

EVIDENCE FOR THE PREPARATION OF A NONSTATIONARY STATE FROM THE OPTICAL DOUBLE RESONANCE SPECTRUM OF NO₂

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In addition to the narrow resonances from the hyperfine structure of the NO₂ excited state, a broad resonance appears in the optical radio frequency double resonance spectrum. It has a pressure-independent linewidth, corresponding to a lifetime of $0.4 \pm 0.1 \mu\text{s}$, which is attributed to the preparation of a nonstationary state by the excitation source.

1. Introduction

One of the puzzles of the visible absorption spectrum of nitrogen dioxide is the discrepancy between the value of the lifetime measured in radiative decay and the lifetime obtained in magnetic depolarization studies (Hanle effect) [1,2]. The difference amounts to a factor of ten or more. In order to solve this riddle a model was introduced [3,4] † which assumes that underlying each level excited in the visible region is a finer structure, called a "bunch structure", consisting of two sublevels whose spacing is about 10 MHz or less. With this bunch structure we were able to show that an intramolecular dephasing process in the isolated molecule causes the coherence time obtained from the Hanle effect measurements to differ from the radiative lifetime. Moreover, it was possible to give a simple explanation for the observed dependence of the coherence time on the rotational quantum number of the excited state. This model makes a fur-

ther prediction, namely, that the radiative excitation prepares the NO₂ molecule in a nonstationary state with a "lifetime" $\tau_0 = 0.5 \mu\text{s}$ in the yellow-red region of the visible absorption spectrum. The present study presents a double resonance experiment carried out on NO₂. This experiment gives results that are in good agreement with this model. In particular, a state with a lifetime of $0.4 \pm 0.1 \mu\text{s}$ is observed.

2. Experimental method

The experimental setup is the same as in the previous double resonance study [8] of NO₂ and will only be described briefly here. A traditional orthogonal geometry is used. The laser beam (single-mode dye laser with a bandwidth of less than 50 MHz) propagates along the X axis. The laser beam is linearly polarized with its electric vector pointing along the Z axis, the same direction as the static magnetic field H_0 . The NO₂ sample, typically at a pressure of 10 mTorr and a temperature of 300 K, is located at the origin. The resulting fluorescence after passing through a polarization analyzer and a Corning 2-58 cutoff filter that suppresses the scattered laser light by a factor of 10^4 is viewed by a photomultiplier along the Y axis. The polarization analyzer is oriented to transmit fluorescence whose electric vector is along the X axis.

A radio frequency field, H_1 , oriented perpendicular to H_0 is applied to the NO₂ sample. The rf field has a fixed amplitude H_1 and a fixed frequency ν . It is

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† In ref. [3], once eqs. (7) and (8) are introduced, the treatment given there follows closely that of an ensemble of spins which do not couple to one another but couple to an external fluctuating field, different at each spin (see ref. [5]). This fluctuating field is provided by the fluctuating internal angular momentum (L), which is related to a tunnelling motion between different equilibrium configurations. See refs. [6,7] for the existence of non C_{2v} symmetry in the NO₂ excited state equilibrium configuration.

brought into resonance with the separation of the excited state magnetic sublevels by scanning the magnetic field H_0 . The resonance condition is

$$h\nu = g\mu_B H_0, \quad (1)$$

where μ_B is the Bohr magneton, g the excited state g factor, and h Planck's constant. To improve the signal-to-noise ratio, we use phase sensitive detection. For this purpose the magnetic field H_0 is modulated at a frequency of about 340 Hz and the output of the photomultiplier is detected by a lock-in amplifier. The resonance signals obtained are to a good approximation derivatives of Lorentzian-shaped curves when plotted as a function of the magnetic field strength H_0 . Previously assigned rotational transitions are selected in the 5933 Å region [9] and the 6125 Å region [10]. Laser power levels are measured with a Spectra Physics model 404 power meter.

3. Results

Fig. 1 presents the resonance structure obtained by exciting the $3_{03} \leftarrow 4_{04}$ transition at 5934.47 Å. Two traces are shown under the same experimental conditions except that the upper trace has twice the rf field power than the lower one. Because of slight optical misalignment of the magnetic field H_0 with the polarization of the laser beam, a Hanle effect signal appears in both traces at zero magnetic field. At higher magnetic field three double resonance signals are evident corresponding to the three hyperfine sublevels of each rotational level (the main constituent of nitrogen dioxide is $^{14}\text{N}^{16}\text{O}_2$ with nuclear spin $I = 1$) [8]. The three narrow resonances whose positions are indicated by the vertical dotted lines are rf power broadened; their shapes are deformed by multiple rf quantum transitions. Extrapolation to zero rf power gives a linewidth of these three resonances which within the precision of the experiment is the same as that of the Hanle effect resonance.

3.1. Observation of a broad resonance signal

Particular attention is called to the broad resonance feature which can be recognized clearly in the upper trace (see the dashed curve) of fig. 1. This resonance structure is obtained with a 30 mW unfocused laser beam 0.5 cm in diameter. Both traces were obtained

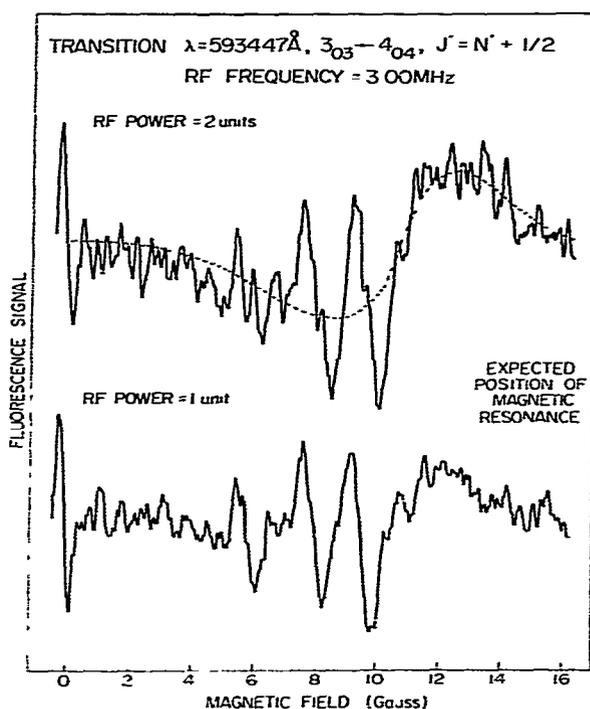


Fig. 1. Double resonance signal as a function of static magnetic field H_0 . Superimposed on the three narrow resonances from the hyperfine components is a broad resonance which becomes more apparent with increasing rf power (compare upper and lower traces). The Hanle signal also appears at $H_0 = 0$.

after signal averaging for 4 h. By focusing the laser beam to a diameter less than 0.1 cm the dependence of the resonance structure on laser power was determined. Fig. 2 shows a plot of the amplitude of the broad structure, the Hanle effect, and the total fluorescence intensity versus laser power. The amplitudes of the narrow double resonance signals are not included in fig. 2. As the laser power increases, the relative amplitudes of the narrow resonances compared to that of the broad structure decreases, making quantitative measurement not possible. Fig. 3 presents a plot of the dependence of the broad resonance structure amplitude on the square of the laser power. Contrary to what is observed for the Hanle effect and for the total fluorescence signal, the broad resonance structure clearly shows a quadratic dependence on laser power.

This broad resonance feature was observed in all

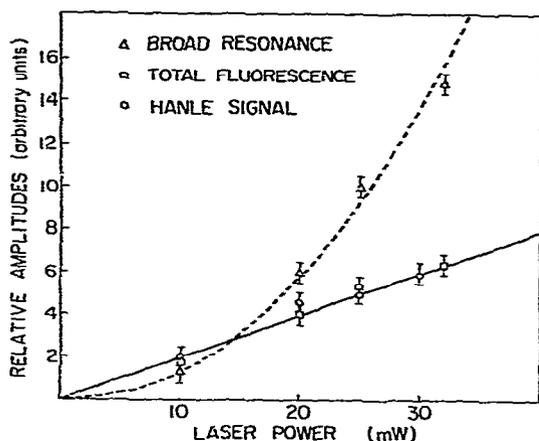


Fig. 2. Plot of the signal amplitudes versus laser power for the Hanle effect, the total fluorescence, and the broad resonance feature.

levels investigated previously (see table 1 of ref. [8]). However the detailed studies reported here were only performed on the transition indicated in fig. 1. Because the NO_2 absorption spectrum is thought to consist of a continuous spectrum underlying the discrete spectrum [11], a search was made for the broad resonance when the laser is tuned between two discrete absorption lines. No resonance signal could be detected under these conditions.

3.2. Dependence on magnetic field strength

A study of the broad resonance as a function of magnetic field strength was also made. It was found

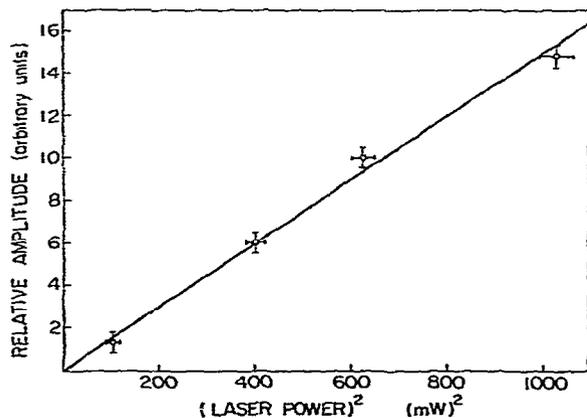


Fig. 3. Plot of the amplitude of the broad resonance feature versus the square of the laser power.

that the amplitude of the broad structure depends on the strength of H_1 as described by the Bloch equations. The broad structure disappears when the rf field is turned off and depends on the frequency ν and the magnetic field H_0 in such a way that eq. (1) is fulfilled for $g = 0.20 \pm 0.02$ in the investigated range ($H_0 \leq 20$ G). This g factor differs markedly from the g factors observed for the three narrow resonances, even when the g values of the hyperfine components are averaged together.

3.3. Dependence on NO_2 pressure

It was found that the amplitude of the broad resonance increases linearly with NO_2 pressure between 1 and 5 mTorr, increases more slowly with yet higher NO_2 pressures, reaching a maximum value around 10 mTorr, and decreases at still higher pressures, vanishing at pressures larger than 50 mTorr. The pressure dependence of the narrow resonance could not be determined because of the poor signal-to-noise ratio.

The width of the broad resonance does not vary with NO_2 pressure in the investigated pressure range (1–20 mTorr). However, the width does show a weak dependence on the magnitude of H_1 . Extrapolation to zero rf power gives a linewidth $\Delta\nu$ (fwhm) of $\Delta\nu = 0.8 \pm 0.2$ MHz which corresponds to a lifetime of

$$\tau = (0.4 \pm 0.1) \times 10^{-6} \text{ s.} \quad (2)$$

4. Discussion

From the above results we conclude that the broad structure with its different lifetime and g value from that of narrow resonances must belong to a state $|b\rangle$ which is not any of the three states $|a\rangle$ ($a = 1, 2, 3$) representing the hyperfine components of the assigned upper level. It might be thought that the laser is exciting an electronic state of NO_2 that lies at twice the frequency of the visible transition. Indeed, such excited states of NO_2 are known, but they do not fluoresce because of predissociation [11]. Moreover, this hypothesis can be ruled out because the broad structure occurs only as a double resonance signal but not in the Hanle effect.

An alternative explanation for the existence of the broad structure is provided by a model for the radiative properties of NO_2 [4] which in part has been de-

scribed previously [3]. In this model the so-called 2B_2 excited state levels $|a\rangle$ consist of bunches of closely lying states, i.e. $|a\rangle = \{|\phi_1\rangle, |\phi_2\rangle, \dots, |\phi_n\rangle\}$. Optical excitation prepares the molecule in a nonstationary state $|a'\rangle$, which is a linear superposition of the $|\phi_i\rangle$. The existence of such a nonstationary state with a "lifetime" τ_0 of about $0.5 \mu\text{s}$ in the yellow-red region was deduced from the Hanle effect and double resonance experiments [3]. We identify this nonstationary state with $|a'\rangle$. Compared to the radiative lifetime τ_R of the states $|a\rangle$ τ_0 is shorter by approximately two orders of magnitude. Moreover, τ_0 is also shorter than the coherence time τ_c , which is related to τ_0 by $\tau_c = (2N + 1)\tau_0$; here N is the rotational quantum number of the state $|a\rangle$. The lengthening of τ_c compared to τ_0 is caused by the molecule's rotation acting as a reservoir of orientation. In the present study we associate $|b\rangle$ with the broad double resonance feature and a "lifetime" τ_b with its width. We find that τ_b is $0.4 \pm 0.1 \mu\text{s}$. Within the precision of the experiment, this is the same as τ_0 .

Therefore we offer the following interpretation for the broad resonance. The radiation field causes $|a\rangle$ and $|b\rangle$ to be coupled by Stark mixing during the time τ_0 that the molecule lives in the nonstationary state $|a'\rangle$. The probability of finding the molecule in the state $|b\rangle$ is proportional to the square of the laser intensity. A dephasing of $|a'\rangle$ probably causes the Stark mixing matrix element to disappear. Assuming that $|b\rangle$ has a low probability for making a radiative transition to the ground state, then the presence of $|b\rangle$ only manifests itself through the fluorescence from $|a\rangle$. However, any perturbation of the orientation in $|b\rangle$ affects also the orientation in $|a\rangle$ due to the coupling of these states during the time τ_0 . A superposition of two resonances signals in the double resonance experiment and in the Hanle experiment are therefore expected, one with a narrow linewidth proportional to $1/\tau_c$ from $|a\rangle$, the other with a broad linewidth proportional to $1/\tau_0$ from $|b\rangle$. This is observed in the double resonance study except that the hyperfine structure of the broad signal is not resolved. However, the situation is quite different in the Hanle effect. Because $|a\rangle$ is nearly completely depolarized at field strengths where the orientation of $|b\rangle$ is almost unaffected (since $\tau_0 < \tau_c$), the Hanle effect signal represents almost completely the narrow signal from $|a\rangle$. Actually, the Hanle signal is expected to be the convolution of

the broad and narrow resonances, but because the broad resonance is nearly flat across the profile of the narrow resonance only the latter is detected.

In summary, we are able to explain the present experiments assuming that the optical excitation prepares the NO_2 molecule in a nonstationary excited state. In another experiment on NO_2 , Herman et al. [12] reported an optical-infrared double resonance study in which the pressure-independent linewidth corresponds to a lifetime of about $0.6 \pm 0.2 \mu\text{s}$. We note that this also is in good agreement with the lifetime τ_0 for the nonstationary excited state. Future studies on the spectroscopy of NO_2 and the excited states of related polyatomic molecules may require one to take into account the detailed nature of the excitation process [13].

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