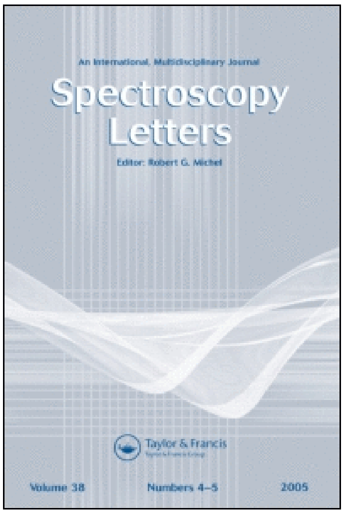

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Q Branch Excited Polarized Fluorescence of Free Polyatomic Molecules

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Q BRANCH EXCITED POLARIZED FLUORESCENCE OF FREE POLYATOMIC MOLECULES.

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ABSTRACT

The formation mechanism of the Q branch excited luminescence polarization of complex molecules in the vapor phase is considered in massive asymmetrical top model. The calculated maps are given together with available experimental values of the degree of polarization and Q branch intensities as functions of the relation of the principal inertia moments and of the absorbing and emitting oscillators orientation. The calculated and measured values of the degree of polarization are compared.

Large polyatomic (complex) molecules possess specific features as a subject of spectroscopy. The large moment of inertia of a massive molecular top results in small values of rotational constants, therefore the molecules have high density of rotational states even at jet-cooling temperatures. Complex molecules, as a rule, are asymmetrical tops and therefore the quantum-mechanical approach to quantitative interpretation of their polarized luminescence requires tedious, time-consuming calculations. It is the reason to develop simple and easy-to-interpret semiclassical methods.

For example, the polarized luminescence of complex molecules in the gas phase excited by noncoherent light can be interpreted as an instant optical excitation and aligning followed by the relaxation of the alignment with regular rotation of molecules. This model can be treated by the semiclassical method of orientational correlation functions [1], which has been developed by Blokhin for asymmetrical molecular tops using the angle-action variables [2,3]. We show here that the polarization of undispersed fluorescence when excited in the Q branch of a rovibronic band is interpreted well by the semiclassical approximation of the massive rigid asymmetrical top model.

It has been shown [3,6] that the movement of the vector **D** fixed in regularly rotating free asymmetrical top is governed by the matrix $D_{mr}(t)$:

$$D_m(t) = \sum_{r=-1}^{1} D_{mr}(t)\cdot D_r = \sum_{n,r=-1}^{1} D_r d^1_{mn}(\beta_0)\exp\Big[-i\big(m\phi_3+n(\phi_2+\omega_2 t)+ \\ + r^2(\phi_1+\omega_2 t)\big)\Big]\cdot\sum_{N=\infty}^{\infty} a^{1N}_{nr}\exp\big[-i\cdot 2N(\phi_1+\omega_1 t)\big], \qquad (1)$$

where D_r are the cyclic components of **D** symmetrized relative to the main inertia planes [3]; $d^1_{mn}(\beta_0)$ are Wigners functions $D^1_{mn}(0,\beta_0,0)$; $\omega_1,\omega_2,\phi_1,\phi_2$ are the frequencies and phases of principal rotational modes of top, β_0 and ϕ_3 are the polar and azimuth angles; a^{1N}_{nr} are the amplitudes of composite rotational modes of frequencies

$$\Omega_{nNr} = n\omega_2+(2N + r^2)\omega_1 .$$

The amplitudes are functions of parameter $z=M^2(2EI_B)^{-1}$, in which M is the magnitude of angular momentum vector, E is the rotational energy of ground state, $I_a \le I_b \le I_c$ are the principal inertia moments of the molecular top. The dipole transition rate constant when oscillator $\mathbf{D} = D_0\mathbf{d}$ ($|\mathbf{d}|=1$) of proper frequency ω_0 in the light field of frequency ω is defined by the known expression :

$$P(t,\omega) = \frac{E_0^2 D_0^2\ \omega_0^2}{4\pi^2\omega^2}\ \frac{d}{dt}\ \left|\int_0^t (\mathbf{e}\cdot\mathbf{d})\exp(-i\Delta\omega\theta)\,d\theta\right|^2, \qquad (2)$$

with $\Delta\omega = \omega - \omega_0$, $\mathbf{E} = E_0 \mathbf{e}$ ($|\mathbf{e}| = 1$) is the amplitude of exciting light.

The time dependence of **d** is given by the simple relation (1). Under the precondition from relations (1) and (2) when coherency time is long (formally $t \to \infty$) it follows:

$$P(\Delta\omega) = \frac{\pi}{4} \frac{E_0^2 D_0^2 \omega_0^2}{h^2 \ \omega^2} \sum_{m,n,N,r} |\mathbf{e}_m|^2 |\mathbf{d}_r|^2 \left(d^1_{mn}(\beta_0) \right)^2 \left(a^{1N}_{nr} \right)^2 \delta(q), \tag{3}$$

$\mathbf{e}_m$ are the cyclic components of the exciting field amplitude **e**; $\delta(q)$ is the delta-function of parameter

$$q = n\omega_2 + (2N + r^2)\omega_1 + \Delta\omega = \frac{M}{I_B} \alpha_{nNr} + \Delta\omega, \tag{4}$$

which defines conditions ($q=0$) of resonance interaction of light field and absorbing oscillator with composite rotation frequency Ω_{nNr}.

Q branch excitation (Q transition in the rigid top model) takes place when $\Delta\omega=0$ and $\Omega_{nNr}=0$, so it holds $\alpha_{nNr}=0$ for all rotational states of molecular top. It is evident that $\alpha_{nNr}=0$ when $n=N=r=0$. From this condition and (1),(3) it follows that the intensity of the transition is proportional to squared stationary harmonic amplitude a^{10}_{00} , which is equal to the time independent part of unit vector projection of main in rotational subspace axes A or C on rotational moment direction, i.e. equal to independent of rotation part of transition dipole moment projection on the angular momentum direction. The rotational phase space of asymmetrical top is divided by stereodynamics of the top movement in subspaces $\Gamma^{(\pm A)}$ and $\Gamma^{(\pm C)}$. Analytical expressions of the top movement in the subspaces are identical in form and differ by the interchange of the A and C axes [7].

If the polarization vector and the main axis of cyclic coordinates ($m=0$) coincide, $(d^1_{00})^2$ is equal to $\cos^2\beta_0$ In the $\Gamma^{(\pm A)}$ subspace Fourier-amplitude a^{10}_{00} and squared projections **d** on A, B and C axes have the form :

$$(a^{10}_{00})^2 = \frac{\pi^2}{4\ K^2(k)} \cdot \frac{y}{z} \cdot \frac{x-z}{x-y} ,$$

$$|d_0|^2=d_A^2,\quad |d_1|^2=d_B^2,\quad |d_{-1}|^2=d_C^2,\quad k^2=\frac{x-1}{1-y}\cdot\frac{z-y}{x-z} \tag{5}$$

and in $\Gamma^{(\pm C)}$

$$(a^{10}_{00})^2=\frac{\pi^2}{4\,K^2(k)}\,\frac{x}{z}\cdot\frac{z-y}{x-y}\ ,$$

$$|d_0|^2=d_C^2,\ |d_1|^2=d_B^2,\ |d_{-1}|^2=d_A^2,\quad k^2=\frac{1-y}{x-1}\cdot\frac{x-z}{z-y} \tag{6}$$

where $K(k)$ is the first kind complete elliptical integral of parameter k; $x=I_C/I_B$; $y=I_A/I_B$.

The transition dipole moment components along the B and C axes in $\Gamma^{(\pm A)}$ and along the A and B axes in $\Gamma^{(\pm C)}$ are forbidden in Q transition, as it is known for the B bands, which have no Q branch. When we use linearly polarized exciting light the fluorescence anisotropy index R is defined by the relation

$$R=\frac{I_{\parallel}-I_{\perp}}{I_{\parallel}+2I_{\perp}}=\left\langle P_2(\mathbf{e}\cdot\mathbf{d}_e)\right\rangle_{\Gamma^*}, \tag{7}$$

in which $I_{\parallel}$ and $I_{\perp}$ are intensities of fluorescence polarized parallel and orthogonal to $\mathbf{e}$, respectively; P_2 is the second kind Legendre polynomial of parameter $(\mathbf{e}\cdot\mathbf{d}_e)$, where $\mathbf{d}_e$ is the emission transition dipole moment. In (7) P_2 is averaged over the ensemble of excited molecules Γ^*. One can show [8] that the time-average of $P_2(\mathbf{e}\cdot\mathbf{d}_e)$ is

$$\left\langle P_2(\mathbf{e}\cdot\mathbf{d}_e)\right\rangle_t=P_2(\mathbf{e}\cdot\mathbf{m})\left\langle P_2(\mathbf{m}\cdot\mathbf{d}_e)\right\rangle_t \tag{8}$$

with $\mathbf{m}=\mathbf{M}/M$, $(\mathbf{e}\cdot\mathbf{m})=\cos\beta_0=d^1_{00}$. Here $\left\langle P_2(\mathbf{m}\cdot\mathbf{d}_e)\right\rangle_t$ is the transition crossection anisotropy index of molecular top with fixed $\mathbf{d}_e$ and x, y, z for a long-time observation . It differs from similar anisotropy index of unrotating transition dipole because of dispersion of $\mathbf{d}_e$ orientation by regular rotation. The analytical form of

$$\left\langle P_2(\mathbf{m}\cdot\mathbf{d}_e)\right\rangle_t=\frac{1}{2}\left[3\left\langle(\mathbf{m}\cdot\mathbf{d}_e)^2\right\rangle_t-1\right]$$

is determined using the known solutions of Euler's equations for a free asymmetrical top. So for $\Gamma^{(\pm A)}$ and $\mathbf{d}_e$ directed along A, B and C axes

$$\left\langle (\mathrm{m}\cdot\mathbf{d}_{eA})^2 \right\rangle_t = \frac{y}{z}\cdot\frac{x-z}{x-y}\cdot\frac{E(k)}{K(k)}; \tag{9.1}$$

$$\left\langle (\mathrm{m}\cdot\mathbf{d}_{eB})^2 \right\rangle_t = \frac{1}{z}\cdot\frac{z-y}{1-y}\cdot\left(1-\frac{E(k)}{K(k)}\right)\cdot\frac{1}{k^2}; \tag{9.2}$$

$$\left\langle (\mathrm{m}\cdot\mathbf{d}_{eC})^2 \right\rangle_t = \frac{x}{z}\cdot\frac{z-y}{x-y}\cdot\left(1-\frac{1}{k^2}\cdot\left(1-\frac{E(k)}{K(k)}\right)\right), \tag{9.3}$$

where E(k) is the second kind complete elliptic integral of parameter k defined in (5) and (6). For $\Gamma^{(\pm C)}$ it is necessary to interchange A and C, x and y in the relations (9.1)-(9.3).

The anisotropy index (7) transforms under the above conditions to

$$R_Q = \frac{\left\langle P_Q \cdot P_2(\mathbf{e}\cdot\mathbf{d}_e) \right\rangle}{\left\langle P_Q \right\rangle}, \tag{10}$$

where P_Q is given by (3) at $\Delta\omega = n = N = r = 0$, $\Gamma = \Gamma^{(\pm A)} + \Gamma^{(\pm C)}$.

We emphasize that the theoretical approach to the Q transitions is correct in spite of the approximate nature of the semiclassical model of a heavy top and of interaction form with the exciting light because at the excitation in the Q branch the transition occurs without interaction of the top with light and error in the magnitude of the pertubation does not play any role.

The expression for P_Q obtained from (3) allows us also to find the relative intensity of Q transition as a function of transition dipole moment orientation and parameters x and y. One can see that equal transition dipole moments oriented along the axes A and C result in different Q branch intensities which are proportional to expressions

$$\sqrt{\frac{y^3}{(x-1)(x-y)^2}}\int_y^1 \frac{dz}{z}\,\frac{\sqrt{x-z}}{K(k)}\,; \quad \sqrt{\frac{x^3 y}{(x-1)(x-y)^2}}\int_1^x \frac{dz}{z}\,\frac{\sqrt{z-y}}{K(k)}\,, \tag{11}$$

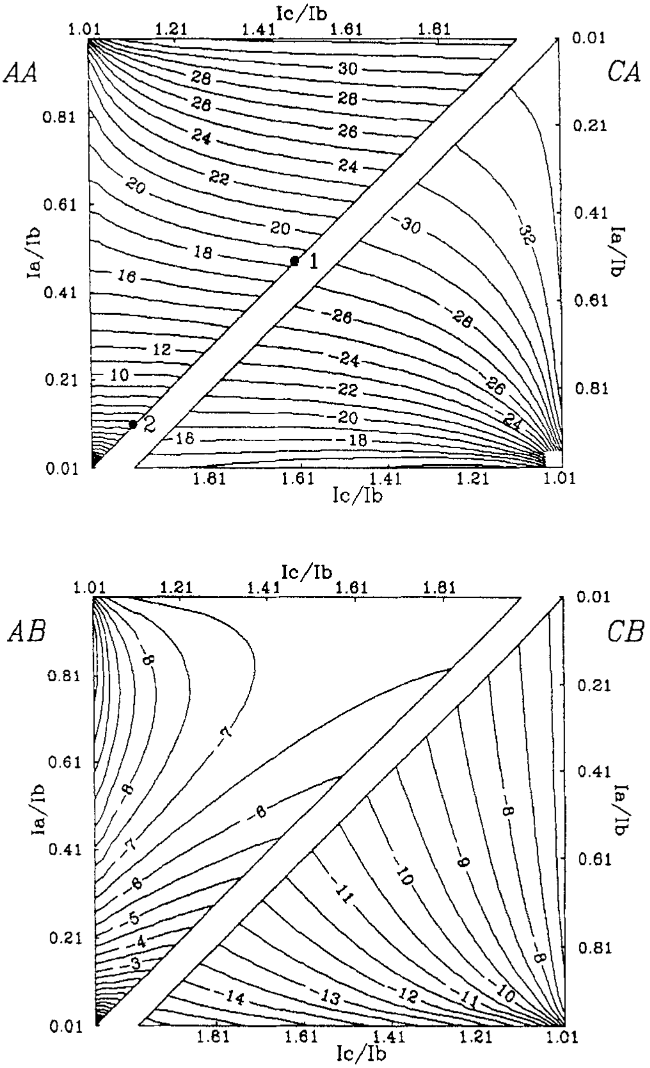

Fig.1. Polarization maps of Q branch excited luminescence as a function of molecular top parameters x, y. The first and second letters mark the type of the excitation and emission band, respectively. Numbered circles: (1) 1,4-diaminoanthraquione, 21.5% [11], (2) thriphendioxazine, 3.6% [11], (3) pyrimidine, 25.0±2% (jet cooling), 26.5±1% (300K) [9]; 26% [10].

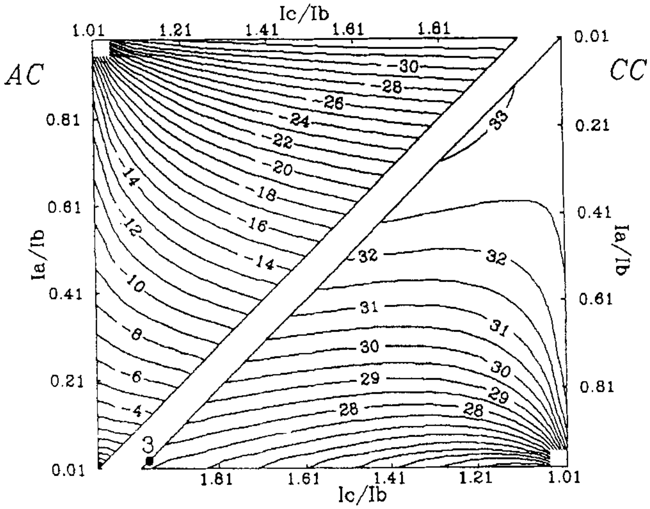

Fig. 1. Continued.

The simplicity of analytical expressions for dependencies of fluorescence polarization and for Q transition intensity on asymmetrical top structure (on the relations of the principal moments of inertia) makes it possible to visualize the general results of the dependencies. In fig.1 the calculated maps of fluorescence polarization degree values and relative intensities of rigid asymmetrical top Q transitions are shown when the absorption transition dipole moment is oriented along the A or C axis and the emitting oscillator is directed along the A, B or C axis. One can see that any arbitrary orientation is a composition of the cases under consideration. The triangular maps correspond to general set of x and y of the rigid asymmetrical top molecular model. The long side of the triangle corresponds to planar molecules (x-y=1), the short sides corresponds to oblate (y=1) and prolate (x=1) tops, point x=y=1 is for spherical top. The values given in the maps are calculated for x>1 and y<1, that is the cases of spherical and sym-

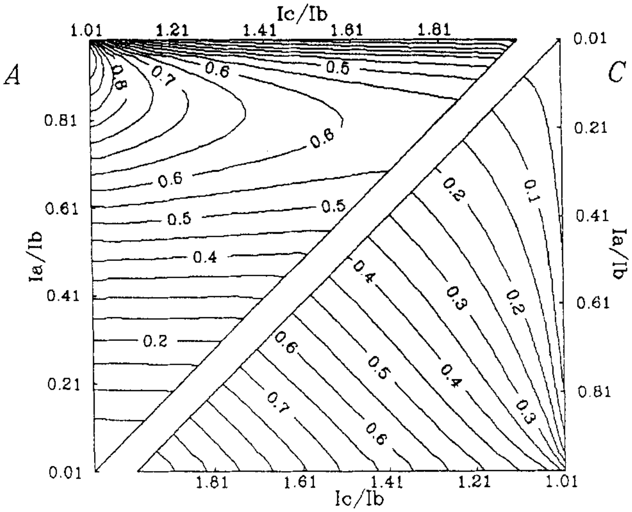

Fig.2. Map of relative intensity of Q branch as a function of molecular top parameters x, y for the A and C bands.

metrical tops are excluded. Numbered circles mark the top configurations for which the values of the degree of polarization have been measured experimentally and the data are reliable. The measured values of the degree of polarization and references are given in the legend. The scanty experimental data nevertheless correlate well. Unfortunately the observed values relate only to planar molecules, therefore it is necessary to have experimental data on other asymmetrical tops.

From the maps it is seen that the fluorescence polarization value essentially depends on the relation of principal moments of inertia and on the intramolecular oscillator orientation. Some of the polarization values exceed 30%, which is never observed or predicted at noncoherent excitation. Maps of relative intensity of the Q transition (Fig.2) show strong dependence of the Q branch intensity on the parameters of the top. Characteristically, for both A and C bands the intensity drops with the top elongation.

The above considerations result in one more interesting conclusion, that the expected value of the degree of fluorescence polarization of a rigid top when both monitoring and excitation are in the Q branch is 50%, as it is observed for diatomic molecules and for rigid isotropic solutions [12].

In general we can state that it is feasible to calculate the anisotropy of fluorescence of complex molecules by a simple and easy-to-interpret method when the fluorescence is excited in the Q branch of a rovibronic band. The dependence of the Q branch excited fluorescence polarization on molecular structure will be useful for molecular spectroscopy and the obtained maps should be important to select the molecular fluorescent polarizational probes, since in this case one needs high polarization and Q band intensity.

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