Explanation of unexpected results with the use of a time-asymmetric evolution in a free molecule

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Recent experiments ("inversion effect") on the free NO_2 molecule reveal unexpected results which are in contradiction to our knowledge on the properties of a small molecule. Making an unconventional assumption on the time evolution of the free NO_2 molecule, we are able to describe these experimental results consistently.

I. INTRODUCTION

In a previous paper (Ref. 1) we reported on a new effect which is observed when the small polyatomic molecule NO_2 is prepared into an electronically excited state by light absorption. As the intensity of the exciting laser light is varied, the degree of polarization of the fluorescence light may undergo a change in sign. We named this effect "inversion effect." It is observed on a collision-free molecule interacting with a narrow-band laser. The conditions of the experiment are such that to all our knowledge the molecule is prepared into a single, isolated and well-defined quantum state. However, the experimental results are in contradiction to our knowledge of the properties and the dynamical behavior of a molecule in a pure quantum state having only spatial degeneracy, because the inversion effect cannot be explained for such a system. This follows from all the experience with laser spectroscopy on atoms and molecules where an effect such as reported in Ref. 1 was never observed (see, for instance, Refs. 2—5). In the accompanying paper (Ref. 6) we describe another experiment on the NO_2 molecule, which confronts us again with the same situation. The experimental results are unexpected and cannot, in our opinion, be explained conventionally.

We conclude from these results that in contradiction to our "knowledge" a more complicated level structure must be assumed in this molecule. Therefore the following physical situation is considered. Laser light induces a transition from the ground state $|a\rangle$ to an excited state $|b\rangle$. However, before $|b\rangle$ decays radiatively the free molecule evolves in an intramolecular process from $|b\rangle$ to a state $|c\rangle$. The fluorescence decay of $|c\rangle$ is observed. We show that the additional assumption of an irreversible evolution of the molecule from $|b\rangle$ to $|c\rangle$ yields a consistent description of the experimental results reported in Refs. 1 and 6.

Irreversibility may be introduced conventionally (see, for instance, Ref. 7) assuming that underlying $|c\rangle$ is a manifold of states sufficiently large to serve as its own thermal bath during the lifetime of the optically excited molecule. However, NO_2 is supposed to have a sparse level structure. Using a narrow-band laser and molecular-beam conditions as in the experiments in Refs. 1 and 6, we expect a situation similar to that of atoms, namely,

preparation of the molecule into a single isolated quantum state and the subsequent radiative decay of this prepared state. It is therefore a contradiction of our knowledge of this molecule to introduce in a conventional way a manifold of states capable of causing an irreversible evolution. Nevertheless, the experimental results in Refs. 1 and 6 seem to be well described by this assumption, and no other explanation seems feasible. We therefore postulate a very unconventional interpretation of the manifold of states associated with the irreversible evolution.

II. THE MODEL

We consider the following situation. Laser light induces a transition from the ground state $|a\rangle$ of the molecule to an excited state $|b\rangle$. However, before $|b\rangle$ decays radiatively the free molecule evolves in an intramolecular process from $|b\rangle$ to a state $|c\rangle$. To describe this situation we assume the Hamiltonian $H = H_0 + V + G + B$. Here $H_0 + V$ is the Hamiltonian of the free molecule, G represents the interaction with the light field of the laser, and B represents the interaction with external magnetic fields. We treat the light field of the laser as classical field and describe the effect of spontaneous emission phenomenologically. The states $|u\rangle = \{|a\rangle, |b\rangle, |c\rangle\}$ with the magnetic sublevels

$$|u,m\rangle = \{|a,m\rangle, |b,m\rangle, |c,m\rangle\}$$

are eigenstates of H_0 with $H_0|u\rangle = E_u|u\rangle$. We assume $E_a < E_b = E_c$. The standard quantum-mechanical equations of motion of an ensemble of molecules represented by the Hamiltonian H in the subspace of states $\{|a\rangle, |b\rangle, |c\rangle\}$ are as follows:

$$\frac{d}{dt}\rho_{uu'}^{mm'} = -\frac{i}{\hbar}(E_u - E_{u'})\rho_{uu'}^{mm'} - \frac{i}{\hbar}\langle u,m |[V,\rho]| u',m'\rangle$$

$$-\frac{i}{\hbar}\langle u,m |[G,\rho]| u',m'\rangle$$

$$-\frac{i}{\hbar}\langle u,m |[B,\rho]| u',m'\rangle$$

$$-\gamma_{uu'}(\rho_{uu'}^{mm'} - \rho^0\delta_{u,a}\delta_{u',a}\delta_{m,m'}) . \tag{2.1}$$

Here $\rho_{\mu\mu'}^{mm'} = \langle u,m |\rho| u',m'\rangle$ designates the density matrix elements. In the above equations the damping term with $\gamma_{uu'}$ describes the effect of spontaneous emission and

also, for $u=u'=a$, the initial state of the molecule without interaction with external fields.

The investigations in Ref. 1 show that it is necessary to assume an irreversible evolution of the molecule from $|b\rangle$ to $|c\rangle$ in order to explain the inversion effect. To introduce irreversibility into the equations of motion we assume that underlying $|c\rangle$ is a manifold of states and $|c\rangle$ represents an average over this manifold. We do not consider this averaging process here. We introduce a modification of the equations of motion and we consider this modification as a result of an unknown averaging process over a manifold of states.

We proceed as follows. We associate the evolution of the molecule from $|b\rangle$ to $|c\rangle$ with the interaction V which is now an average quantity like $|c\rangle$. We assume the properties

$$\langle u,m \,|\, V \,|\, u',m'\rangle = \hbar V_{uu'}\delta_{mm'} \,,$$
$$\tag{2.2}$$
$$V_{ab}=V_{ac}=0, \quad V_{bc}\neq 0 \,.$$

Furthermore, we assume that Eqs. (2.1) for $(d/dt)\rho_{uu'}^{mm'}$ are formally not changed for $u'=u$ but only for $u'\neq u$. More precisely, the terms $\langle u,m \,|\, [V,\rho] \,|\, u',m'\rangle$ with $u'=u$ are not changed but those with $u'\neq u$ are changed. We assume the following replacements:

$$i\hbar^{-1}\langle a,m \,|\, [V,\rho] \,|\, u,m'\rangle \rightarrow \alpha_{au}\rho_{au}^{mm'} \,, \tag{2.3}$$

$$i\hbar^{-1}\langle b,m \,|\, [V,\rho] \,|\, c,m'\rangle \rightarrow \alpha_{bc}\rho_{bc}^{mm'}-iV_{bc}\rho_{bb}^{mm'} \,, \tag{2.4}$$

where $\alpha_{au}=\alpha_{ua}$ and $\alpha_{bc}=\alpha_{cb}$ are positive real numbers and $u\neq a$. These replacements mean that the effect of V on the time dependence of $\rho_{uu'}^{mm'}$ with $u\neq u'$ is phenomenologically described by a pure relaxation term except for $\rho_{bc}^{mm'}$. The term $-iV_{bc}\rho_{bb}^{mm'}$ appearing in the time dependence of $\rho_{bc}^{mm'}$ is necessary in order to describe the evolution of the molecule from $|b\rangle$ to $|c\rangle$.

The matrix elements representing the interaction with the light field of the laser are $\langle u,m \,|\, G \,|\, u',m'\rangle = \hbar G_{uu'}^{mm'}$. We assume that $G_{ac}^{mm'}=G_{bc}^{mm'}=0$ and only $G_{ab}^{mm'}\neq 0$. This means that the laser induces transitions between $|a\rangle$ and $|b\rangle$ but not between $|a\rangle$ and $|c\rangle$. This assumption is also considered in the discussion in Sec. V.

The magnetic field interaction matrix elements have the form

$$\langle u,m \,|\, B \,|\, u',m'\rangle = \hbar\omega_u m\,\delta_{m,m'}\delta_{u,u'}+\hbar B_{uu'}^{mm'}\delta_{uu'} \,. \tag{2.5}$$

The first term represents the interaction with the static magnetic field directed along the quantization axis (z axis). $\hbar\omega_u$ is the Zeeman splitting of the magnetic sublevels $|u,m\rangle$ with $u=a,b,c$. We assume in the following that $\omega_b=\omega_c$. $B_{uu'}^{mm'}$ represents the interaction with a radiofrequency field. We suppose $B_{uu'}^{mm'}=0$ for $m=m'$.

With these assumptions we obtain

$$\frac{d}{dt}=\rho_{cc}^{mm'}=-\gamma_{cc}\rho_{cc}^{mm'}-i\sum_n (B_{cc}^{mn}\rho_{cc}^{nm'}-\rho_{cc}^{mn}B_{cc}^{nm'})$$

$$-i(V_{cb}\rho_{bc}^{mm'}-\rho_{cb}^{mm'}V_{bc}) \tag{2.6}$$

and similar equations for $(d/dt)\rho_{aa}^{mm'}$ and $(d/dt)\rho_{bb}^{mm'}$. The conditions for irreversibility [Eqs. (2.3) and (2.4)] appear only in the matrix elements off diagonal in u:

$$\frac{d}{dt}\rho_{ab}^{mm'} = -Z_{ab}^{mm'}\rho_{ab}^{mm'}-i\sum_n (G_{ab}^{mn}\rho_{bb}^{nm'}-\rho_{aa}^{mn}G_{ab}^{nm'})$$

$$-i\sum_n (B_{aa}^{mn}\rho_{ab}^{nm'}-\rho_{ab}^{mn}B_{bb}^{nm'}) \,, \tag{2.7}$$

$$\frac{d}{dt}\rho_{ac}^{mm'} = -Z_{ac}^{mm'}\rho_{ac}^{mm'}-i\sum_n G_{ab}^{mn}\rho_{bc}^{nm'}$$

$$-i\sum_n (B_{aa}^{mn}\rho_{ac}^{nm'}-\rho_{ac}^{mn}B_{cc}^{nm'}) \,, \tag{2.8}$$

$$\frac{d}{dt}\rho_{bc}^{mm'} = -Z_{bc}^{mm'}\rho_{bc}^{mm'}+iV_{bc}\rho_{bb}^{mm'}-i\sum_n G_{ba}^{mn}\rho_{ac}^{nm'}$$

$$-i\sum_n (B_{bb}^{mn}\rho_{bc}^{nm'}-\rho_{bc}^{mn}B_{cc}^{nm'}) \,, \tag{2.9}$$

$$Z_{uu'}^{mm'} = i\hbar^{-1}(E_u-E_{u'})+i(m\omega_u-m'\omega_{u'})+\Gamma_{uu'} \,, \tag{2.10}$$

where $\Gamma_{uu'}=\gamma_{uu'}+\alpha_{uu'}$ with $u\neq u'$, and $Z_{bc}^{mm}=\Gamma_{bc}$. We use these equations in the following to derive two phenomena, the inversion effect and the broad rf resonance.

III. INVERSION EFFECT

The following experimental situation is considered here (see Ref. 1). A beam of NO_2 molecules is propagating along the z axis in an x,y,z coordinate system. We idealize the molecular beam assuming that all molecules have the same velocity $\mathbf{v}=v_z$. The molecules are considered to be free. Any interaction between the molecules and the environment is neglected. A laser beam (cw single-mode laser) crosses the molecular beam at a right angle. The diameter of the laser beam defines the transit time T_L of the molecules through the light field of the laser. T_L is in general shorter than the lifetime of the molecules in the electronically excited state. We define an observation volume with an extension along the molecular beam which covers the interaction volume with the light field of the laser and which is also sufficiently large so that all excited molecules decay radiatively within this volume. The laser light is linearly polarized parallel to the quantization axis (the z axis). The interaction matrix elements are $G_{ab}^{mm'}=0$ for $m\neq m'$. An external static magnetic field directed along the z axis causes a Zeeman splitting $\hbar\omega_u$ of the magnetic sublevels $|u,m\rangle$ with $u=a,b,c$. There is no radiofrequency field. Thus we have $B_{uu'}^{mm'}=0$.

We consider a stationary-state situation. As many molecules enter into the observation volume as are leaving it. The laser light is continuously turned on and the molecules interact all the time with the static magnetic field. To obtain the stationary-state solutions of the equations of motion under these conditions we proceed as follows. Integration of Eq. (2.9) yields $\rho_{bc}^{mm'}(t)$ as a function of $\rho_{bb}^{mm'}(t)$ and $\rho_{ac}^{mm'}(t)$. Integration of Eq. (2.8) gives $\rho_{ac}^{mm'}(t)$ as a function of $\rho_{bc}^{mm'}(t)$. From both equations we obtain with the initial condition $\rho_{bc}^{mm'}(-\infty)=0$, and similar conditions for the other matrix elements,

$$\rho_{bc}^{mm'}(t)=i\int_{-\infty}^t ds\,V_{bc}(s)\rho_{bb}^{mm'}(s)$$

$$\times\exp[-\Gamma_{bc}(t-s)]+K_m \,, \tag{3.1}$$

$$K_m = -\exp[-\Gamma_{bc}(t-t')]$$

$$\times \int_{t'-T_L}^{t'} ds \int_{-\infty}^{0} dr\, G_{ba}^{mm}(s)G_{ab}^{m}(s+r)\rho_{bc}^{mm}(s+r)$$

$$\times \exp[-\Gamma_{bc}(t'-s)+rZ_{ac}^{mm}] . \tag{3.2}$$

Here we take into account that the molecules interact with the light field only in the time interval $t'-(t'-T_L)$. Next we introduce two simplifications. First, it is assumed that $V_{bc}(s)$ is time independent. Second, we neglect the correlation between $G_{ba}^{mm}(s)$ and $G_{ab}^{mm}(s+r)$ on the one hand, and $\rho_{bc}^{mm}(s+r)$ on the other hand, and insert the first-order correlation function (see, for instance, Ref. 8),

$$G_{ba}^{mm}(s)G_{ab}^{mm}(s+r) = |G_{ab}^{mm}|^2 \exp[-|r|(i\omega_L+b_L)] , \tag{3.3}$$

into Eq. (3.2) Here ω_L is the circular frequency of the laser light and b_L the spectral width of the laser light as seen by the molecules during the transit time T_L.

The second simplification means that we separate the interaction of the molecule with the light field into two independent processes. In a first interaction the molecule is prepared into the state $|b\rangle$. The density matrix elements ρ_{bb}^{mm} are created. Subsequently the molecule experiences the interaction V which drives it into the state $|c\rangle$ as well as a second interaction with the radiation field. The second interaction is operative as long as coherence exists between $|b\rangle$ and $|c\rangle$.

$\rho_{bc}^{mm}(t)$ as given by Eq. (3.1) is a solution of the equations of motion at the time t when the molecules were interacting with the light field at the time t' before. The stationary-state solution (we represent it by ρ_{bc}^{mm} here) is obtained by averaging over the explicit dependence on t' and by replacing $\rho_{bc}^{mm}(t)$ and $\rho_{bb}^{mm}(t)$ in the integrals by the stationary-state solutions ρ_{bc}^{mm} and ρ_{bb}^{mm}. This gives

$$\rho_{bc}^{mm} = iV_{bc}\rho_{bb}^{mm} \int_{-\infty}^{t} ds\, \exp[-\Gamma_{bc}(t-s)]$$

$$-\rho_{bc}^{mm}|G_{ab}^{mm}|^2\Gamma_{bc} \int_{-\infty}^{t} dt'\exp[-\Gamma_{bc}(t-t')] \int_{t'-T_L}^{t'} ds \int_{-\infty}^{0} dr\, \exp[-\Gamma_{bc}(t'-s)+r(Z_{ac}^{mm}+i\omega_L+b_L)] . \tag{3.4}$$

In averaging over t' we multiplied Eq. (3.2) with the statistical weight $\Gamma_{bc}dt'$.

Similarly, Eq. (2.6) gives $\gamma_{cc}\rho_{cc}^{mm} = -iV_{cb}\rho_{bc}^{mm}+\text{c.c.}$ where c.c. means conjugate complex. Thus we obtain

$$\rho_{cc}^{mm} = \rho_{bb}^{mm}(\lambda_m/\gamma_{cc}) , \tag{3.5}$$

$$\lambda_m = \frac{|V_{bc}|^2}{\Gamma_{bc} + \dfrac{|G_{ba}^{mm}|^2[1-\exp(-\Gamma_{bc}T_L)]}{Z_{ac}^{mm}+i\omega_L+b_L}} + \text{c.c.} \tag{3.6}$$

The experimental results in Ref. 1 were described starting from a system of rate equations for the sublevels $|a,m\rangle$, $|b,m\rangle$, and $|c,m\rangle$. These rate equations are in agreement with the present results. Using similar simplifications as in the derivation of Eqs. (3.5) and (3.6) we obtain

$$\dot{a}_m = -\gamma_{aa}(a_m-\rho^0)+\gamma_m b_m-\gamma_m a_m ,$$

$$\dot{b}_m = -\gamma_{bb}b_m+\gamma_m a_m-\gamma_m b_m-\lambda_m b_m , \tag{3.7}$$

$$\dot{c}_m = -\gamma_{cc}c_m+\lambda_m b_m ,$$

with $a_m=\rho_{aa}^{mm}$, $b_m=\rho_{bb}^{mm}$, and $c_m=\rho_{cc}^{mm}$ if $\dot{a}_m=\dot{b}_m=\dot{c}_m=0$. γ_m can be written approximately as (for $\Gamma_{bc}T_L \gtrsim 1$)

$$\gamma_m = |G_{ab}^{mm}|^2(Z_{ab}^{mm}+i\omega_L+b_L)^{-1}+\text{c.c.} \tag{3.8}$$

To have full agreement with the equations used in Ref. 1 it is necessary to assume that the laser light is tuned to resonance, for instance $Z_{ac}^{mm}+i\omega_L+b_L=\Gamma_{ac}+b_L$, and that the term $\gamma_{bb}\rho_{bb}^{mm}$ describing radiative decay of the sublevel $|b,m\rangle$ can be neglected.

Equation (3.6) and (3.7) describe the inversion effect in complete detail, as a comparison with Eqs. (3)—(6) of Ref. 1 shows. The inversion effect is a consequence of the

dependence of λ_m on the light intensity and on the quantum numbers m, i.e., on $|G_{ab}^{mm}|^2$. Due to this dependence the occupation probability distribution for the ρ_{bb}^{mm} and the ρ_{cc}^{mm} may be "inverse" to each other for high light intensities. Equation (3.6) shows that the inversion effect also depends strongly on the transit time T_L of the molecules through the light field. It disappears for $\Gamma_{bc}T_L < 1$. Also, this result is in good agreement with the experiments. According to Eqs. (3.7) λ_m may be interpreted as decay rate of $|b,m\rangle$ into $|c,m\rangle$. Increasing light intensity decreases this decay rate. We name this phenomenon "light-induced stabilization" of the state $|b\rangle$. Obviously, the state $|b\rangle$ gains stability from the interaction with the light field of the laser.

We note that the calculation is performed with a light field having only one frequency ω_L. In Eq. (3.5), for instance, this frequency determines the resonance in ρ_{bb}^{mm} and λ_m. The explicit dependence on ω_L is only calculated for λ_m here. In the experiments we need to average over all frequencies ω_L which a molecule sees when it passes through the light field of the laser. It follows immediately that the stabilization effect is only strong if the interaction with the light field is simultaneously resonant in ρ_{bb}^{mm} and in λ_m. As a consequence the stabilization effect depends very critically on the divergence of the light beam which the molecules fly through during the transit time T_L. The effects connected with the divergence of the light beam are discussed in Ref. 6. Also, the broad rf resonance which we describe in Sec. IV is connected with resonant interaction of the light field in the term λ_m. The effects connected with the divergence of the light beam can therefore best be studied on this resonance. However, the total fluorescence intensity (the term $\sum_m \rho_{cc}^{mm}$) also depends strongly on the divergence of the light beam as a consequence of the stabilization effect.

IV. THE BROAD rf RESONANCE

The experimental situation is the same as in Sec. III, except that the molecules interact additionally with a rf field. The magnetic field interaction matrix elements are given by Eq. (2.5) with $B_{uu}^{mm'}=0$ for $m=m'$. Our aim is to evaluate the quantity $P=\sum_m \rho_{cc}^{mm}$ under stationary-state conditions. The calculation proceeds in the same way as in Sec. III. Equation (2.6) yields $\gamma_{cc}P = -iV_{cb}\sum_m \rho_{bc}^{mm}+$c.c. because the term $\sum_{m,n}(B_{cc}^{mn}\rho_{cc}^{nm} -\rho_{cc}^{mn}B_{cc}^{nm})$ is identically zero. This term describes magnetic resonance in the sublevels $|c,m\rangle$. However, these rf-field-induced transitions do not change the total occupation probability P of $|c\rangle$. Integration of Eq. (2.9) gives

$$\sum_m \rho_{bc}^{mm}(t)=i\sum_m \int_{-\infty}^t ds\, V_{bc}(s)\rho_{bb}^{mm}(s)$$

$$\times \exp[-\Gamma_{bc}(t-s)]+Y\,, \quad (4.1)$$

$$Y=-i\sum_m \exp[-\Gamma_{bc}(t-t')]$$

$$\times \int_{t'-T_L}^{t'} ds\, G_{ba}^{mm}(s)\rho_{ac}^{mm}(s)$$

$$\times \exp[-\Gamma_{bc}(t'-s)]\,. \quad (4.2)$$

Here we used $\omega_b=\omega_c$ and therefore $B_{bb}^{mn}=B_{cc}^{mn}$. The matrix elements $\rho_{ac}^{mm}(s)$ can be written as a function of $\rho_{bc}^{mm}(s)$, $\rho_{ac}^{nm}(s)$, and $\rho_{ac}^{mn}(s)$ using Eq. (2.8). We assume that $\rho_{ac}^{nm}(s)$ and $\rho_{ac}^{mn}(s)$ are functions of $\rho_{ac}^{mm}(s)$ and $\rho_{ac}^{nn}(s)$ only. This approximation is permissible for low rf-field powers because it means neglecting higher-order terms in the rf-field power. Furthermore, we also neglect terms containing the product $B_{aa}^{mn}\rho_{ac}^{nn}B_{cc}^{nm}$. This is permissible if we assume that the Zeeman splitting in the states $|a\rangle$ and $|c\rangle$ is sufficiently different so that magnetic resonances simultaneously in $|a\rangle$ and $|c\rangle$ can be excluded. However, we note here that this condition may not be fulfilled if the g factors of the ground and excited state are very close or if experiments are performed at low magnetic fields. Under these conditions the term $B_{aa}^{mn}\rho_{ac}^{nn}B_{cc}^{nm}$ may cause a shift (an attraction of rf resonances in the ground and excited state of the laser-induced transition) of the magnetic resonance. Finally, we obtain an integral for $\rho_{ac}^{mm}(s)$ containing the three terms $G_{ab}^{mm}(s)\rho_{bc}^{mm}(s)$, $B_{aa}^{mm}(s)B_{aa}^{nm}(s)\rho_{ac}^{mm}(s)$, and $\rho_{ac}^{mm}(s)B_{cc}^{mn}(s)B_{cc}^{nm}(s)$. By iterative approximation the $\rho_{ac}^{mm}(s)$ in the two last terms are expressed by the leading term $G_{ab}^{mm}(s)\rho_{bc}^{mm}(s)$. This result for $\rho_{ac}^{mm}(s)$ is inserted into Eq. (4.2). We write $Y=Y_1+Y_2+Y_3$ and obtain $Y_1=\sum_m K_m$ with K_m given in Eq. (3.2) and

$$Y_2=\sum_{m,n} \exp[-\Gamma_{bc}(t-t')]\int_{t'-T_L}^{t'} ds \int_{-\infty}^0 dr \int_{-\infty}^0 du \int_{-\infty}^0 dw\, G_{ba}^{mm}(s)R_{aa}^{mn}(s+r)R_{aa}^{nm}(s+r+u)G_{ab}^{mm}(s+r+u+w)$$

$$\times \rho_{bc}^{mm}(s+r+u+w)$$

$$\times \exp[-(t'-s)\Gamma_{bc}+(r+w)Z_{ac}^{mm}+uZ_{ac}^{nm}]\,. \quad (4.3)$$

Y_3 is identical with Y_2 if we replace B_{aa}^{mn} by B_{cc}^{nm} and Z_{ac}^{nm} by Z_{ac}^{mn}. We express the product of the light- and rf-field transition matrix elements by the product of the light- and rf-field correlation functions

$$|G_{ba}^{mm}|^2\exp[(r+u+w)(b_L+i\omega_L)] \quad (4.4)$$

$$\times |R_{aa}^{mn}|^2\exp\{u[b_s+i(m-n)\omega_s]\}$$

using Eq. (3.3) and a similar equation for the rf-field. Here ω_s is the circular frequency and b_s the spectral width of the rf field. r, u, and w are negative variables.

The calculation is now continued as in Sec. III. The final result is

$$P=\sum_m \rho_{cc}^{mm}=\sum_m \rho_{bb}^{mm}(\lambda_m^s/\gamma_{cc})\,, \quad (4.5)$$

$$\lambda_m^s=\frac{|V_{bc}|^2}{\Gamma_{bc}+\dfrac{|G_{ba}^{mm}|^2[1-\exp(-\Gamma_{bc}T_L)]}{Z_{ac}^{mm}+i\omega_L+b_L}(1-W_m)}+\text{c.c.}\,, \quad (4.6)$$

$$W_m=\frac{1}{(ix_m+\Gamma_{ac}+b_L)}$$

$$\times \sum_r \left[\frac{|B_{aa}^{m\,m+r}|^2}{i[x_m+r(\omega_a-\omega_s)]+(\Gamma_{ac}+b_L+b_s)}\right.$$

$$\left.+\frac{|B_{cc}^{m\,m-r}|^2}{i[x_m+r(\omega_c-\omega_s)]+(\Gamma_{ac}+b_L+b_s)}\right]\,. \quad (4.7)$$

Here $x_m=(E_a-E_c)/\hbar+m(\omega_a-\omega_c)+\omega_L$ and $r=n-m$. The rf field appears only in W_m. Without rf field we have $W_m=0$ and $\lambda_m^s=\lambda_m$, in agreement with the results in Sec. III. With the laser light tuned to optical resonance ($x_m=0$) the quantity W_m shows magnetic resonances whenever the Zeeman splitting in the ground or excited state is in resonance with the rf field, i.e., for $\omega_a=\omega_s$ and $\omega_c=\omega_s$. We name these resonances "broad rf resonances" because their width is in general bigger than the width of the ordinary optical-rf double-resonance signals, as Ref. 6 shows. We note here that $|W_m|$ is assumed to be less than 1 in consequence of the above-introduced low rf-power approximation.

For a comparison with the experiments we evaluate the quantity $S=(P-P_0)/P_0$ where $P_0=P$ for $W_m=0$. We

use an approximation for low light intensity (development of λ_m^s in powers of $|G_{ab}^{mm}|^2$ up to terms linear in $|G_{ab}^{mm}|^2$). Further, we use $b_s = 0$ because the spectral width b_s of the rf field is much smaller than the spectral width b_L of the light field. We give the result only for the resonance in the ground state ($S = S_a$),

$$S_a = \frac{[1 - \exp(-\Gamma_{bc} T_L)]}{\Gamma_{bc}} \sum_{m,r} A_m |G_{ab}^{mm}|^2 |B_{aa}^{m\,m+r}|^2 \frac{(\Gamma_{ac} + b_L)[(\Gamma_{ac} + b_L)^2 - 3x_m^2 - 2x_m r(\omega_a - \omega_s)]}{[x_m^2 + (\Gamma_{ac} + b_L)^2]^2 \{[x_m + r(\omega_a - \omega_s)]^2 + (\Gamma_{ac} + b_L)^2\}} . \quad (4.8)$$

Here $A_m = \rho_{bb}^{mm}(\sum_n \rho_{bb}^{nn})^{-1}$. The resonance connected with the excited state is simply obtained from this expression if one replaces $B_{aa}^{m\,m+r}$ by $B_{cc}^{m\,m-r}$ and ω_a by ω_c. We may assume $r = \pm 1$ because only rf-field transitions between neighboring sublevels are important.

V. DISCUSSION

From the equations of motion [Eqs. (2.6)—(2.10)] introduced in Sec. II we derived two phenomena, the inversion effect and the broad rf resonance. Both phenomena are in good agreement with the experiments reported in Refs. 1 and 6. Moreover, we do not know of any alternative description of these experimental results. This is a strong support for our assumptions. However, we are confronted with the question of how to interpret the model introduced in Sec. II.

The physical situation underlying the inversion effect and the broad rf resonance appears in our description as follows. The interaction of the molecule with the light field is separated into two processes. First the laser light induces a transition in the molecule from the ground state $|a\rangle$ to an excited state $|b\rangle$. The density matrix elements ρ_{ab}^{mm} and ρ_{bb}^{mm} are created. Being in $|b\rangle$ the molecule experiences an internal interaction which drives it away from $|b\rangle$ into the state $|c\rangle$ and simultaneously a "second" interaction with the radiation field. Only the second interaction is explicitly being considered in the calculations in Secs. III and IV. The second interaction causes coherence between $|a\rangle$ and $|c\rangle$ (the matrix elements ρ_{ac}^{mm}) as long as there is coherence between $|b\rangle$ and $|c\rangle$ (the matrix elements ρ_{bc}^{mm}). Thus the second interaction is only operative during a given coherence lifetime. The stronger ρ_{ac}^{mm} the slower is the evolution of the molecule from $|b\rangle$ to $|c\rangle$ (stabilization effect). On the other hand, the longer the molecule is in $|b\rangle$, the higher the probability for a transition into $|a\rangle$ by induced emission, because there is no electric dipole transition moment between $|a\rangle$ and $|c\rangle$. As described in Ref. 1, the inversion effect demonstrates the dependence of the stabilization effect on the orientational quantum numbers m. On the other hand, the broad rf resonance demonstrates, as described in Ref. 6, that the stabilization effect is only operative if the first and the second interactions of the molecule with the radiation field take place during a time $\Gamma_{bc}^{-1} \approx \Gamma_{ac}^{-1} \approx 3$ μs, which is short compared to the radiative decay time (≈ 30 μs) of the molecule.

A "lifetime" of about 3 μs has been expected for this molecule for a long time. Douglas noticed that the lifetime τ_R from radiative decay measurements is anomalous-

ly longer than the radiative lifetime τ_m evaluated from the integrated absorption coefficient (Ref. 9). In the spectral range of interest for us ($\lambda = 593$ nm) Donnelly and Kaufman calculated the value $\tau_m \approx 3$ μs (Ref. 10). Radiative decay measurements under molecular-beam conditions in the same spectral region yield single-exponential decay with a lifetime $\tau_R \approx 30$ μs (Ref. 11). This result for τ_R is in agreement with the widths of our optical-rf double-resonance and zero-field level-crossing (Hanle-effect) measurements on the same transitions where the broad rf resonances are also investigated (Ref. 12). Therefore two characteristic times $\tau_R \approx 30$ μs and $\tau_m \approx (\Gamma_{bc})^{-1} \approx 3$ μs have to be associated with each excited state in the spectral region near 593 nm.

We assumed that the equations of motion introduced in Sec. II are a result of an unknown averaging process over a manifold of states underlying $|c\rangle$. As mentioned in Sec. I, there is no conventional way to assume such a manifold of states in NO_2 because this molecule is supposed to have a sparse level structure (compare Refs. 13 and 14 and references given therein). We therefore interpret the assumed manifold of states as follows. As in hidden-variables theories (Ref. 15) we add a new variable L to the well known set of quantum numbers which are conventionally used to describe a pure quantum state of a molecule. We assume $L = 0$ for $|b\rangle$ and $L \neq 0$ for $|c\rangle$. If states with $L = 0$ and $L \neq 0$ are possible in the electronically excited state we assume the same for the ground state too. Thus there are states $|a\rangle$ with $L = 0$ and $|a'\rangle$ with $L \neq 0$, both having the same set of conventionally used quantum numbers. Further, we assume that the same intramolecular process which is operative between $|b\rangle$ and $|c\rangle$ is also operative between $|a\rangle$ and $|a'\rangle$. This intramolecular process is associated with a stability criterion. Prepared into a "pure" quantum-mechanical state with a given set of conventionally used quantum numbers the molecule tends irreversibly ("relaxes") toward a preferred L configuration. In an optical transition in absorption as well as in emission the L configuration is conserved because electric field dipole transitions cause a strong correlation between both states involved in the transition. If $L = 0$ is the stable L configuration in the electronic ground state of the molecule we expect that $|a\rangle$ and $|b\rangle$ have $L = 0$. But $L = 0$ may not be a stable L configuration in the electronically excited state. Therefore the molecule relaxes into $|c\rangle$ with $L \neq 0$. A radiative transition from $|c\rangle$ to the ground state of the molecule brings the molecule into a configuration with $L \neq 0$ from which it relaxes into a configuration with $L = 0$.

The meaning of L is not clear. Tentatively we may as-

sociate L with the symmetry of the molecule as we did in Ref. 16, with $L=0$ designating a symmetric configuration in which the two NO bond lengths are equal and with $L\neq 0$ designating deviations from this symmetric configuration. The characteristic time $\Gamma_{bc}^{-1}\approx 3$ μs may be associated with the lifetime of the state $|b\rangle$. This time is surprisingly long for a configurational adjustment of the molecule. We have no explanation for this. Finally, we mention that the model can be tested by further experiments. For instance, it is possible to study the process of induced emission from $|c\rangle$ to $|a'\rangle$. Some first experiments already indicate results which are in favor of the considered model.

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