Effect of inversion of polarization in laser-excited molecular beams

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In the paper by Weber, Bylicki, and Miksch [Phys. Rev. A **30**, 270 (1984)] the "inversion effect" of the Hanle and rf double-resonance signals in NO_2 molecules is explained with the questionable assumption of a "light-induced stability of the optically prepared state." We give an alternative explanation of the "inversion effect" which is based on the nonstationarity of molecular perturbation by a laser and which is consistent with the present knowledge of interaction of laser light with matter.

In recent papers (Ref. 1 and references therein) Weber and co-workers have reported on the unexpected behavior of the Hanle and double-resonance signals observed after excitation of NO_2 with laser light in the 593-nm band. A particularly unusual feature of those signals is the "inversion effect," i.e., the inversion of their signs with an increase of the intensity of the light beam and/or its diameter.

In the opinion of the authors of Ref. 1 the experimental observations may not be explained in terms of standard theories and require a novel interpretation with quite strong assumptions. A model of a molecular structure is presented where in addition to levels a and b directly perturbed by a laser, an additional hypothetical state c (or even a continuum of states) is included. The upper level b, although populated by light absorption from the lower level a, does not return radiatively to a but undergoes a radiationless irreversible transition to level c, which subsequently decays with fluorescence emission. Moreover, steady-state conditions are assumed when solving the rate equations for the populations of levels a, b, and c. The above assumptions lead the authors of Ref. 1 to a conclusion about the "light-induced stability of the optically prepared state" which is in contradiction with the present knowledge of the radiative decay of quantum states.

In this Comment we wish to present an alternative explanation of the inversion effect in terms of nonstationarity of the molecular interaction with light. Such an interpretation does not require any problematic assumptions and is consistent with the well-known principles of the interaction of laser light with matter. It offers a satisfactory qualitative explanation of the inversion effect.[1] We also believe that it plays an important role in other effects observed by Weber *et al.*[2] For the sake of brevity we concentrate here only on the inversion effect on the transition

$$|N=1,K=0,J=\tfrac{3}{2},F=\tfrac{5}{2}\rangle\text{-}|N=2,K=0,J=\tfrac{5}{2},F'=\tfrac{7}{2}\rangle$$

labeled as line 1 in Ref. 1.

Our analysis is closely related with the studies of nonstationary effects of optical pumping.[3–8] Unlike in Refs. 3–8, however, we do not make a weak-field rate-equations approximation, but solve an exact density-matrix equation. Also, because of very long lifetimes of the molecular states, the effects of a finite laser linewidth are much more important here than in the earlier works.

The key point of our treatment (and those of Refs. 3–8 as well) is the consideration of a time evolution of individual molecules moving across the laser beam rather than using the steady-state approximation and phenomenological relaxation rates to account for finite laser-beam transit times. The steady-state approximation is unjustified under the experimental conditions of Ref. 1 because the time of molecular interaction with the laser beam, i.e., the transit time, is comparable with evolution times of the perturbed molecular states.

We start from the equations for the density matrix of the NO_2 molecule interacting with a linearly π-polarized monochromatic light beam of frequency ω_L close to frequency ω_0 of the $|F,m\rangle$-$|F',\mu\rangle$ molecular transition:

$$\begin{aligned}
\dot{n}_m &= -\Gamma n_m + i\beta_{m\mu}(\rho_{\mu m}-\rho_{m\mu}) ,\\
\dot{n}_\mu &= \Gamma' \sum_{m'} p_{m'\mu} n_{m'} - i\beta_{m\mu}(\rho_{\mu m}-\rho_{m\mu}) ,\\
\dot{\rho}_{m\mu} &= \left[i\delta - \frac{\Gamma}{2} \right] \rho_{m\mu} + i\beta_{m\mu}(n_\mu - n_m) ,
\end{aligned} \tag{1}$$

where n_m and n_μ are the populations of the magnetic sublevels of the excited and ground states, respectively, and $\rho_{m\mu}$ is the off-diagonal density-matrix element (optical coherence) between sublevels m and μ; Γ denotes spontaneous emission rate from the upper level F to all possible lower levels, whereas Γ' is the rate of spontaneous emission at the transition F-F'; $\delta=\omega_L-\omega_0$; $p_{m\mu}$ is the relative transition probability between a given pair (m,μ) ($\sum_\mu p_{m\mu}=1$ for each value of m); and $\beta_{m\mu}$ denotes the Rabi frequencies for the transitions $|F,m\rangle$-$|F',\mu\rangle$ ($\beta_{m\mu}=\beta\sqrt{p_{m\mu}}$, β being the Rabi frequency of the F-F' transition).

As mentioned earlier, there are no phenomenological relaxation constants in Eqs. (1) associated with a finite laser-beam transit time. Transit-time effects are fully accounted for when performing ensemble averaging of the solutions of Eqs. (1) over the velocity distribution.[4–7]

The time-dependent solutions of Eqs. (1) describe the dynamics of the evolution of the molecular populations. We assume that at $t=0$ the molecule is exclusively in its ground state [$n_\mu(t=0)=1$] and all elements $\rho_{m\mu}(t=0)$ and

$n_m(t=0)=0$. It is noteworthy that molecular systems, because of a wealth of states to which the excited state may decay, usually have $\Gamma' \ll \Gamma$, so that a spontaneous-emission repopulation of the ground state may be neglected. Under such conditions the solution of Eqs. (1) is particularly simple because the complex molecular system of the F and F' states may be decomposed into $2F+1$ two-level subsystems (m,μ) which can be then solved analytically yielding the well-known oscillating solutions (Rabi nutation) for $\beta_{m\mu} > \Gamma/2$ and nonoscillating aperiodic $n_m(t)$ dependence for $\beta_{m\mu} \leq \Gamma/2$.

The evolution of a molecular system under laser irradiation depends mainly upon the time and strength of the interaction with laser light and on the molecular structure, in particular on the specific values of $p_{m\mu}$ (and $\beta_{m\mu}$) for different μ. Figure 1 shows the time dependence of the excited-state populations of an individual molecule obtained from Eqs. (1) for the $|F=\frac{5}{2}\rangle$-$|F'=\frac{7}{2}\rangle$ transition (line 1 in Ref. 1) with $\Gamma=100\Gamma'$ and for $\beta=\Gamma$ [Fig. 1(a)] and $\beta=4\Gamma$ [Fig. 1(b)]. The amplitudes of signals observed in Ref. 1 are related with the quantity

$$S \propto (4N_{1/2}+N_{3/2}-5N_{5/2})/(N_{1/2}+N_{3/2}+N_{5/2}) ,$$

where N_m are the ensemble-averaged populations. For better visualization of the inversion effect we have plotted in Fig. 1 the time dependences of $4\bar{n}_{1/2}+\bar{n}_{3/2}$ and $5\bar{n}_{5/2}$, rather than each population $\bar{n}_m(t)$ ($\bar{n}_m$ denotes the Doppler-averaged population n_m).

Figure 1 shows that just after the molecule has entered the laser beam at $t=0$ the upper-state sublevels with smaller value of $|m|$ are excited faster than those with large $|m|$ because of different $p_{m\mu}$'s (on the contrary, for the $F \rightarrow F$ transition the levels with higher $|m|$ are populated faster). According to Ref. 1 such an alignment of the upper state yields negative rf double-resonance and positive Hanle signals (when the resonant rf field saturates transitions between sublevels m, all n_m are equal and $S=0$). After an initial buildup of the excited-state populations they start to decrease either because of an oscillatory behavior of $n_m(t)$ in the Rabi regime ($\beta_{m\mu} > \Gamma/2$) or because of the lower-state depletion due to optical pumping to all lower-lying molecular states not directly perturbed by the laser if $\beta_{m\mu} \leq \Gamma/2$. If the optical excitation is weak [Fig. 1(a)] or lasts only for a brief period of time with respect to the radiative decay of the upper state [e.g., T_1 in Fig. 1(b)], the upper-state alignment does not reverse its sign. The situation changes, however, when the intensity of the light and/or the interaction time increases so much that the Rabi oscillation for a given (m,μ) enters its second half-period, or in the case of $\beta_{m\mu} \leq \Gamma/2$, when the lower state becomes appreciably depleted during the interaction. In such cases the upper-state sublevels which were initially mostly populated, i.e., those with small $|m|$, are weaker populated than those with large $|m|$ for which $\beta_{m\mu}$ is smaller [see $n_m(T_2)$ in Fig. 1(b)]. This result obviously disagrees with the conclusion of Ref. 1 that the inversion of population distribution will never appear for the upper state of an optical transition and proves that the inversion of the upper-state alignment may be explained without any unusual assumptions on the molecular structure and dynamics. Still, a direct comparison of the results of our analysis with the observations of Weber *et al.*[1] requires some attention. Firstly, in the nonoscillatory regime the inversion effect is predicted by our model for $t > 1/\Gamma$, whereas the experimental results indicate that it happens when $t < 1/\Gamma$. It is interesting that a possible prealignment of the ground molecular state (e.g., due to collisions in the beam nozzle) can shift the onset of the inversion effect towards time shorter than $1/\Gamma$, but under the conditions of Ref. 1 there was no evidence of such prealignment.[9] Secondly, in the Rabi regime with exactly monochromatic light many inversions are possible since the curves representing oscillating $4n_{1/2}(t)+n_{3/2}(t)$ and $5n_{5/2}(t)$ may intersect many times within the interaction time t, provided that t and β are appropriately large, whereas only single inversions were observed in Ref. 1. It has to be noted, however, that Eqs. (1) describe an individual molecule interacting with monochromatic laser light. Therefore, a proper averaging procedure is necessary to make the above results comparable with the experiment of Weber *et al.*[1] where not perfectly monochromatic laser was used and the molecular beam was not collimated which resulted in an inhomogeneous broadening of not less than 50 MHz. Assuming a phase-diffusion model of the interaction with a laser of a finite bandwidth,[10] we can average the density-matrix equations (1) over the laser fluctuations, and integrate its solutions over the residual Doppler distribution of δ. Details of such averaging need not be discussed here. The important result which follows is a considerable smoothing of the oscillatory structure in the $n_m(t)$ dependence after the first maximum, i.e., after about the first period of Rabi nuta-

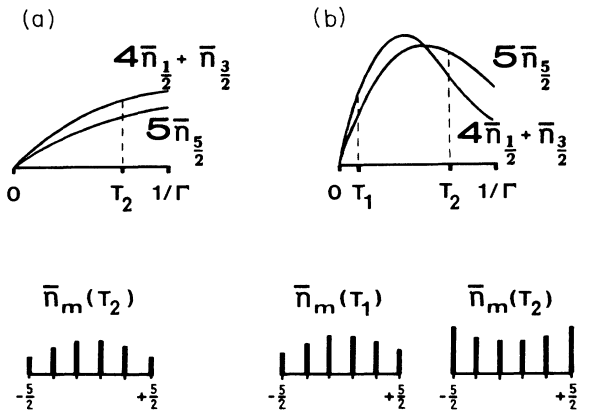

FIG. 1. Time dependence of the populations of the excited molecular sublevels $|F,m\rangle$ calculated for the $|F=\frac{5}{2}\rangle$-$|F'=\frac{7}{2}\rangle$ transition and for (a) $\beta=\Gamma$ and (b) $\beta=4\Gamma$, and averaged over the Doppler distribution of resonance frequencies of individual molecules in the uncollimated beam. Time scale is from 0 to the radiative lifetime of the excited level ($1/\Gamma$). It is assumed that $\Gamma=100\Gamma'$, and that at $t=0$ all $n_m=0$. Lower diagrams represent schematically the distributions of populations $\bar{n}_m(t)$ over sublevels m for short (T_1) and long (T_2) interaction times. The "inversion effect" may occur when the curves $4\bar{n}_{1/2}(t)+\bar{n}_{3/2}(t)$ and $5\bar{n}_{5/2}(t)$ intersect, i.e., for an appropriately long and strong interaction.

tions. It is interesting to note that for the appearance of the inversion effect the Rabi frequencies of individual subsystems (m,μ) within the F-F' transition must not differ too drastically. If they differ so much as, for example, in the case of transition $F=\frac{5}{2}$-$F'=\frac{5}{2}$ (line 2'R in Ref. 1), where $\beta_{1/2,1/2}:\beta_{3/2,3/2}:\beta_{5/2,5/2}=1:3:5$, then the averaged alignment does not change sign which is consistent with the experimental observations.[1] On the other hand, if the Rabi frequencies are not very different, as, for example, in the case of line 1 ($F=\frac{5}{2}$-$F'=\frac{7}{2}$), where $\beta_{1/2,1/2}:\beta_{3/2,3/2}:\beta_{5/2,5/2}=1:0.91:0.71$, the averaged alignment does reverse its sign for appropriately large β and t.

It is impossible to perform a precise comparison of our model with the experimental results of Ref. 1 without all necessary data. Nevertheless, assuming realistic values of unknown parameters, the above model offers a satisfactory qualitative agreement with the observations of Weber *et al.*[1]

It is important to realize that the inversion of the upper-state alignment occurs under nonstationary conditions when the n_m populations are decaying with a rate of the order of Γ. These are the conditions which are entirely opposite to what is meant by the "light-stabilization effect" in Ref. 1. Moreover, in our interpretation we do not find any particular features which have no analogy in atomic physics. Even the assumption $\Gamma' \ll \Gamma$, which is typical for molecules, in principle, could be relaxed. The solutions obtained numerically for the case when $\Gamma' \lesssim \Gamma$ behave similarly to those discussed above. We therefore regard the inversion effect as a very interesting manifestation of the nonstationary effects of the interaction of laser light with molecules and atoms, and not as evidence of the inadequacy of quantum mechanics.

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