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## Alignment–orientation transition at optical excitation of molecules in magnetic field

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Angular momentum alignment–orientation transition is analyzed for the ground state of diatomic or linear molecules subjected to the dynamic Stark effect. Analytical expressions are derived for the orientation value. It is shown that, first, orientation of angular momenta resulting from the action of the dynamic Stark effect is a nonlinear process which depends quadratically on the intensity of the irradiating light; second, it is a quantum effect and disappears for the states with large angular momenta; and, third, it occurs only in the presence of an external magnetic field.

### 1. INTRODUCTION

As a result of linearly polarized light absorption alignment of the angular momentum of the excited state of the ensemble of atoms or molecules occurs. For diatomic molecules in the gas phase this means, in particular, that there appears a preferred plane in which the optically excited molecules predominantly rotate.

Various mechanisms of an alignment–orientation transition have been studied. Such a transition means that in the selected plane the direction of the rotation is also defined, and the angular momentum of the ensemble of molecules become oriented. For review see [1] and references therein. The orientation of the molecular ensemble can be detected as appearance of circularly polarized radiation in the laser induced fluorescence. To achieve such a transition an external anisotropic perturbing factor—external field or anisotropic collisions—is necessary, in addition to the exciting light.

The influence of the external field manifests itself as the removal of the degeneracy of the rotational level  $J$  over the magnetic quantum number  $M$  as a result of the energy  $E_M$  shift of the magnetic sublevel  $|J, M\rangle$ . In the frequency scale the splitting of magnetic sublevels can be written as  $\omega_{MM'} = (E_M - E_{M'})/\hbar$ . In the case of broad band linear absorption (weak exciting light) and external field as a perturbing factor the necessary condition for the alignment–orientation transition is [1]

$$\omega_{MM\pm 1} \neq \omega_{-M\mp 1-M}. \quad (1)$$

This means that the external magnetic field which causes ordinary Zeeman effect, when  $E_M \propto M$  can not cause the alignment–orientation transition in the case of weak excitation.

The situation is different in the case of strong exciting light when the absorption is nonlinear. Now light with a wide spectral range in the case the center of the profile

of the exciting light does not coincide with the center of the absorption line, and, in the presence of the external magnetic field, an alignment-orientation transition can take place as a result of the dynamic Stark effect. This requires the Stark shift of the absorption frequency

$$\omega_S = \frac{1}{\hbar^2} \text{v.p.} \int \frac{I(\omega_l) |\langle J' || \hat{d} || J'' \rangle|^2 \omega_0}{2(\omega_l^2 - \omega_0^2)} d\omega_l, \quad (2)$$

where  $\langle J' || \hat{d} || J'' \rangle$  is the reduced matrix element of the dipole transition from the ground state with angular momentum  $J''$  into a state with angular momentum  $J'$ ,  $\omega_0$  is the frequency of this transition, and  $I(\omega_l)$  is the spectral profile of the excitation line.

## 2. THEORY

To describe the interaction of an ensemble of gas-phase molecules with light having a wide spectral profile of arbitrary intensity we shall use the equations of motion of the polarization moments (PM)

$$\begin{aligned} \dot{f}_Q^K &= \Gamma_p \sum_{X\kappa} {}^K F^{X\kappa} \{ \Phi^{(X)} \otimes \varphi^{(\kappa)} \}_Q^K \\ &\quad - \Gamma_p \left( \frac{\Pi_{J'}}{\Pi_{J''}} \right)^2 \sum_{XK'} {}^K A_{1+}^{XK'} \{ \Phi^{(X)} \otimes f^{(K')} \}_Q^K \\ &\quad + 2i\omega_S \left( \frac{\Pi_{J'}}{\Pi_{J''}} \right)^2 \sum_{XK'} {}^K A_{1-}^{XK'} \{ \Phi^{(X)} \otimes f^{(K')} \}_Q^K - (\Gamma_K - iQ\omega_{J'}) f_Q^K, \end{aligned} \quad (3)$$

$$\begin{aligned} \dot{\varphi}_q^\kappa &= -\Gamma_p \sum_{X\kappa'} {}^\kappa A_+^{X\kappa'} \{ \Phi^{(X)} \otimes \varphi^{(\kappa')} \}_q^\kappa \\ &\quad + \Gamma_p \left( \frac{\Pi_{J'}}{\Pi_{J''}} \right)^2 \sum_{XK} {}^\kappa F_1^{XK} \{ \Phi^{(X)} \otimes f^{(K)} \}_q^\kappa \\ &\quad + 2i\omega_S \sum_{X\kappa'} {}^\kappa A_-^{X\kappa'} \{ \Phi^{(X)} \otimes \varphi^{(\kappa')} \}_q^\kappa - (\gamma_\kappa - iq\omega_{J''}) \varphi_q^\kappa \\ &\quad + \Gamma_{J'J''} C_\kappa \delta_{K\kappa} \delta_{Qq} f_Q^K + \lambda_q^\kappa \delta_{\kappa 0} \delta_{q 0}. \end{aligned} \quad (4)$$

Here  $f_Q^K$  and  $\varphi_q^\kappa$  are the polarization moments of the excited and ground states and  $\Gamma_K$  and  $\gamma_\kappa$  are their relaxation rates,

$${}^K F^{X\kappa} = \frac{\Pi_{J'}^3 \Pi_{X\kappa}^2}{\Pi_{J''K}} (-1)^{X+1} \begin{Bmatrix} K & J' & J' \\ X & 1 & 1 \\ \kappa & J'' & J'' \end{Bmatrix}. \quad (5)$$

$${}^\kappa A_{\pm}^{X\kappa'} = \frac{1 \pm (-1)^{\kappa+X+\kappa'}}{2} \frac{\Pi_{J'X\kappa'}^2}{\Pi_\kappa} (-1)^{J'-J''+\kappa'} \begin{Bmatrix} \kappa & X & \kappa' \\ J'' & J'' & J'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & X \\ J'' & J'' & J' \end{Bmatrix}. \quad (6)$$

$$C_\kappa = (-1)^{J'-J''+\kappa+1} \Pi_{J''J'} \begin{Bmatrix} J'' & J'' & \kappa \\ J' & J' & 1 \end{Bmatrix}. \quad (7)$$

Expressions for the coefficients  ${}^{\kappa}A_{1\pm}^{X\kappa'}$  and  ${}^{\kappa}F_1^{XK}$  are obtained from Eqs. (6) and (5) by exchanging  $J''$  and  $J'$ . In Eqs. (5)–(7) the braces denote 9j- and 6j-symbols [2]. The functions  $\Phi_{\xi}^X$  describe the polarization of the exciting light and factor  $\Pi_{ab\dots} = \sqrt{(2a+1)(2b+1)\dots}$ . The symbol  $\otimes$  denotes the irreducible tensor product [2].

In Eqs. (3) and (4) the first term describes light absorption, the second term describes stimulated emission, the third term describes the effect of the dynamic Stark effect, and the fourth term describes the relaxation of the polarization moments and the action of an external field leading to Zeeman splitting  $\omega_{J''}$  and  $\omega_{J'}$  of the ground and excited state. The last two terms in Eq. (4) describe reverse spontaneous transition and isotropic filling of the lower level.

If an ensemble of molecules is excited by linearly polarized light when only the  $\Phi_{\xi}^X$  components with rank  $X = 0, 2$  differs from zero, then the angular momenta become aligned only for  $\omega_S = 0$  in the ensemble (these components describe the polarization moments of even rank  $K$  and  $\kappa$ ), since the coefficients  ${}^K F^{X\kappa}$ ,  ${}^{\kappa} F_1^{XK}$ ,  ${}^K A_{1+}^{XK'}$ , and  ${}^{\kappa} A_{+}^{X\kappa'}$  equal zero if the sum of the upper indexes is odd.

In the case  $\omega_S$  differs from zero an alignment–orientation transition occurs, since the  ${}^K A_{1-}^{XK'}$  and  ${}^{\kappa} A_{-}^{X\kappa'}$  coefficients are different from zero only if the sum of the upper indexes is odd. In this case the fluorescence is expected to be circularly polarized.

The coefficient  ${}^{\kappa} A_{-}^{X\kappa'}$  characterizes the efficiency of the alignment–orientation transition for the ground state level and the coefficient  ${}^K A_{1-}^{XK'}$  characterizes the same for the excited state level. Using explicit expressions for the 6j symbols, for example, for the ground state, we find for the three allowed types of molecular transitions  $Q(J'' = J')$ ,  $P(J'' = J' + 1)$ , and  $R(J'' = J' - 1)$  [3]

$$\begin{aligned} {}^1A_{-}^{22}(Q) &= \frac{5[3 - 4J''(J'' + 1)]}{J''(J'' + 1)\sqrt{3(2J'' - 1)(2J'' + 3)}}, \\ {}^1A_{-}^{22}(P) &= \frac{5}{\sqrt{3}} \sqrt{\frac{2J'' - 1}{2J'' + 3}} \frac{2J''^2 + 5J'' + 3}{J''(J'' - 1)(2J'' + 1)}, \\ {}^1A_{-}^{22}(R) &= \frac{5}{\sqrt{3}} \frac{\sqrt{2J'' + 3}(2J'' - 1)}{(2J'' + 1)(J'' + 1)}. \end{aligned} \quad (8)$$

These quantities show the efficiency of the quadrupole alignment ( $\kappa' = 2$ ) transition under action of dynamic Stark effect at linearly polarized excitation ( $X = 0, 2$ ) to the dipole orientation ( $\kappa = 1$ ). As  $J''$  increases the coefficients  $|{}^1A_{-}^{22}|$  decrease approaching

$${}^1A_{-}^{22}(P) = {}^1A_{-}^{22}(R) = \frac{5}{\sqrt{3}} \frac{1}{J''}, \quad (9)$$

$${}^1A_{-}^{22}(Q) = -\frac{10}{\sqrt{3}} \frac{1}{J''} \quad (10)$$

asymptotically for large  $J''$ .

### 3. EXAMPLE

For  $Q$ -type transition with  $J'' = J' = 1$ , expanding the solution for PM in a power series in the parameters  $\omega_S/\gamma_{\kappa}$  and  $\Gamma_p/\gamma_{\kappa}$ , we can find the orientation  $\varphi_q^1$ . If the polarization

vector of the exciting light is described by spherical angles  $\theta$  and  $\varphi$ , then in the second order of the expansion we find

$$\varphi_0^1 = \frac{\omega_S \Gamma_p \omega_{J''} \sqrt{2}}{12\gamma_1} \sin^2 \theta \left( \frac{\sin^2 \theta}{\gamma_2^2 + 4\omega_{J''}^2} + \frac{\cos^2 \theta}{\gamma_2^2 + \omega_{J''}^2} \right), \quad (11)$$

$$\begin{aligned} \varphi_1^1 = (\varphi_{-1}^1)^* = i e^{i\varphi} \frac{\omega_S \Gamma_p}{24(\gamma_1 - i\omega_{J''})} & \left[ \sin^3 \theta \cos \theta \left( \frac{\gamma_2 + 2i\omega_{J''}}{\gamma_2^2 + 4\omega_{J''}^2} - \frac{\gamma_2 - i\omega_{J''}}{\gamma_2^2 + \omega_{J''}^2} \right) \right. \\ & \left. + (3 \cos^2 \theta - 1) \cos \theta \sin \theta \left( \frac{\gamma_2 + i\omega_{J''}}{\gamma_2^2 + \omega_{J''}^2} - \frac{1}{\gamma_2} \right) \right]. \end{aligned} \quad (12)$$

#### 4. CONCLUSIONS

It is obvious from Eqs. (11) and (12) that when magnetic field  $\mathbf{B}$  (which defines the  $z$  axis) and the  $\mathbf{E}$  vector of the exciting light are orthogonal ( $\theta = \pi/2$ ), only longitudinal orientation  $\varphi_0^1$  occurs. In other cases transversal orientation  $\varphi_{\pm 1}^1$  also is produced.

The effect, as it can be seen, is proportional to the  $\omega_S \Gamma_p$ . In other words it is proportional to the squared intensity of the exciting light. It is of pure quantum origin and disappears at the large  $J$  limit, as it is seen from (9) and (10).

As it can be easily seen from the above example, in absence of the external magnetic field ( $\omega_{J''} = 0$ ) the alignment-orientation transition will not occur.

It is important to stress that all above conclusions are valid for broad band excitation, when no such effects as magnetic scanning take place and all magnetic sublevels are in equally good resonance with the exciting light.

The produced orientation may be of the considerable value and can very strongly affect the observable signals. Thus, the correct accounting for alignment-orientation transition is of great importance in proper interpretation of the experiments utilizing optical pumping of molecules [4].

At the same time optical alignment of molecules is considered as a good method for the preparation of polarized state of reagents in chemical reaction stereodynamics experiments. In such experiments accounting for the alignment-orientation transition is also of great importance.

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