

Magnetically induced increase in the probability for radiative excitation and many-photon dissociation of gas molecules: an analog of the Senftleben effect

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Precession of rotating molecules in a magnetic field can substantially increase the probability for their photoexcitation.

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1. The many-photon dissociation of polyatomic molecules by the beam from a CO_2 laser has been the object of intense recent research, both experimental and theoretical (see the review by Letokhov and Makarov,¹ for example). Although the mechanism for many-photon dissociation is still not completely clear, it has been hypothesized² that transitions between states with approximately equal energies (state mixing) should substantially raise the probability for many-photon dissociation, regardless of the actual dissociation mechanism. In the present letter we will examine the effect of one possible mixing agent: a magnetic field. We will see that the overall state mixing in the case of a magnetic field may be thought of as an analog of the Senftleben effect in the kinetics of gases.^{3,4} We will derive an equation [Eq. (3)] which describes the effect of the magnetic field on many-photon dissociation and which contains only observable quantities. It would be a very simple matter to verify or refute Eq. (3) experimentally.

Duperrex and van der Bergh⁵ have observed that a magnetic field increases the probability for the many-photon dissociation of CF_2HCl molecules. They studied certain aspects of this effect (we will return to this question in Sec. 4).

The experimental results of Ref. 5 are in qualitative agreement with the theoretical model which we will outline below. A quantitative comparison of theory and experiment on the basis of Eq. (3) will probably become possible in the near future after experimental data have been obtained to supplement those of Ref. 5.

2. The physical mechanism for the effect of a magnetic field \mathbf{B} on many-photon dissociation becomes completely clear when we consider the following factors.

I. Most molecules do not have an electron spin or orbital angular momentum in their ground state. Let us assume for simplicity that the spins of all the nuclei are also zero. Even such molecules, however, will have a magnetic moment by virtue of their rotation; the motion of the nuclei is not completely offset by the motion of the electron cloud.⁶ The magnetic moment $\vec{\mu}$, which is generated by the rotation of the molecule, is usually written in the form $\vec{\mu} = -g\mu_n \mathbf{J}/\hbar$, where \mathbf{J} is the mechanical moment, and μ_n is the nuclear magneton. The dimensionless quantity g , the "rotational constant," depends strongly on the extent of slippage of the electron clouds of the atoms. For

polyatomic molecules, this constant usually lies in the range⁶ $g = 0.1-0.5$. In a magnetic field \mathbf{B} , the moments $\vec{\mu}$ and \mathbf{J} (or the expectation values of the corresponding operators in a quantum-mechanical treatment) begin to precess around \mathbf{B} at the frequency $\Omega = g\mu_n B/\hbar$. In a field $B = 14$ kG (Ref. 5) the precession frequency $2\pi/\Omega$ is comparable to the duration of the laser pulse, t_l .

II. In an electromagnetic field with wave vector \mathbf{k} the excitation probability may depend on the orientation of the moment \mathbf{J} of the excited system with respect to \mathbf{k} . In an unpolarized radiation field, for example, the single-photon dipole transition with $J \rightarrow J + 1$, which is accompanied by the change $M \rightarrow M \pm 1$, where M is the projection of the moment on \mathbf{k} , has a probability proportional to⁷ $(J + M + 2)(J + M + 1) + (J - M + 2)(J - M + 1) \simeq 2J^2(1 + \cos^2 \theta)$, where θ is the angle between \mathbf{J} and \mathbf{k} (we are assuming $J, M \gg 1$). The theory for many-photon dissociation as it exists today cannot tell us the θ dependence of w (the probability per pulse of the many-photon dissociation) unless we resort to some far-reaching model-based simplifications. It is nevertheless completely reasonable to assume that w is a rather strong function of θ . [This might be the case, for example, in an n -photon transition involving the change $J \rightarrow J + n$ in a circularly polarized electromagnetic field; here $w \sim (1 + \cos \theta)^{2n}$. For simplicity, we will consider this particular case, bearing in mind that all the results remain valid for the general case.] Because of the strong θ dependence of w , the only molecules which enter the "hot" ensemble and dissociate are those for which \mathbf{J} is oriented in a certain manner with respect to \mathbf{k} . In the case at hand, \mathbf{J} and \mathbf{k} must form an angle no greater than θ_c . The relative number of such molecules, $f(0)$, is roughly equal to the relative area enclosed by the solid angle θ_c :

$$f(0) \simeq \frac{\theta_c^2}{4}$$

(we are assuming $\theta_c \ll 1$).

3. We now consider many-photon dissociation in a magnetic field \mathbf{B} which is perpendicular to \mathbf{k} . We assume that the dissociation conditions are such that the effect of collisions can be ignored during the pulse. We consider a sphere defined by the tips of the initial vectors \mathbf{J} (Fig. 1). Without the field \mathbf{B} , the orientation of \mathbf{J} will not change, and dissociation occurs only from region A , with a relative area $f(0)$. In the presence of a field \mathbf{B} , the precession in the magnetic field causes the moment \mathbf{J} to rotate through an angle Ωt_l during the pulse, of duration t_l .

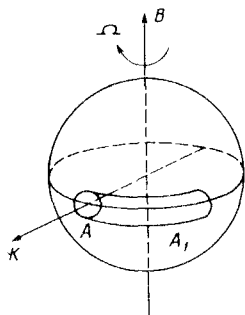


FIG. 1.

We assume

$$\theta_c \ll \Omega t_l < 2\pi, \quad (1)$$

The relative area of the region A_1 , in which dissociation can occur over the time t_l , is then

$$f(B) = \frac{\theta_c \Omega t_l}{2\pi}.$$

In Fig. 1, region A is a circle, while A_1 is a band. When \mathbf{J} falls in region A as a result of the precession, the molecule will dissociate. The quantity $f(B)$ is the relative number of molecules which dissociate in the presence of the field \mathbf{B} . We note that the quantities $f(0)$ and $f(B)$ can be observed directly in the laboratory.

Introducing the ratio $R = f(B)/f(0)$, and expressing θ_c in terms of $f(0)$, we find

$$R = \Omega t_l / \pi \sqrt{f(0)}. \quad (2)$$

According to (2), the ratio R increases linearly with increasing B over a broad range of \mathbf{B} , which can be found from conditions (1). [When B becomes so high that the second condition in (1) is violated, the ratio R should exhibit a plateau as a function of B .] If \mathbf{B} and \mathbf{k} are not perpendicular and instead form an angle α , we should introduce a factor $\sin \alpha$ on the right side of (2). We may thus make the following assertion: In experiments with different values of \mathbf{I} , t_l , \mathbf{B} , and $\sin \alpha$, the following combination K of observable quantities should remain constant:

$$K = \frac{R \sqrt{f(0)}}{t_l B \sin \alpha} = \text{const} (I, t_l, B, \sin \alpha), \quad (3)$$

where \mathbf{I} is the average intensity of the electromagnetic radiation over the pulse length t_l . (The electromagnetic flux is $F = It_l$.) For different experiments differing only in the value of \mathbf{I} , the combination $R \sqrt{f(0)}$ should remain constant, according to (3).

Equations (2) and (3) hold if $f(0) \ll 1$ and $f(B) \ll 1$ and if the ratio R is much greater than unity.

Because of the approximate nature of the model adopted here, combinations of this type will not, of course, remain strictly constant. The relative changes, however, should be smaller than the relative changes in the quantities making up these combinations.

4. In experiments involving the irradiation of CF_2HCl molecules by the beam from a CO_2 laser with a constant frequency and different values of F in the pulse, Duperrex and van der Bergh⁵ observed a monotonic decrease in R from 3 to 1 as F was increased from 1 to 3 J/cm^2 . If the change in F was achieved by changing I , while holding t_l constant (Duperrex and van der Bergh⁵ did not state how F was changed), a decrease in R with increasing F is in qualitative agreement with Eqs. (2) and (3), since the dissociation probability in the absence of a magnetic field, $f(0)$, increases rapidly with increasing F for all known molecules. As mentioned earlier, a meaningful quantitative test of Eqs. (2) and (3) could be carried out under the conditions $R \gg 1$.

When the magnetic field \mathbf{B} is parallel to the laser beam ($\alpha = 0$), the model of this paper predicts $R = 1$, i.e., that the magnetic field will not affect the many-photon dissociation. An experimental verification of this assertion would be a good verifica-

tion of our model, since this assertion remains valid even if the condition $R \gg 1$ does not hold at $\alpha = \pi/2$. The field \mathbf{B} might affect many-photon dissociation in the case $\alpha = 0$ by virtue of other processes, e.g., a change in the precession of the molecules around \mathbf{J} for nonspherical molecules.

5. In many-photon dissociation, as in the kinetics of gases, the rotational degrees of freedom provide the channel by which the magnetic field affects the corresponding process. This effect can be explained by a mixing of states. In the case at hand, states with different orientations of the moment \mathbf{J} with respect to \mathbf{k} are mixed by the precession of \mathbf{J} in the field \mathbf{B} . Since this is such a general effect, this mixing should affect not only many-photon dissociation but also other processes involving photoexcitation of molecules.⁸

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