Magnetic predissociation in Te_2 B 1_u.

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ABSTRACT

We report a registration of magnetic predissociation (MPD) of electronically excited molecules via peculiarities in magnetic field **B** induced alignment–orientation conversion (AOC). Non-linear magnetic energy shift and heterogeneous MPD produce dispersion type fluorescence circularity signals $C(B)$ of different sign. Measurements on $B\,1_u^-$, $v(J)$=2(96) state of $^{130}Te_2$ yielded natural $C_v^{het} = \pm 6$ $s^{-1/2}$ and magnetic $\alpha_v^{het} = \mp 9 \times 10^3$ $s^{-1/2}T^{-1}$ rate constants of heterogeneous PD, supposing that the $B\,1_u^-$ state PD takes place through 0_u^- state continuum.

1. INTRODUCTION

It has been interest for a long time[1] in the perturbing factors, which are able to break the reflection symmetry of the aligned angular momenta ensemble, causing the AOC phenomenon. One may imagine that alignment behaves like a double-headed arrow (⇔), whereas orientation behaves like a single-headed one (⇒). In particular, excitation with linear polarized light creates alignment only, and **E**-vector defines the axis of cylindrical symmetry. As it was revealed[2,3,4], Zeeman effect in simple molecules, under special conditions, is able to cause the AOC effect, manifesting itself as the appearance of fluorescence circularity $C(B)$ under linearly polarized broad spectral line excitation. The present paper contains simulations[5] of expected fluorescence circularity signal under linear polarized excitation in conditions typical for $B^3\Sigma_u^-$ state of Te_2 molecule as well as fitting of experimentally obtained data.

2. THEORETICAL APPROACH

It is easy to understand the main reasons for Zeeman induced AOC[2,4] if one remembers that the ensemble density matrix element $f_{MM'}$, which describes the coherence between sublevels with magnetic quantum numbers M and M' in the state with definite angular momentum J value, contains a factor $f_{MM'} \sim (\Gamma_{MM'} + i\omega_{MM'})^{-1}$, $\omega_{MM'}$ and $\Gamma_{MM'}$ being the splitting energy and the coherence relaxation rate, respectively, in the system of Zeeman sublevels E_M, $E_{M'}$. Let us assume that the exciting light linear polarization vector $\mathbf{E}(\vartheta, \varphi)$ is directed at angles ϑ, φ with respect to the quantization axis $\mathbf{z}||\mathbf{B}$, whilst fluorescence is observed along y axis. The expression for the difference $I_r - I_l$ which describes the appearance of orientation $C=(I_r - I_l)/(I_r+I_l)$, $I_{r,\,l}$ being right-handed and left-handed circularly polarized fluorescence intensities, can be written[2,4] as

$$I_r - I_l \propto \Gamma_p \frac{\sin 2\theta}{2} \sum_M \frac{\Gamma_{MM+1} \sin\varphi + \omega_{MM+1} \cos\varphi}{\Gamma^2_{MM+1} + \omega^2_{MM-1}}$$

$$\times\left(C^{J'M}_{J''M+11-1} C^{J'M-1}_{J''M+110} - C^{J'M}_{J''M10} C^{J'M+1}_{J''M11}\right)$$

$$\times\left(C^{J'M}_{J_1''M10} C^{J'M+1}_{J_1''M11} + C^{J'M}_{J_1''M+11-1} C^{J'M+1}_{J_1''M+110}\right) \qquad (1)$$

Hence, for the appearance of AOC at broad spectral line excitation, one must have asymmetry, with respect to M. M', either in Zeeman energy splitting, (i)$\omega_{MM\pm1} \neq \omega_{-M\mp1-M}$ or (ii) in M-dependent coherence relaxation rate $\Gamma_{MM\pm1} \neq \Gamma_{-M\mp1-M}$. Condition (i) is met at quadratic Zeeman energy E_M dependence on magnetic field (B) and magnetic quantum number (M), which can be caused by the second-order paramagnetic term, which is called "high-frequency term" (HFT), according to Van Vleck[6], and by the first-order diamagnetic term. Condition (ii) is fulfilled when the M-selective magnetic predissociation (MPD) takes place[7]. We will consider the case when AOC is produced by HFT and MPD, which are caused by the same paramagnetic Hamiltonian $\hat{\mathbf{H}}_{pm} = -\mu_B B(g_l \mathbf{J}_a + (g_s - g_l)\mathbf{S})$, g_l and g_s are orbital and spin electronic g-factors, $\mathbf{J}_a = \mathbf{L} + \mathbf{S}$ is the total electronic angular momentum. It is clear that HFT and MPD are resulting from the simultaneous effect of external magnetic field and intramolecular interaction, thus AOC represents an exclusively sensitive method to investigate the interaction between both bonded and continuum electronic states Ω, Ω'. Applying the primitive Hund's (c)-case coupling scheme, the perturbation $G = \langle\Omega| \hat{\mathbf{H}}_{pm} |\Omega'\rangle$ can be divided into homogeneous ($\Omega = \Omega'$) part, when $G_z = g_l\Omega\delta_{\Omega\Omega'} + (g_s - g_l)\langle\Omega| \hat{\mathbf{S}}_z |\Omega'\rangle$, and heterogeneous ($\Omega' = \Omega \pm 1$) part, when $G_\pm = g_l\langle\Omega| \hat{\mathbf{J}}_{a\pm} |\Omega'\rangle + (g_s - g_l)\langle\Omega| \hat{\mathbf{S}}_\pm |\Omega'\rangle$. It was revealed that parameters G_z, $G_\pm$ and the electronic mixing matrix element $\eta = g_l\langle\Omega| \hat{\mathbf{J}}_{a\pm} |\Omega'\rangle$ describe both $\omega_{MM'}$ and $\Gamma_{MM'}$ contribution into AOC signal, and, in its turn, can be gained from $C(B)$ signal processing[5].

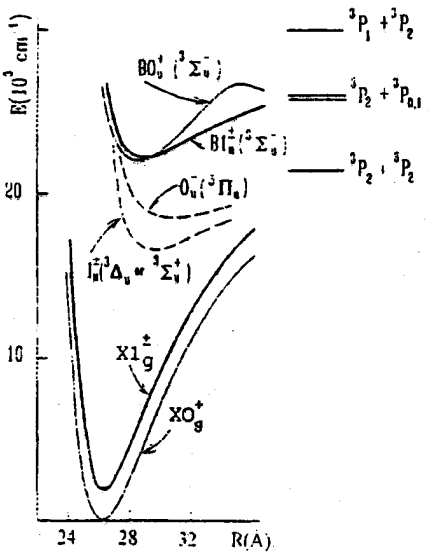

Fig.1. Te_2 term pattern.

The unified perturbation treatment of quadratic Zeeman energy shift and MPD has been accomplished[5], accounting for magnetic and intramolecular perturbations via interaction with bonded or continuum states, dividing the Hund's (c)-case intramolecular perturbation operator into homogeneous ($\Delta\Omega = 0$) and heterogeneous ($\Delta\Omega = \pm1$) parts. We suppose that the $0_u^-\left({}^3\Pi_u\right)$ and $1_u^\pm$ (${}^3\sum_u^+$ and ${}^3\Delta_u$) states, Fig.1, are responsible for $B\,1_u^-$ state PD. Numerical simulation, see Fig.2, have been carried out for the conditions relevant to the $B\,{}^3\sum_u^-$ complex of $^{130}Te_2$, molecule, see Fig.1. $C(B) = (I_r - I_l)/(I_r + I_l)$ signal is absent completely at linear Zeeman effect (curve 1 in Fig. 2). The HFT, or $\omega_{MM'}$ contribution into AOC due to quadratic Zeeman effect, is shown by curve 2, while curve 4 demonstrates the $\Gamma_{MM'}$ contribution due to both heterogeneous and homogeneous MPD (neglecting of the latter leaves the signal almost unchanged, see curve 5). The influence of $\omega_{MM'}$ and $\Gamma_{MM'}$ produce circularity of different sign and shape, and the structure remains pronounced also

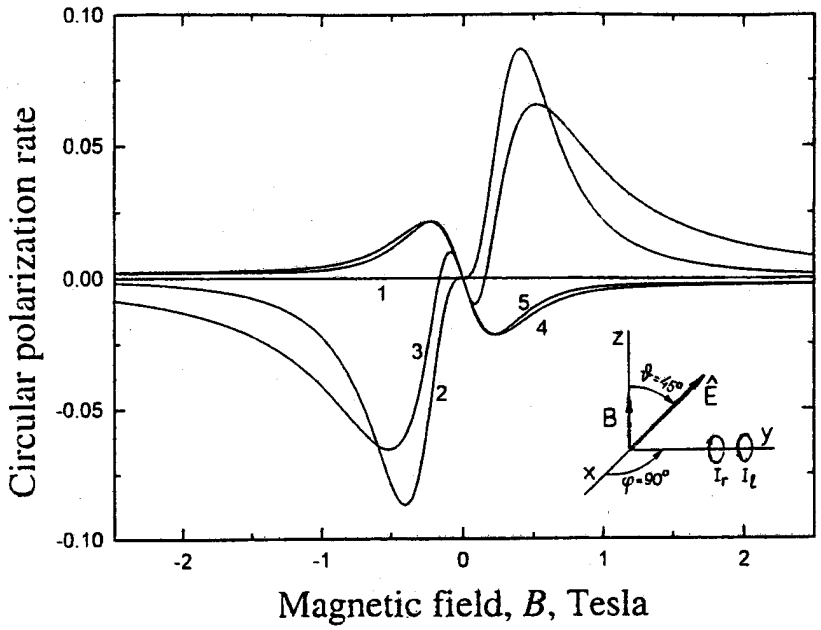

Fig.2. Calculated magnetic field dependence $C(B)$ of the degree of fluorescence circular polarization, or AOC signal (the geometry is shown in the setting-up). 1- signal in case of linear Zeeman effect term LPT; 2 - accounting for LPT and for non-linear Zeeman term HFT; 3 - accounting for LPT, HFT, homogeneous and heterogeneous magnetic PD; 4 - accounting for LPT, heterogeneous and homogeneous magnetic PD; 5 - accounting for LPT and heterogeneous magnetic PD. The PD parameters used in calculations are: C^{het}_{ν}=-6$s^{-1/2}$, α^{het}_{ν}=$10^4 s^{-1/2}T^{-1}$, C^{hom}_{ν}=$10^3 s^{-1/2}$ and α^{hom}_{ν}=$10^3 s^{-1/2}T^{-2}$.

in the summary signal 3, which accounts for all effects. It is possible to judge, from the first glance, about the heterogeneous type of MPD since the homogeneous MPD is unable in this case to produce the additional peaks which can be distinguished in curve 3.

3. RESULTS AND DISCUSSION

AOC signal was registered[3] in $B\ 1_u^-$-component of the Te_2, $B^3\Sigma_u^-$ state, Fig. 1, as the appearance of $C(B)$ up to 0.05, for B up to 0.4 T, under absorption (ν''=4, J''=95) $X^1\Sigma_g^-$ → (ν'=2, J'=96) $B\ 1_u^-$ of linearly polarized 514.5 nm Ar^+ – laser line at ϑ= 45°, φ= 90° in the equation (1).

Fig. 3 demonstrates the results of fitting of experimental $C(B)$ signal (dots in Fig. 3). Curve 2 demonstrates AOC signal caused exclusively by B^2 - Zeeman term and differs markedly from curve 2', which was calculated without accounting for $B\ 1_u \sim B\ 0_u^+$ wave function mixing[3]. Curve 3' accounts for $B\ 1_u^- \sim 0_u^-$ heterogeneous MPD and demonstrates dispersion type $C(B)$ signals with different sign than in case of curve 2. Fitting of experimental data, see curve 3', allowed to determine the electronic matrix element of paramagnetic Hamiltonian $\left\langle \Omega = 0 \middle| \hat{\mathbf{H}}_{pm} \middle| \Omega = 1 \right\rangle \equiv G_{\pm} = 2.7$, as well as the natural $C^{het}_{\nu} = \pm 6\ s^{-1/2}$ and the magnetic $\alpha^{het}_{\nu} = \mp 9 \times 10^3\ s^{-1/2}T^{-1}$ rate constants of heterogeneous PD, supposing that the $B\ 1_u^-$ state PD takes place through 0_u^- state continuum, Fig. 1. Comparison of curve 3' with the curve 3, which

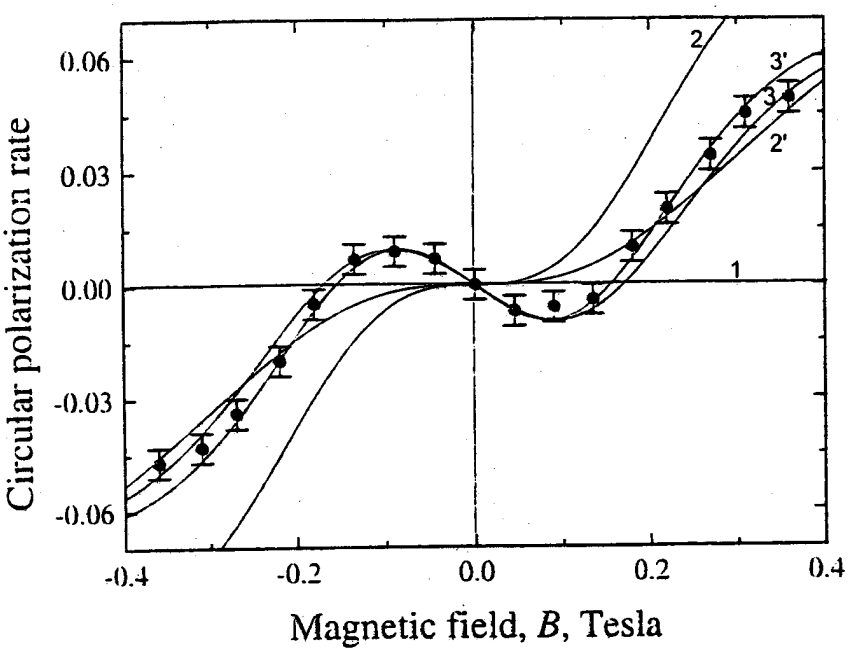

Fig.3. Fitting of experimentally obtained AOC signal in $C(B)$ at the same geometry as in Fig.2. Curves 1-3 are the same as in Fig.2. Curve 2' ignores the interference term E^{int}_{HFT} in quadratic Zeeman effect, whilst curve 3' differs from curve 3 by ignoring homogeneous PD. The parameters obtained by fitting are: C^{het}_v=-6s$^{-1/2}$, α^{het}_v=9x10^{3}s$^{-1/2}$T^{-1}, $G_{\pm}$=2.7.

was calculated by including into calculation the estimated upper limits of homogeneous PD parameters $C_v^{hom} = 10^3$ s$^{-1/2}$ and $\alpha_v^{hom} = 10^3$ s$^{-1/2}$T^{-1}, confirms that accounting for $B\,1_u^- \sim 1_u^{\pm}$ PD practically does not imply the fitting. The results obtained allowed to suggest that MPD takes part mainly through $0_u^-(^3\Pi_u)$ state continuum and to prove that quadratic Zeeman energy shift is caused by magnetic field induced $\Delta J = \pm 1$ $B\,1_u^- \sim B\,0_u^+$ and $B\,1_u^- \sim B\,1_u^+$ mixing within $B\,^3\Sigma_u^-$ state complex. As it is known from I_2 studies[7], the interference term $\alpha_v C_v$ allows to determine very weak natural PD rate C_v, also in case of $^{130}Te_2$ ($B\,^3\Sigma_u^-$) we obtained $C_v^{het} J(J+1) \cong 6.7 \times 10^5$ s^{-1} which is only about 8% of the full relaxation rate $\Gamma = 8.55 \times 10^6$ s^{-1} for $B\,1_u^-$, v=2(96) level. Thus, the studies of $\Gamma_{MM'}$ contribution in AOC signal give new possibilities in investigating PD phenomena.

As it can be shown[5], it is possible to use the PD parameters, obtained for the $B\,1_u^-$ state of Te_2, in order to evaluate the ratio of electronic matrix elements $\eta_v^{het} \equiv \eta$ and $G_{\pm}$:

$$\frac{\alpha_v^{het}}{C_v^{het}} \cong \frac{\sqrt{2\pi}\langle v|\varepsilon\rangle \mu_B G_{\pm}}{\sqrt{2\pi}\langle v|\varepsilon\rangle \frac{\eta}{2\mu R_c^2}} = 2\mu R_c^2 \mu_B \frac{G_{\pm}}{\eta} \,. \qquad (2)$$

Using the evaluated $\hbar^2/(2\mu R_c^2) \cong 0.1$ cm^{-1} value and taking $\mu_B = 0.467$ cm^{-1}T^{-1}, one obtains the following $G_{\pm}/\eta$ value:

$$\frac{G_{\pm}}{\eta} = \frac{g_l J_{a\pm} + (g_s - g_l) S_{\pm}}{J_{a\pm}} \cong 1 + \frac{S_{\pm}}{J_{a\pm}} \cong \frac{\alpha_v^{het}}{C_v^{het} 2\mu R_c^2 \mu_B} \cong -3.2 \times 10^2 \ . \qquad (3)$$

The fact that $G_{\pm}/\eta$ ratio is so large means that almost complete cancellation of $L_{\pm}$ and $S_{\pm}$ takes place. Indeed, since $\hat{\mathbf{J}}_{a\pm} = \hat{\mathbf{L}}_{\pm} + \hat{\mathbf{S}}_{\mp}$, Eq. (3) yields $L_{\pm} \cong -1.0031 S_{\pm}$. Hence, for $B\ 1_u^-$ state of Te_2 the values of electronic matrix elements $L_{\pm}$ and $S_{\pm}$ almost coincide, being opposite in signs. This striking point was observed also for the $B\ ^3\Pi_{0_u^+}$ state of I_2 molecule[7], where the ratio $L_{\pm} \cong -1.0435 S_{\pm}$ was obtained.

4. ACKNOWLEDGMENTS

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