A SIMPLE MODEL FOR THE DIFFERENCE BETWEEN COHERENCE TIME AND RADIATIVE LIFETIME IN NO_2

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An intramolecular mechanism is proposed to reconcile the different lifetimes obtained from direct radiative decay measurements and from Hanle effect measurements on NO_2. This mechanism predicts a dependence of the coherence lifetime on the excited state rotational quantum number which is in good agreement with the previous experiments.

1. Introduction

The lifetimes of the electronic states of NO_2 responsible for its visible absorption spectrum have long been a puzzle [1]. The difference between the lifetime values directly measured by fluorescence decay and those deduced from integrated absorption measurements appears to be qualitatively understood [2,3]. However, there remains another discrepancy regarding the value of the lifetimes obtained in radiative decay, τ_R, and in magnetic depolarization (Hanle effect) measurements of the coherence time, τ_C.

Hanle effect measurements on NO_2 have been carried out by two groups. One group [4] studied the yellow and red region of the absorption spectrum (5933–6126 Å), the other [5] the blue and green (4880 Å and 5145 Å). In these experiments the product $g\tau_C$ is obtained from the width of the depolarization signal as a function of magnetic field. Here g is the excited state Landé g factor and τ_C the dephasing time of that state. If one assumes that the values of the g factors are given by the Hund's case (b) angular momentum coupling scheme, then τ_C is smaller than τ_R by a factor of about 10 in the yellow-red region, and a factor of about 100 in the blue-green region. Direct measurements of the g factors by optical–radiofrequency double resonance [6] and by Zeeman scanning [5] confirmed that the g factors behave well in the same levels in which the Hanle effect was investigated. We therefore confront here the question of why τ_C differs from τ_R.

It is useful to review in what way the Hanle effect gives different information about the molecule's excited state behavior than direct lifetime measurements. In the Hanle effect one prepares the molecules in a coherent superposition of magnetic sublevels of that manifold of states that are excited by the radiation field. This coherent superposition of magnetic sublevels corresponds to an orientation of the molecules in the excited state, which results in the case of linearly polarized excitation in an alignment of the excited state magnetic moment along a fixed axis of a chosen coordinate system. The subsequent fluorescence is then polarized along this axis. The application of a magnetic field perpendicular to this axis causes the magnetic moment to precess about the magnetic field direction, resulting in a depolarization of the fluorescence. The depolarization curve as a function of magnetic field strength B_0 has a lorentzian shape whose linewidth ΔB_0 (fwhm) is related to the disorientation rate $1/\tau_C$ by

$$(g\beta/\hbar)\Delta B_0 = 1/\tau_C\,, \tag{1}$$

where β is the electronic Bohr magneton.

In the absence of all other effects, the spontaneous emission rate $1/\tau_R$ is equal to $1/\tau_C$. Often collision

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processes contribute to the disorientation rate, making $1/\tau_C$ larger than $1/\tau_R$. In the Hanle experiments on NO_2 in the yellow-red, corrections were made for the effects of collisional dephasing by extrapolating the linewidth ΔB_0 to zero pressure, the lowest data points being taken at 0.5 mtorr. In the Hanle experiments on NO_2 in the blue-green region the collisional dephasing was eliminated by the use of a molecular beam. Based on the results of both experiments we conclude that the measured coherence time τ_C is that of an isolated molecule. As was previously suggested [4,5], an intramolecular mechanism must be responsible for the difference between τ_R and τ_C.

2. The model

We present a simple phenomenological model for the intramolecular dephasing in the NO_2 molecule which is based on work by one of us (H.G.W.) to describe the radiative properties of this molecule [7]. The excited state of the NO_2 molecule including fine and hyperfine structure is assumed to have a density of levels described as a sparse intermediate case [8], where each level is separated by a spacing that is large compared to the natural linewidth. We further assume that underlying each level is a finer structure consisting of levels whose spacing is comparable to the linewidth calculated from integrated absorption measurements. We call these close-lying levels a "bunch". According to this structure of the NO_2 molecule, the hamiltonian H for the combined system, molecule plus radiation field is represented by two terms

$$H = H_0 + V \,, \tag{2}$$

where H_0 is the sum of the radiative hamiltonian, the molecule–photon interaction, and the major part of the molecular hamiltonian, and V describes the molecular interaction giving rise to the bunch structure.

The absorption of radiation by the molecule prepares it in an eigenstate of H_0 having the eigenfunction Ψ_0. The latter may be written as a superposition of eigenfunctions Ψ_n of H

$$\Psi_0 = \sum_n a_n \Psi_n \,. \tag{3}$$

The prepared state Ψ_0 has a definite total angular momentum $\boldsymbol{J}$ (in the absence of an external field). To simplify the discussion, we treat the NO_2 molecule as if it had no hyperfine structure, since its inclusion only complicates the treatment without introducing any changes. Because Ψ_0 is a degenerate state, we assume that there exists a non-zero expectation value of some internal angular momentum $\boldsymbol{L}$, whose origin will be discussed later. Then the expectation value of the total angular momentum $\boldsymbol{J}$ satisfies the relation

$$\langle \boldsymbol{J} \rangle = \langle \boldsymbol{N} \rangle + \langle \boldsymbol{S} \rangle + \langle \boldsymbol{L} \rangle \,, \tag{4}$$

where $\boldsymbol{N}$ is the rotational angular momentum and $\boldsymbol{S}$ the electronic spin angular momentum. Eq. (4) should not be interpreted to imply that N, L, or S are good quantum numbers, but rather that the sum of expectation values equals the expectation value of the good quantum number J.

The interaction term V removes (or changes) the degeneracy of Ψ_0 and quenches the expectation value of $\boldsymbol{L}$. As $\langle \boldsymbol{L} \rangle$ is quenched, $\langle \boldsymbol{N} \rangle$ and $\langle \boldsymbol{S} \rangle$ must adjust so that their sum is $\langle \boldsymbol{J} \rangle$. After this quenching process, there are n excited states Ψ_n, each with its own radiative lifetime. The following shows that the adjustment of $\langle \boldsymbol{S} \rangle$ and $\langle \boldsymbol{N} \rangle$ determines the coherence time for the excited state.

The interaction between $\boldsymbol{S}$ and $\boldsymbol{N}$ is part of the coarse structure, while that between $\boldsymbol{S}$ and $\boldsymbol{L}$ is of the order of the bunch structure. Therefore $|\langle \boldsymbol{L} \rangle|$ must be much less than $|\langle \boldsymbol{N} \rangle|$ and $|\langle \boldsymbol{S} \rangle|$ and the relation $\langle \boldsymbol{J} \rangle = \langle \boldsymbol{N} \rangle + \langle \boldsymbol{S} \rangle$ must be a good approximation at all times. With this approximation we derive from the vector model

$$\langle \boldsymbol{S} \rangle = \pm(2N+1)^{-1} \langle \boldsymbol{J} \rangle \,, \tag{5}$$

where the plus sign is for $J = N + 1/2$ and the minus sign for $J = N - 1/2$.

We replace the interaction of $\boldsymbol{S}$ with $\boldsymbol{L}$ by an effective hamiltonian

$$H_{\mathrm{eff}} = -\gamma \boldsymbol{S} \cdot \boldsymbol{B}_1(t) \,, \tag{6}$$

which is assumed to act on only one level Ψ_n. Here $\boldsymbol{B}_1(t)$ is a time dependent magnetic field acting on the magnetic moment associated with the electron spin $\boldsymbol{S}$ and γ is the gyromagnetic ratio. The motion of the total angular momentum $\boldsymbol{J}$ of the molecule in a particular state Ψ_n placed in an external magnetic field B_0 (lying along the z axis) is described by the Bloch equation [10]

$$\mathrm{d}\langle J\rangle \mathrm{d}t = (g\beta/\hbar)[\langle J\rangle \times B(t)] - (1/\tau_R)[\langle J\rangle - \langle J\rangle_0] , \quad (7)$$

where

$$B(t) = B_0\hat{z} \pm (\gamma\hbar/g\beta)(2N+1)^{-1} \times [B_{1x}(t)\hat{x} + B_{1y}(t)\hat{y} + B_{1z}(t)\hat{z}] . \quad (8)$$

In eq. (7) τ_R is the radiative lifetime of the state Ψ_n and $\langle J\rangle_0$ the equilibrium value of $\langle J\rangle$ toward which the system relaxes under the action of the radiative decay only. Because spontaneous emission is an isotropic process, the transverse and longitudinal relaxation times in the absence of collisions are the same, namely, τ_R.

In order to discuss how $\langle J\rangle$ develops in time we distinguish the effect of the x, y, and z components of the field $B_1(t)$. The $B_{1z}(t)$ component causes the precession rate of $\langle J\rangle$ around B_0 to be faster or slower than determined by B_0 alone. Because we have an ensemble of molecules that have been excited at different times, this introduces a spread in the precession frequency $\omega_0 = (g\beta/\hbar)B_0$ by an amount $\delta\omega = \pm\gamma\bar{B}_{10}/(2N+1)$ and contributes to a destruction of the coherence of the precessing angular momentum $\langle J\rangle$. Here $\bar{B}_{10}$ is the Fourier component of $B_{1z}(t)$ in the frequency domain corresponding to the reciprocal of the energy spread in the bunch structure. A coherence lifetime τ_C can be defined by the relation that $|\delta\omega\tau_C| = 1$. Thus we find that

$$1/\tau_C = |\gamma|\bar{B}_{10}/(2N+1) . \quad (9)$$

The z component of $B_1(t)$ does not affect the component $\langle J_z\rangle$ but only the transverse components $\langle J_x\rangle$ and $\langle J_y\rangle$. On the other hand, the x and y components of $B_1(t)$ combined with $B_0\hat{z}$ can change all three components of $\langle J\rangle$. These transverse components of $B_1(t)$ introduce transitions between the magnetic sublevels, shortening the coherence time. We have assumed in the present treatment that the radiative lifetime τ_R is long compared to the dephasing time due to the presence of the bunch structure. Therefore we have associated the disorientation rate $1/\tau_C$ with the expression given in eq. (9) which depends only on $\bar{B}_{10}$; in a more complete treatment, we must also include the contribution from the spontaneous emission to $1/\tau_C$.

To appreciate the above, we consider the special case where $\langle J\rangle_0$ has only the value $\langle J_z\rangle_0$. We further assume that the transverse components of $B_1(t)$ can be approximated by a rotating magnetic field of frequency ω and amplitude $\bar{B}_{10}$, while the longitudinal component of $B_1(t)$ can be neglected. Then the steady-state solution of the Bloch equation [eq. (7)] in a rotating frame (designated here by a prime) with frequency ω is well known [9]. In particular, the y' component of $\langle J'\rangle$ has the solution

$$\langle J'_y\rangle = \langle J_z\rangle_0 \frac{\omega_1\tau_R}{1 + (\omega-\omega_0)^2\tau_R^2 + \omega_1^2\tau_R^2} , \quad (10)$$

where $\omega_1 = \gamma\bar{B}_{10}/(2N+1)$. Eq. (10) gives the following transverse relaxation rate, $1/T_2$, for $\langle J'_z\rangle$

$$(1/T_2)^2 = (1/\tau_R)^2 + \omega_1^2 . \quad (11)$$

Neglecting the spontaneous emission rate, we once again recover eq. (9), where we identify the transverse relaxation rate with $1/\tau_C$.

3. Discussion

The model described here predicts a coherence lifetime that depends on the excited state rotational quantum number N in the following way

$$\tau_C = \tau_0(2N+1) . \quad (12)$$

Here $1/\tau_0 = |\gamma|\bar{B}_{10}$ expresses the rate with which the interaction term V removes the degeneracy of the initial prepared state Ψ_0. We now analyze the previous Hanle effect data using eq. (12) and the expression for the g factor [4]

$$|g(N)| = 2.002/(2N+1) , \quad (13)$$

where eq. (13) neglects hyperfine structure. Table 1 summarizes the results. We find that the measured values of the product $g\tau_C$ are independent of the quantum number N, as predicted by eqs. (12) and (13). Furthermore, the values of τ_0 are the same within a given study, the average value for the yellow-red region being 0.5 μs and for the blue-green region 0.09 μs. Presently, we do not know whether the difference in the τ_0 values for the two studies represents the different behavior of the molecule as a function of excitation energy or reflects the different experimental approaches to the measurement of the Hanle effect. From τ_0 we can estimate the order of magnitude of the bunch structure from the approximate expression

$$\tau_0|\langle\Psi_0|V|\Psi_0\rangle| = \hbar , \quad (14)$$

since we can relate $\gamma\hbar\bar{B}_{1z}$ to $\langle\Psi_0|V|\Psi_0\rangle$. Accordingly,

Table 1
Hanle effect data of refs. [4,5]

Band (A)	N'	K'_a	$g\tau_C(10^{-7}$ s)	$\tau_0(10^{-7}$ s)
5933	3	0	21 ± 12	10.5 ± 6
5933	3	0	13 ± 5	6.5 ± 3
5933	3	1	13 ± 1	6.5 ± 0.5
5933	15	0	7.6 ± 1.2	3.8 ± 0.6
6117	17	0	11 ± 1	5.5 ± 0.5
6117	17	1	8.8 ± 1.9	4.4 ± 1
6117	17	1	9.1 ± 1.7	4.6 ± 0.9
6125	7	1	7.3 ± 0.4	3.6 ± 0.2
6125	13	1	11 ± 1	5.5 ± 0.5
6125	22	1	9.5 ± 0.9	4.8 ± 0.5
6126	3	1	6.5 ± 0.4	3.3 ± 0.2
6126	6	1	10 ± 3	5.0 ± 1.5
6126	8	1	9.0 ± 0.4	4.5 ± 0.5
5145	4		1.7 ± 0.1	1.0 ± 0.5 a)
5145	4		1.8 ± 0.1	0.93 ± 0.5 a)
5145	4		1.7 ± 0.1	0.69 ± 0.5 a)
5145	9		1.7 ± 0.1	0.86 ± 0.5 a)
5145	9		1.7 ± 0.1	0.95 ± 0.5 a)
5145	6		1.7 ± 0.1	0.85 ± 0.5 a)
4880	11		1.5 ± 0.2	0.75 ± 0.1
4880	11		1.7 ± 0.2	0.85 ± 0.1

a) For these measurements to deduce τ_0 we use the g factor given in ref. [5], which takes into account the particular hyperfine component excited.

this interaction matrix element is of a few MHz in magnitude.

The bunch structure is introduced phenomenologically since the conventionally assumed structure of the NO_2 molecule fails to explain the difference between coherence and radiative lifetime. We find that the postulation of the bunch structure (1) explains the difference between τ_C and τ_R, (2) predicts the observed rotational dependence of τ_C, and (3) does not contradict the highest resolution spectrum of the NO_2 visible system [10,11]. Moreover, this model avoids the necessity of introducing a dense background structure to describe intramolecular dephasing as done in the statistical limit for large polyatomic molecules [8].

One possible rationalization of the bunch structure starts from a consideration of the asymmetric distortion of the molecule in the excited state which appears to make the two NO bond lengths in the NO_2 molecule different on the average, corresponding to the mixing of $^2A_1$ and $^2B_2$ character [12]. In the excited state this molecule can therefore be regarded as having two identical nuclei occupying two nonequivalent sites. The equivalence of the two identical nuclei is established by tunneling or hopping so that each nucleus can occupy both sites. This process can be described as a large amplitude motion which makes the molecule oscillate (or rotate) between two configurations which differ only by an exchange of the two identical nuclei and an overall rotation of the molecule [13]. It is this internal motion, which introduces the bunch structure (obviously a doublet structure) and which produces the internal angular momentum $\langle L \rangle$.

Thus the prepared state Ψ_0 is not a stationary state but evolves under the action of V into two stationary states Ψ_n ($n = 1, 2$), which may have different radiative lifetimes τ_R, in agreement with reports of non-exponential decay [1], and which also may give rise to quantum beats on a time scale of 0.1 μs. The time τ_0, defined in eq. (14), characterizes the "lifetime" of the non-stationary state. We find that τ_0 is shorter than τ_C because the rotational angular momentum N, which to a first approximation is unaffected by the interaction V (V causes predominantly the coupling of L with S), acts like a reservoir of orientation and coherence for the total angular momentum. Since the bunch structure is more than two orders of magnitude smaller than the coarse structure, it effects negligibly the qualities of the coarse structure, for instance the quantum numbers N and S and the g factor. On the other hand, its presence causes the molecule to dephase itself on a time τ_C shorter than the radiative time τ_R.

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