

“Latent” optical activity of molecules

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We consider the question of the appearance of optical activity in an ensemble of oriented symmetrical molecules that are optically inactive when their orientation is random. We present experimental data that confirm the existence of such a “latent” optical activity and demonstrate the feasibility of using this method to investigate molecules.

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Circular dichroism (CD) spectroscopy has proved itself as an effective method for the investigation of molecular structure, and has found extensive applications in physics, chemistry, and biology. However, so far this method has been restricted to the investigation of asymmetrical molecules. The torque $R_{o\alpha}$ which characterizes the sign and intensity of the CD band for a transition of a molecule from the ground state o to the excited state α can be described in the case of isotropic distribution by the formula^[1]

$$R_{o\alpha} = \text{Im}(\vec{\mu}_{o\alpha} \mathbf{m}_{\alpha o}), \quad (1)$$

where $\mu_{o\alpha}$ and $\mathbf{m}_{\alpha o}$ are the transition matrix elements of the electric and magnetic dipole-moment operators. Expression (1) imposes a restriction on the symmetry of the molecules: the only optically active molecules are those having no inversion center and symmetry planes. The situation is different for oriented systems. A study of the CD spectra of oriented molecules yields more complete information on their structure, and it is precisely this circumstance which has attracted the attention of researchers to this problem. Strange as it may seem, however, no attention was paid to another no less important aspect, namely the fact that orientation makes it possible to increase greatly the number of investigated molecules.

The optical activity of an ensemble of oriented molecules is described by the torque tensor \mathcal{R}_{ij} , which can be represented as a sum of two tensors^[2] \mathcal{R}_{ij}^M and \mathcal{R}_{ij}^Q

$$\mathcal{R}_{ij} = \mathcal{R}_{ij}^M + \mathcal{R}_{ij}^Q, \quad (2)$$

$$\mathcal{R}_{ij}^M = \frac{3}{2} \text{Im} [(\vec{\mu}_{\alpha a} m_{\alpha a}) \sigma_{ij} - m_{i\alpha a} \mu_{j\alpha a}], \quad (3)$$

$$\mathcal{R}_{ij}^Q = - \left(\frac{3 \omega_{\alpha a}}{4c} \right) \text{Re} (e_{ikl} \vec{\mu}_{l\alpha a} Q_{kja\alpha}), \quad (4)$$

where \mathcal{R}_{ij}^M and \mathcal{R}_{ij}^Q are the torque tensors connected with the magnetic-dipole and electric quadrupole transition moments $m_{\alpha a}$ and $(Q_{kj})_{\alpha a}$, respectively; e_{ikl} is the Levi-Civita symbol, σ_{ij} is the Kronecker symbol, $\omega_{\alpha a}$ is the transition frequency, and c is the speed of light. Spatial averaging causes the tensor \mathcal{R}_{ij}^M to degenerate into the pseudoscalar (1), while the tensor \mathcal{R}_{ij}^Q averages out to zero. Expressions (3) and (4) impose less stringent restrictions on the molecule than (1), and require only that it has no inversion center, but admits of the existence of symmetry planes. Thus, introduction of orientation can in principle lead to the appearance of optical activity in molecules that are optically inactive in the case of random orientation, we shall call this phenomenon "latent" optical activity.

Let us dwell on that part of the tensor \mathcal{R}_{ij} which is connected with the magnetic-dipole transition element. For molecules without an inversion center but with symmetry planes, the first term in (3) is equal to zero, therefore

$$\mathcal{R}_{ij}^M = - \frac{3}{2} \text{Im} [m_{i\alpha a} \mu_{j\alpha a}]. \quad (5)$$

We consider the situation when the molecules are arranged on a helical matrix, as shown in Fig. 1. This arrangement of the molecule simulates, for example, the arrangement of the ligands in helical biopolymers and cholesteric liquid crystals. By virtue of the axial symmetry of the system along the z axis, the tensor \mathcal{R}_{ij}^M becomes partially averaged out and assumes the diagonal form (in the coordinates x, y, z)

$$\mathcal{R}^M = \begin{pmatrix} R_{\perp} & 0 & 0 \\ 0 & R_{\perp} & 0 \\ 0 & 0 & R_{\parallel} \end{pmatrix}, \quad (6)$$

where

$$R_{\perp}^M \equiv R_{xx}^M = R_{yy}^M = \frac{3}{4} \text{Im} [\mu_{z\alpha a} m_{z\alpha a}], \quad (7a)$$

$$R_{\parallel}^M \equiv R_{zz}^M = \frac{3}{2} \text{Im} (\vec{\mu}_{\perp\alpha a} m_{\perp\alpha a}). \quad (7b)$$

Here $\mu_{\perp\alpha a}$ and $m_{\perp\alpha a}$ are the projections of the vectors $\mu_{\alpha a}$ and $m_{\alpha a}$ on the xy plane. If the arrangement of the molecules in the matrix is such that the vector $m_{\alpha a}$ lies in the plane of the vectors $\mu_{\alpha a}$ and z then expressions (7) take the form

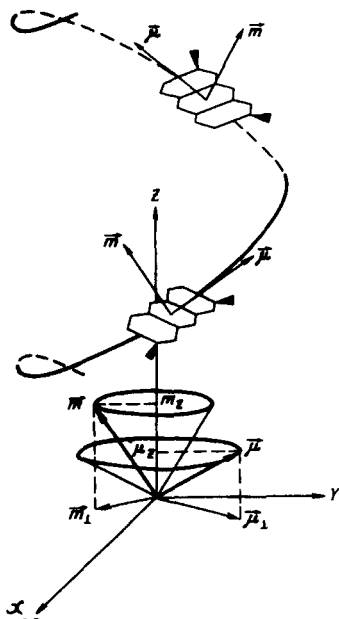


FIG. 1. Arrangement of the molecules in a helical matrix and orientations of the transition moments μ and m .

$$R_{\perp}^M = \frac{3}{8} \sin 2\alpha \text{Im}[\mu_{\alpha} m_{\alpha}], \quad (8a)$$

$$R_{\parallel}^M = -\frac{3}{4} \sin 2\alpha \text{Im}[\mu_{\alpha} m_{\alpha}], \quad (8b)$$

where α is the angle of inclination of the vector μ_{α} to the xy plane. As seen from (8), the components R_{\perp}^M and R_{\parallel}^M reach their maximum absolute value at the angle $\alpha = 45^{\circ}$. In this case observation along the z axis will reveal the maximum effect of "latent" optical activity. At $\alpha = 0$ and $\alpha = 90^{\circ}$, the components of the torque tensor are equal to zero, corresponding to excitation of either only the electric or only the magnetic dipole moment. We present below experimental data that confirms the existence of "latent" optical activity in planar molecules and demonstrate the potential capabilities of the proposed method.

We investigated the CD spectra of proflavine molecules (symmetry group c_{2v}) adsorbed on double-helix molecules DNA and RNA. The complexes DNA-PF and RNA-PF were oriented in a flow-through cell, the construction of which made it possible to register the CD in the direction of the preferred orientation of the polymers and to avoid effects of linear dichroism.^[3,4] Figure 2 shows the CD spectra of these complexes in the dye absorption region with maximum at 460 nm. In both cases, orientation gives rise to "latent" optical activity, this effect being most strongly pronounced in the case of the complex of the proflavine with DNA, as is evidenced by the total absence of CD for the non-oriented solution. The electric transition dipole moment of the 460-nm band lies in the plane of the proflavine molecule and is directed along its long axis. The corresponding magnetic moment is perpendicular to the plane of the molecule. A comparison of the experimental results with the theory [formula (8)] leads to the following significant conclusions: a) The planes of the dye molecules in the complexes DNA-PF and RNA-PF are not perpendicular to the axis of the polymer helix, but make a certain angle with the plane normal to the axis. b)

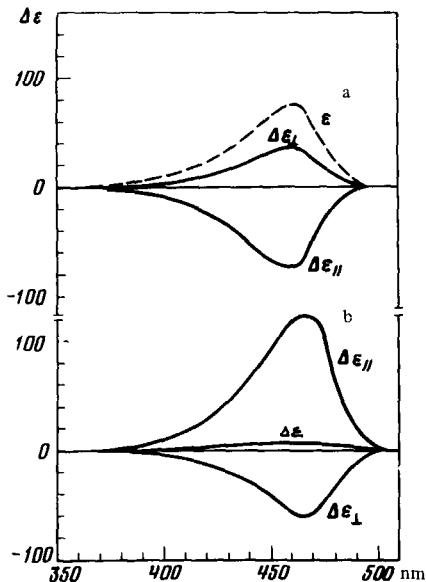


FIG. 2. Optical activity of oriented proflavine molecules: a—CD spectra of the DNA-proflavine complex, b—CD spectra of the RNA-proflavine complex, $\Delta\epsilon$, $\Delta\epsilon_{\parallel}$, $\Delta\epsilon_{\perp}$ —isotropic, longitudinal, and transverse circular dichroism, ϵ —absorption (in molar quantities).

The sign of the inclination of the dye in the DNA-PF complex is opposite to the sign of the inclination in the RNA-PF complex. c) The magnitude of the dye inclination angle in the complex RNA-PF is approximately double that in the complex DNA-PF. This result agrees qualitatively with the intercalation model,^[5] according to which the molecules of the dye are interleaved between pairs of DNA and RNA bases and are parallel to them. Using the known values of the angle of inclination of the bases in DNA ($\alpha \approx 3^\circ$), the dipole $\mu_{\alpha\alpha}$ of the 465-nm band (5.9 D), and expression (8), we obtain an estimate of the magnetic-transition moment of the dye: $m_{\alpha\sigma} \approx 4 \mu_B$. Of course, this is only some effective value that includes a possible contribution of the quadrupole moment.¹⁾

Summarizing, we can state that the phenomenon of "latent" optical activity, which is closely connected with magnetic-dipole and quadrupole transition moments, uncovers new possibilities for the study of the electronic structure of molecules and of the spatial structure of the complexes with different polymers (including those of biological origin).

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¹⁾The quadrupole component of the torque tensor is described in this case, apart from a coefficient, by an expression analogous to (8), where $\text{Im}(\mu_{\alpha\alpha} m_{\alpha\sigma})$ is replaced by $\text{Re}(\mu_{\alpha\alpha} Q_{\alpha\sigma})$.

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