hyperfine structure parameters in the $v'=3, N'=1$ level which used a coincidence of the 1961-Å selenium line.⁹ For this level $\gamma = -82.7 \pm 1.0$ MHz and $b = 39.2 \pm 1.5$ MHz. If these parameters are assumed to be independent of vibrational level, the ratio of the hyperfine to the spin-rotation splitting in the $v'=1, N'=10$ level is less than $\frac{1}{20}$. This suggests that case ($b_{\beta J}$) coupling is even a better approximation than our polarization measurements indicate.

D. Radiative Lifetime

With Hund's case ($b_{\beta J}$) established, we can extract the radiative lifetime of the $v'=1, N'=10$ level from the Hanle linewidth using the case ($b_{\beta J}$) g values given in Table II. In principle, the Hanle signal for the $v'=1, N'=10$ level is a superposition of six Lorentzians, each having a linewidth inversely proportional to its hyperfine g value. However, the population of the $J'=10.5$ spin component is found by relative intensity measurements (see Fig. 2) to be about six times greater than that of the $J'=9.5$ spin component. Thus the contribution from the three hyperfine levels associated with

$J'=9.5$ can be neglected in the analysis. Note that, in any case, the g values of these hyperfine components are roughly the same as the g values of the three hyperfine components of the $J'=10.5$ level. Since the g values are within 20% of one another, it may be assumed that the resultant Hanle signal can be treated as a single Lorentzian having a linewidth inversely proportional to an effective average g value, given by the mean of the three case ($b_{\beta J}$) g values. This treatment further assumes that the g values are equally weighted because the spectral profile of the Te line is flat across the excited state hyperfine splittings, an approximation which seems entirely reasonable considering the small hyperfine splitting. A more refined treatment has been attempted in which the average effective g value was calculated (1) by computing the g values using intermediate coupling for the smallest ratio of γ to b which still satisfies the polarization measurements, and (2) by weighting each g value by its Hanle-effect contribution. However, the average effective g value obtained in this manner differs by less than 3% from the average case ($b_{\beta J}$) g value of 0.095.

With this g value we determine the radiative lifetime of the $v'=1$, $N'=10$ level of the NO $A^2\Sigma^+$ state to be 178 ± 19 nsec, in embarrassingly good agreement with the previous Hanle determination of GZC of 181 ± 22 nsec for the $v'=1$, $N'=13$ level. In both cases, the quoted errors reflect only the statistical uncertainty (three standard deviations) in the determination of the Hanle linewidth. We are unable to account for the discrepancy with the lifetime values obtained by Fink and Welge or by Copeland (see Table I).

E. Destruction of Alignment

The slope of the Hanle pressure broadening plot shown in Fig. 3, along with the determined radiative lifetime, may be used to calculate the rate for the destruction of alignment. For the $v'=1$, $N'=10$ level we find that $R=(6.54\pm 1.1)\times 10^{-10}$ cm³ sec⁻¹ and for the $v'=1$, $N'=13$ level the data of GZC¹⁸ yields $R=(6.53\pm 0.53)\times 10^{-10}$ cm³ sec⁻¹. These rate constants represent all processes that alter the M_F distribution in the excited state or shorten its lifetime. In atomic excited states, quenching or excitation transfer collisions are often much less important than collisions that reorient the angular momentum of the excited state. However, in molecular excited states, the reverse is often true. It is interesting to see to what extent R can be viewed as the sum of other collisional processes that already have been studied in this molecule.

Callear and Pilling¹⁹ determined the quenching rate

constant to be $(2.3\pm 0.2)\times 10^{-10}$ cm³ sec⁻¹. This is the total rate constant for collisional removal from the $v'=1$ level of the NO $A^2\Sigma^+$ state. Broida and Carrington²⁰ determined the total rate constant for change of the rotational quantum number J within the $v'=1$ level to be $(2.1\pm 0.4)\times 10^{-10}$ cm³ sec⁻¹. The sum of these two rate constants is $(4.4\pm 1.1)\times 10^{-10}$ cm³ sec⁻¹. There has been no direct measurement of the rate constant for alignment relaxation within the manifold of magnetic sublevels for the v' , J' level. However, our measured rate constant for the total destruction of alignment suggests that this rate constant is about 2×10^{-10} cm³ sec⁻¹.

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