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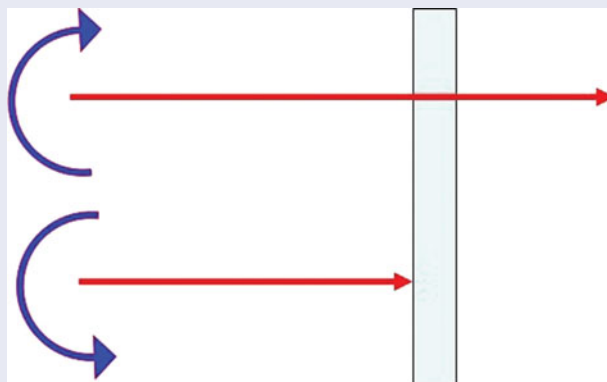
Origin of the giant circular dichroism of vibronic f – f transitions

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ABSTRACT

Taking into account the space inhomogeneity of the light electromagnetic wave, a new quantum mechanical expression for the natural optical activity (NOA) of electron transitions has been obtained, which is consistent with the phenomenological theory. It is shown that properties of the NOA of parity forbidden f – f transitions substantially differ from those of allowed transitions. The experimentally observed large NOA of the f – f transitions and extremely large (close to unity) NOA of vibrational repetitions of the f – f transitions are qualitatively explained on the basis of the obtained theoretical expression.



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1. Introduction

Natural circular dichroism (NCD) is widely used in study of organic materials. NCD of inorganic compounds, and $4f$ compounds in particular, was investigated less extensively, (see, e.g. [1–8]). Recently, a very large (close to unity) natural optical activity (NOA) of the electron-vibrational (vibronic) transitions was revealed in $\text{ErAl}_3(\text{BO}_3)_4$ [9] and in $\text{HoAl}_3(\text{BO}_3)_4$ [10] crystals. Such a large NOA should be explained.

The widely used theory of the NCD [11] gives the following expression for the NOA of a transition $i \rightarrow f$:

$$A = \text{Im}[\langle i|\vec{d}|f\rangle\langle f|\vec{m}|i\rangle]/|\langle i|\vec{d}|f\rangle|^2. \quad (1)$$

Here, Im denotes the imaginary part of a quantity, \vec{d} and \vec{m} are the electric and magnetic dipole moments, respectively. The electric dipole character transition is

considered. This formula was obtained for a sample composed of randomly oriented chiral systems; however, majority of researches use it for crystals as well. This formula lies in the background of a number of the subsequent theoretical works (see, e.g., [1,12–18]). According to Equation (1), none of the electron transitions can be almost completely circularly polarised, as it takes place in Refs. [9,10], since this would require equality of matrix elements of the electric and magnetic dipole moments. Influence of the crystal symmetry on the optical activity was considered, e.g. in Ref. [19]. According to the phenomenological theory, the formula for the NOA should contain the light wave number in the explicit form. Thus, the space dispersion should be taken into account [20,21].

2. Results and discussion

According to the Onsager principle, the electric polarizability tensor follows the relation: $\alpha_{nm}(\vec{k}) = \alpha_{nm}(-\vec{k})$

where \vec{k} is the light wave vector which characterises the space dispersion. Consequently, the tensor can be decomposed into symmetric and anti-symmetric parts. The symmetric part is the even function of \vec{k} and the anti-symmetric part is the odd function of \vec{k} . If a crystal has the centre of inversion, then the anti-symmetric part is equal to zero, since vector \vec{k} change sign as a result of the space inversion. If there is no absorption, then α_{mn} is the Hermitian tensor and, consequently, the symmetric components are the real and anti-symmetric ones are the imaginary values. If the light propagates along the z -axis which is the optical axis of the crystal, then the symmetric tensor is the diagonal one, but anti-symmetric tensor has only components $\alpha_{xy} = -\alpha_{yx}$. Just these components give rise to the NCD and birefringence: $\alpha_+ - \alpha_- = g = i\alpha_{xy}$, where α_+ and α_- are polarisabilities for + and - circularly polarised waves. It is important to note that in order to describe the circular dichroism and birefringence, basing on the Maxwell equations it is enough if only the electric polarisability tensor differs from zero and depends on \vec{k} . Thus, it is not necessary to take into account magnetic dipole transitions probability, when the electron transition has certainly electric dipole character.

Basing on results of Ref. [20], it is possible to write the electric polarisability tensor of a molecule corresponding to the electron transition $i \rightarrow f$ in the form:

$$\alpha_{nm}(\omega, \vec{k}) \left[\frac{M_{if}^n(-\vec{k})M_{fi}^m(\vec{k})}{\omega_{if} + \omega} + \frac{M_{fi}^n(-\vec{k})M_{if}^m(\vec{k})}{\omega_{if} - \omega} \right] \quad (2)$$

Here, $\hat{M}(\vec{k}) = \hat{p}e^{i\vec{k}\vec{r}} + e^{i\vec{k}\vec{r}}\hat{p}$ and $\hat{p} = -i\hbar\frac{\partial}{\partial\vec{r}}$, that is, the space dispersion was taken into account. The perturbation inducing the electron transition is: $\hat{U} \sim \vec{E}_0(\hat{M}(\vec{k})e^{-i\omega t} + \hat{M}^*(\vec{k})e^{i\omega t})$, where \vec{E}_0 is the amplitude of the light wave electric field. Consequently, at $k = 0$ operator $\hat{M}(\vec{k} = 0) = 2\hat{p}$ is proportional to the electric dipole operator. Taking into account that $M_{if} = M_{fi}^*$, from (2) it is possible to obtain:

$$\alpha_{nm}(\omega, \vec{k}) \sim \frac{\omega_{if}\text{Re} \left[M_{if}^n(-\vec{k})M_{fi}^m(\vec{k}) \right] + i\omega\text{Im} \left[M_{if}^n(-\vec{k})M_{fi}^m(\vec{k}) \right]}{\omega_{if}^2 - \omega^2}. \quad (3)$$

Formula (2) was obtained in [19] in assumption that there is no absorption. Therefore, according to the phenomenological theory, the first term in (3) gives the symmetric part of the polarisability tensor and the second one gives the anti-symmetric part (gyration tensor),

responsible for the circular birefringence and dichroism. In order to transfer to the resonance region, it is necessary to replace function $1/(\omega_{if}^2 - \omega^2)$ by the complex Lorentz function: $1/[(\omega_{if}^2 - \omega^2) - i\gamma\omega]$, where γ is the line width. The imaginary part of this function will give dispersion of absorption and dichroism.

Since $e^{i\vec{k}\vec{r}} \approx 1 + i\vec{k}\vec{r}$, we can write

$$\begin{aligned} \hat{M}(\vec{k}) &\approx 2\hat{p} + i(\hat{p}\vec{k}\vec{r} + \vec{k}\vec{r}\hat{p}) \\ &= 2\hat{p} + ik(\hat{p}r_k + r_k\hat{p}) \equiv 2\hat{p} + k\Delta\hat{p}. \end{aligned} \quad (4)$$

Here, r_k is the projection of \vec{r} on the \vec{k} direction. Substituting (4) into (3), we obtain for the value in the brackets:

$$\begin{aligned} [\dots] &= 4p_{if}^n p_{if}^{m*} + 2k \left(\Delta p_{if}^{m*} p_{if}^n - \Delta p_{if}^n p_{if}^{m*} \right) \\ &\quad - k^2 \Delta p_{if}^n \Delta p_{if}^{m*}. \end{aligned} \quad (5)$$

It is possible to show that the second term in (5) is always imaginary one, and also because it is proportional to k it is responsible for the anti-symmetric components of the polarisability tensor. Let us consider now the usual experimental situation when the light propagates along the z -axis which is the optical axis of the crystal. Then, as mentioned above, the symmetric part of the polarisability tensor is the diagonal one and the anti-symmetric components are $\alpha_{xy} = -\alpha_{yx}$. Additionally, $r_k = z$ and according to (4)

$$\Delta\hat{p}^{x,y} = i(\hat{p}^{x,y}z + z\hat{p}^{x,y}). \quad (6)$$

Due to the axial symmetry, matrix elements of the x and y components of the operators are identical that is reflected in double superscripts in (6). Then we obtain:

$$[\dots] = 4|p_{if}^x|^2 + 2k \left(\Delta p_{if}^{x*} p_{if}^x - \Delta p_{if}^x p_{if}^{x*} \right) - k^2 |\Delta p_{if}^x|^2. \quad (7)$$

Thus, the NOA of the transition $i \rightarrow f$ is:

$$A = \frac{\text{Im}2k \left(\Delta p_{if}^{x*} p_{if}^x - \Delta p_{if}^x p_{if}^{x*} \right)}{4|p_{if}^x|^2 - k^2 |\Delta p_{if}^x|^2}. \quad (8)$$

A difference in the frequency dependencies of α_{xy} and α_x , which is appreciable only far from the resonance, is not taken into account in (8).

If a crystal has the centre of inversion and the electric dipole transition is parity allowed, then the matrix element p_{if}^x is not zero, but the matrix element Δp_{if}^x is equal to zero, since according to (6) $\Delta\hat{p}$ is the even function. Thus, the crystal must not have the centre of inversion in order to have the NCD in agreement with the

phenomenological theory, and for the allowed transition we find from (8):

$$A \sim kr = \frac{r}{\lambda}, \quad (9)$$

where r is the radius of the object, absorbing the quantum of the light and λ is the light wave length. Additionally, the NOA is proportional to the deviation of the crystal field from the centrally symmetrical one.

Another situation takes place for the parity forbidden f - f transitions. In this case, the absence of the centre of inversion is necessary for allowance of the transitions themselves. If there is the centre of inversion, the matrix element Δp_{if}^x , on the contrary, is not zero for f - f transitions, and it weakly depends on the noncentrosymmetrical distortions. When these distortions decrease the matrix element p_{if}^x tends to zero but Equation (8) increases. Thus, it is possible to expect, that NOA of the parity forbidden f - f transitions can be larger than that of the parity allowed ones. Indeed, the radius of the rare earth ions is of the order of 0.1 nm. Then according to (9) the NOA of the allowed transitions in the visible spectral range should be of the order of $2 \cdot 10^{-4}$. In reality, the NOA of f - f transitions rich values of about 0.1 [2,5]. The value (8) is also called the dissymmetry factor, having in mind that the NOA should be proportional to the noncentro-symmetrical distortions. However, we see that this statement is valid only for the parity allowed transitions. For the parity forbidden ones, the circular dichroism itself, i.e. numerator in (8), will be probably more suitable characteristic of the optical activity of the transition. This value, indeed, is proportional to the noncentrosymmetrical distortions.

According to the said above, already little intensity of vibronic transitions can be the cause of their large NOA. However, the electron vibrational nature of such transitions can give additional contribution into the NOA. In crystals with the centre of inversion, odd vibrations mix wave functions of the opposite parity and so the vibrational repetitions of the parity forbidden electron transition become to be allowed (Herzberg–Teller interaction). Even vibrations mix wave functions of the same parity and therefore they can create repetitions of already allowed transitions. Intensities of such vibrational repetitions of the purely electronic transition are proportional to the Stokes losses during the vibronic transitions. Majority of the rare earth compounds have no centre of inversion (mentioned above crystals including) and the f - f transitions are allowed due to the static odd distortions and are purely electronic ones. Conception of even and odd vibrations, strictly speaking, loses sense in such crystals, but the vibrations can be decomposed

Table 1. Selection rules for electric dipole transitions between Kramers states in D_3 symmetry.

	$E_{1/2}$	$E_{3/2}$
$E_{1/2}$	$\pi, \sigma(\alpha)$	$\sigma(\alpha)$
$E_{3/2}$	$\sigma(\alpha)$	π

Table 2. Selection rules for electric dipole transitions between non Kramers states in D_3 symmetry.

	A_1	A_2	E
A_1	–	π	$\sigma(\alpha)$
A_2	π	–	$\sigma(\alpha)$
E	$\sigma(\alpha)$	$\sigma(\alpha)$	$\pi, \sigma(\alpha)$

into odd and even parts. However, the vibrations partially preserve the mentioned properties, because deviation from the centro symmetrical structure is small. Thus, the mainly odd vibrations admix wave functions of the opposite parity and increase intensity of f - f transitions but do not increase the circular dichroism. The mainly even vibrations, on the contrary, admix wave functions of the same parity and do not increase intensity of f - f transitions but increase the circular dichroism. This can be the origin of the particularly large NOA of the vibronic transitions [9,10]. Additionally, the electron-vibrational interaction and covalency of bonds can increase delocalisation of the electron wave functions and can additionally increase the NOA.

Er^{3+} and Ho^{3+} ions in $\text{ErAl}_3(\text{BO}_3)_4$ [9] and in $\text{HoAl}_3(\text{BO}_3)_4$ [10] crystals are in the D_3 symmetry positions. In this symmetry, p^x transforms according to E irreducible representation and the coordinate z transforms according to A_2 irreducible representation. Then the function zp^x , giving NOA, transforms according to

$$\Gamma(zp^x) = A_2 \times E = E \quad (10)$$

representation. Consequently, the symmetry selection rules for the NOA coincide with those for the α -polarised absorption (Tables 1, 2), and all symmetry allowed transitions (the f - f transitions including) can have NOA. Similar situation takes place also in other uniaxial crystals.

It is known that intensity of the parity forbidden f - f transitions cannot be reliably found totally theoretically, and it is described by the semi-empirical Judd–Ofelt theory [22–24]. In the network of this theory, practically all f - f transitions are partially allowed (if there is no centre of inversion) due to the selection rule: $\Delta J \leq \lambda$ ($\lambda = 2, 4, 6$), where J is the total momentum of the ion. Matrix elements $(zp^x)_{if}$, characterising the NCD, probably, can be found theoretically for the f - f transitions, since for these transitions they are parity allowed. For the parity allowed transitions situation is opposite. Thus, in both cases, the

possibility of the totally theoretical calculation of the NOA is doubtful.

3. Conclusions

Taking into account the space inhomogeneity of the light electromagnetic wave, the new quantum mechanical expression for the NOA of electron transitions has been obtained. In contrast to the traditional expression, the new one is consistent with the phenomenological theory. In particular, it gives proportionality of the effect to the light wave number and it shows that the active object must have no centre of inversion. NOA of the electric dipole transitions should not contain matrix elements of the magnetic dipole operator. It is shown that properties of the NOA of the parity forbidden f - f transitions substantially differ from those of allowed transitions. In particular, NOA of f - f transitions is on the average much larger than that of allowed transitions. The experimentally observed peculiarities of the NOA of f - f transitions and their vibrational repetitions were qualitatively explained on the basis of the obtained theoretical expression. The possibility of the totally theoretical calculation of the NOA both of allowed and parity forbidden electron transitions is doubtful.

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No potential conflict of interest was reported by the author.

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