Reinvestigation of the Hanle Effect for the NO $^2\Sigma^+$ State

K. R. German* and R. N. Zare

Department of Chemistry, Columbia University, New York, New York 10027

AND

D. R. Crosley

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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The coincidence of the Cd II 2144.38-A line with the $^2\Sigma^+\leftrightarrow^2\Pi$ lines of the (1, 0) band of the NO $^2\Sigma$ system is used to perform a measurement of the molecular Hanle effect on the $(\nu'=1, \nu''=13)$ vibration–rotation level of the excited state. A linear fit to the pressure-broadening data yields an intercept of 4.25±0.3 G for the zero-pressure linewidth and a slope of 16.3±0.2 mg/morr. This is in disagreement with the value of 5.5±0.5 G reported by Gouedard and Lehmann for the half-width at half-maximum. If we assume a g value calculated for Hund's case (b) coupling, the radiative lifetime calculated from our half-width at half-maximum is in good agreement with the work of Jeunehomme. The previous results of Crosley and Zare are shown to be spurious because of mercury vapor contamination.

INTRODUCTION

Recently, Crosley and Zare have reported measurements of the Hanle effect and optical radio-frequency double resonance in the NO $^2\Sigma^+$ state of NO using selective excitation with zinc and cadmium emission lines. Based on their results, $g$ and $g\sigma$ were concluded to be the same for both excitations, despite the fact that they populate significantly different rotational levels of the upper-state vibrational level. In addition, their measured $g$ value is not compatible with any straightforward angular-momentum coupling scheme for the excited state.

We have re-examined this system and find that the previous results were caused by mercury vapor contamination in both the metal lamp and the fluorescence cell. Consequently, we now know that what was actually observed was the well-studied $^2\Pi_1$ state. Using Cd excitation at 2144 Å, we have remeasured the Hanle effect in NO by observing a single fluorescence line through a spectrometer and by observing all fluorescence bands through a mercury-vapor absorption filter. The Hanle-effect linewidth extrapolated to zero pressure is 4.25±0.3 G. If we accept the radiative lifetime reported by Jeunehomme ($\tau=1.965\pm0.63\times10^{-9}$ sec), our results are consistent with the $g$ value obtained for a Hund's case (b) coupling scheme. The variation of the linewidth with pressure of 16.3±0.2 mg/morr yields a cross section for the destruction of alignment of 114±8 Å².

Gouedard and Lehmann have recently carried out quite similar studies on the NO molecule. Using excitation from a Cd lamp and a spectrometer to disperse the molecular fluorescence, they obtained a half-width at half-maximum of 5.5±0.5 G. A suggestion is offered as to how their data may be in accord with our own.

EXPERIMENTAL

Figure 1 shows a block diagram of the experimental apparatus. The cadmium lamp is an electrodeless microwave discharge contained in an air-heated quartz jacket. A standard right-angle geometry is used to observe the fluorescence which is dispersed through a 1/4-m Jarrell–Ash spectrometer. Additional coils not illustrated in this figure are used to null the local magnetic fields and to modulate the magnetic field produced by the Helmholtz sweep coils. The photomultiplier output is fed into a lock-in amplifier, and the results of successive sweeps are stored in a PDP-8/L signal averager. After enough sweeps have accumulated to render the signal-to-noise ratio adequate, the output of the signal averager is recorded on punched paper tape, and these data are used to perform a full line fit to the theoretical line shape.

Excitation of nitric oxide is accomplished using the 2144-Å Cd II emission line. Broida and Carrington have shown that this line excites only the $\nu'=1, \nu''=13$ vibration–rotation level of the $^2\Sigma^+$ electronic state of NO. The fluorescence spectrum from this level consists of $P$, $Q$, and $R$ lines terminating on each vibrational level of the $^2\Pi_1$ and $^2\Pi_3$ ground substates; it extends from the exciting line to about 3300 Å, peaking at several bands around 2500–2700 Å.

Figure 2 shows a dc trace of the spectrometer output of the (1, 5) fluorescence band in second order, where the branch notation is that adopted previously by Broida and Carrington. This is the most intense fluorescence band, and the figure shows the resolution used in this experiment. The strength and sign of the Hanle effect vary from branch to branch. We find that the strongest Hanle signal is from the $Q_0+9R_12$ branches and has a magnitude of 8%±4% of the total light. The signs shown in parentheses of Fig. 2 correspond to the sign of the degree of polarization. A positive sign refers to an increase in fluorescent intensity with increasing magnetic field. The sign of the $9P_9$ branch is uncertain, as the signal-to-noise ratio was only about 1:1 after 4 h of integration. Our assignment of signs agrees with that of Gouedard and Lehmann in those cases where they were able to determine the sign of the Hanle effect for the individual lines.

Obviously, the Hanle signal for an entire fluores-

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cence band is reduced because of cancellation of the effects of the various branches. However, the sign of the Hanle effect for the whole band is still positive.

Unfortunately, the 2537-Å line of mercury occurs in the middle of the (1, 4) fluorescence band of NO. Moreover, the degree of polarization in mercury is of the order of 80% of the total fluorescence and hence causes a very strong Hanle signal. Indeed, under our experimental conditions, it was found that the Hanle signal caused by mercury contamination was approximately 300 times stronger than that of the undispersed NO fluorescence.

Two methods of measurement, both of which avoided the mercury contamination problem, were used: (1) the $Q_2$ and $QR_{12}$ branches of the (1, 5) band were observed through a spectrometer; and (2) the undispersed fluorescence was observed through a mercury absorption cell. Efforts to remove the mercury contamination from either the scattering cell or the cadmium lamp were unsuccessful.

We believe the mercury in the cadmium lamp to be trace mercury impurities in the cadmium metal, as elaborate trapping and cleaning procedures always failed to produce a mercury-free lamp. The source of mercury in the scattering cell appears to be twofold. It is likely that the contamination in the previous measurements was caused primarily by the use of a mercury McLeod gauge in measuring the NO pressure. However, as even removing the gauge and rebuilding the vacuum system failed to eliminate the problem completely, we suspect that mercury might be in the NO gas.

For the present series of experiments, the NO pressure was measured with a thermocouple gauge which was later calibrated against a McLeod gauge after completion of the experiments.

**ANALYSIS OF DATA**

For the right-angle geometry shown in Fig. 1, the ideal theoretical line shape is an inverted Lorentzian for dc detection. In practice, optical misalignment and the finite size of detection adds a small dispersion-shaped component. In our experiment we employ magnetic field modulation. The line shape obtained using ac detection is thus expected to be the derivative of the Lorentzian and dispersion components in the limit of small modulation fields. At the finite modulation fields necessary to produce detectable ac signals, the line shape is broadened by the modulation. Let $n$ be the modulation amplitude in gauss, $x$ be the magnetic field in gauss, and $\Gamma$ be the linewidth in gauss. Then, in terms of the dimensionless parameters,

$$ h = x/\Gamma, \quad A = h^2 - m^2 - 1, $$

and

$$ m = n/\Gamma, \quad B = (A^2 + 4h^2)^{1/2}, $$

FIG. 1. Schematic experimental setup.
Fig. 2. Fluorescence spectrum (second order) of the (1, 5) band of the NO γ system with the resolution used in the Hanle measurements. The signs in parentheses indicate whether the sign of the degree of polarization is positive or negative.

the theoretical line shape may be written for $h > 0$ as

$$V(1) [\frac{(B+A)}{\sqrt{h(B-A)}}] (mB)^{-1} + V(2) \times \left| 1 - \frac{[h(B+A)]^{1/2} - (B-A)^{1/2}}{(2^{1/2}B)} \right| m^{-1}, \quad (1)$$

and for $h < 0$ as

$$V(1) [\frac{(B+A)}{\sqrt{-h(B-A)}}] (mB)^{-1} + V(2) \times \left| 1 - \frac{[h(B+A)]^{1/2} + (B-A)^{1/2}}{(2^{1/2}B)} \right| m^{-1}, \quad (2)$$

where $V(1)$ and $V(2)$ are the coefficients, respectively, of the Lorentzian and dispersion contributions to the total dc signal.\(^8\)

The data were fit to the above expression using a nonlinear least squares program to determine the coefficients $V(1)$ and $V(2)$ and the linewidth $\Gamma$. A typical result of such a fit is shown in Fig. 3.

In the absence of pressure broadening, the linewidth $\Gamma$ is related to the radiative lifetime $\tau$ and the magnetic moment $g_\mu_B$ by

$$\Gamma = \frac{\hbar}{2g_\mu_B\tau}. \quad (3)$$

A simple pressure-broadening model in which collisions merely randomize the phase of the emission oscillator leads to the calculation of an effective coherence time $T$ as

$$T^{-1} = \tau^{-1} + n\sigma v, \quad (4)$$

where $n$ and $v$ are the number density and the mean velocity of the colliding species, and $\sigma$ is their average cross section. At finite pressure, $T$ replaces $\tau$ in Eq. (3), giving rise to a linear broadening of $\Gamma$ with pressure.

Figure 4 illustrates the variation of the linewidth with NO pressure. The solid circles refer to data taken through the spectrometer on the $Q_2 + Q_{R12}$ branches, while the open circles refer to data taken on all bands through the mercury absorption filter.

A linear least squares fit to the solid circles gives an intercept of $4.25 \pm 0.3$ G and a slope of $16.3 \pm 0.2$ mG/mtorr, where the uncertainties represent 95% confidence limits. We might expect deviations from a linear dependence of the linewidth on pressure because of (1) NO dimer formation and (2) radiation trapping. We have estimated the magnitude of both these effects and find them to be negligible as compared with the accuracy of our measurements.
The dimerization constant $K$ for the reaction

$$2\text{NO} \rightarrow (\text{NO})_2$$

was determined by Guggenheim\textsuperscript{9} from second virial coefficient data over the temperature range 120-300°K. These data have been reanalyzed by Scott,\textsuperscript{10} who finds

$$K(\text{atm}^{-1}) = \frac{[(\text{NO})_2]/[\text{NO}]^2}{\exp[-10.90 + 752/T(\text{OK})]}.$$

For the highest pressures used in this experiment, about $5 \times 10^{-3}$ atm NO, the concentration of NO dimer at 300°K is about one part in $10^8$ of the NO concentration.

When resonance radiation of a given molecular species passes through vapor of the same species, it becomes partially absorbed, only to be re-emitted at a later time. Thus the imprisonment of resonance radiation causes the apparent lifetime of the excited state of the molecule to increase. A closely related phenomenon accompanying radiation trapping is that of coherence narrowing, whereby the width of the level-crossing curve is found to narrow as multiple scattering of resonance photons becomes important. Coherence narrowing has a simple physical interpretation in terms of an ensemble of classical oscillators in a static magnetic field. When one precessing oscillator decays, and the radiation emitted excites another oscillator, the second oscillator, because of the polarization of the radiation, will tend to precess in phase with the first oscillator. To an outside observer, the effect will be the same as if the first oscillator were endowed with a longer lifetime, leading to a narrower level-crossing signal. We note that this increase in lifetime is not quite the same as the apparent increase in lifetime of the excited state, as the lifetime with which we are concerned is the “in-phase” lifetime of the oscillator. We shall follow the practice of calling this the “coherence time” of the excited state.

Considerable insight into the nature of coherence narrowing may be obtained by treating radiation trapping in the density-matrix formalism.\textsuperscript{11,12} In particular, Saloman and Happer\textsuperscript{13} showed that the coherence time $T$, which is the same for all fluorescence branches, is given by

$$T = \frac{\tau}{1 - \sum_i x_i \beta_i},$$

where $\tau$ is the radiative lifetime of the excited state, $\beta_i$ is the branching ratio to the $i$th branch, $x_i$ is the trapping probability for photons associated with the $i$th branch, and $\alpha_i$ is an angular factor. For the right-angle geometry employed in our experiment, $\alpha_i$ is given by

$$\alpha_i = \frac{3}{16} (2J' + 1) \left[ \begin{array}{ccc} J' & J' & 2 \\ 1 & 1 & J \end{array} \right]^2,$$

where $J'$ and $J$ are the angular momenta of the excited-state and ground-state levels, respectively. Equation (6) shows that the most effective branch for radiation trapping is the $\Delta J = 0$ branch, for which $\alpha_i$ approaches the value 7/25 with increasing $J$. The $\Delta J = \pm 1$ branches approach the same limiting value of 7/100.

An upper limit to the effect of coherence narrowing may be obtained using a branching ratio of 13% for molecular fluorescence in the (1,0) band and an average absorption coefficient of 0.44 cm$^{-1}$ (mm Hg)$^{-1}$. At 300 mtorr of NO, we calculate a roughly 1% narrowing of the Hanle curve as compared to that at zero pressure. However, as the hyperfine structure is within the Doppler width of the fluorescence lines, it contributes oppositely signed Hanle signals which tend to cancel each other out. We therefore expect this narrowing to be an overestimate.

**DISCUSSION AND RESULTS**

The measurement of the linewidth $\Gamma$ yields the product $g\tau$. In order to determine both $g$ and $\tau$, it would be necessary to measure either quantity separately. An effort was made to measure $g$ by the technique of optical radio-frequency double resonance,\textsuperscript{14} but this was unsuccessful because of the low transmission of polarizers at 2144 Å and the large rf magnetic fields required for a system with such a short lifetime and small magnetic moment.
In the absence of hyperfine structure, a $\Sigma$ state satisfies Hund's case (b) coupling and is expected to have a $g$ value given by

$$g_{\Sigma} = \frac{N}{2} \pm \frac{1}{2} = \pm \frac{1}{2}. \quad (7)$$

For our case, $N = 13$ and $g_{\Sigma} = \pm 0.074$.

When hyperfine structure is present, two idealized coupling schemes are possible,\(^1\) the choice of which depends on whether the $p$-type doubling or the hyperfine splitting dominates. In the former case [Hund's case (b$_{g}$)], $\mathbf{N}$ and $\mathbf{S}$ couple to form $\mathbf{J}$, which in turn couples with $\mathbf{I}$ to give a resultant $\mathbf{F}$; whereas in the latter case [Hund's case (b$_{h}$)], $\mathbf{I}$ and $\mathbf{S}$ couple to form $\mathbf{G}$, which couples with $\mathbf{N}$ to give a resultant $\mathbf{F}$. Of course, intermediate coupling is also possible.

The excited states of NO are characterized by a clear division into two separate classes: Rydberg states, in which a single electron is excited into a Rydberg-type orbital outside the NO$^{+}$ $\Sigma^{+}$ molecular core; and non-Rydberg states, in which the electrons occupy different unfilled-shell configurations of the $2p$ electrons. The $A$ $\Sigma^{+}$ state of NO has an electronic configuration, $(\sigma_{1s})^{2}(\sigma^{*}1s)^{2}(\sigma_{2p})^{5}(\sigma_{3p})^{4}(\sigma_{3s})^{4}$ and is the lowest-lying member of the $\alpha \sigma$ molecular Rydberg series. Because the outermost electron is well removed from the molecular core, splittings caused by spin-rotation or hyperfine interaction are expected to be quite small in this state. Indeed, the magnitude of the $p$-type doubling constant as well as the hyperfine splitting parameters are not known for the NO $A$ $\Sigma^{+}$ state, and thus we are unable to assign the coupling scheme for this state without some ambiguity. Nevertheless, there are two compelling reasons to believe that the $p$-type doubling for the $N'=13$ level is greater than or comparable to the hyperfine splittings, so that Hund's case (b$_{g}$) may be used to derive an estimate for the $g$ value. Calculations\(^1\) show that both the polarizations and the relative intensities would not be as observed if the hyperfine splittings were larger than the $p$-type doubling.

Fortunately, $N$ is much larger than $I$, and the influence of hyperfine structure on the $g$ value for case (b$_{g}$) is expected to be small. For example, $g_{p}$ deviates from $g_{\Sigma}$ by no more than 8% in the most unfavorable instance. Note that even if we were certain of the coupling scheme, we would not know the relative populations of the different hyperfine levels excited by the Cd lamp and, hence, could not determine an effective $g$ value. Using the value of $g_{\Sigma}=0.074$, we deduce a radiative lifetime of $1.81\times10^{-7}$ sec for the $v'=1, N'=13$ level of the $A$ $\Sigma^{+}$ state. From absolute $f$-value measurements for the $\gamma$-band system determined by Weber and Penner, Bethke, and others, Callear and Smith\(^1\) have calculated the mean radiative lifetimes for the $v'=0, 1,$ and 2 vibrational levels to be $2.3\times10^{-2}$, $2.1\times10^{-2}$, and $2.1\times10^{-2}$ sec, respectively. These lifetimes were found to be compatible with their CO$_{2}$ quenching studies. Subsequently, Jeunehomme\(^1\) determined the radiative lifetime for the $v'=0$ vibrational level to be $1.965\pm0.03\times10^{-7}$ sec, using electron-impact excitation and the phase-shift technique. Most recently, Copeland\(^1\) has directly measured the radiative lifetime of the NO $A$ $\Sigma^{+}$ state using a delayed coincidence technique. For $v'=0$, 1, and 2, he found the values $r=1.19\pm0.06\times10^{-7}$, $1.21\pm0.07\times10^{-7}$, and $1.15\pm0.08\times10^{-7}$ sec, respectively, which are smaller by a factor of $\sim 2$ than the previous results. Although our estimate of the lifetime suffers from lack of knowledge of the effect of hyperfine structure on the $g$ value, we see no way to reconcile our lifetime with that of Copeland. Accepting the radiative lifetime for NO reported by Jeunehomme, we have determined the average cross section for the destruction of alignment, based on our pressure-broadening data, to be $114\pm8 \text{ Å}^{2}$.

As we mentioned before, Gouedard and Lehmann performed level-crossing experiments on NO very similar to our own, but found a half-width at a half-maximum of $5.5\pm0.5 \text{ G}$ as opposed to our value of $4.25\pm0.3 \text{ G}$. We would like to suggest a possible explanation for this disagreement. Gouedard and Lehmann report that they could not detect effects of pressure broadening below 100 mtorr. It is likely then that their value for the linewidth applies to NO at this pressure. We note that at the same pressure we find for the linewidth (see Fig. 4) a value of $5.9\pm0.3 \text{ G}$, which is in agreement with their value.

In the interest of scientific discovery, it is worth noting that the validity of the NO Hanle measurements of Crosley and Zare was first questioned in an experiment performed on the same apparatus used earlier by them, when a silica glass filter with a cutoff at 2300 Å was interposed between the cadmium lamp and the scattering cell, but failed to diminish significantly the alleged NO Hanle effect. A search of the spectrum of the Cd lamp used by these authors revealed the presence of the Hg 2537-Å line, which unfortunately occurs in the middle of the passband of the interference filter used in the prior investigations. Another experiment showed that the Hg 2537-Å line was ineffective in exciting NO fluorescence.

The Hanle linewidths measured using either the Cd lamp or the Zn lamp were identical with each other and with the linewidth for Hg $^{3}P_{1}$; moreover, the $g$ value of 1.5 determined by the double resonance measurements for both excitations was also equal to the $g$ value of Hg $^{3}P_{1}$. These facts support our contention that the results of the level-crossing and double resonance measurements of Crosley and Zare were caused solely by mercury contamination.

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Role of Spin Symmetry Conversion in Nuclear Relaxation in Solids

DANIEL WALLACH*

Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802

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The rates of nuclear transitions in molecules which are able to rotate about a single axis in the solid are considered. Only the effects of intramolecular dipolar interactions are taken into account. In molecules with threefold or higher symmetry about the rotation axis, only transitions which alter the symmetry of the nuclear state can occur. In molecules with twofold symmetry, if the angle between the internuclear vector and the rotation axis is 90°, only transitions which retain the nuclear symmetry can occur. If that angle is not 90°, both nuclear transitions which alter and which conserve symmetry are allowed. The detailed mechanisms which cause these two types of nuclear transitions are similar.

I. INTRODUCTION

One method of studying torsional motions in solids is by NMR experiments. The torsional motions impart a time dependence to the nuclear dipole–dipole interactions, and this time dependence causes nuclear relaxation.

The detailed expression for the nuclear relaxation time depends on the model chosen to describe the torsional motions. Commonly, one of two classical models is used. The rotation is assumed either to be diffusional or to consist of random jumps among potential minimum sites. In either case the nuclear relaxation time is related to an angular correlation time \( \tau_0 \), where \( \tau_{\text{r}} \) is proportional either to the rotational diffusion constant or to the jump frequency. The other torsional parameter which appears is \( \tau_0 \), the height of the barrier to rotation. It is assumed that \( \tau_{\text{r}} \) varies with temperature as

\[
\tau_{\text{r}} \propto \exp(\alpha_0/kT).
\]

A classical model of the rotation is not always adequate. At sufficiently low temperatures, for example, the spacing between torsional levels will be large compared to the level widths, and quantum effects must be considered. In addition, however, quantum effects may occur because of symmetry restrictions on the over-all wavefunction. Hydrogen provides the best known example of such effects. If \( \text{H}_2 \) is in the vibrational and electronic ground state, the Pauli principle requires that rotational wavefunctions which are symmetric with respect to interchange of the two protons can only occur in combination with nuclear wavefunctions which are antisymmetric, and vice versa. These restrictions have an important bearing on the nuclear relaxation process because they imply that there are two...