

Splitting of polarized impurity-fluorescence bands in the steady-state spectrum of an isotropic solution

E. M. Aver'yanov

L. V. Kirenskiĭ Physics Institute, Siberian Branch of the Russian Academy of Sciences, 660036 Krasnoyarsk, Russia

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A difference is predicted between the peaks, ν_{VV} and ν_{VH} , of the polarized components $J_{VV}(\nu)$ and $J_{VH}(\nu)$ in the steady-state spectrum of impurity fluorescence in an isotropic solution. This difference would result from a temporal correlation between an orientational Brownian diffusion of excited fluorescing molecules and a structural relaxation of the surrounding matrix molecules.

1. The splitting of polarized spectral bands of condensed molecular media is usually associated with the presence of a macroscopic structural anisotropy of the medium due to a long-range translational or orientational order of the molecules. This is correct for the known types of splitting of polarized absorption bands: resonant (Davydov) splitting of exciton bands in molecular crystals,¹ its analog in liquid crystals,² static splitting of electron bands of impurity absorption in liquid crystals and in anisotropic polymer films,^{3,4} and splitting of nonuniformly polarized bands of impurity absorption in anisotropic media.⁵ In the case of a steady-state impurity fluctuation, however, a splitting of its polarization components can occur even in an isotropic solution under several conditions, specified below, which might be realized experimentally.

2. We consider a dilute isotropic solution of fluorescent molecules which absorb and emit light in the transmission region of the matrix in the absence of exchange effects by virtue of an excitation in the impurity–impurity and impurity–matrix systems. To avoid making the physical side of the picture too complicated, we assume that the fluorescent molecules are uniaxial, that one of the absorption or emission oscillators is parallel to the molecular axis, and that the other is oriented at an angle β from this axis. The component $J_{ij}(\nu)$ of the steady-state impurity-fluorescence spectrum is given by

$$J_{ij}(\nu) = \int_0^{\infty} dt F(t) I_{ij}(t) \rho(\nu, t), \quad (1)$$

where we have omitted the isotropic coefficients, the indices i and j specify the polarizations of respectively the absorbed and emitted light in the laboratory coordinate system, $F(t) = \exp(-t/\tau_F)/\tau_F$, and τ_F is the effective decay time of the fluorescence. The independent components $I_{VV}(t)$ and $I_{VH}(t)$ in the cases of vertical (V) and horizontal (H) polarizations of the light are given by⁶

$$I_{VV}(t) = 1 + \frac{4}{5} S_{\beta} \exp(-t/\tau_R), \quad I_{VH}(t) = 1 - \frac{2}{5} S_{\beta} \exp(-t/\tau_R), \quad (2)$$

where $S_\beta = (3\cos^2\beta - 1)/2$, and τ_R is the time scale of the rotational Brownian relaxation of the orientational correlation functions:

$$\Phi_{n0}(t) = \langle D_{n0}^2(\Omega_0) D_{n0}^{2*}(\Omega_t) \rangle = 0.2 \exp(-t/\tau_R)$$

with $n=0.2$.

In accordance with the experiments of Refs. 7-9, we assume that the shape of the band $\rho(\nu, t)$ of the instantaneous fluorescence spectrum at the time t , excited by a δ -function pulse at $t=0$, is independent of t , although the shift of its peak, $\nu_0(t)$, is approximated by the familiar expression^{8,9}

$$\nu_0(t) = \nu_0(\infty) + \Delta\nu \exp(-t/\tau_0), \quad (3)$$

where $\Delta\nu = \nu_0(0) - \nu_0(\infty)$. The change in $\nu_0(t)$ stems from a structural relaxation of the environment of the fluorescent molecules during their lifetime in the excited state.

The position of the maximum ν_{ij} of the $J_{ij}(\nu)$ band satisfies the equation

$$\int dt F(t) I_{ij}(t) \rho'(\nu, t) = 0. \quad (4)$$

Since $\Delta\nu$ is much smaller than the half-width Γ of the $\rho(\nu, t)$ band,⁷⁻⁹ we can find a solution of Eq. (4) by expanding the derivative $\rho'(\nu, t)$ in a series in $\nu - \nu_0(t)$ in the neighborhood of $\nu_0(t)$ and retaining only the linear approximation. As a result, we have

$$\begin{aligned} \nu_{VV} &= \nu_0 + \frac{4}{5} S_\beta \delta_{\nu R} \left[1 + \frac{4}{5} S_\beta \tau_R / (\tau_R + \tau_F) \right]^{-1}, \\ \nu_{VH} &= \nu_0 - \frac{2}{5} S_\beta \delta_{\nu R} \left[1 - \frac{2}{5} S_\beta \tau_R / (\tau_R + \tau_F) \right]^{-1}, \end{aligned} \quad (5)$$

where

$$\begin{aligned} \nu_0 &= \int dt F(t) \nu_0(t), \\ \delta_{\nu R} &= \int dt F(t) \nu_0(t) \exp(-t/\tau_R) - \nu_0 \tau_R / (\tau_R + \tau_F). \end{aligned} \quad (6)$$

The quantity ν_0 gives us the position of the maximum of the band,

$$\rho(\nu) = \int dt F(t) \rho(\nu, t) = \frac{1}{3} [J_{VV}(\nu) + 2J_{VH}(\nu)], \quad (7)$$

found at the magic angle $\theta_M = 54.7^\circ$ between the polarizations of the exciting and analyzing light. If the shape $\rho(\nu, t)$ remains constant over time, regardless of the relation between $\Delta\nu$ and Γ , expressions (5) are exact and are of the same form for the centers of gravity $\bar{\nu}_{ij}$ of the $J_{ij}(\nu)$ bands, with $\nu_0(t)$ and ν_0 being replaced by the centers of gravity $\bar{\nu}(t)$ and $\bar{\nu}$ of the $\rho(\nu, t)$ and $\rho(\nu)$ bands.

Substituting (3) into (6), we find

$$\delta_{vR} = \frac{\Delta\nu\tau_0\tau_R\tau_F^2}{(\tau_0 + \tau_F)(\tau_R + \tau_F)[(\tau_0 + \tau_F)(\tau_R + \tau_F) - \tau_F^2]} \quad (8)$$

The parameter δ_{vR} , which is responsible for the difference between ν_{VV} and ν_{VH} , is a measure of the temporal correlation between two relaxation processes: the rotational Brownian diffusion of the excited fluorescent molecules and the restructuring of the coordination neighborhoods of these molecules. In contrast with the effect of the correlation between these relaxation processes on polarization aspects of the $J_{ij}(\nu, t)$ spectra, which were discussed in Ref. 10, the difference ν_{ij} in which we are interested in the present paper pertains to only the steady-state spectrum $J_{ij}(\nu)$. It does not exist for the maxima $\nu_{ij}(t) = \nu_0(t)$ of the $J_{ij}(\nu, t)$ bands in the isotropic phase.⁶ The parameter δ_{vR} vanishes if at least one of the following conditions holds: $\tau_0 \gg \tau_F$, $\tau_R \gg \tau_F$, and the inverse inequalities. The physical reason for the difference between ν_{VV} and ν_{VH} is that under the condition $S_\beta \Delta\nu > 0$ the component $J_{VV}(\nu)$ [$J_{VH}(\nu)$] is dominated by the short-lived (long-lived) molecules with the higher-frequency (lower-frequency) position of the $\rho(\nu, t)$ spectrum.

3. Looking at experimental consequences of (5), we note that, with $\tau_0 = \tau_R = \tau_F$, $\beta = 0$, and the typical value $\Delta\nu \approx 10^3 \text{ cm}^{-1}$, the magnitude of the splitting, $\nu_{VV} - \nu_{VH} \approx 10^2 \text{ cm}^{-1}$, would be large enough to be seen experimentally. It would be comparable to the difference $\nu_{xx} - \nu_{zz}$ in the steady-state $J_{ij}(\nu)$ spectrum of the impurity fluorescence of nematic liquid crystals.⁶ In the case of Stokes excitation of fluorescence we would have $\Delta\nu > 0$ (Refs. 8 and 9), and the inequalities $\beta \geq \theta_M$ would correspond to the inequalities $\nu_{VV} \geq \nu_{VH}$. In the case of anti-Stokes excitation of the fluorescence in viscous solutions we would have^{7,11} $\Delta\nu < 0$, and in the cases $\beta \geq \theta_M$ we would have $\nu_{VV} \geq \nu_{VH}$.

The difference between ν_{VV} and ν_{VH} is directly related to the spectral variation of the fluorescence anisotropy,

$$r(\nu) = \frac{J_{VV}(\nu) - J_{VH}(\nu)}{J_{VV}(\nu) + 2J_{VH}(\nu)}, \quad (9)$$

or the degree of polarization of the fluorescence, $P(\nu) = 3r(\nu)/[2 + r(\nu)]$. To demonstrate this assertion, we use the representation

$$J_{VV}(\nu) = \rho(\nu)[1 + 2r(\nu)], \quad J_{VH}(\nu) = \rho(\nu)[1 - r(\nu)]. \quad (10)$$

We easily find the following expressions for the maxima of these bands:

$$\begin{aligned} \nu_{VV} &= \nu_0 + \frac{2r'(\nu_0)/\alpha}{1 + 2[r(\nu_0) - r''(\nu_0)/\alpha]}, \\ \nu_{VH} &= \nu_0 - \frac{r'(\nu_0)/\alpha}{1 - [r(\nu_0) - r''(\nu_0)/\alpha]}, \end{aligned} \quad (11)$$

where $\alpha = |\rho''(\nu_0)|/\rho(\nu_0)$. At the same level of accuracy of the $\rho'(\nu, t)$ expansion, using (2), we can convert expression (11) into (5); the sign of $r'(\nu_0)$ will be the same as the sign of the product $S_\beta \Delta\nu$. The difference between the components ν_{VV} and ν_{VH} is therefore larger for broad $\rho(\nu)$ bands with a flat maximum. Despite the fact

that the $r(\nu)$ and $P(\nu)$ spectra are well known for isotropic solutions with a $\nu_0(t)$ relaxation,^{8,9} a difference between the components ν_{VV} and ν_{VH} might have previously been perceived as a manifestation of parasitic, instrumental, depolarizing factors.⁹

4. In summary, a difference between the ν_{VV} and ν_{VH} maxima of the steady-state components $J_{VV}(\nu)$ and $J_{VH}(\nu)$ of polarized impurity fluorescence in an isotropic solution expands our understanding of the anisotropic spectral properties of isotropic media, and it adds to the possibilities for the practical utilization of these properties. The parameters τ_0 , τ_R , and $\Delta\nu$ might be optimized to increase the difference $\nu_{VV} - \nu_{VH}$ through an appropriate change in the temperature (or viscosity) and polarity of the solvent. By varying the angle (θ) between the polarizations of the exciting and analyzing light, we could continuously tune the maximum of the steady-state fluorescence band over the entire frequency interval from ν_{VV} to ν_{VH} .

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