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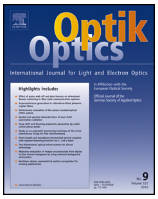

Optical activity originated by ring of coupled oscillators

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ABSTRACT

This paper presents the theory of the optical activity of ring of coupled based on the generalized Rosenberg relations for the complex rotatory power. The rotational strengths of the quantum-mechanical transitions of normal modes of vibrations for the arbitrary propagation direction of the electromagnetic wave are calculated by relatively simple way. In real materials, the valence electrons can be represented by the harmonic oscillators. Therefore, this theory can be used for the solution of the optical activity of molecules when the optical activity is based on the dipole–dipole interactions between the valence electrons. One of such molecules can be the molecules of the SUA crystal, the optical activity of which follows from the optical activity of single molecules. It is shown that using the model of ring of coupled oscillators, better dispersion relations for the optical activity of this crystal can be obtained. As example, the interpretation of one isolated peak of the circular dichroism of the SUA crystal is shown as an example.

1. Introduction

It is known that the optically active medium reacts differently on the propagation of the left and the right circularly polarized waves, in which the incident linear polarized wave is decomposed in this medium. The circularly polarized waves propagate with different velocities. Therefore, after the composition of these waves on the output of the medium, the linear polarized wave results again but with a rotated plane of polarization with respect to the incident wave. The variation of this rotation with frequency or wavelength is called the optical rotatory dispersion (ORD). Furthermore, specific spectral bands exist in the spectrum of the optically active medium, in which the circularly polarized waves are absorbed differently. Then, two circularly polarized waves, with different amplitudes, are composed in the slightly elliptically polarized wave. This effect is known as a circular dichroism (CD) and consequently the frequencies in the corresponding spectral bands are addressed as dichroic frequencies. In this case the rotation of the principal axis of the plarization ellipse is considered as the angle of rotation. From the point of view of basic optical characteristics, the optically active medium is described by complex refractive indices $\overline{n}_l$ and $\overline{n}_r$ for the left and the right circularly polarized waves respectively. By means of complex refractive indices, the complex rotatory power $\overline{\rho}$ of the medium is defined as the fundamental characteristic of the optically active medium in the known form

$$\overline{\rho} = \rho + \mathrm{i}\sigma = \frac{\omega}{2c}(\overline{n}_l - \overline{n}_r) = \frac{\omega}{2c}\left[(n_l - n_r) + \mathrm{i}(\kappa_l - \kappa_r)\right], \tag{1}$$

where ρ denotes the ORD and, to an excellent approximation, σ is the CD. The quantities n_l, n_r and κ_l, κ_r are real and imaginary parts of the complex refractive indices $\overline{n}_l$ and $\overline{n}_r$. Let's remind that the ORD and CD, as the dispersive and the absorptive aspects arising from the interaction of the radiation with the matter, are connected by the Kramers–Kronig transforms [1].

Optical activity (OA) can be of molecular and/or crystalline origin. It means that OA describes the dissymetry of molecules or crystals following from the fact that a molecule or crystal is nonsuperimposable on its mirror image. Considering this fact, a theoretical structural optically active units can be defined and the results of the OA solutions of these units can be used for better explanation and description of the OA of real matter. A ring of coupled oscillators, i.e. the system of mutually coupled oscillators lying on the circle when the directions of vibrations of the oscillators contain an angle with the plane of the circle, can be considered to be one of such units. The linear harmonic oscillators represent the valence electrons of the most polarizing atoms in the molecule. We would like to demonstrate that this model

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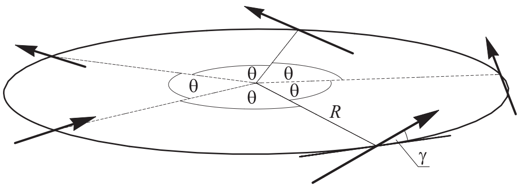

Fig. 1. Ring of coupled oscillators.

can improve the interpretation and description of the OA experimental data of e.g. cubic crystal of sodium uranyl acetate (SUA) and most of all the contribution of the uranyl acetate complex to the resulting OA.

Let us note that the ab initio methods are used in the solutions of the molecular OA most frequently. These methods are powerful tool for the needs of structural chemistry. Different levels of quantum mechanical theory of molecules such as Hartree–Fock (HF), coupled clusters (CC) or most of all the time-dependent density functional theory (TDDFT) are used (see e.g. [2–6]). The theory of coupled oscillators is often used in the calculations of the OA of crystalline origin (see e.g. [7–13,16]). However, the ab initio methods do not provide more complicated forms of dispersion relations. On the other hand, the methods of coupled oscillators provide accurate forms of dispersion relations depending on complexity of the model used and therefore they are more convenient for exact interpretation of the OA experimental data in wide intervals of frequencies or wavelengths. The ab initio methods calculate the ORD and CD independently using a different algorithms [14]. The methods of coupled oscillators can obtain the ORD and CD dispersion relations by means of one calculation procedure, when the damping of the oscillators is taken into account.

The model of coupled oscillators in the OA also can be solved following different calculation ways. Chandrasekhar [7] and later many other authors used the dispersion theory of refractive indices of the medium, represented by the coupled oscillators units, for the propagation of the circularly polarized electromagnetic waves. Following the Condon relations [15], the propagation of the linear polarized waves through the optically active medium can be solved [16,17]. This solution is considered more precise. However, it was proved [12,13] that the tedious calculations, which are required by the above mentioned methods, can be simplified when we use the direct calculation of the rotational strengths of the quantum-mechanical transitions. For that reason, this solution method of the OA, based on the model of coupled oscillators, will be used in the following text.

2. General theory

The valence elctrons of most polarizable atoms are represented by mutually coupled linear harmonic oscillators with defined positions an directions of vibrations. In the model of ring of oscillators, the situation can be described as follows. Let's have oscillator denoted No. 1. Starting from this oscillator on the circle, the position and the direction of vibrations of another oscillator (No. 2) can be obtained as the result of moving round the circle axis of the oscillator No. 1 to the position of the oscillator No. 2 (Fig. 1). The angle θ of the rotation is determined by the number of oscillators in the model. The oscillators are positioned regularly on the circle in the most frequent cases, i.e. $\theta = 2\pi/n$, where n is the number of single oscillators in the unit of the coupled oscillators, i.e. in one compound oscillator. All the oscillators lying on one circle are coupled, whereas the oscillators lying on different circles are supposed to be uncoupled. This supposition follows from the conception of longer distances between the oscillators lying of different circles in comparison with distances between the oscillators on one circle. Therefore, the rings of oscillators contribute to the resulting OA independently. The orientation of the ring of oscillators is random with regard to the direction of propagation of the electromagnetic wave.

The opticaly active quantum-mechanical transition from the ground state $|0\rangle$ to any excited state $|k\rangle$ of the system is characterized by the rotational strength defined as

$$R_{k0} = \mathrm{Im}\left(\langle 0|\hat{\mathbf{p}}|k\rangle \cdot \langle k|\hat{\mathbf{m}}|0\rangle\right), \tag{2}$$

where $\hat{\mathbf{p}}$ and $\hat{\mathbf{m}}$ are operators of electric and magnetic dipole moments induced by the propagating electromagnetic wave and the oscillator strengths fulfill the Kuhn sum rule [18]

$$\sum_k R_{k0} = 0. \tag{3}$$

Using the rotational strengths, the complex rotatory power $\overline{\rho}$ of any molecular system is defined according to the Rosenfeld formula [19]

$$\overline{\rho}(\omega) = \frac{8\pi N}{3\hbar c}\sum_k \frac{R_{k0}\omega^2}{\omega_{k0}^2 - \omega^2 - 2\mathrm{i}\gamma_{k0}\omega} \tag{4}$$

where the original formula is extended to the dichroic frequency region. In Eq. (4), N is the number of molecules in the volume unit, ω_{k0} is the transition frequency from the ground state to the excited state, γ_{k0} is the damping constant. The connection of the ORD and CD with $\overline{\rho}$ follows from Eq. (1).

The above mentioned relations have to be modified for the system of coupled oscillators. Such systems are usually solved using the system of normal coordinates because of split of the characteristic frequency of the single oscillator into n frequencies of normal modes η of vibrations, $\eta = 1, 2, \ldots, n$. Then the rotational strengths of the normal modes

$$R_{\eta_{k0}} = \mathrm{Im}\left(\langle \eta_0|\hat{\mathbf{p}}_{q_\eta}|\eta_k\rangle \cdot \langle \eta_k|\hat{\mathbf{m}}_{q_\eta}|\eta_0\rangle\right) \tag{5}$$