Observation of quantum beats in the kinetics of the thermalization of diatomic molecules in the electronic ground state

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Quantum magnetic beats have been discovered experimentally in the kinetics of the thermalization of a vibrational-rotational level of the ground state of diatomic molecules after emptying by a laser pulse.

"Free" quantum beats in radiation kinetics are the most obvious evidence of the presence of a coherent superposition of nondegenerate states in a system and can be used to determine the splitting of these states.[1] This method has been used previously in atomic systems and in excited states of molecules. We have now observed the first case of beats between Zeeman sublevels of a vibrational-rotational level v'', J'' of the electronic ground state α'' of diatomic molecules in an external magnetic field. An important point here is that although the coherence between sublevels is produced in a nonlinear process of optical pumping through "emptying"[2] during absorption, $(v'', J'')\alpha'' \rightarrow (v', J')\alpha'$ where $(v', J')\alpha'$ refers to the electronically excited state, the beats are observed after the intense emptying laser pulse, in the kinetics of a fluorescence caused by a weak probing beam. In this case, the system is completely free of the nonlinear distortions which have occurred in the method of a beat resonance during harmonic modulation of an excitation, where the presence of a strong light field has led to a broadening and a shift of the signal.[3,4] A precise determination of the frequency of the quantum beats unambiguously determines the magnetic moment (Landé factor) of a fixed vibrational-rotational level. It thus becomes possible to study in detail that magnetism of certain vibrational-rotational levels of diamagnetic electronic ground states of dimers which is caused by an admixture of some other (paramagnetic) states.

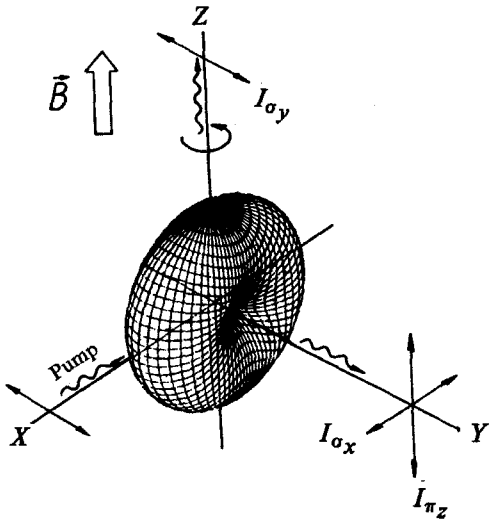

FIG. 1. The experimental geometry and the distribution of angular momenta of the lower level, $(v'', J'')\alpha''$, from calculations for an optical alignment through "emptying" with $\Gamma_p/\gamma = 10/3$ and $\Gamma/\Gamma_p = 86.2$.

Let us examine the mechanism for the formation of the beats. We assume that an optical alignment of the level $(v'', J'')\alpha''$ is caused by laser light propagating along the X axis and linearly polarized along the Y axis as in Fig. 1. In a typical situation, the emptying of the vibrational-rotational level (v'', J'') during the absorption process, at a rate Γ_p, competes primarily with the filling of this level by radiationless transitions at a rate γ within the state α''. If $\Gamma_p \gtrsim \gamma$, there is a significant optical alignment of the lower level, $(v'', J'')\alpha''$. Figure 1 shows the spatial distribution of the angular momenta of an ensemble of particles in this level in the limit of large angular momenta for the case of Q absorption, i.e., for the case $J' = J''$. We see that the ensemble acquires a nonvanishing quadrupole moment.

We choose the pump light in the form of the pulse in Fig. 2, whose length Δt is much shorter than the period of the precession in the external magnetic field $\mathbf{B}||Z$ and also shorter than the relaxation time γ^{-1}. On the other hand, the pump pulse is long enough to cause a significant alignment. After the end of the pulse (or its weakening to the level of the probing light), at the time t_0, the distribution of angular momenta in Fig. 1 precesses around $\mathbf{B}$ at a frequency $\omega = \mu_0 g B/\hbar$, where g is the Landé factor, and μ_0 is the Bohr magneton. At the same time, the distribution becomes filled in to the point that it becomes spherically symmetric, at a rate γ during the relaxation (thermalization). If the decay rate of the excited state satisfies $\Gamma \gg \gamma$, and if its precession frequency satisfies $\Omega \ll \Gamma$ (this is the actual situation for, e.g., the alkali dimers Li_2, Na_2, and K_2), the kinetics of the resonant fluorescence series from $(v' J')\alpha'$, excited by the weak light at the pedestal of the pulse at $t > t_0$, reflects a transition process in the $(v'', J'')\alpha''$ ground state (Fig. 2). When a magnetic field $\mathbf{B}$ is imposed, we should see a harmonic modulation at a frequency 2ω against the background of an intensification described by a single exponential function with a constant γ (the validity of this approximation is discussed in Ref. 5), since the frequency 2ω is the frequency at which the distribution of angular momenta in Fig. 1 reproduces itself.

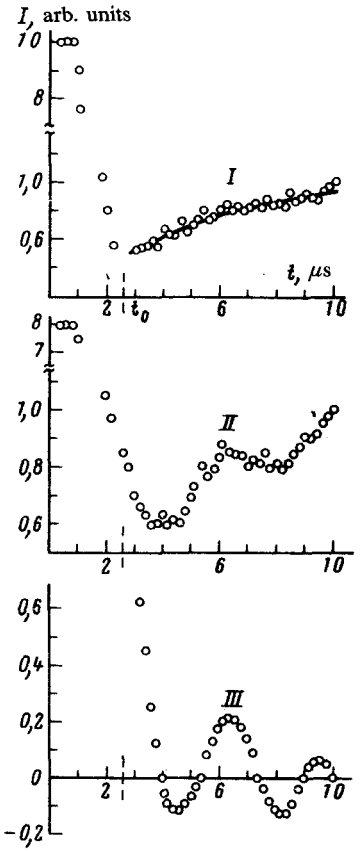

FIG. 2. I—Kinetics of the fluorescence signal I_{σ_y} in the absence of a magnetic field; II—in a field $B = 0.8$ T; III—the difference between signals II and I, after the noise is smoothed out.

We can now write an expression for the expected intensity of the fluorescence in the transient process at $t > t_0$ for the case in which the I_{σ_y} component, which is polarized along the Y axis, is observed along the Z axis:

$$I_{\sigma_y} = I(\infty) - [I(\infty) - I(0)]e^{-\gamma(t-t_0)} + Ce^{-\gamma(t-t_0)}\cos[2\omega(t-t_0)+\varphi], \quad (1)$$

where $\sim I(\infty)$ is the fluorescence intensity for the low-lying state with a thermally equilibrium population as $(t - t_0) \to \infty$, $I(0)$ is the intensity at $t = t_0$, C is a positive constant, and γ is the phase shift which arises from the finite width of the pump pulse. This result is confirmed by a more rigorous analysis. It can be shown that in observation along the Y axis (Fig. 1) beats are seen in the signal I_{π_z} with frequencies of 2ω and 4ω, while beats are seen in I_{σ_x} only at 4ω. The contribution from the component of the hexadecapole moment, which generates the frequency 4ω, is very small.

As the object of the experimental study we selected K_2 molecules in a cell containing saturated potassium vapor. A side arm with metallic potassium is held at 441 K, at which the potassium atom density is $N_K = 0.29 \times 10^{14}$ cm^{-3}, while the density of dimers is $N_{K_2} = 0.13 \times 10^{11}$ cm^{-3}. This cell is connected to a vacuum system that maintains a vacuum no worse than 10^{-6} torr. The beam at 632.8 nm from an LG-38 He-Ne laser, with a power of about 60 mW, excites the transition $(1.72)X\,^1\Sigma_g^+$

$\rightarrow(8.72)B\,^1\Pi_u$ most efficiently. An ML-102 electro-optic modulator controlled by a G5–15 pulse generator produces pulses 1.8 μs long with a modulation depth of about 0.85. The fluorescence I_{σ_y} is measured in the Q_{16} line of the resonant series, isolated with a DFS-12 monochromator. A cooled PM-79 photomultiplier is used in the photon-counting mode. The time dependence is determined by a delayed-coincidence method, with a statistical analysis of the appearance of individual photons, with time-to-amplitude conversion, and with data accumulation in an AI-256-6 pulse-height analyzer.

The experimental results are shown in Fig. 2. When the magnetic field is applied, the monotonic exponential increase of the signal shown by curve I gives way to the periodic beats shown by curve II. To single out the harmonic component, we use expression (1), taking the difference between signals II and I; the difference, after smoothing, is shown by curve III in Fig. 2. The frequency of the quantum beats (curve III) can be used for a preliminary determination of the Landé factor of the $(1.72)X\,^1\Sigma_g^+$ state of the K_2 molecule: $g = 1.2\times 10^{-5}$. This value agrees approximately with that found by Brooks *et al.*[6] for the entire X state of K_2 by a molecular-beam method and also with the value found by Auzin'sh and Ferber[4] by a method of a nonlinear beat resonance. We will refine the value of g through more-careful measurements. We would like to achieve a large value of the ratio ω/γ.

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