

Occurrence of circular polarization in Te<sub>2</sub> fluorescence due to quadratic Zeeman effect

M.P.Auzinsh, I.P.Klincare, A.V.Stolyarov\*,  
Ya.Tamanis and R.S.Ferber

University of Latvia, Department of Physics,  
Riga, Latvia, LV-1586  
\*Moscow M.Lomonosov State University, Department of Chemistry,  
Moscow W-234, 119899

ABSTRACT

This paper reports the observation of the molecular fluorescence circularity under irradiation with linear polarized light. The phenomenon arises as a result of partial transformation from alignment of the ensemble of molecular angular momenta into orientation due to quadratic correction to Zeeman effect. Circularity rate up to 0.05 at magnetic field 0.4 T was registered in  $B^3\Sigma_u^-(1\bar{u}) \rightarrow X^3\Sigma_g^-(0_g^+)$  fluorescence of <sup>130</sup>Te<sub>2</sub> molecules. Data fitting showed that the electronic part of g factor caused by  $1\bar{u}^0\bar{u}$  interaction is equal to  $G_{\pm} \approx \langle 0_u | J_{\pm} | 1_u \rangle + 1.0023 \langle 0_u | S_{\pm} | 1_u \rangle = 2.72$ .

1. INTRODUCTION

Orientation of angular momenta under excitation by broad band linear polarized light appears when external perturbation is applied causing asymmetric splitting between coherent  $M, M\pm 1$  magnetic sublevels when the corresponding magnetic splitting frequencies  $\omega_{M, M\pm 1} \neq \omega_{-M, -M}$ . Significant interest in such a phenomenon of alignment-orientation conversion is connected with changing the symmetry type of angular momenta distribution. As far as we know, there exist only a few direct experimental observations, of the mentioned effect performed on atoms under anisotropic collisions.

An interesting possibility appears to use the quadratic correction to the Zeeman effect in diatomic molecules. We have chosen the closely positioned  $B0_u^+$  and  $1\bar{u}^+$  states of the Te<sub>2</sub> molecule as a convenient object for analysis and experimental observation of the effect. Heterogeneous electron-rotation  $\Delta J=0$  interaction mixes  $B0_u^+$  and  $1\bar{u}^+$  states but the  $1\bar{u}$  component can be considered as unperturbed. When external magnetic field  $\vec{B}$  is applied interaction between the levels with  $\Delta J=\pm 1$  arises, leading to a quadratic Zeeman energy dependence on field strength. For this reason the  $1\bar{u}$  component was chosen here in order to demonstrate the appearance of alignment-orientation transformation induced by quadratic Zeeman effect.

2. CALCULATION OF THE EXPECTED SIGNAL

The Zeeman operator  $\mathcal{H}_{\text{mag}}$  for a Hund's (c) coupling case can be written in the form:

$$\mathcal{H}_{\text{mag}} = -\mu_B \vec{B} [g_1 J_{\text{az}} + (g_s - g_1) S]. \quad (1)$$

We suppose here that the space-fixed  $z$  axis of quantization is directed along the external magnetic field  $\vec{B}$ ,  $g_l=1$  is the orbital electronic  $g$  factor,  $g_s=2.0023$  is the spin electronic  $g$  factor,  $J_s=L+S$  is an overall electronic orbital and electronic spin angular momentum of the molecule,  $\mu_B$  is the Bohr magneton.

In contrast to intramolecular perturbations a magnetic field is able to induce interaction between levels with different  $J$  in  $0_u^+ - 1_u^+$  complex of  $B^3\Sigma_u^-$  state. As follows from selection rule, total parity  $+$  or  $-$  is conserved, cf. Fig.1. This means that allowed interactions with  $\Delta J=\pm 1$  are  $1_u^- - 1_u^+$  and  $1_u^- - 0_u^+$ . Neglecting diamagnetic terms the quadratic over  $B$  contribution  $\Delta E_M$  to magnetic energy can be written for  $1_u^-$  state as

$$\Delta E_M(1_u^-, v_1, J) = \frac{\langle 1_u^-(J) | \mathcal{H}_{mag} | 1_u^+(J\pm 1) \rangle^2}{E_{v_1^-}^J - E_{v_1^+}^{J\pm 1}} + \frac{\langle 1_u^-(J) | \mathcal{H}_{mag} | 0_u^+(J\pm 1) \rangle^2}{E_{v_1^-}^J - E_{v_0^+}^{J\pm 1}}, \quad (2)$$

Here  $v_0^+$  and  $v_1^\pm$  denote the vibrational levels of  $0_u^+$  and  $1_u$  state, respectively. The total magnetic energy of a certain rovibronic level  $(v_1, J)$  takes the form:

$$E_M(1_u^-, v_1, J) = gM\mu_B B + G_z^2 A(M, J) \mu_B^2 B^2 + G_\pm^2 B(M, J) \mu_B^2 B^2, \quad (3)$$

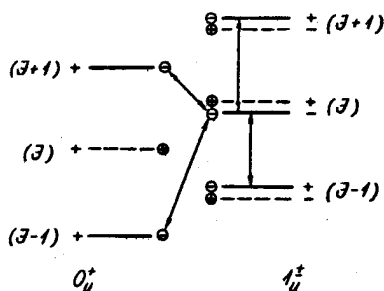


Fig.1. Magnetic field induced mixing between  $1_u^-$  and  $1_u^+, 0_u^+$  state levels with  $\Delta J=\pm 1$ . An even isotope possesses even  $J(1_u^-)$  values and the levels shown with dashed lines are not realized due to symmetry considerations.  $\oplus, \ominus$  denote the total parity, whilst  $\oplus, \ominus$  denote the electronic parity.

where the first term corresponds to linear Zeeman effect.  $G_z$  is the electronic part of the molecular  $g$  factor in the  $\Omega=1$  state. The second term of Eq.(3), in agreement with Eq.(2), is emerging due to  $1_u^- - 1_u^+$ ,  $\Delta J=\pm 1$  interaction.  $A(M, J)$  and  $B(M, J)$  are "geometric" factors<sup>2</sup>.

The second quadratic term in Eq.(3) describes the magnetic field induced  $1_u^- - 0_u^+$ ,  $\Delta J=\pm 1$  interaction, and  $G_\pm$  is the component of the electronic part of the  $g$  factor caused by heterogeneous ( $\Delta\Omega=1$ ) interaction<sup>2</sup>:

$$G_\pm = g_l \langle \Omega | J_{s\pm} | \Omega^* \rangle + (g_s - g_l) \langle \Omega | S_\pm | \Omega^* \rangle. \quad (4)$$

Thus, the problem of getting Zeeman energy  $E_M(1_u^-, v, J)$  values accounted for quadratic terms arising due to magnetic field induced interaction, cf. Eq.(3), is reduced to two adjustable parameters, namely  $G_z$  and  $G_\pm$ .

Eq.(3) satisfies the condition

$$\omega_{M+1} \neq \omega_{M-1} - M, \quad (5)$$

due to  $M^2$  dependence of "geometric" factors<sup>2</sup>

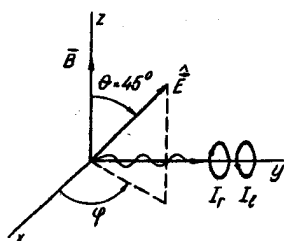


Fig.2. Excitation and observation geometry.

and hence the appearance of circularity  $I_r - I_l$  is expected,  $I_r, I_l$  being fluorescence intensities in the cycle  $J'' \rightarrow J' \rightarrow J_1$  possessing right-handed and left-handed circular polarization, respectively. The geometry of excitation and observation is shown in Fig.2. The  $\hat{E}$ -vector of linear polarized excitation is directed at spherical angles  $\theta, \varphi$ . The direction of observation is chosen along  $y$  axis. Expressions for  $I_r - I_l$  and  $I_r + I_l$  at arbitrary  $\theta, \varphi$  are given in Ref.3. The optimal  $\theta$  value equal to  $\pi/4$ , will be supposed in further treatment, and we obtain:

$$I_r - I_l = \frac{\Gamma_p (\Gamma \sin \varphi + \omega_{M, M+1} \cos \varphi)}{M \Gamma^2 + \omega_{M, M+1}^2} \left( C_{J'' M+11-1}^{J' M} C_{J'' M+110}^{J' M+1} - C_{J'' M10}^{J' M} C_{J'' M+11}^{J' M+1} \right) \times \left( C_{J_1 M+10}^{J' M} C_{J_1 M+11}^{J' M+1} + C_{J_1 M+11-1}^{J' M} C_{J_1 M+10}^{J' M+1} \right), \quad (6)$$

where  $C_{\alpha\alpha\beta\beta}^{C\gamma}$  are Clebsch-Gordan coefficients,  $\Gamma$  is the excited state relaxation rate and  $\Gamma_p$  is the pumping (excitation) rate. Figure 3 demonstrates the results of numeric calculation of the expected value of circularity rate  $C = (I_r - I_l) / (I_r + I_l)$  at  $\theta = \pi/4, \varphi = \pi/2$  as dependent on a dimensionless parameter  $\omega_L / \Gamma$ , where  $\omega_L = \frac{G_z}{J(J+1)} \frac{\mu_B B}{\hbar}$ , at different values of  $G_{\pm}$ . The  $I_r + I_l$  value has been calculated according to Eq.(15) from Ref.3. We would like to mention the high sensitivity of the appeared orientation signal to  $G_{\pm}$  changes. Hence, it is promising to use the alignment-orientation conversion effect in order to determine  $G_{\pm}$  values.

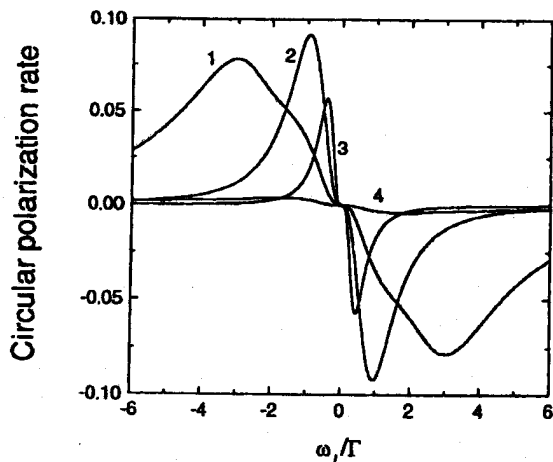


Fig.3. Calculated circularity rate as dependent on parameter  $\omega_L / \Gamma$  for different  $G_{\pm}$  values: 1- $G_{\pm}=8$ , 2- $G_{\pm}=4$ , 3- $G_{\pm}=2$ , 4- $G_{\pm}=1$ . Here  $G_z = -1.86$ ;  $\Gamma = 8.55 \times 10^6 \text{ s}^{-1}$ .

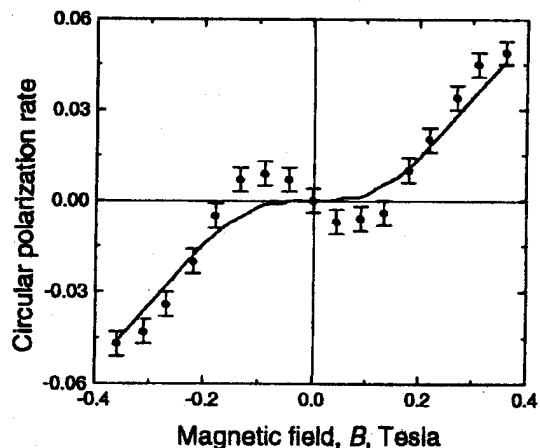


Fig.4. Measured circularity signal for  $v_1=2 (J=96)$  level of  $B^3\Sigma_u^+(1u)$  state in  $^{130}\text{Te}_2$ . Full line is obtained by data fitting.

### 3. EXPERIMENTAL RESULTS AND DISCUSSION

Molecular fluorescence from isotopic  $^{130}\text{Te}_2$  vapor was induced by a linear polarized line (514.5 nm) from an Ar<sup>+</sup> laser. The tellurium isotope was held in a fused silica cell at a temperature  $T=650\text{K}$  and connected with a vacuum system through a dry valve. The R-type molecular transition ( $X1\bar{g}, v''=4, J''=95$ )  $\rightarrow$  ( $B1\bar{u}, v=2, J=96$ ) was excited.

The degree of circularity was measured at the geometry of Fig.2 when  $\theta=\pi/4$ ,  $\phi=\pi/2$ . The external magnetic field was varied between  $B=-0.4$  T and  $+0.4$  T. The results for a fluorescence transition ( $B1\bar{u}, v=2, J=96$ )  $\rightarrow$  ( $X1\bar{g}, v=8, J=97$ ) are presented in Fig.4 showing the appearance of circularity up to  $C=0.05$ . The solid line was calculated using  $G_{\pm}$  as the only nonlinear fitting parameter, and we obtained the value  $G_{\pm}=2.72$ . The calculated dependence reflects, to a major extent, the main behavior of the measured circularity values. However, one can notice some distinction which is beyond the statistical error limit. The discrepancy in the small  $B$  region can not be explained by accounting for the simultaneous  $l\bar{u}$ ,  $O\bar{u}$  and  $l\bar{u}$  interaction which is able to change only slightly the  $G_{\pm}$  value yielded by fitting, without changing the shape of the signal at small magnetic field. We can only suppose that the discrepancy may be due to either some systematic experimental errors or, possibly, because the broad excitation line approximation is not valid with sufficient precision.

It is interesting to compare the information available from magnetic field induced alignment - orientation conversion with that yielded by conventional Landé factor measurements supposing the linear Zeeman effect conditions. Landé factors of a diamagnetic ( $\Omega=0$ )  $B0\bar{u}$  state of  $\text{Te}_2$  were obtained in Ref.4. The  $g(B0\bar{u})$  factor values are determined by electron - rotation  $O\bar{u} \sim l\bar{u}$  interaction with  $\Delta J=0$ . The  $g$  factor data interpretation needs however the notion of  $G_{\pm}$  as well as the mixing coefficients  $c(O\bar{u})$  and  $c(l\bar{u})$  for the coupled  $O\bar{u}$  and  $l\bar{u}$  states. For weakly coupled levels we get

$$g(B0\bar{u}) = 2G_{\pm} \eta \frac{\langle v_0 | B(R) | v_1 \rangle \langle v_0 | v_1 \rangle}{\sum_{v_1} \frac{E_{v_1}^J}{E_{B0\bar{u}}^J} - \frac{E_{v_1}^J}{E_{A1\bar{u}}^J}} \quad (7)$$

where  $\eta = \langle \Omega | J_{\pm} | \Omega^* \rangle$  is the electronic matrix element for heterogeneous electron-rotation state mixing  $|\Omega - \Omega^*|=1$ . Hence, the  $g$  factor data yield only the product  $\eta G_{\pm}$  and does not allow to determine  $G_{\pm}$  in a direct way. The  $\eta$  value for  $O\bar{u} \sim l\bar{u}$  mixing in  $\text{Te}_2$  was determined<sup>5</sup> from energetic and radiative data as  $\eta \approx 1.43$ . This leads to  $G_{\pm} \approx 2.9$  for the  $B0\bar{u}$  state level  $v_0=0$  ( $J=179$ ). This result is in a good agreement with the  $G_{\pm}$  values obtained in a direct and independent way in the present work. In fact, this confirms that the  $G_{\pm}$  value is very close to  $2\eta$ , and thus we have an additional reason for the conclusion that the  $\text{Te}_2(1u)$  state studied here is basically a  $^3\Sigma_1^-$  component of the  $B^3\Sigma_u^-$  state.

It is worth mentioning that the alignment-orientation conversion induced by nonlinear Zeeman mixing gives the possibility to study the

weak interaction effects via magnetic characteristics of not only diamagnetic but paramagnetic states as well. For instance, the  $1\bar{u}$  state of  $\text{Te}_2$  studied here was always treated as unperturbed by  $1u^+0_0^+$  interaction and its magnetic properties were described by the  $G_z$  value only.

#### 4. CONCLUDING REMARKS

We demonstrated and analyzed the transformation of alignment of molecular angular momenta into their orientation under the influence of nonlinear Zeeman effect. This effect of breaking the cylindrical symmetry manifests itself in the occurrence of fluorescence circularity under linear polarized excitation. Sufficiently effective alignment-orientation conversion was registered in a  $1\bar{u}$ -component of  $B^3\Sigma_u^-$  state of  $\text{Te}_2$  caused predominantly by magnetic field induced  $1\bar{u}^+0_0^+$  state mixing with  $\Delta J=\pm 1$ . It is important to mention that since the linear Zeeman effect is not able to cause orientation, the registration of circularity at linear polarized excitation makes it possible to separate this effect from the own  $1u$ -state paramagnetism. Hence, the measurement of magnetic properties can be used to study intramolecular interaction not only in diamagnetic  $\Lambda=0$  or  $\Omega=0$  states which appeared to be an extremely sensitive test of weak perturbations, but can be applied also to paramagnetic states.

#### 5. REFERENCES

1. H.Lefebvre-Brion and R.W.Field, *Perturbations in the Spectra of Diatomic molecules*, Academic Press, New York, 1986.
2. I.P.Klincare, M.Ya.Tamanis, A.V.Stolyarov, M.P.Auzinsh and R.S.Ferber, "Alignment-orientation conversion by quadratic Zeeman effect: Analysis and observation for  $\text{Te}_2$ ", *J.Chem.Phys.*, submitted.
3. M.P.Auzinsh and R.S.Ferber, "Emergence of circularity at linear polarized Excitation of molecules", *J.Chem.Phys.*, submitted.
4. I.P.Klitsare, A.V.Stolyarov, M.Ya.Tamanis, R.S.Ferber and Ya.A.Kharya, "Anomalous behaviour of Landé factors of the  $\text{Te}_2(B0_u^+)$  molecule and of the intensities of the  $B0_u^+-X1_g^+$  transition", *Opt.Spectr.(USSR)*, Vol.66, pp.595-597, 1989.
5. E.A.Pazyuk, A.V.Stolyarov, M.Ya.Tamanis, and R.S.Ferber, "Global deperturbation analysis from energetic, magnetic and radiative measurements:Application to  $\text{Te}_2$ ", *J.Chem.Phys.*, submitted.