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Measurement of NO_2 $^2B_2$ State g Values by Optical Radio Frequency Double Resonance

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The g values for some selected levels of the NO_2 6126 and 5933 Å bands were measured using optical radio frequency double resonance. The g values are found to be well described by the Hund's case (b) coupling scheme.

INTRODUCTION

Despite considerable efforts to understand the visible spectrum of NO_2 and the radiative properties of this molecule, many mysteries remain (*1*). In particular, the depolarization of NO_2 fluorescence by a magnetic field (the Hanle effect) shows anomalous behavior, as reported by two groups (*2*, *3*). From the rate of depolarization as a function of field strength one obtains the product $g\tau_c$, where g describes the magnetic moment of the excited state and τ_c its dephasing lifetime. It is found that the $g\tau_c$ product is much smaller than expected, even when the measurements are extrapolated to zero total pressure to be free of radiation trapping and collisional effects. If the g values behave as predicted for Hund's case (b) coupling, then τ_c is a factor of 5 to 10 times shorter than τ_r the observed lifetime for total fluorescence decay in the red region and even larger in the blue-green region. This implies that the molecule may undergo intrinsic dephasing on a time scale shorter than its radiative lifetime, a result quite unexpected for so small a molecule.

The aim of the present study is to measure directly the g value for some of the same levels for which the Hanle effect has already been observed. This is accomplished by using optical radio frequency double resonance to measure the separation between the magnetic sublevels at a known field strength (*4*). We find that the g value is well behaved and hence is not the cause of the Hanle effect anomaly.

EXPERIMENTAL DETAILS

Figure 1 shows the experimental setup which is similar to the Hanle studies of Figger *et al.* (*2*). A cylindrical cell (15 cm long, 6 cm in diameter) contains the NO_2 sample at a typical pressure of 10 mTorr. A single-mode dye laser, linearly polarized in the vertical direction, excites a specific rotational level of the $^2B_2$ state of NO_2. The fluorescence from this state is observed along a perpendicular

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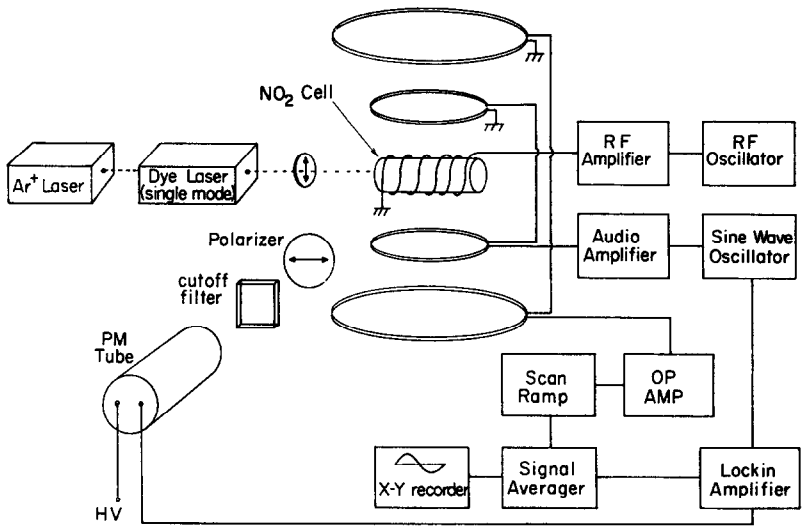

FIG. 1. Schematic diagram of the experimental setup. Coils for the compensation of the Earth's magnetic field are not shown.

axis to the laser after passing through a horizontal polarizer. When the NO_2 sample is subjected to a radio frequency field a change in the fluorescence intensity passing through the polarizer is observed as the rf field is brought into resonance with the separation of the magnetic sublevels of the excited state, i.e., the resonance condition

$$h\nu = g\mu_B H_0 \qquad [1]$$

is met. Here, ν is the radio frequency, H_0 is the vertical magnetic field (dc), μ_B is the Bohr magneton, and g is the excited state g factor.

In this experiment, these resonances are observed by maintaining the rf field at a fixed frequency and amplitude while scanning the magnetic field H_0. In addition H_0 is modulated on the order of the expected half-width of the signal and the fluorescence is detected with a lock-in amplifier giving to first order the derivative of the resonance signal.

The NO_2 sample (Matheson, 99.5% pure) is purified by trap to trap distillation (*5*) and stored in a liquid nitrogen cooled cold finger. From this finger the cell is filled to a pressure of 10 mTorr as measured by a thermocouple gauge. The gas sample is changed after every 30 min of irradiation because the laser light seems to produce a photochemical reaction that decreases the signal amplitude and increases the total pressure up to 50% at 50 mW laser power.

The excitation source is a single mode dye laser, as described previously (*2*). The bandwidth of this laser is typically smaller than 50 MHz and the average power is 50 mW (at 5934 Å). An unfocused beam of 0.3-cm diameter is used. This laser is tuned to excite a $^2B_2$ level with definite quantum numbers N' and K' whose assignments are known (5–7). Table I lists the transitions investigated. The excited state levels are chosen to be those for which Hanle effect measurements (*2*) and radiative lifetime measurements (*2*, *7*) have been made. Before

TABLE I

Transitions Used in the Present Double Resonance Study

Band (Å)	λ(Å)	$N'_{K_{-1},K_{+1}} \leftarrow N''_{K_{-1},K_{+1}}$
5933	5934.41	$3_{03} \leftarrow 4_{04}$ [a]
5933	5934.47	$3_{03} \leftarrow 4_{04}$ [a]
5933	5934.53	$3_{12} \leftarrow 4_{13}$
6126	6129.16	$8_{18} \leftarrow 9_{19}$

[a] Based on the measured g values, the 5934.41Å transition is the $J' = 5/2$ spin component and the 5934.47Å transition the $J' = 7/2$ spin component (see text).

each measurement a Spex ¾-m spectrometer (not shown in Fig. 1) is used to set the laser to the desired transition within 0.05 Å. Fine tuning is obtained by taking the excitation spectrum of NO_2 over a small interval and comparing this to a microdensitometer trace of the assigned absorption spectrum (*5*, *7*).

A pair of Helmholtz coils (40 cm in diameter) produces a vertical dc field, H_0, to be scanned from 0 to 25 G defining the z axis. Coaxial with these coils is a smaller pair of Helmholtz coils (30 cm in diameter). These coils produce a 340 Hz modulating field (0.25 G amplitude) superimposed on H_0. Not shown in Fig. 1 are two sets of Helmholtz coils located along the x and y axes which serve to nullify the Earth's magnetic field in these directions. The remaining component of the Earth's field produces a dc offset to H_0. The inhomogeneity of the applied magnetic field over the dimensions of the cell is no more than 10 mG as measured by a Hall probe Gaussmeter (Bell Model 640). The dc magnetic field, H_0, is scanned by supplying a sawtooth voltage to an operational amplifier powering the main coils. The magnetic field is calibrated versus the current in the drive circuit (measured by the voltage across a 1 Ω precision resistor) using the Hall probe Gaussmeter. Thus the magnetic field at any point in the scan can be read directly from this voltage to a precision of 2% in the region of interest. A 55-turn coil closely wound around the NO_2 cell produces a horizontal radio frequency field, H_1, defining the x axis. A resonant tank circuit drives the coil in the region of 1.5 to 3 MHz at a typical rms amplitude of 0.3 G.

The laser induced fluorescence of NO_2 is viewed along the y axis by a photomultiplier tube (Centronic Q4283SA-25). This light is collected by a lens (15-cm focal length, $F = 1.5$) after passing through a polaroid sheet polarizer oriented parallel to the x axis. A cutoff filter (Corning 2-58), which passes light with wavelength longer than 6200 Å, is used to suppress scattered laser light by a factor of 10^4. The signal from the photomultiplier is enhanced by a band-pass amplifier (Keithley Model 823 Nanovolt Amplifier) and fed into a lock-in amplifier (PAR HR-8).

The signal-to-noise ratio in the present experiment is less than one. Compared

to the Hanle signal, the double resonance signal is about a factor of 100 smaller. Nearly noise-free Hanle signals can be obtained with this setup in a single sweep, whereas for the detection of a typical double resonance signal, as exemplified by Fig. 2, signal averaging (HP Model 5480 A hard wired signal averager or a PDP-8L Computer) for about 4 hr is required. This typical signal plot shows three double resonance signals and a Hanle signal around $H_0 = 0$. The "small" Hanle signal is due to an unavoidable misalignment between the field and beam directions as well as that between the polarizer shown in Fig. 1. The main noise results from the amplitude instability of the laser.

RESULTS AND DISCUSSION

Table I lists the levels of the 5933 and 6126 Å bands that have been investigated and Fig. 2 presents a typical trace of the fluorescence signal versus magnetic field for the 5934.47-Å transition. According to a Hund's case (b) coupling scheme (*8*) in which the nuclear spin I (quantum number I) couples to the rotational angular momentum J' to produce a total angular momentum F', the molecular g factor is given by

$$g(N',J',F') = \frac{(1.001)[F'(F'+1) + J'(J'+1) - I(I+1)]}{(2N'+1)F'(F'+1)}, \qquad (2)$$

where N' is the nuclear rotational angular momentum. Because the main consti-

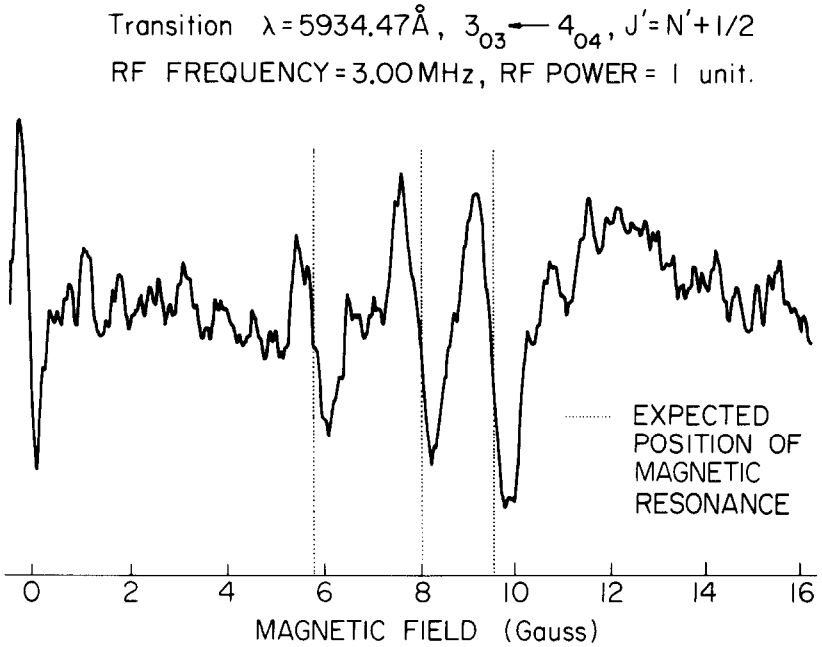

FIG. 2. Plot of the fluorescence signal derivative versus magnetic field, H_0, showing the Hanle signal at $H_0 = 0$ and the double resonance signals for the three hyperfine components of the designated transition.

tuent of the NO_2 sample is $^{14}N^{16}O_2$, the nuclear spin quantum number I is 1. Thus each upper state N', J' spin level has three hyperfine components $F' = J' + 1$, $F' = J'$, and $F' = J' - 1$, each of which according to Eq. [2] has a slightly different g value.

As Fig. 2 shows, three double resonance signals appear. Moreover, the three resonances are at the magnetic fields predicted by Eq. [1] using the g values calculated from Eq. [2]. Equation [1] applies to the weak field limit where the Zeeman splittings are strictly linear with field strength. To test the validity of Eq. [1], measurements were carried out at 2 and 3 MHz rf fields. No change of $g(N', J', F')$ could be observed within the precision of the experiment, estimated to be better than 20%. This finding not only confirms the validity of Eq. [1] but shows that the excited state g values are given correctly by Eq. [2]. Certainly it is possible to carry out more precise determinations of the value of $g(N', J', F')$ by improving, for example, our magnetic field calibration. However, since the main purpose of this study is to determine whether or not the upper state g values are well behaved, further refinements were not attempted.

Figure 2 also shows the Hanle signal at $H_0 = 0$. The linewidths of the Hanle signal and the three double resonance signals are approximately equal. The double resonance signals in Fig. 2 are power broadened, but measurement with different rf field amplitudes indicate that the double resonance linewidths when extrapolated to zero rf power agree fairly well with the width of the Hanle signal.

For the 6129.16-Å transition a similar resonance structure is found, showing three well-resolved double resonance signals. Again the g values correspond to those predicted from Eq. [2]. Studies of the 5934.41- and 5934.53-Å transitions yield definite resonance signals at the expected magnetic fields but for these transitions the three hyperfine double resonances overlap one another to such an extent that we were unable to resolve them. The signal-to-noise ratio for these transitions was smaller than for the 5934.47-Å transition, causing us to use a larger rf field strength to bring out the double resonance signal. However, the resultant power broadening of the resonance structure and the deformation of this signal by multiple rf quantum transitions prevented a measurement of individual $g(N', J', F')$ values. A Bloch–Siegert shift, which is also present for the other transitions studied, is negligible compared to the precision of the experiment. The results reported here are obtained using low laser intensity. If the laser power is increased, a broad structure appears upon which the double resonances are superimposed. The nature of this new feature is presently under study.

The observation of optical radio frequency double resonance signals can also be used to assign the quantum numbers N' and J'. The latter is of particular interest since analysis of the laser-induced fluorescence spectrum readily gives the value of N' of a given level but not in general that of J' (*5*). For the 5934.47-Å transition corresponding to one of the $N' = 3$ spin doublets the g values we measure permit us to assign $J' = 7/2$ and thus the other spin component at 5934.41 Å as $J' = 5/2$. These assignments agree with those found previously (*5*, *6*). Unfortunately this assignment procedure was not possible for the 5934.53- and the 6129.16-Å transitions because the double resonance structure for the former is

not sufficiently resolved and the g values for the latter do not unambiguously permit the value of J' to be known within our measurement uncertainty.

The present investigation shows that the excited state molecular g factors for the NO_2 $^2B_2$ state are correctly expressed by Eq. [2]. Thus the behavior of the g values cannot be responsible for the anomalous results of the Hanle effect measurements (*2*). Therefore an understanding of the source of this discrepancy must be directed at resolving the question why the measured radiative lifetime and the coherence lifetime obtained from the Hanle effect differ in the absence of collisions.

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