Induction of gyrotropy as a new method of study in the physics of condensed media

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The essential advantages of spectroscopic investigations by chiroptical methods based on studying gyrotropy are pointed out. The phenomena of induction of gyrotropy in nongyrotropic media by chiral matrices or chiral admixtures are described and the physical mechanism of the phenomena is analyzed. A set of methods is presented that allows one to study optically inactive molecules and nongyrotropic substances. The potentialities of the methods and their advantages are indicated with a set of examples. The methods are indicated to be highly promising and are insufficiently used in solid-state physics.

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1. INTRODUCTION

The phenomenon of gyrotropy (first-order spatial dispersion) has been widely employed for a long time to study the structure of matter and interparticle interactions. At first its most striking manifestation was studied—rotation of the plane of polarization of light, or optical activity. From the time of Pasteur, Le Bel, and van't Hoff, and later Chugaev, a theory of the spatial structure of molecules has been constructed on this basis.[1-3]

The usual measurements of optical activity are performed in the region 180–1000 nm. Measurements of circular dichroism have proved more informative owing to better resolution. At present they have been extended into the infrared region[4,5] and thus they encompass the region of vibrational frequencies and even of lattice vibrations.[6,7] On the other hand, they have been extended into the vacuum ultraviolet[8a] and the x-ray region.[8b] Methods have also been developed of measuring the Raman scattering of gyrotropic objects.[9-11] All these methods yield information on the unexcited electronic states. The development of a method of measuring circularly polarized luminescence[12] has made it possible to study the excited states as well. The contemporary methods of studying the Rayleigh scattering of chiral objects enable one to study the specifics of fluctuations and supermolecular structures.[13,14] A method has also been developed of making measurements in anisotropic media.[15,16]

Studies of the gyrotropy of chiral molecules are also being performed in photoelectron spectroscopy.[17] Thus, in essence, an entire separate field of spectroscopy has arisen—the spectroscopy of circularly polarized radiation. Methods have also been developed of measuring acoustic gyrotropy, which are important for studying crystal lattices.

Studying matter in terms of its gyrotropy has a number of advantages over many other spectroscopic methods[1-3]:

1. The gyrotropy parameter is highly sensitive to the symmetry of objects and to the smallest perturbations of it. Displacements of atoms in a molecule that alter its symmetry or displacements of molecules in a crystal can be detected in this way, starting with magnitudes of the order of 0.1–0.001 Å. It is possible to reveal and determine the arrangement and interaction of asymmetric centers.

2. The existence of an additional parameter of circularly polarized absorption bands—the signs—enables one to obtain more information in the changes, e.g., in the circular dichroism, than in ordinary absorption measurements (Fig. 1). The same pertains also to measurements of rotatory dispersion and other methods (different selection rules).

3. Studies of gyrotropy enable one to reveal and study weak, forbidden magnetic-dipole and electric-quadrupole transitions that are masked in ordinary spectral measurements by adjacent strong allowed absorption bands, and also weak singlet-triplet and triplet-triplet transitions.

4. One can determine the orientation of the moments of the stated transitions.

5. Studies of gyrotropy yield additional information on vibronic interactions, while the resolution in circular-dichroism spectra is usually higher than in absorption spectra, owing to the more rigorous selection rules.

6. One can reveal and study the effects of mixing of states of different parity and the borrowing thereby of oscillator strength by weak transitions from neighboring strong ones.

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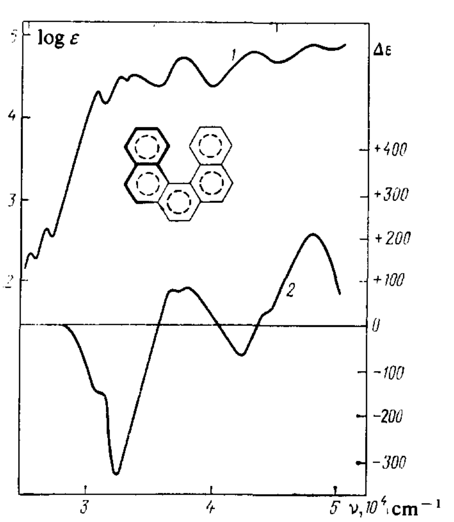


FIG. 1. Absorption (*1*) and circular-dichroism (*2*) spectra of pentahelicene in solution. The greater information content of the circular-dichroism spectrum can be seen.

Initially one studied the structure and properties of molecules, mainly in solution: the structures, conformations, coordination of ligands, etc., were determined. Subsequently it has turned out that the study of gyrotropy in its different manifestations yields much information on the structure of more complicated formations—macromolecules and polymers.

As early as the studies of Chugaev, Kuhn and a number of others, gyrotropy was found to be extremely sensitive also to intermolecular interactions: e.g., in its sensitivity to temperature variation (Fig. 2), to the effect of the solvent, to polymerization, association, etc., it greatly surpasses all other molecular parameters. This enables one to use gyrotropy as an indicator to study a number of problems of the physics of liquids (e.g., their behavior at the critical point[18a]), of glassy materials (processes of vitrification), of plastic crystals, of liquid crystals (phase transitions and pretransition phenomena[18b]) and many general manifestations of intermolecular interactions.

Study of the gyrotropy of crystals is also highly informative—one can obtain information on the structure, internal field, and collective effects. The possibility has been explored of detecting infinitesimal deformations of molecules and of more complex structural elements (e.g., metal complexes, island compounds) upon crystallization. This enables us to make our understanding of this important, ill-studied process[1] more exact; a possibility also arises of studying structural defects, impurity centers, and details of phase transitions (e.g., in ferroelectrics; see Refs. 1 and 19).

One can also obtain information on the structure of biological objects.

Without exaggeration, we can describe the methods of studying the properties of matter from its gyrotropy as having been firmly installed now in the arsenal of methods of the physics of condensed states, in particular, solid-state physics.

However, before the seventies the application of the methods was naturally restricted to the set of gyrotropic substances, which limited the generality and applicability of the method. In the past decade the methods of artificial induction of gyrotropy in materials not gyrotropic by nature have become widespread: molecules, condensed phases, impurity centers, etc. This has substantially expanded the set of materials amenable to study, and it seems to promise to make these methods very universal.

For example, it turns out to be possible to study the structure and nature of the energy levels of rare-earth ions, uranyl ions, transition-metal ions, various impurity centers, and to study the structure of any liquid crystals, solid and polymeric matrices, vacancies in semiconductors, and molecules of any structure.

This review takes as its goal the presentation of this method of studies, its theoretical foundations, and the methods of realizing and applying the obtained results.

2. GENERAL INFORMATION

Rotation of the plane of polarization, circular dichroism, and circular polarization of luminescence are special manifestations of gyrotropy—first-order spatial dispersion.

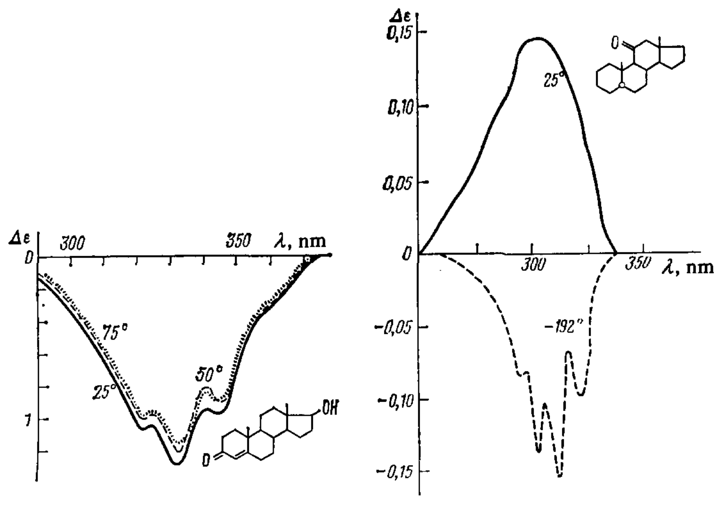


FIG. 2. Dependence of the circular dichroism on the temperature (°C) for two steroids.

As is known, spatial dispersion is a consequence of the nonlocality of the connections between the field vectors, i.e., the influence on the processes at a given point of the medium of processes occurring in adjacent regions, when this influence is transmitted at a velocity comparable with the velocity of light in the medium.

The appearance of gyrotropy requires:

1) an appreciable variation in the phase of the light wave at the characteristic distance R of the interaction that gives rise to spatial dispersion:

2) the existence in the object of study of a definite dissymmetry[1)] above all, the absence of a center of symmetry.[1-3,19]

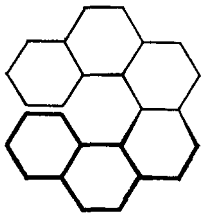
In the general case both intramolecular and intermolecular interactions or the dynamic behavior of the free carriers can make a substantial contribution to the spatial dispersion. The corresponding parameter R will have a differing physical meaning.

If the intramolecular interactions and excitations localized in the molecule play the determining role, we must identify this parameter with the dimensions of the molecule and the intramolecular distances. In this case one speaks of "molecular" gyrotropy caused by "optically active molecules".

Whenever the source of gyrotropy is the intermolecular interactions and delocalized excitations or movement of free carriers, respectively the intermolecular distances, the radius of molecular action, the lattice constant, and the mean free path of an exciton or a free carrier, etc., serve as the parameter. In this case one speaks of "crystal" gyrotropy.

In line with what has been said above, the second necessary property—dissymmetry—must in the first case be inherent in the internal structure of the molecule, while in the second case the molecules in the free state can even be symmetric, but the structure of the polymer of crystal, etc., must be dissymmetric. Evidently states that differ substantially in nature can exist simultaneously and contribute to the gyrotropy. In line with this, both types of gyrotropy can appear simultaneously.

The processes that give rise to molecular optical activity can encompass the molecule as a whole. A typical example is the molecule of hexahelicene:



Here the chain of benzene rings lie along a helix. Here all the processes of photon scattering take place in the dissymmetric cloud of completely delocalized electrons. That is, the entire molecule is excited.

In other cases the optical activity of a molecule can involve the presence in its structure of an asymmetric center. An example is the asymmetric carbon atom well-known in stereo chemistry—a carbon atom linked to four different substituents.

In the theory of optical activity a "chirophore" denotes such an element that possesses characteristic bands in the circular-dichroism spectrum. These chirophores are termed "intrinsically optically active", since their activity involves their internal dissymmetry (chirality).

Along with these chirophores, one often encounters others that have symmetry elements in the free state that rule out optical activity. The existence of the latter in any electronic transition of such a chirophore involves "induction"—asymmetric perturbation by the other parts of the molecule. The role of this perturbation can be played by the static Coulomb field of these parts. On the other hand, this can also be a dynamic perturbation of the orbitals of the electrons and the chirophore by the motion of electrons localized in other parts of the molecule. The set of these phenomena and the symmetry requirements have been analyzed in Refs. 19–21. Such chirophores are called "induced optically active". An example can be the carbonyl group ($C = 0$), a characteristic chirophore unusually sensitive to the slightest changes of symmetry, which alters not only the magnitude but also the sign of the optical activity in different compounds, depending on the position in the molecule and the near environment.

Another example is the cobalt ion (and ions of all other

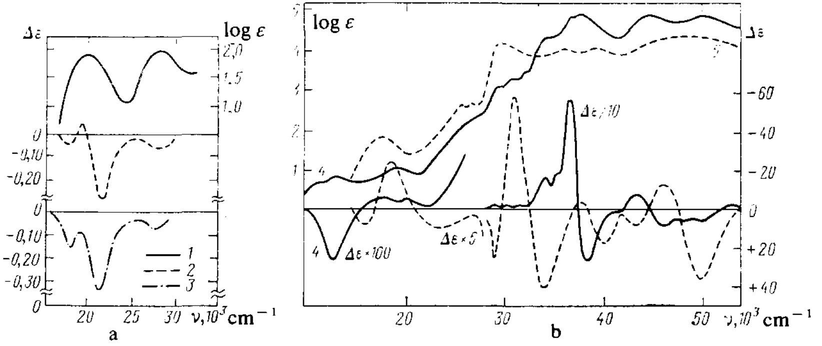


FIG. 3. a) Absorption spectrum of two Co tetraammine complexes (with leucine and valine—*1*) and circular-dichroism spectra (complex with leucine—*2*; complex with valine—*3*; circular dichroism reveals the difference[22]); b) absorption (above) and circular dichroism (below) spectra of Ni phenaminate (*4*) and Cr pentadionate (*5*)[2] (the greater information content of the circular-dichroism spectrum can be seen).

transition metals). In the free state the electron shells of cobalt atoms and ions have a center and a plane of symmetry. Hence they are optically inactive. In the complexes of coordination compounds of cobalt with organic ligands, where it enters in the form of an ion, optical activity arises in the absorption bands of the latter, induced by the asymmetric field of the ligands (Fig. 3).[22] We see that the circular-dichroism spectrum is more informative than is the absorption spectrum. One can say the same about the rare-earth ions and the uranyl ion.[23,24]

In the theoretical analysis optical activity is treated as a two-photon process of light scattering by the molecule with absorption of one photon and emission of another. In the process these two photon modes interfere; one must take into account all the possible forms of interactions, i.e., all combinations of possible modes: electric-dipole–electric-dipole ($\mathbf{p}\cdot\mathbf{p}$), electric-dipole–magnetic-dipole ($\mathbf{p}\cdot\mathbf{m}$), electric-dipole–electric-quadrupole ($\mathbf{p}\cdot\hat{\mathbf{q}}$), etc.

A detailed analysis (see Refs. 1, 19, 20) shows that the fundamental contribution always comes from the scalar product of transition moments $\mathbf{p}\cdot\mathbf{m}$. When the arrangement of the molecules is disordered, only this product contributes. With an ordered arrangement one must generally also take into account both the vector product $\mathbf{p}\otimes\mathbf{m}$ and the contributions $\mathbf{p}\cdot\mathbf{q}$ ($\hat{\mathbf{q}}$ is the tensor of the moment of the electric-quadrupole transition), etc., although they are considerably smaller as a rule.[25]

Group-theoretic analysis shows that the moments **p** and **m** differ simultaneously from zero only in the noncentrosymmetric symmetry groups. The scalar product $\mathbf{p}\cdot\mathbf{m}$, which plays the fundamental role, differs from zero only in chiral (enantiomorphic) groups. Therefore one observes especially marked manifestations of gyrotropy in objects possessing chirality; in line with this, the presented methods are termed chiroptical. The quantity

$$\hat{\mathsf{R}} = \mathrm{Im}\,\langle 0 \mid \mathbf{p} \mid n\rangle\cdot\langle n \mid \mathbf{m} \mid 0\rangle \qquad (1)$$

is called the rotatory strength of the transition 0–n; it determines the magnitude of the effect (the rotatory strength is an analog of the dipole strength in dispersion theory, $D_{0n}\,|<0|\mathbf{p}|n\rangle|^2$).

In the general case when the orientations are correlated, and in ordered systems, $\hat{\mathsf{R}}$ is a tensor whose components depend on **p**, **m**, $\hat{\mathbf{q}}$, and the distribution function and the orientation of the particles[26–28]).[2]

The presented ideas pertain to free molecules, i.e., hence to the intramolecular interactions. Evidently, they are applicable also to the intermolecular interactions: a chiral field, however created, can cause a dissymmetric distortion of the internal field of the molecule, deformation of the electron cloud, or even of the nuclear framework of a part of an achiral molecule or all of it as a whole and render it "optically active by induction". These interactions can even give rise to supermolecular chiral structures having a dissymmetric internal field. Naturally, such phenomena are especially notable in condensed phases, where the role of the internal field of the medium is considerable.

As we shall see, the phenomena of induction and their mechanisms are rather varied, just as the forms of intermolecular interaction are.

However, there is a common feature in all cases—in the most general meaning of the word, one can term as induction any change in the local or overall symmetry of the local field around the object and/or a change of the symmetry of its structure by this field owing to some interaction with the environment—a change that leads to appearance in the object of chirality and gyrotropy. One can propose the following working classification.

1) Induction of gyrotropy in an achiral molecule[3] by the asymmetric field of the van der Waals forces exerted by neighbors and a local chiral light field (see below), without change in the equilibrium distribution of charges in the molecule.

2) Orientation of achiral impurities by a chiral matrix.

3) Onset of chiral structures (supermolecular) under the action of Van der Waals forces.

4) Creation of chiral structures upon formation of hydrogen bonds and of associations.

5) Asymmetrization of the electron shell of a molecule involving the shift of its energy levels.

6) Asymmetrization (chiral deformation) of the nuclear framework of a molecule.

7) Creation in an achiral matrix of a chiral structure upon introducing an optically active impurity.

In general, the classification of the effects is highly provisional and somewhat artificial, since several of the cited factors act jointly in most cases.

3. MECHANISM OF INDUCTION

The physical mechanism of induction has been analyzed by several authors.[29–32] The interactions have been assumed weak enough that the molecules do not change their arrangement and orientation. Most studies have used the wave functions of the free molecules. That is, they have not taken full account of the deformation of the electron shell and the shift of the energy levels (in contrast to the calculations for "intramolecular induction", which have taken account of the deformation of both the nuclear framework and of the electron shell of the molecule). The calculations were performed for a mixture consisting of two materials—with chiral (C) and achiral (A) molecules, while the binary interactions were considered. Here two factors play a role: 1) the interactions of the electron shells, which asymmetrize the shell of molecule A (absorption of a photon by molecule C, emission of a virtual photon by molecule C, and absorption of it by molecule A); 2) interference of photons scattered by C and absorbed by A, whereby an asymmetric light field is created.

Naturally, the results of the calculations depend on the relative orientation of the molecules A and C. Moreover, the macroscopic result depends on the process of averaging over the orientations of all the molecules in summing their contributions.

We shall present below the results of the calculations, following Ref. 32 in the main.

The form of the derived formulas depends on whether the molecule A has an allowed magnetic-dipole or an allowed electric-dipole transition. In the former case, when the magnetic-dipole transition 0–$\bar{s}$ is allowed in A, while there is a transition 0–v in C, the rotatory strength for "ideal disorder" is determined by the expression

$$\hat{\mathsf{R}}_s^{\mathrm{M}} = -\frac{1}{6} R_{\mathrm{AC}}^{-6} C_{\mathrm{M}} \sum_u \sum_t \mathrm{Im}\,\{[\mathbf{p}_{\mathrm{A}}^{0t}\mathbf{p}_{\mathrm{A}}^{ts}]\cdot\mathbf{m}_{\mathrm{A}}^{s0}\,[\mathbf{p}_{\mathrm{C}}^{0u}\mathbf{p}_{\mathrm{C}}^{uv}]\cdot\mathbf{p}_{\mathrm{C}}^{v0}\}. \tag{2}$$

Here the superscript t pertains to the intermediate states of A, and u to the intermediate states of C.

In the latter case, the following electric-dipole transition is allowed in A:

$$\hat{\mathsf{R}} = \hat{\mathsf{R}}_s^{e} + \hat{\mathsf{R}}_{\mathrm{binding}}. \tag{3}$$

Here $\mathsf{R}_{\mathrm{binding}}$ is the contribution of binding of the oscillators of A and C (with strong coupling between them). In this case the electric-quadrupole moments of the transitions in A contribute:

$$\hat{\mathsf{R}}_s^{e} = \frac{8}{3} R_{\mathrm{AC}}^{-6} C_{\mathrm{e}} \sum_u (\mathbf{p}_{\mathrm{A}}^{0s}\cdot\mathbf{p}_{\mathrm{A}}^{s0})\,\{\mathrm{Im}\,[(\mathbf{p}_{\mathrm{C}}^{0u}\cdot\mathbf{p}_{\mathrm{C}}^{v0})\,(\mathbf{p}_{\mathrm{C}}^{0v}\cdot\mathbf{m}_{\mathrm{C}}^{u0})]$$

$$+ C'_{\mathrm{e}}\,(1-\delta_{uv})\,\mathrm{Im}\,[(\mathbf{p}_{\mathrm{C}}^{0v}\cdot\mathbf{p}_{\mathrm{C}}^{u0})\,(\mathbf{p}_{\mathrm{C}}^{0u}\cdot\mathbf{m}_{\mathrm{C}}^{v0})]\}, \tag{4}$$

$$\hat{\mathsf{R}}_{\mathrm{binding}} = \frac{C_{\mathrm{M}}}{10} R_{\mathrm{AC}}^{-6} \sum \sum \{(\mathbf{p}_{\mathrm{A}}^{0t}\hat{q}_{\mathrm{A}}^{ts}\mathbf{p}_{\mathrm{A}}^{s0} - \mathbf{p}_{\mathrm{A}}^{ts}\hat{q}_{\mathrm{A}}^{0t}\mathbf{p}_{\mathrm{A}}^{s0})\,[\mathbf{p}_{\mathrm{C}}^{0u}\mathbf{p}_{\mathrm{C}}^{uv}]\cdot\mathbf{p}_{\mathrm{C}}^{v0}\}. \tag{5}$$

The coefficients G_i determine the frequency-dependence; they depend in a rather complex way on the energies of the levels s and v and the energy differences among the levels s, v, u, and t. This dependence is of resonance type.

Roughly speaking, the order of magnitude of all the terms is the same.[4)] Phenomena are observed both at distances corresponding solely to the long-range components and at close distances. For very close distances ($R_{\mathrm{AC}} \ll \lambda$),[31] formulas of similar type have been derived. However, here additional terms arise having a $1/R^9$ dependence on the distance.

One can represent the expressions (2) and (4) in the following form (while neglecting $\hat{\mathsf{R}}_{\mathrm{binding}}$): instead of (2) we have

$$\hat{\mathsf{R}}_s^{\mathrm{M}} = -\frac{1}{6} R_{\mathrm{AC}}^{-6} C_{\mathrm{M}} \sum_u \sum_t \Omega_{\mathrm{M}}^{\mathrm{A}}(s,\,t)\,\Lambda_{\mathrm{M}}^{\mathrm{C}}(u,\,v). \tag{6}$$

Instead of (4) we have

$$\hat{\mathsf{R}}_s^{e} = \frac{8}{3} R_{\mathrm{AC}}^{-6} C''_{\mathrm{e}} \sum_u \Omega_{\mathrm{e}}^{\mathrm{A}}(s)\,\Lambda_{\mathrm{e}}^{\mathrm{C}}(u). \tag{7}$$

Here

$$\Omega_{\mathrm{M}}^{\mathrm{A}}(s,\,t) = \mathrm{Im}\,([\mathbf{p}_{\mathrm{A}}^{0t}\mathbf{p}_{\mathrm{A}}^{ts}]\cdot\mathbf{m}_{\mathrm{A}}^{s0}, \tag{8}$$

$$\Omega_{\mathrm{e}}^{\mathrm{A}}(s) = (\mathbf{p}_{\mathrm{A}}^{0s}\cdot\mathbf{p}_{\mathrm{A}}^{s0}) \tag{9}$$

are the "magnetic and electric inducibilities of A", while

$$\Lambda_{\mathrm{M}}^{\mathrm{C}}(u,\,v) = [\mathbf{p}_{\mathrm{C}}^{0u}\mathbf{p}_{\mathrm{C}}^{uv}]\cdot\mathbf{p}_{\mathrm{C}}^{v0}, \tag{10}$$

$$\Lambda_{\mathrm{e}}^{\mathrm{C}}(u,\,v) = \mathrm{Im}\,\{(\mathbf{p}_{\mathrm{C}}^{0u}\cdot\mathbf{p}_{\mathrm{C}}^{v0})\,(\mathbf{p}_{\mathrm{C}}^{0v}\cdot\mathbf{m}_{\mathrm{C}}^{u0})\} \tag{11}$$

are the "electric and magnetic inductive strengths of C". The quantities $\hat{\mathsf{R}}_{\mathrm{M}}$ and $\hat{\mathsf{R}}_{\mathrm{e}}$ (which we can call the "induced rotatory strengths") usually have the same order of magnitude.

In some achiral symmetry groups both transitions can be allowed in A, but the induction will be governed by one of them, since the moments are orthogonal in these molecules.

In orientational disorder, as has been pointed out, the distance-dependence is mainly of the R^{-6} type. However, in the presence of ordered orientations[5)] terms proportional to R^{-3} arise.[29a] Naturally the degree of order depends on the thermal motion; relationships of the type of $(kT)^{-1}$ and $(kT)^{-2}$ have been obtained in Refs. 29.

Reference 31 has treated the contribution of the vibronic interactions. As we shall show below, they can be considerable.

Reference 30 has treated also the interaction inducing optical activity of one molecule of A with N molecules of C (i.e., the course of the phenomenon for a solution or an impurity); for the simplest case of one molecule of A and two identical molecules of C the following expression was derived:

$$\hat{\mathsf{R}}_A = (G_2 + G_3)\,\mathrm{Im}\,\frac{\mathbf{p}_{\mathrm{A}}^2\mathbf{p}_{\mathrm{C}}^2\ (\mathbf{p}\,_{\mathrm{C}}\cdot\mathbf{m}\mathrm{C})}{\Delta\varepsilon^2} \tag{12}$$

Here G_2 and G_3 are coefficients that depend on the geometric arrangement of the molecules as a function R^{-6} of the distances, while $\Delta\varepsilon$ is the spacing between their levels.

A calculation of the induction phenomenon and of the Maxwellian field of a chiral molecule influencing achiral neighbors has been performed in the most rigorous form[29b] by methods of quantum electrodynamics. For the case in which an electric-dipole transition is allowed in A, the circular dichroism that arises was calculated for very close distances ($kR \ll 1$):

$$\Delta\Gamma = C\,\frac{k}{R}\,\Omega_{\mathrm{e}}^{\mathrm{A}}(s)\,G_{jj}^{\mathrm{C}}(k,\,u). \tag{13}$$

Here

$$G_{jj}^{\mathrm{C}}(k,\,u) = \mathrm{Im}\sum_u \left(\frac{\mathbf{p}_j^{0u}\cdot\mathbf{m}_j^{u0}}{\omega_{u0}-\omega} + \frac{\mathbf{m}_j^{0u}\cdot\mathbf{p}_j^{u0}}{\omega_{u0}+\omega}\right) \tag{14}$$

is an analog of the expressions $C_{\mathrm{e}}\ \Lambda_{\mathrm{e}}^{\mathrm{C}}$ in (7). The frequency-dependence here is the same as in the expression given by quantum electrodynamics for the "ordinary" polarizability tensor:

$$\alpha_{jk}(k,\,u) = \sum_u \left(\frac{\mathbf{p}_j^{0u}\cdot\mathbf{p}_k^{u0}}{\omega_{u0}-\omega} + \frac{\mathbf{p}_k^{0u}\cdot\mathbf{p}_j^{u0}}{\omega_{u0}+\omega}\right)\cdot$$

The overall form of the presented formulas is analogous to the preceding ones, but the R^{-1} dependence strikes the eye, the differs substantially from (2)–(7) and alters the course of the phenomena; at large distances the relationship varies from R^{-3} to R^{-6}.

We note that an additional quadrupole term arises for an ordered arrangement of A and C with the form

$$A_{ijk} = \sum_u \left(\frac{p_i^{0u}q_{jk}^{u0}}{\omega_{u0}-\omega} + \frac{q_{jk}^{0u}p_i^{u0}}{\omega_{u0}+\omega}\right).$$

As we have already said, the effects are especially sharply marked for resonant or close-lying levels in A and C. However, we can see that the phenomenon of induction is very

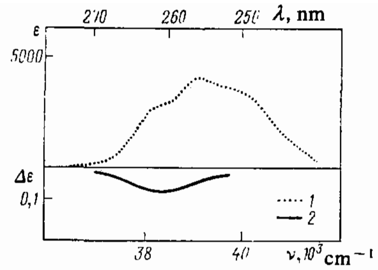


FIG. 4. Absorption (*1*) and circular-dichroism (*2*) spectra of achiral pyridine in a chiral solvent.[39] The magnetic-dipole transition is seen to be singled out.

universal and is manifested in any pairs A and C (with account taken of the presented symmetry considerations; see Ref. 26 and the references cited there), since the transition in A can be practically any one whatever. In particular, a weak magnetic-dipole in A can play an important role that is almost inappreciable in the absorption spectrum (Fig. 4). Similar effects of the mutual-induction type also occur between two—differing or identical—chiral molecules.

Experimental studies of the induction effect and tests of the theory have been performed in many studies, in particular in Refs. 33–38. The effect is quite significant and easily detectable, and is observed in all cases. Reference 33 has also estimated the distance-dependence R^{-n}; values $3<n<12$ were obtained for different materials, while $n\approx 6$ on the average[6)].

In particular, induction is manifested upon dissolving achiral substances in a chiral solvent[33,34,36,37]—optical activity arises in the bands of the solute in solvents of the most varied nature. This indicates the universal character of the interaction, which is not associated with any chemical processes; only the fact of making a solution is required. Since the effect is universal, while one can select the chiral solvent from a very broad range for the most varied materials, the method can be applied for practically any molecules (e.g., for the octahedral complex $Mo(CO)_6$ and the tetrahedral ion $[CrO_4]^{-2}$,[39] the NO_3^- ion, etc.).

A characteristic example can be the induction of optical activity in the plane symmetric ion $[PtCl_4]^{2-}$ (symmetry D_{4h}) in a chiral solvent.[34] We see in Fig. 5 that circular dichroism arises in only one of the three absorption bands, this enables one to discover the difference in their mechanisms of origin.

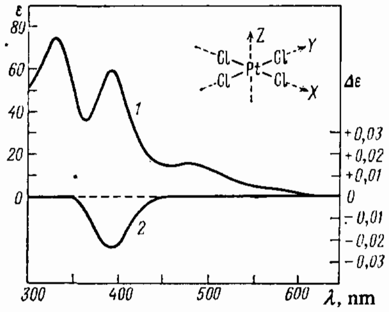


FIG. 5. Absorption (*1*) and circular-dichroism (*2*) spectra of a solution of $PtCl_4$ in chiral (−) — 2,3-butanediol.[34]

Induction by a chiral solvent can also be detected from the appearance of circularly polarized fluorescence and phosphorescence. Besides all else, this method offers the important possibility of revealing and studying weak triplet-singlet and triplet-triplet transitions (see, e.g., Refs. 40 and 41). In certain cases of induction by a solvent the formation of associations has been proposed (see below). Often it suffices to assume the correlation of orientations. Attempts have been made in the literature to describe the phenomenon of induction by a macroscopic calculation—introduction of Lorentz-type corrections for the chiral internal field of the medium.[42] However, this still requires a considerable theoretical development.

The induction effect is also important for studying chiral molecules for which the potential barrier between the dextro and levo forms is so low that direct study of their activity is impossible. The chiral matrix fixes a single form. Induction is no less important in preparing crystals of materials having chiral molecules. Without going into the details (see Ref. 1, Chaps. 2 and 3), we point out that one can obtain either racemic or chiral crystals, depending on the conditions of crystallization. A chiral solvent induces formation of the latter, allowing study of gyrotropy.

All that we have presented pertains also to solid materials. At present methods are being developed at a heightened pace of carrying out reactions in a crystalline phase. Here the chirality of the source matrix induces chirality of the reaction product. If this product possesses an intrinsic gyrotropy, the presence of the chiral matrix induces formation of molecules of only the one corresponding sign; see, e.g., Refs. 43 and 44.

The formulas given above offer a good qualitative description of the course of the phenomena. A sufficiently complete and rounded test of the quantitative relationships has not yet been performed. The expected orders of magnitude, to the extent that one can estimate them, correspond to experiment.

4. EFFECT OF ORIENTATION

Above we have been treating the van der Waals forces acting among fixed molecules whose arrangement and orientation are given by some distribution function. However, these forces themselves can give rise to certain correlations in the orientations of the molecules; if the field of these forces is chiral, chiral supermolecular structures arise. A model object for demonstrating this type of phenomena is the liquid crystals. As is known, a certain orientational order exists in these crystals in the absence of coordinational order. In the so-called nematic liquid crystals, which consist of axially symmetric molecules, long-chain and seemingly rodlike, the long axes of the molecules are oriented in parallel[45] If the molecules are chiral and optically active, such a distribution of adjacent molecules is energetically more favorable in the field formed by the van der Waals forces in which their axes lie at a certain angle. As a result (for details, see Ref. 46) helical (chiral) structures arise, whose characteristic di-

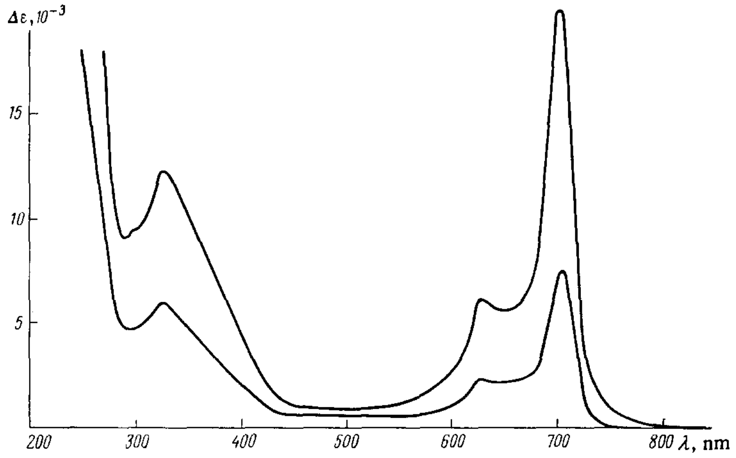


FIG. 6. Circular-dichroism spectrum of achiral copper phthalocyanine in a chiral liquid-crystalline matrix (cholesteryl nonanoate, $\lambda_{abs} < 230$ nm) at different temperatures. The upper curve is for the lower temperature.

mensions (pitch of the helix) are of the order of thousands of Angström units, and which extend for 50 to 100 μm and farther. In particular, the cholesteric liquid crystals—derivatives of cholesterol ("cholesterics")—are of this type. Owing to their chirality, these structures yield a rotation of the plane of polarization of tens of thousands of degrees, and correspondingly a very large circular dichroism. This effect does not stem from phenomena of spatial dispersion, but from Bragg diffraction by the chiral structure and selective reflection of light of one circular polarization, while the role of the chiral field of the van der Waals forces consists in creating this structure.

Two processes arise upon introducing achiral and optically inactive molecules into such a matrix. On the one hand, an impurity—especially if somewhat similar in form—can be incorporated into the helical structure. That is, a helical arrangement of the impurity molecules and a certain orientation of them are created.[7)] Our studies[48] have obtained ordered incorporation into a cholesteric liquid crystal of even such nonlinear and large molecules as phthalocyanine (Fig. 6) or chlorophyll. On the other hand, the molecules experience the action of the internal chiral field of the matrix, and the induction effect that was treated above arises. As we have pointed out, in the presence of orientational order a contribution to the gyrotropy (of both the matrix and the impurity) arises also from the quadrupole moments (see (4) and (5)) and from the product $\mathbf{p} \otimes \mathbf{m}$.

Both effects are observed experimentally. If the impurity molecule has low symmetry and possesses an appreciable linear dichroism, a considerable and easily measurable circular dichroism will be observed in its absorption bands owing to the specific orientation. This can be calculated[47] from the linear dichroism and the parameters of the helical structure (see, e.g., Ref. 48). Conversely, if ones measures the circular dichroism, one can obtain data on the structure, the degree of order, etc. Of course, an induction effect also takes place.

If there is no linear dichroism—the impurity molecule is highly symmetric—one observes only induction in "pure" form. Thus, for example, circular dichroism and optical activity are induced in the octahedral complex $Mo(CO)_6$.[42] For a review of similar phenomena see Refs. 27 b and 49 and the bibliographies given there. For molecules of lower symmetry, and possessing linear dichroism, the measurements become more complex. However, methods have been proposed for separate determination of the linear dichroism and the circular dichroism proper induced in the impurity.[28,48,50,51] In particular, a universal principle has been proposed in our laboratory.[16] Methods also exist for measurements using luminescence, which is circularly polarized in these cases.[51]

A convenience of a chiral cholesteric matrix is the possibility of obtaining in a single specimen a chiral structure (with arbitrary variation of the pitch of the helix) and a nematic (achiral) structure, with conversion to an ordinary isotropic liquid by an external agent (temperature, electric or magnetic field).[46]

We should note that the chiral field of a liquid-crystalline matrix can even deform (asymmetrize) the nuclear framework of an impurity center (see below):

Of course, one can observe processes of this type not only in liquid crystals, where orientation arises in its purest form (the optical activity of their molecules is relatively small—the "inductive strength" is small). It has been known long and well that, when achiral dyes or other molecules are adsorbed on polymeric chiral structures, induced optical activity arises in the absorption bands of the dyes.[52–55] This has been shown on the examples of protein polymers, structures of nucleic acids, cellulose polymers, and other polysaccharides. Here both an orientational effect and induction occur, in the sense of Sec. 2, owing to the chiral field of the adsorbent. Thus the possibility arises, on the one hand, of studying the structure of the adsorbate by studying the induced activity, and on the other hand, to study the structure of the adsorbent, or polymer matrix, from the optical activity of markers that arises (such studies have become a standard method of studying biological chiral structures).

Since one can choose highly varied adsorbents, while also a broad range of substances can be adsorbed, the method

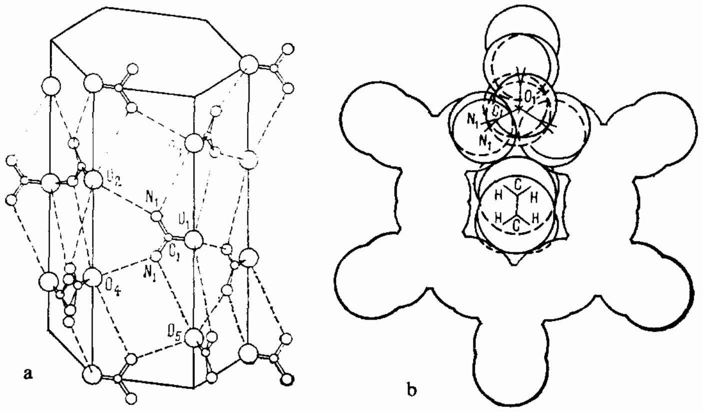


FIG. 7. a) Structure of a urea complex; b) incorporation of hexadecane along the axis of the complex (top view).

is rather universal. Let us point as an example the study of the structure of the levels of europium introduced into a chiral substrate and revealing optical activity in its absorption bands.[56] Reference 57a has treated on the basis of a bound-oscillator model[8)] the induction (by van der Waals forces) of chirality and optical activity upon incorporating various achiral molecules into chiral complexes containing many chromophores. The dependence of the phenomenon on the symmetry of the guest and host and the orientation of the impurity was studied, and rules were given that enable one to predict the sign—"selection rules", which simplify the analysis. Let us stress again that in many cases a chiral deformation of the adsorbate is very likely; it is difficult to demarcate these effects.

To effect induction by a matrix, it is very convenient, in particular, to employ a somewhat special object—crystalline structures or those reminiscent of polymers, the so-called inclusion compounds. These matrices are molecular-crystal structures into whose pores or cavities the molecules under study are incorporated under the action of van der Waals forces and steric interactions without forming chemical bonds. A characteristic example is the adducts of urea, $NH_2CO \cdot NH_2$. The molecules of urea belong to the point group C_{2v}, while the structure of the urea crystal is described by the space group D_{2d}^3. That is, urea is neither chiral in solution nor in the crystal. However, upon forming a so-called clathrate complex of urea with a saturated hydrocarbon, e.g., hexadecane ($C_{16}H_{34}$), the molecule of which is also achiral, a relative orientation of their molecules occurs. The structure of the crystal of the new complex is described by the space group D_6^2 or D_6^3, according to which the urea molecules ($z = 6$) are arranged, as shown in Fig. 7, while the hexadecane molecules lie in the channels in the urea structure under the action of van der Waals forces. The complexes that are formed are chiral and optically active. That is, onset of chirality occurs here in components achiral in the free state. Instead of hexadecane, chiral molecules can also lie in the channels, e.g., 2-chlorooctane ($C_8H_{17}Cl$). In this case four variants of the complex can exist; a D- or L-crystal incorporating D- or L-chlorooctane. Naturally the probability of forming the variants will differ (for details see Ref. 58), just like the optical activity of the complex as a whole. However, the sign of the "guest" dictates the favorability of formation of the urea complex of a certain sign. On the other hand, if one employs a chiral matrix as the "host", e.g., cy-

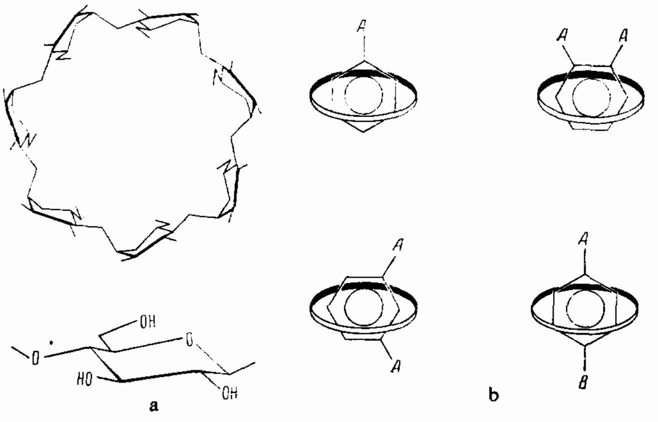


FIG. 8. a) Structure of cyclodextrin (below—individual link of a glucose residue); b) diagram of the "incorporation" of different molecules into the complex.[57]

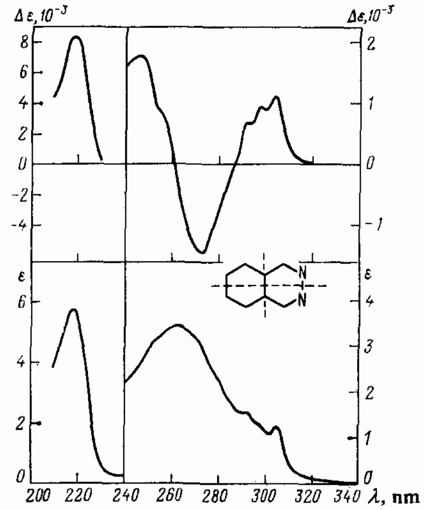


FIG. 9. Absorption (below) and circular-dichroism (above) spectra of molecules of achiral phthalazine incorporated into cyclodextrin.[61] The greater information content of the circular-dichroism spectrum can be seen.

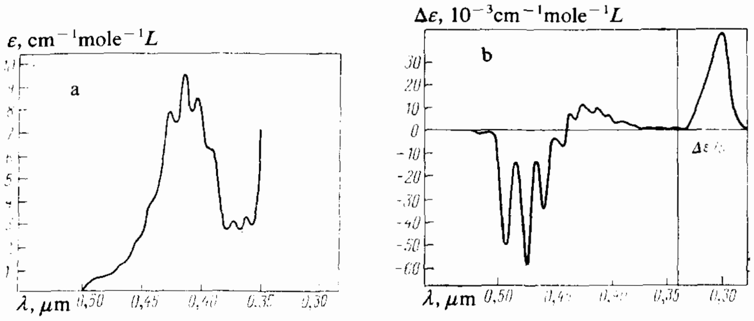


FIG. 10. Absorption (a) and circular-dichroism (b) spectra of a solution of achiral uranyl nitrate in chiral (−)-2,3-butanediol.[64]

clodextrin, a considerable activity of a definite sign can be induced in an achiral guest.[59–61] The theory of Ref. 57 is also applicable here. By studying the gyrotropy of the complex, one can decide on the structures of the guest or the host. At present such matrices are used rather widely (Figs. 8, 9), since one can incorporate an extremely large set of substances, organic and inorganic.

5. ROLE OF HYDROGEN BONDS

Induction is effected not only by van der Waals forces, but also by hydrogen bonds and the associations that they give rise to. These problems, which pertain to semichemical interactions, lie somewhat outside our topic, yet merit a brief mention. Several factors act here.

In the association of the chiral C molecule and the achiral A molecule, the intermolecular distance is decreased, and a certain relative orientation is produced: according to (2), (5), and (12), this enhances the induction effect, as the distance-dependence is expected to be R^{-2}-R^{-3}.[62] It has also been noted[29b] that the effect increases by an order of magnitude upon interpenetration of the electron shells.

Moreover, a certain asymmetric deformation of the electron shell of A is created, or more often, chiral complexes arise. Thus, upon introducing the inactive salts of the linear uranyl ion into a weakly rotatory solvent (1 deg/cm), an induced rotation of the order of 500 deg/cm arose in the absorption bands of the former.[63] Such effects enable one to elucidate more exactly the coordination of ligands; the asymmetrization of the field of the ligands yields information on the number and nature of the levels of the coordinated ion. Thus, for example, solutions of inactive uranyl nitrate in an optically active solvent, butanediol, have been studied in our laboratory.[64] Optical activity arises in the absorption bands of $UO_2(NO_3)_2 \cdot 6H_2O$, probably induced by formation of an association via hydrogen bonds, including the asymmetric carbon atom, i.e., a chiral complex. Such methods are especially convenient for studying all objects with *ff*-shells being filled, which conserve spectroscopic individuality to a considerable degree (Fig. 10). A number of studies of rare-earth ions by this method are known.

Moreover, hydrogen bonds can also give rise to chiral structures anew. Thus, phenol molecules (achiral in the liquid) are bound by hydrogen bonds in the crystal into a structure with a pseudo-threefold axis to form the chiral space group C_2^2. Molecules of orthocresol, also achiral in the free state, are bound by hydrogen bonds upon crystallization into a structure with a threefold screw axis (space group C_3^2).[65] In the phenomena discussed above of induction upon adsorption on polymers, one can suspect a role of association in a number of cases.[35,56] An example is shown in Fig. 11.

6. DEFORMATION OF MOLECULES

Now let us examine the problem of asymmetrization by deformation of the nuclear framework of molecules in a chiral field.

Here we should distinguish three processes:

1. Deformation of molecules of an individual substance upon crystallizing to yield a chiral structure.
2. Deformation of achiral impurity centers in a chiral matrix.
3. Deformation of an achiral matrix by a chiral impurity.

The first process, which leads to formation of gyrotropic crystals by substances whose molecules are inactive in the free state, is interesting for crystal physics from the general standpoint in allowing one to trace the highly important process of deformation of molecules forming a crystal.

There is no general theory of deformation processes, and probably it would be highly difficult to construct it. It is well known from the experimental material of modern crys-

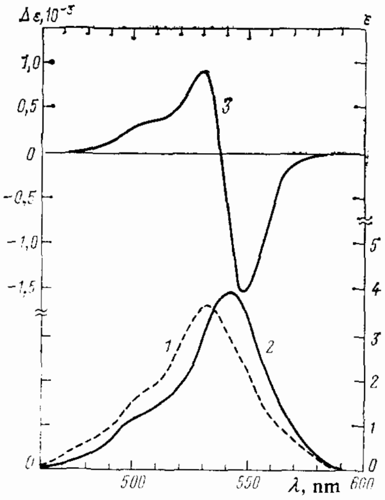
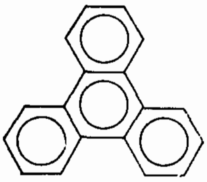


FIG. 11. Absorption spectrum of achiral pyronine in an achiral solvent (*1*), in a complex with α-chymotrypsin (*2*), and the circular-dichroism spectrum of the complex (*3*).[35]

tal physics that a considerable deformation often occurs upon crystallization, not only of the electron shell, but also of the nuclear framework—as a rule, toward lowered symmetry.[66] This is true even in molecular crystals, in which the interparticle interactions are relatively weak.

The physical reason for this is obvious—deformation proves energetically favorable because it makes possible a denser packing, which entails a gain in energy greater than the cost of it in deformation.

We can illustrate what we have said with the example of triphenylene ($C_{18}H_{12}$). Its molecule in the free state has high symmetry (point group D_{3h}):



Hence it is nonpolar and inactive. Upon crystallizing it is deformed and becomes asymmetric and polar. The crystal that is formed is gyrotropic and belongs to the class D_2^4.

One can propose the following explanation here: positions having the site symmetry D_{3h} exist in the space groups $D_{3h}^{1,3}, D_{3h}^{1,3,4}$, but these groups do not allow very close and closest packing. Hence deformation of the molecules proves favorable. In the group D_2^4 indicated above the highest site symmetry is E. Here dense packings of the molecules can be effected with a low symmetry of the molecules. The detection of circular dichroism in the absorption bands of the molecule proves the loss of its center of symmetry. Thus this method enables one to elucidate the character of the deformation of the molecule in the process of crystallization. Mixing of states of different parity occurs in the asymmetric deformation of a molecule or complex by the internal field of the medium. The lowered symmetry renders previously forbidden transitions allowed. Here a "borrowing of intensity" can arise from the vibronic interactions. Namely, in the presence of a certain state A close enough to the state B and combining with the lower state C, the intensity of the transition $B \rightleftarrows C$ can be substantially amplified owing to vibronic interactions with the transition $A \rightleftarrows C$. Borrowing requires fulfillment of certain demands on the symmetry of the states: the direct product of their symmetry types must be totally symmetric and the components of the dipole moments for which the transitions are allowed must be parallel. Thus borrowing of intensities can occur from close-lying—and sometimes even far-lying—powerful allowed transitions. Precisely in such cases, in which the transition becomes allowed both as an electric dipole transition and as a magnetic-dipole one, gyrotropy arises, according to which one can explain the little-studied process of mixing of states.

An example of what has been said is the crystal of sodium uranyl acetate ($Na[UO_2(CH_3COO)_3]$), a complex compound that forms island structures in the crystal. Its anionic complex in the free state has the symmetry D_{6h}, and the material in solution is inactive. The complex is deformed[91] on crystallization to the symmetry C_3 and forms a crystal with the symmetry group T^4, which contains no site symmetries other than C_3. The detailed analysis conducted in our studies[1,67–74] showed the deformations to differ in the first and in the subsequent coordination spheres owing to the interactions among the ligands. This is precisely why the states of different parity become mixed to yield $\mathbf{p} \cdot \mathbf{m}$ modes in previously forbidden transitions and optical activity in the absorption bands of the uranyl ion (mainly associated with the ff-shell of uranium). One can use the projection-operator technique to show[1] that, with a sufficient lowering of symmetry—to C_3, practically any transition becomes allowed, both in the electric-dipole and in the magnetic-dipole approximation. It can become a carrier of optical activity, having borrowed[72] intensity from other transitions. Here the vibronic interactions play a substantial role; the degree and character of the borrowing depend on the symmetry of the vibration. Generally speaking, the moments $\mathbf{p}$ and $\mathbf{m}$ can borrow intensity also from different transitions. As was pointed out above, the relative orientation of the transition moments plays an important role in borrowing. One can decide on the orientation of the moments from the sign of the circular dichroism that arises and from its magnitude. There is practically no borrowing when they are orthogonal. Thus studies of gyrotropy enable one to elucidate the mechanism of borrowing arising from the mixing of states. The same phenomena have been observed in crystals of the series of

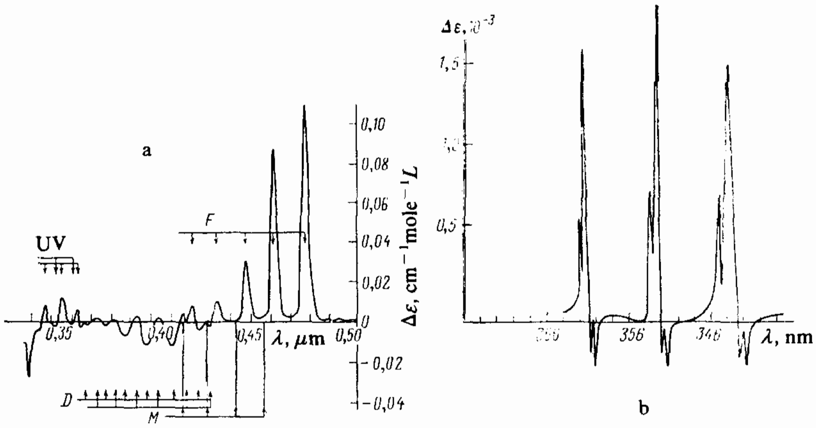


FIG. 12. Circular-dichroism spectrum of crystals of Na uranyl acetate at 300 K (a) and Rb uranyl propionate at 10 K (b).[76,77]

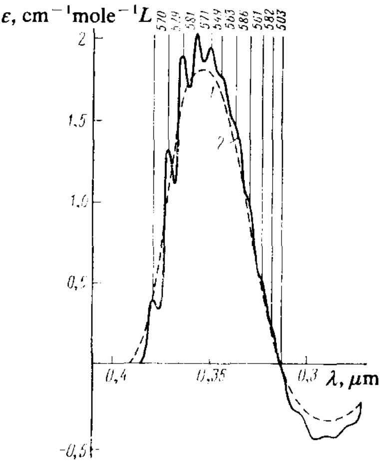


FIG. 13. Circular-dichroism spectrum of a crystal of barium nitrite at 80 K.[79]

uranyl propionates. Here it has been shown that the magnitude of the asymmetric deformation increases with increasing ionic radius in the series of cations K, NH_4, Rb, and Cs, and one can decide from the rotatory strength on the magnitude of the deformation. One can see that such studies yield a fair amount of information of general character. It proved possible later in studies of our laboratory[75–77] to distinguish three new electronic transitions in the uranyl ion, and to indicate the symmetry of the states. Using the symmetry changes of the ion upon crystallization pointed out above, it has been possible to distinguish the type of vibrations (asymmetric) that cooperate in the borrowing of intensities. Figure 12 shows examples of induced circular-dichroism spectra obtained in these studies.

In speaking of the role of vibronic interactions, we point out again that gyrotropy has been demonstrated[1,78] in the crystal $Ba(NO_2)_2 \cdot H_2O$, involving perturbation of the ionic group NO_2, which is triatomic and hence cannot have intrinsic activity. Subsequent studies of our laboratory[79] have shown that the induction is caused by perturbations involving external vibrations—excitation in the lattice of phonons of asymmetric type. Perhaps this makes the moments **p** and **m** nonorthogonal. A vibrational structure can be seen in Fig. 13.

The gyrotropy of the nitrates of *Rb* and *Cs* was studied in Ref. 80, and a considerable contribution to it from vibronic interactions was shown. In our laboratory[80b] we could subsequently trace the orientational disordering upon heating, which leads to a phase transition.

Hydrogen bonds can also take part in the deformation of some particular complex. Thus, $NiSO_4$ crystallizes from aqueous solution as crystals of $NiSO_4 \cdot 6H_2O$. Here the highly symmetric octahedron of the $Ni(H_2O)_6^{2+}$ complexes proves to distort to the symmetry C_2 owing to the presence of hydrogen bonds with the SO_4^{2-} tetrahedra surrounding it. Consequently optical activity and circular dichroism arise in the bands of Ni. The mechanism of origin of gyrotropy is analogous to that described above. Borrowing occurs here from the strong transitions in the far ultraviolet region (electric-dipole moment) and from the near transitions (magnetic-dipole moment), again with participation of the vibronic interactions.[1]

As we see, such studies are of substantial interest. However, they are restricted to a selection of chiral substances. Hence a method is desirable that would enable one to go outside this set. One can achieve this by using chiral matrices into which the molecules, ions, or complexes of interest have been introduced, or conversely, by introducing chiral probes into the substances of interest used as a matrix. Here again one must resort to examples, since it is difficult to construct a general theory.

One can conduct a number of studies by using as the matrix the chiral crystal ethylenediamine sulfate (symmetry group $D_4^{4,8}$)-$C_2H_4(NH_2)_2 \cdot H_2SO_4$, which is transparent in the visible and ultraviolet. Let us study the introduction of the anion CrO_4^{2-} as the impurity. In the free state it is symmetrical (tetrahedral) and inactive, but it isomorphously replaces the SO_4^{2-} group. When it is introduced into ethylenediamine sulfate,[1] optical activity and circular dichroism are found in the absorption bands of the ion (lying in the visible), involving the lowering of its symmetry in the matrix to C_2 (there are no other site symmetries in the group D_4). At the same time, its absorption spectra vary little from those in solution, so as to allow a comparison. Figure 14 shows the absorption spectra of the matrix containing the impurity and the circular dichroism spectra. Here the appearance of at least six bands in the circular-dichroism spectrum is clearly evident, whereas only two are visible in the absorption spectrum. This indicates the substantially greater resolving power of the former method and the existence of a number of transitions that are masked in the absorption spectrum by more intense neighboring transitions allowed in the electric-dipole approximation.[80,81]

These studies have made possible a substantial refinement of the pattern of energy levels and vibronic vibrations in the ion. In particular, three new transitions have been found that are forbidden in the free ion, together with the presence of vibrations of nonsymmetrical type. We stress that the forbidden and allowed transitions in the circular-dichroism spectrum prove to be of the same order of intensity. Yet in the absorption spectra they differ substantially. On the other hand, since the existing data show the replacement of the SO_4^{2-} ion by the CrO_4^{2-} ion to be isomorphous to a good approximation, and the CrO_4^{2-} ion has orientation and symmetry close to those for the SO_4^{2-} ion, it is logical to assume that the element (or one of the elements) responsible for the gyrotropy of the matrix is the SO_4^{2-} group. Here we see that the method has made it possible to shift the study of the matrix from the far ultraviolet to the visible region. This is its undoubted merit, and it has made it possible to elucidate the nature of the gyrotropy of the matrix.

This method has been developed and expanded by introducing the same ion into other matrices.[82] Thus, upon introducing the CrO_4^{2-} ion into crystals of α-$NiSO_4 \cdot 6H_2O$ and α-$NiSeO_4 \cdot 6H_2O$, the gyrotropy induced in the ion proves to differ somewhat (although the symmetry group of the matrix is the same $D_4^{4,8}$, and hence the site symmetry is the same). This indicates that the position and orientation of

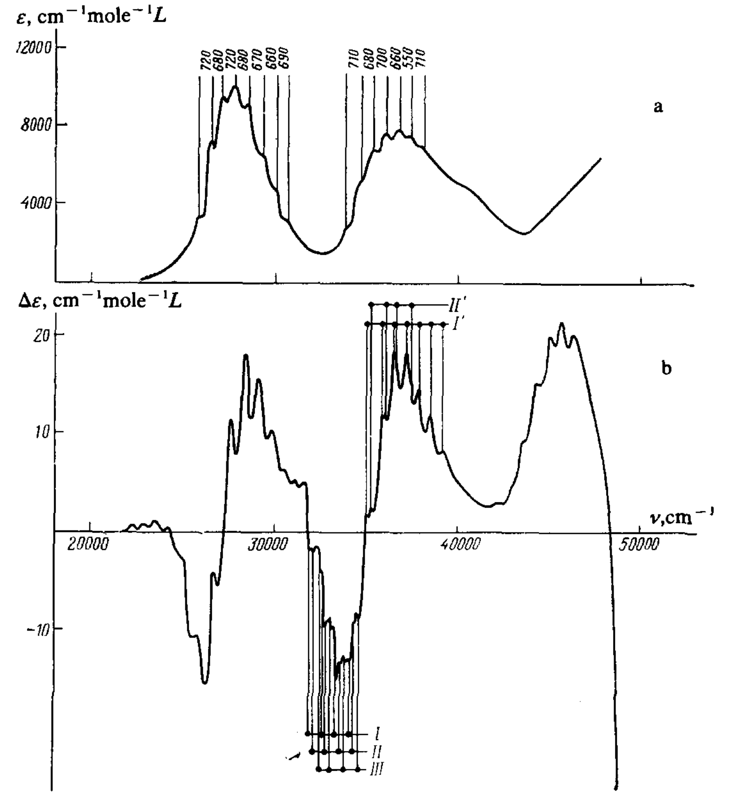


FIG. 14. Absorption (a) and circular-dichroism (b) spectra of the ion CrO_4^{2-} in a crystal of ethylenediamine sulfate.[81] The Roman numerals indicate the resolved vibrational series.

the ion differ somewhat here. Moreover, the replacement of S by Se proves to be detectable. In line with what has been said above, this indicates that the elements of SO_4 and SeO_4 contribute to the gyrotropy. Upon introducing the ion into the matrix of $ZnSeO_4 \cdot 6H_2O$ (which has no absorption bands in the visible, which is very convenient), the pattern also varies somewhat (Fig. 15a). Finally, one can introduce the same ion into the matrix of $KLiSO_4$[83,84] (Fig. 15b). Since the matrix has the symmetry group C_6^6, in which site symmetries C_3 are possible, the environment of the ion differs, and hence its circular dichroism proves to differ. Thus, by placing the same ion in different matrices, one can refine the obtained ideas concerning the structure of its levels, making a comparison also with its spectra[85] in the achiral matrix KBr and in a chiral solvent,[30b] where there is apparently no deformation.

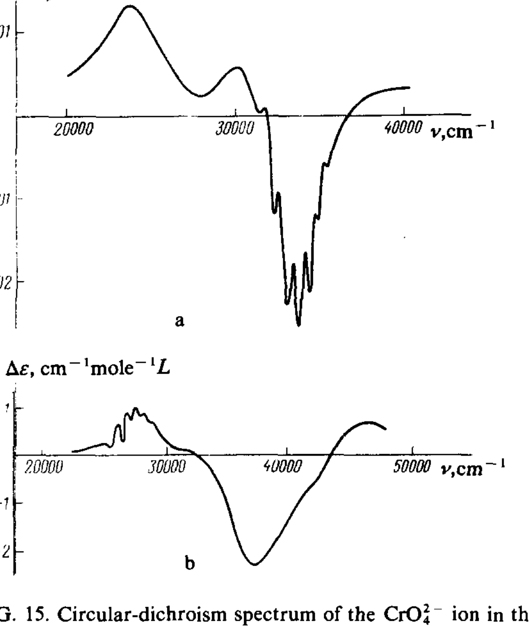


FIG. 15. Circular-dichroism spectrum of the CrO_4^{2-} ion in the crystals $ZnSeO_4 \cdot 6H_2O$ (a) and $KLiSO_4$ (b) at 80 K.[84]

By replacing an impurity ion, one can by comparing the data investigate the change in the nature of the implantation. Thus, in our laboratory the ion MoO_4^{2-} was introduced into a matrix of ethylenediamine sulfate. It also isomorphously replaces the SO_4^{2-} ion. The position of the ion in the lattice was shown to differ somewhat from that of the ion CrO_4^{2-}. This arises from the fact that the ionic radius of MoO_4 is ~1.97 Å, whereas it is ~1.65 Å for CrO_4. As we see, the method responds to these fine differences.

It has been shown[86] in our laboratory by the same methods that MnO_4 ions enter into the $LiIO_4$ crystal with a different degree of oxidation, and correspondingly with a different coordination.

Another example of applying this method is the studies of the behavior of impurities in a matrix of $ZnSeO_4 \cdot 6H_2O$ (which has no absorption bands in the visible and ultraviolet regions). The Zn ion can be replaced by the ions of Co, Cu, Mn, Fe, and Ni. Since the dimensions and ionic radii of these ions differ somewhat from one another and from the Zn ion, certain distortions of the matrix arise, which are especially noticeable at low temperatures. These distortions also yield some information on processes in the matrix—its deformation upon introducing impurities; on the other hand, the cited ions, which have absorption bands in a region of the spectrum convenient for working, can be studied in considerable detail by this method.[1] The circular dichroism of an Ni impurity in the $LiIO_3$ matrix mentioned above proves to differ from that in the $ZnSeO_4 \cdot 6H_2O$ matrix. Hence also the nature of the implantation of the impurity differs. For a complete utilization of the method, it is convenient to compare it with the behavior in achiral matrices.[87]

We have conducted the same type of studies[84,88,89] for the rare-earth ions in a matrix of the double yttrium aluminum borate $YAl_3(BO_3)_4$, where the yttrium ion was replaced by ions of the rare earth Nd (partially) and Eu (completely) (Fig. 16). For the Eu^{3+} ion, the manifestation of higher multiplicities was shown from the appearance of weak transitions forbidden in the dipole approximations. A weak splitting of the type-E Stark components was established from the sign-varying circular dichroism. This indicates a certain distortion of the environment of the Eu^{3+} ion (triangular prisms formed by O atoms), which is probably orthorhombic. As we see, the method is very sensitive to slight lattice distortions, especially of the near environment.[10)]

It was possible to demonstrate a different nature of the borrowing of intensities for Nd ions from that for Eu, and to point out the preferentially electric-dipole character of the transition.[89b] However, apparently, one must take into account also a certain contribution of the quadrupole moments.

We see from what we have presented that one can study very many ions by selecting the matrix, elucidate the nature of the incorporation of these ions, and, finally, determine a number of properties of the matrix itself.

It was shown in Ref. 89c that, in the presence of a Jahn-Teller effect, a contribution to the induction can arise from the nondegenerate vibrational modes of pseudoscalar symmetry (since the rotatory strength is always pseudoscalar, as we see from (1)). This concept can expand the set of problems that can be studied.

One can draw conclusions concerning the course of the process of implanting an impurity and the nature of this implantation also in another way by using the gyrotropy at the silicon vacancies that has been observed.[90] Study of the broad-band semiconductor $Bi_{12}SiO_{20}$ (symmetry class T^5) has established that it contains Si vacancies when grown by the usual methods. These vacancies manifest themselves also in gyrotropy—one observes an additional band of opposite sign at the edge of the circular-dichroism band corresponding to the fundamental absorption (Fig. 17). Upon introducing Al ions into such a crystal, the additional band vanishes—apparently these ions fill the vacancies. Thus one can

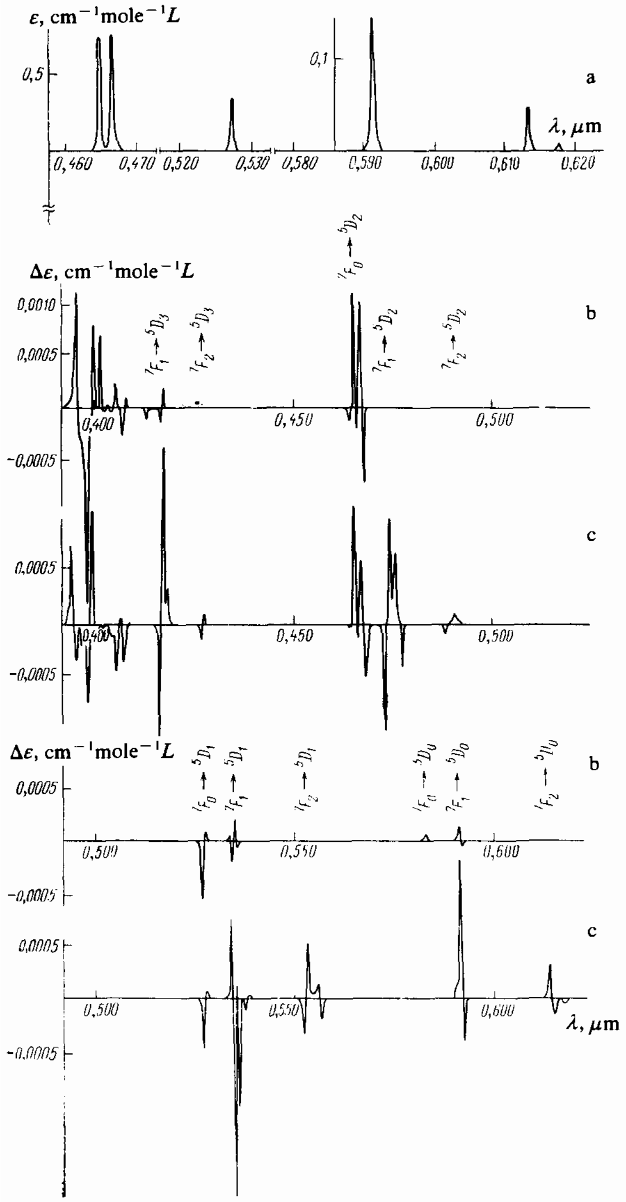


FIG. 16. Axial absorption spectrum of Eu^{3+} in a crystal of $EuAl_3(BO_3)_4$ (a) and its circular-dichroism spectra at 80 K (b) and 300 K (c).[84,89a]

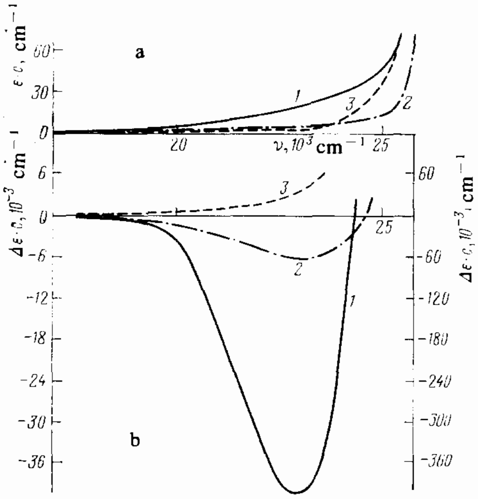


FIG. 17. Absorption (a) and circular-dichroism (b) spectra of crystals of $Bi_{12}SiO_{20}$ (*1*), $Bi_{12}SiO_{20}$ + 0.01% Al (*2*), and $Bi_{12}SiO_{20}$ + 0.032% Al (*3*).[90]

detect vacancies, trace their replacement, and thus elucidate the nature of the implantation of the impurity. Subsequently[90b] a substitution with Fe ions was also carried out; here one can estimate the concentration of ions and their local symmetry from the intrinsic absorption band of Fe. The behavior of Ga ions was also studied; by the same method the incorporation of Cu ions into lead germanate has been studied.

Evidently, such methods yield extensive information, and in principle they allow one to study a broad set of substances. However, the difficulty of choosing matrices or impurities suitable for growing crystals and the difficulties of growing them restrict their possibilities. Therefore, it would seem that the special problem of the asymmetrization of the framework of molecules in a liquid-crystalline matrix is important. This method is experimentally feasible with considerably greater ease, and the requirements on "implantability" of impurities are much lower (although, probably, the deformation here is smaller and the nature of the implantation is less evident).

Generally, the phenomena of asymmetric deformation are observed not only in solid crystalline media, where they are most perspicuous and strongly marked, but also in other matrices. Thus, for example, in the chiral liquid-crystalline matrix discussed above, when one introduces into it such highly symmetric complexes as $Mo(CO)_6$ and $W(CO)_6$ (octahedral), circular dichroism arises in their absorption bands. One cannot explain this by a chiral arrangement, since they lack linear dichroism (only the octupole moment differs from zero). For the same reason the induction effect will be small.[30b] An appreciable deformation was shown[91] to take place, which lowers the symmetry of the complex at least to D_{4d}, when a quadrupole moment can arise. This problem merits more detailed study.

Here we should point out that the methods presented above can also be applied to studies of processes of polymerization[28] and vitrification, employing both the influence of orientation and of deformation. One can also determine the nature of the incorporation of impurities into a polymer.[92]

7. INDUCTION BY A CHIRAL IMPURITY

The high sensitivity of the gyrotropy of molecules and of the conformation of the described supermolecular structures to changes in the symmetry of the local field enables one to use the reverse of the effect that we have been discussing—the effect of a chiral impurity on an achiral matrix. And here the model object can be a liquid-crystalline matrix.

When one introduces a small amount (0.05–5%) of a chiral impurity into a nematic liquid crystal, structures of cholesteric type arise in them. Similar effects are observed also in discotic liquid crystals.[93,94] The phenomenon has been well studied empirically,[95–97] and a large assortment of "strongly twisting additives" has been selected. Thus the van der Waals forces exerted by the small impurities can induce a chiral structure in the material as a whole. Theoretically, the microscopical mechanism of the phenomenon is not clear enough. A role of the steric properties of the impurity has been shown experimentally.[98] However, the small amount of the required admixture indicates also a contribution from long-range forces, or more likely, a transfer of orienting influence via adjacent molecules,[99] solvation shells, etc. Experiment shows that not only the magnitude, but also the sign of the twist of the induced structure depend on the amount of impurity. This indicates the complexity of the phenomenon and the possibility of different combinations of relative orientations[100] and points out the need of taking account of at least ternary interactions.

The effect of twisting substantially expands the set of possible chiral matrices and facilitates the choice of matrices for a substance of interest. On the other hand, the onset of a chiral structure induced by an impurity can serve as a convenient indicator for studying the properties of the impurity by considerably amplifying the effect arising from its intrinsic optical activity. Thus a nematic matrix has been employed[101] for studying aminoalcohols possessing a very weak optical activity. When these alcohols were introduced into a nematic, they induced a chiral structure in it. Owing to this supermolecular structure, the rotation of the plane of polarization increased by a factor of a thousand. A concentration of impurity of the order of 0.05–1% sufficed (we stress that this indicates a very strong effect of the impurity on the structure of the matrix). It became possible to study an infinitesimal amount of material with a vast amplification of activity. In exactly the same way, it becomes possible to distinguish isomers and conformers introduced into chiral or achiral matrices.

Of course, such an induction by impurities occurs not only in liquid crystals, where it is manifested most strikingly. Thus, a set of polymers is known (see, e.g., Refs. 36 and 102) in which the introduction of a chiral impurity into an ordinary inactive solution induces activity in the achiral solvent. Here both interactions via surrounding molecules (solvation shells) and AC associations can occur as extra effects.[63] One can observe this also in solid-state matrices.

The method of induction by a chiral impurity proves valuable also in studying substances consisting of chiral molecules. The point is that the production of dextro and levo molecules is equally probable in all ordinary reactions for preparing these substances. Consequently the obtained material as a whole proves to be inactive (a "racemate").[11)] Preparing substances in a "chirally pure" form (separation of antipodes) is very complicated.

Introduction of a chiral impurity (1–5%, sometimes less) into a racemate creates a considerable preponderance of molecules of one sign, and enables one to study the gyrotropy.[104,105] This also occurs in a solid phase upon forming crystals[12)] (for more details, see Refs. 1 and 107). We note here in passing that another method exists of studying a racemate involving selective photoexcitation of one of the antipodes with light of the appropriate circular polarization[108] (see also Ref. 109).

8. CONCLUSION

The overall conclusion from all that we have presented in this review can be formulated as follows. In molecular physics and spectroscopy and in the physics of liquids and solutions, methods of induction of gyrotropy have been developed and are being successfully applied for a broad set of nongyrotropic objects. They enable one to include a very broad group of materials in the set of studies by the highly informative chiroptical methods. Application of this method in solid-state physics is essentially just beginning, but has already yielded valuable results and merits further development.

[1] Dissymmetry-chirality—is the absence of a center and of planes of symmetry. Asymmetry is the complete absence of elements of symmetry.

[2] Evidently its symmetry will generally vary when nontotally symmetric vibrations arise in the object.

[3] Here and below we provisionally employ the term "molecule", although all that we have said pertains to ions, complexes, polymers, etc.

[4] This is precisely the fact that favors the manifestations of weak magnetic-dipole and electric-quadrupole transitions.

[5] In the presence of correlation of orientations, and especially in the presence of order, one must not neglect R_{binding} and the quadrupole moments.

[6] The sign of the effect induced in A may not agree with the sign for C.

[7] Creation of orientation enables one to study activity also in molecules that have a plane of symmetry (see above). The absence of a center of symmetry suffices.[25]

[8] An earlier treatment was given in Ref. 57b.

[9] Displacements from 0.02 to 0.28 Å.

[10] Possibly this is just the explanation of an increase in dichroism with temperature in Fig. 16.

[11] The only exceptions are some substances of biological origin that have a fixed sign; see Ref. 103 for the reasons for this.

[12] The method of separation by spontaneous crystallization known since the time of Pasteur is applicable to a very restricted set of substances.[106]

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