OPTICAL ROTATORY DISPERSION OF $\alpha$-QUARTZ

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ABSTRACT: It is shown that some formulae describing optical rotatory dispersion of $\alpha$-quartz with the aid of two Drude’s terms reduce to the combined formula containing one Drude’s and one Chandrasekhar’s term. Comparison of various formulae describing the experimental data of $\alpha$-quartz leads to the conclusion that the optical activity of this crystal is due to its crystal structure only, that means the optical activity is not of molecular origin. Further the rotatory strengths are discussed with the regard to coupled oscillator model and to the structure of $\alpha$-quartz.

1 Introduction

Burkov et alii have undertaken an exhaustive study of formulae describing optical rotatory dispersion (ORD) of $\alpha$-quartz. This study is based on precise measurements of various authors in the region from 0.15$\mu$m to 3.2$\mu$m. Beside the well known formula of Drude

$$\rho(\lambda) = \sum_i \frac{K_i^{(1)}}{\lambda^2 - \lambda_i^2}$$

(1)

Burkov et alii have used the following formulae:

$$\rho(\lambda) = \sum_i \frac{K_i^{(1)} \lambda^2}{(\lambda^2 - \lambda_i^2)^2}$$

(2)

derived by Chandrasekhar, the combined formula

$$\rho(\lambda) = \sum_i \left[ \frac{K_i^{(1)}}{\lambda^2 - \lambda_i^2} + \frac{K_i^{(2)} \lambda^2}{(\lambda^2 - \lambda_i^2)^2} \right]$$

(3)
derived by one of us [8] and also by Nelson [9] and formula

$$\rho(\lambda) = \sum_i K_i^{(3)} \left( \frac{\lambda^2 + \lambda_i^2}{(\lambda^2 - \lambda_i^2)^2} \right)$$  \hspace{1cm} (4)

derived by Agranovich [10, 11] and by Tsvirko [12]. In these formulae $\rho$ is the rotatory power, $\lambda_i$ is the characteristic wavelength and $K_i^{(j)}$ are the constants including molecular and crystalline properties of $\alpha$-quartz. Formulae (2) and (3) are based on the theory of coupled oscillators and the formula (4) is based on the excitons theory. It should be noted that measurements and theories for light propagating along the optic axis have been taken into account only. The applicability of the above mentioned formulae have been judged by Burkov et alii with the aid of root-mean-square deviation defined by

$$g = \sum_n (\rho_{\text{exp}} - \rho_{\text{teor}})^2$$ \hspace{1cm} (5)

where $\rho_{\text{exp}}$ are experimental data and $\rho_{\text{teor}}$ fitted data following from formulae (I) - (IV). Further $n$ is a number of measured data and the analysis of Burkov et alii comprises forty-five points from 0.15$\mu$m to 3.2$\mu$m. These authors have found that formulae (I) and (IV) with one term are inconvenient because $g$ is very great. They have found good agreement in the case of formula (I) with two terms of opposite signs, in the case of formula (2) with one or two terms and in the case of formula (3) with different $K_1^{(1)}$ and $K_2^{(2)}$ but with one $\lambda_i$. In some cases they have introduced the constant term corresponding to ORD in infra-red region. The results of the most convenient formulae are presented in Tab. 1.

| Nr. | Formula | $g$ |
|-----|---------|----|
| I   | $\rho(\lambda) = \frac{7.17\lambda^2}{(\lambda^2 - 0.0928^2)^2}$ | 3.91 |
| II  | $\rho(\lambda) = \frac{-0.05}{\lambda^2 - 0.0926^2} + \frac{7.266\lambda^2}{(\lambda^2 - 0.0926^2)^2}$ | 3.90 |
| III | $\rho(\lambda) = \frac{184.22}{\lambda^2 - 0.09355^2} + \frac{-177.04}{\lambda^2 - 0.09170^2}$ | 3.90 |
| IV  | $\rho(\lambda) = \frac{-1.05\lambda^2}{(\lambda^2 - 0.09998^2)^2} + \frac{8.22\lambda^2}{(\lambda^2 - 0.09387^2)^2}$ | 3.82 |
| V   | $\rho(\lambda) = \frac{219.47}{\lambda^2 - 0.09332^2} + \frac{-212.30}{\lambda^2 - 0.09176^2} + 0.0361$ | 3.89 |
| VI  | $\rho(\lambda) = \frac{-1.335\lambda^2}{(\lambda^2 - 0.1012^2)^2} + \frac{8.49\lambda^2}{(\lambda^2 - 0.0944^2)^2} + 0.0964$ | 3.74 |

In addition it should be noted that Katzin and Bùrer [13, 14] have worked out a formula for ORD of $\alpha$-quartz in the range from 0.23$\mu$m to 3.5$\mu$m. Their
formula has the form

$$\rho(\lambda) = \frac{127.02476}{\lambda^2 - 0.0979^2} - \frac{119.77145}{\lambda^2 - 0.0958^2} - 0.1879. \quad (6)$$

The experimental data are fitted to a root-mean-square deviation of about 0.038 deg. It is the most accurate formula worked out for this spectral range. However, this formula deviates notably from important measurements of Servant in the far ultraviolet. In the range from 0.1850 µm to 0.15235 µm the deviations are of systematic nature and become very great. E. g. for λ = 0.15235 µm rotatory power is 779.9 deg/mm whereas formula (6) gives 791.7 deg/mm.

The good agreement of formulae containing the wave dependence $\lambda^2/(\lambda^2 - \lambda^2 i)^2$ is not surprising because this dependence holds for some other crystals which are, like α-quartz, optically active in crystalline state only. On the other hand good approximation with the aid of formulae containing Drude’s terms only such as the formulae III and V from Tab. I is surprising because we are suspicious, in agreement with Hennessey and Vedam, of the formulae containing Drude’s term only. These terms are typical for optically active molecules. The molecular origin of optical activity of α-quartz is highly improbable because of the high symmetry of SiO$_2$ groups. Of course, they are some crystals the ORD of which can be fitted by Drude’s formula although they consist from symmetrical molecules. In this case the optical activity is of a pseudomolecular origin. The molecules of these crystals are symmetrical when isolated but they lose their symmetry in the crystalline state. They play then the same role as chromophors in optically active molecules. But it seems that this situation occurs in the case when crystals are composed from large molecules. We shall see that the loss of symmetry of SiO$_2$ groups in α-quartz is very little. We shall show that the formulae containing only Drude’s terms reduce to our formula (3), where Chandrasekhar’s terms plays a predominant role and Drude’s terms represents a little contribution. It means that formulae III and V differs very little from formula II.

### 2 Coupled Oscillators Model

ORD of α-quartz via coupled oscillators model has been firstly studied by Chandrasekhar and then by us. This model has been also generalized to the case of absorption region, where circular dichroism occurs. In this section we shall improve this model in order to obtain equations containing explicitly the rotational strengths for normal modes of vibrations which are the specific features of this model. We shall restrict our considerations to the crystals structure belonging to the space group of symmetry $D_3^4$ or its enantiomer $D_3^6$ because α-quartz is its typical representative. The crystal structure of α-quartz shows that an axial channel which results in a lower specific gravity than would be found from closer packing of the atoms. Fusion, rather than giving a
higher density from closer packing, results in an even lower specific gravity. This implies a molecular SiO\textsubscript{2} structural unit rather than an ionic crystalline constitution \[18, 19\]. Unit cell contains three molecules which are arranged spirally about a set of parallel c-axes. This arrangement together with the interaction between molecules causes a gyratory effect. In order to describe the optical properties of medium under the consideration it is natural to start from the properties of an isolated molecule and interactions between molecules are neglected because they play the role of little contributions. But it is not possible in the study of the optical activity of crystals consisting from inactive molecules. Therefore the above mentioned chiral structure together with the interaction between molecules must be simultaneously taken into account. In the study of interaction of an isolated molecule with an electromagnetic radiation each molecule behaves like a linear harmonic oscillator by which it may be represented. In the study of the optical activity the interaction between molecules can be considered with the aid of a compound oscillator consisting from two linear harmonic oscillators coupled together.

According to crystal structure of α-quartz let the first single oscillator, representing an isolated SiO\textsubscript{2} group, be situated at the origin of co-ordinate system with its vibration direction along α, β, γ, where α, β, γ are the direction cosines. Each oscillator is a charged particle which is assumed to be bound elastically to its own equilibrium position and capable of vibrating along a line. In the case of α-quartz we assume the vibrations along the line joining the centers of gravity of oxygen atoms. The second oscillator is situated at x, y, z with its vibration direction turned through an angel θ about c-axis with respect to the first one. For α-quartz θ = 120 deg. Each oscillator, when uncoupled, has the natural frequency ω\textsubscript{0}. As a result of the coupling, ω\textsubscript{0} would be split into two normal frequencies ω\textsubscript{1} and ω\textsubscript{2}. These normal frequencies of the compound oscillator are

\[ ω_1 = ω_0^2 + 2π^2ε, \quad ω_2 = ω_0^2 - 2π^2ε. \] (7)

Here ε is a coupling constant. The exact nature of the coupling is not essential in the following considerations but we consider it as small. We can neglect all terms containing ε\textsuperscript{2}. In our case it means that we assume the interactions of valence shall electrons of each isolated SiO\textsubscript{2} group.

The above mentioned model enables us to evaluate \( n_1 \) and \( n_r \) as it has been performed by Chandrasekhar \[3, 7\]. He has assumed that both normal modes have the same oscillator strengths. We have removed this simplification \[8\] obtaining for rotatory power ρ the following expression

\[ ρ(ω) = \frac{ω}{2c} (n_1 - n_r) = \pi Ne^2(α^2 + β^2) d sin θ \cdot \left( \frac{f_{q2}ω^2}{ω_2^2 - ω^2} - \frac{f_{q1}ω^2}{ω_1^2 - ω^2} \right). \] (8)
or in wave lengths
\[ \rho(\lambda) = \frac{\pi N e^2 (\alpha^2 + \beta^2) d \sin \theta}{mc^2} \cdot \left( \frac{f_{q_2} \lambda_2^2}{\lambda^2 - \lambda_2^2} - \frac{f_{q_1} \lambda_1^2}{\lambda^2 - \lambda_1^2} \right). \] (9)

From eqs. (7) and (8) one gets
\[ \rho(\lambda) = \frac{\pi N e^2 (\alpha^2 + \beta^2) d \sin \theta}{mc^2} \cdot \left[ \frac{\epsilon (f_{q_1} + f_{q_2}) \lambda_0^4 \lambda^2}{2 e^2 (\lambda^2 - \lambda_0^2)^2} + \frac{(f_{q_2} - f_{q_1}) \lambda_0^2}{\lambda^2 - \lambda_0^2} \right]. \] (10)

Here \( N \) is a number of single oscillators per unit volume, \( d \) is a linear distance between two single oscillators and \( f_{q_1}, f_{q_2} \) are oscillator strengths of both normal modes of vibrations.

We see that this model does not contain rotational strengths explicitly. It is because this model is a classical one. The rotational strengths follows from the quantum mechanical equations of motion of coupled oscillators. It will be shown in Appendix. Each normal mode has a proper rotational strengths. The strengths are
\[ R_{q_1} = -\frac{\hbar e^2 d (\alpha^2 + \beta^2) f_{q_1} \sin \theta}{8mc} \]
\[ R_{q_2} = \frac{\hbar e^2 d (\alpha^2 + \beta^2) f_{q_2} \sin \theta}{8mc}. \] (11)

Substituting from eq. (11) into eq. (9) we have
\[ \rho(\lambda) = \frac{8\pi N \epsilon (R_{q_2} - R_{q_1}) \lambda_0^4}{\hbar c} \cdot \frac{\lambda^2}{(\lambda^2 - \lambda_0^2)^2} + \frac{8\pi N (R_{q_1} + R_{q_2}) \lambda_0^2}{\hbar c} \cdot \frac{1}{\lambda^2 - \lambda_0^2}. \] (12)

or with the aid of eq. (7)
\[ \rho(\lambda) = \frac{4\pi N \epsilon (R_{q_2} - R_{q_1}) \lambda_0^4}{\hbar c} \cdot \frac{\lambda^2}{(\lambda^2 - \lambda_0^2)^2} + \frac{8\pi N (R_{q_1} + R_{q_2}) \lambda_0^2}{\hbar c} \cdot \frac{1}{\lambda^2 - \lambda_0^2}. \] (13)

It is clear that eqs. (12) and (13) are identical but under the condition that the difference between \( \lambda_1 \) and \( \lambda_2 \) is very small. This little difference follows from the assumption that \( \epsilon \) is small. Now we see that eq. (13) contains two terms the first of which is of Chandrasekhar’s type while the second one is of Drude’s type. In the case of \( f_{q_1} = f_{q_2} \) we have \( R_{q_1} = -R_{q_2} \) and Drude’s term in eq. (13) vanishes. Comparing eqs. (12) and (13) with the formulae in Tab. 1 we see that formulae III and V, being of Drude’s type, contain \( \lambda_1 \) and \( \lambda_0 \) which are very near and that the constants are also very near in numerical values but of opposite signs. We can also expect that these formulae reduce to our combined formula (3). Let us suppose that both constants in formulae of the type of III and V are
the same in numerical values but with opposite signs, then these formulae reduce to Chandrasekhar’s one. We can also expect that formulae III and V reduce to the formula which should be very near to formula II of Tab. [4] We shall see in the next section that this is true.

3 Discussion of Formulae

Let us compare formula III with eq. (12). We rewrite eq. (12) as follows

\[ \rho(\lambda) = \frac{A_{q_2} \lambda_2^2}{\lambda^2 - \lambda_2^2} + \frac{A_{q_1} \lambda_1^2}{\lambda^2 - \lambda_1^2}. \]  

(14)

We must take care of units. In formulae I - IV \( \rho \) is expressed in \( \text{deg/mm} \) and in theoretical considerations we express it in \( \text{rad/cm} \). In eq. (14) \( \rho \) and \( A_{q_2} \) and \( A_{q_1} \) are in the same units. Comparing eqs. (12) and (14) we see that 

\[ A_{q_1,2} = \frac{8\pi NR_{q_1,2}}{\hbar c}. \]  

(15)

Substituting from eq. (15) for \( R_{q_1,2} \) and for \( R_{q_1} + R_{q_2} \) into eq. (13) one gets

\[ \rho(\lambda) = \frac{(\epsilon \lambda_0^4/2c^2)(A_{q_2} - A_{q_1}) \lambda^2}{(\lambda^2 - \lambda_0^2)^2} + \frac{(A_{q_1} + A_{q_2}) \lambda_0^2}{\lambda^2 - \lambda_0^2}, \]  

where \( \lambda_0 = (\lambda_1 + \lambda_2)/2 \). Using eq. (7) we get

\[ \epsilon \lambda_0^4 \frac{2\lambda_0}{c^2} = \frac{1}{2} \left( \lambda_2^2 - \lambda_1^2 \right) = \lambda_0 \Delta \lambda. \]  

(17)

Here \( \Delta \lambda = \lambda_2 - \lambda_1 \). It follows from formula III that \( A_{q_2} = 2.1049 \cdot 10^4 \) and \( A_{q_1} = -2.1053 \cdot 10^4 \) in units of \( \rho \). Further \( \lambda_0 = 0.09265\mu m \) and \( \Delta \lambda = 1.5nm \). Substituting these values into eq. (16) we have

\[ \rho(\lambda) = \frac{7.214\lambda^2}{(\lambda^2 - 0.09265^2)^2} - \frac{0.034}{\lambda^2 - 0.09265^2}. \]  

(18)

In a similar way we obtain instead of formula V

\[ \rho(\lambda) = \frac{7.281\lambda^2}{(\lambda^2 - 0.09254^2)^2} - \frac{0.013}{\lambda^2 - 0.09254^2} + 0.036. \]  

(19)

In this case \( \lambda_0 = 0.09254\mu m \) and \( \Delta \lambda = 1.5nm \). We are able to evaluate \( \epsilon \) from eq. (17). It is \( 4.25 \cdot 10^{29} \text{sec}^{-2} \) for formula III and \( 3.54 \cdot 10^{29} \text{sec}^{-2} \) for formula V. Because \( \omega_0^2 \) is of order \( 10^{32} \text{sec}^{-2} \) we see that \( \epsilon \) is really small as we have assumed. Chandrasekhar [5] has also evaluated \( \epsilon \) for \( \alpha \)-quartz but he had to
use beside his formula I the formula for ordinary refractive dispersion. His value is $6.35 \cdot 10^{29} \text{sec}^{-2}$.

We see that there is a little difference among formulae I, II, III and V. We conclude that formulae III and V are nothing but formula II.

Now let us discuss the rotational strengths which may be evaluated from eqs. (12) and (14). In this case we must multiply both sides of eq. (14) by $\pi/18$. Then we obtain

$$\rho = \frac{3.664 \cdot 10^3 \lambda^2}{\lambda^2 - \lambda_0^2} - \frac{3.674 \cdot 10^3 \lambda_0^2}{\lambda^2 - \lambda_0^2}$$

or

$$R_{q_1} = -\frac{3.674 \cdot 10^3 \hbar c}{8\pi N}, \quad R_{q_2} = \frac{3.664 \cdot 10^3 \hbar c}{8\pi N}. \quad (21)$$

We have for $\alpha$-quartz $N = 2.68 \cdot 10^{22}$ and therefore $R_{q_1} = -1.732 \cdot 10^{-37}$ and $R_{q_2} = 1.727 \cdot 10^{-37}$ in cgs units.

We are now able to evaluate oscillator strengths $f_{q_1}$ and $f_{q_2}$. We have for $\alpha$-quartz $\alpha^2 = 0.64$, $\beta^2 = 0.0232$, $d = 1.8 \cdot 10^{-28} \text{cm}$, $\sin \theta = \sqrt{3}/2$. We get from eq. (11)

$$R_{q_1} = -1.155 \cdot 10^{-38} f_{q_1} = -1.732 \cdot 10^{-37}$$

$$R_{q_2} = 1.155 \cdot 10^{-38} f_{q_2} = 1.727 \cdot 10^{-37}. \quad (22)$$

From thus $f_{q_1} = 14.99$ and $f_{q_2} = 14.95$ and the average value $f_0 = (f_{q_1} + f_{q_2})/2 = 14.97$. This actual value of oscillator strengths corresponds to the number of valence - shell electrons of the oxygen and silica bring into $SiO_2$ molecule.

Using the same procedure in the case of formula V we get for $R_{q_1} = -2.0675 \cdot 10^{-37}$ and for $R_{q_2} = 2.0677 \cdot 10^{-37}$. The splitting of oscillator strengths is very little because $f_{q_1} = 18.852$ and $f_{q_2} = 18.851$. For these reasons Drude’s term plays a negligible role in formula V. The averaged value of $f_0 = 18.8515$ seems to be in high regard to the number of valence - shell electrons in $SiO_2$. Chandrasekhar [8] combining formulae for ORD and refractive dispersion has obtained

$$\frac{\alpha^2 + \beta^2}{2} f_0 = 6.5. \quad (23)$$

From thus $f_0 = 19.68$ which is also higher then the valence-shell electrons in $SiO_2$.

### 4 Conclusions

Performing the analysis we may conclude that all formulae from Tab. [9] reduce to formula in which the term $\lambda^2/(\lambda^2 - \lambda_0^2)^2$ plays a predominant role. This wave dependence arises from the model of coupled oscillators. Although this model is not sufficiently general to be rigorously valid for a crystal, it brings out
clearly a type of interactions which may be important in determining ORD of crystals which are optically active in crystalline state only. It has been shown that formulae containing two Drude’s terms with opposite signs and involving \(\lambda_1\) and \(\lambda_2\) which are close to each other reduce in fact to combined formula in which Chandrasekhar’s term plays a predominant role.

Nelson [9] has analysed the mechanism of crystalline optical activity and concluded that the quadratic term in formula II is due to lattice dynamics, while the electric-dipole–magnetic-dipole or electric-dipole–electric-quadrupole interference leads to the known Drude’s term.

The evaluated rotational strengths of both modes of vibrations are of an order \(10^{-37}\). This value is acceptable for crystals in visible and in uv region. On the other hand it seems that only the formula III and for these reasons also the formula II gives the actual value of \(f_0\) corresponding to the number of valence-shell electrons in SiO₂.

The location of \(\lambda_0\) is also of great importance and facilitates to understade the mechanism of ORD in \(\alpha\)-quartz. Platzöder [20] has measured the vacuum uv reflectance of \(\alpha\)-quartz and has found that the sharp peak at 0.1190\(\mu m\) is due to this exciton transition and that the other peaks at 0.105\(\mu m\), 0.0840\(\mu m\) and 0.0710\(\mu m\) are due to the interband transitions. The characteristic wave lengths in formulae I - III and V are located at the bottom of the dip between two peaks at 0.084 and 0.105\(\mu m\). The bottom is at 0.0940\(\mu m\) and it is in agreement with ORD formulae. On the other hand characteristic wave lengths in two - termed formulae IV and VI belong to two different interband transitions. The peak at 0.105\(\mu m\) is, in fact, split into three very near peaks. Two bottoms are located between 0.10 and 0.11\(\mu m\). The characteristic wave lengths in first terms in formulae IV and VI are then very close to above mentioned values. Both other terms contain \(\lambda_0\) which is located at \(\approx 0.084\mu m\).

The connection between characteristic wave lengths and interband transitions is in agreement with the model theory of coupled oscillators. The normal modes of vibrations are nothing but the tight-binding exciton model in quantum mechanical term.

Natori [21] has pointed out that coupled oscillator model pays no attention to the effect of the electron transfer from atom to atom that gives rise to the ordinary electronic band. For this reason Natori has discussed ORD in term of the ordinary energy band theory. He has obtained for \(\alpha\)-quartz following formula

\[
\rho(\omega) = 911.22\left(\sqrt{10.834 - h\omega} + \sqrt{10.834 + h\omega} - 2\sqrt{10.834}\right) + \\
6708.8\left(\frac{1}{\sqrt{10.834 - h\omega}} + \frac{1}{\sqrt{10.834 + h\omega}} - \frac{2}{\sqrt{10.834}}\right),
\]

(24)

where \(h\omega\) is measured in eV. In this formula he has taken into account 11 points of measurements from 0.6708 to 0.1525\(\mu m\) and calculated \(\rho\) with the aid of eq. (24). But in this region \(g = 2.16\) while Chandrasekhar’s formula gives \(g = 0.992\).
Moreover it follows that the deviations $\Delta \rho = \rho_{\text{exp}} - \rho_{\text{cal}}$ are of systematic nature when using formula (24). In the region from 0.6708 to 0.3403$\mu m$ $\Delta \rho$ in negative and the deviations have decreasing tendency from $-0.11$ to zero at $\lambda = 0.3403\mu m$. In the region from 0.3403 to 0.1525$\mu m$ $\Delta \rho$ is positive with increasing tendency from zero to $+3.9$ at $\lambda = 0.1725\mu m$. The deviation $\Delta \rho$ at $\lambda = 0.1525\mu m$ is again negative but very great, that is $-5.8$. In formula (25) $\hbar \omega_0 = 10.834eV$. It means that $\lambda_0 = 0.11443\mu m$ which located it at the bottom of the dip between two peaks at 0.105 and 0.1190$\mu m$. Natori has pointed out that this location of $\lambda_0$ is in agreement with the used model and that the formula (24) is more preferable than Chandrasekhar’s formula. But as we have shown his formula does not enable good approximation of experimental data.

The analysis cannot stop here but we can conclude that ORD of $\alpha$-quartz is due to its crystal structure because in all appropriate formulae Chandrasekhar’s terms play a predominant role and just these terms reflects the optical activity of crystalline origin. It should be noted that Drude’s term in our formula does not reflect optical activity of molecular origin as judged by some authors (see e. g. [22] and references in this paper). This term reflects the splitting of rotatory strengths of normal modes of vibrations (see Appendix). Meanwhile, we do not know the cause of this splitting but we expect that this splitting is caused by crystalline field. We hope in the future to apply the model of coupled oscillators to some real crystals including the effects of crystalline field.

Some authors [22] ascribe our combined formula to Agranovich [10, 11]. But Agranovich has pointed out that Drude’s term vanishes in his formula when taking into account crystal consisting from optically inactive molecules. The difference between our formula and formula of Born [23] has been discussed by us in [8]. In the Appendix we shall show that formula of Agranovich and Tsvirko is special case of our combined formula as well as formula derived recently by Kato et alii [24].

**Appendix: Rotational Strengths of Normal Modes of Vibrations**

A transition is optically active when it has non-vanishing rotational strengths. For a transition from some ground state $|0\rangle$ to the excited state $|n\rangle$ the rotational strength is a imaginary part of scalar product of the electric dipole moment $\vec{\mu}_e$ and the magnetic dipole moment $\vec{\mu}_m$. These moment are $\langle 0|\vec{\mu}_e|n\rangle$ and $\langle n|\vec{\mu}_m|0\rangle$ so that

$$R_{0n} = \text{Im}\langle 0|\vec{\mu}_e|n\rangle\langle n|\vec{\mu}_m|0\rangle.$$  \hspace{1cm} (25)

In the case of coupled oscillators the excited state $|n\rangle$ is split into two states $|1n\rangle$ and $|2n\rangle$. Therefore the rotational strength needs be considered between ground state and both excited states. The total electric moment of compound
oscillator is

\[
\vec{\mu}_e = e (\vec{r}_1 + \vec{r}_2) = e [\vec{r}_1 + \vec{r}_2 + \vec{r} (\alpha \cos \theta - \beta \sin \theta) r_2 + \vec{r} (\alpha \sin \theta + \beta \cos \theta) r_2].
\] (26)

Here \(\vec{r}\) and \(\vec{f}\) are the unit vectors along \(x\) and \(y\) axis and \(\vec{r}_1\) and \(\vec{r}_2\) are position vectors of vibrating electrons in both single oscillators. Because we study the rotational strengths for light propagating along \(c\)-axis we taken into account the vibrations along \(x\) and \(y\) axes. Using the normal coordinates

\[
r_1 = \frac{1}{\sqrt{2}} (q_1 + q_2), \quad r_2 = \frac{1}{\sqrt{2}} (q_1 - q_2)
\] (27)

we obtain from eq. (26) the normal components of \(\vec{\mu}_e\) as follows

\[
\vec{\mu}_{e_{1}} = \frac{e}{\sqrt{2}} \{\vec{r} [\alpha (1 + \cos \theta) - \beta \sin \theta] + \vec{f} [\beta (1 + \cos \theta) + \alpha \sin \theta] \} q_1
\] (28)

and

\[
\vec{\mu}_{e_{2}} = \frac{e}{\sqrt{2}} \{\vec{r} [\alpha (1 - \cos \theta) + \beta \sin \theta] + \vec{f} [\beta (1 - \cos \theta) - \alpha \sin \theta] \} q_2.
\] (29)

The magnetic dipole moment of compound oscillator is

\[
\vec{\mu}_m = \frac{e}{2c} \left[ \left( \frac{d}{2} \times \dot{\vec{r}}_2 \right) - \left( \frac{d}{2} \times \dot{\vec{r}}_1 \right) \right],
\] (30)

where \(d\) is linear distance between two centers of gravity of both single oscillators. We can write instead of eq. (30)

\[
\vec{\mu}_m = \frac{-ed}{4c} \left[ \vec{k} \times (\dot{\vec{r}}_1 - \dot{\vec{r}}_2) \right].
\] (31)

Here \(\vec{k}\) is the unit vector along \(z\)-axis which is identical with crystal \(c\)-axis. We see that magnetic dipole moment arises from a particular spatial distribution of coupled oscillators. When \(\vec{r}_1\) and \(\vec{r}_2\) colinear the magnetic dipole moment is zeroth. The normal components of \(\vec{\mu}_m\) are

\[
\vec{\mu}_{m_{1}} = \frac{-ed}{\sqrt{32}c} \left\{ \vec{f} [\alpha (1 - \cos \theta) + \beta \sin \theta] - \vec{r} [\beta (1 - \cos \theta) - \alpha \sin \theta] \right\} \dot{q}_1
\] (32)

and

\[
\vec{\mu}_{m_{2}} = \frac{-ed}{\sqrt{32}c} \left\{ \vec{f} [\alpha (1 + \cos \theta) - \beta \sin \theta] - \vec{r} [\beta (1 + \cos \theta) + \alpha \sin \theta] \right\} \dot{q}_2.
\] (33)
According to eq. (25) we get
\[ R_{1n0} = \text{Im} \left[ -\frac{2e^2d(\alpha^2 + \beta^2) \sin \theta \langle 0|q_1|1n\rangle \langle 1n|\dot{q}_1|0\rangle}{8c} \right] \] (34)
and
\[ R_{2n0} = \text{Im} \left[ \frac{2e^2d(\alpha^2 + \beta^2) \sin \theta \langle 0|q_2|2n\rangle \langle 2n|\dot{q}_2|0\rangle}{8c} \right] . \] (35)

The matrix elements \( \langle \eta n|\dot{q}_n|0\rangle \) may be written as follows
\[ \langle \eta n|\dot{q}_n|0\rangle = i\omega_{\eta n0} \langle \eta n|q_n|0\rangle \] (36)
and using definition of oscillator strength
\[ f_{q_n} = \frac{2m\omega_{\eta n0}|\langle \eta n|q_n|0\rangle|^2}{\hbar} \] (37)
we obtain for \( R_{1n0} \) and \( R_{2n0} \)
\[ R_{1n0} = -\frac{\hbar e^2d(\alpha^2 + \beta^2) f_{q1} \sin \theta}{8mc} \] (38)
and
\[ R_{2n0} = \frac{\hbar e^2d(\alpha^2 + \beta^2) f_{q2} \sin \theta}{8mc} . \] (39)

We see that \( R_{1n0} \) and \( R_{2n0} \) substituted into eq. (12) gives directly eq. (9) and from eq. (13) we get eq. (10).

In linear harmonic oscillator approximation one may evaluate the matrix elements in eq. (37), that is
\[ |\langle \eta n|q_n|0\rangle|^2 = \frac{\hbar}{2m\omega_{\eta n0}} \] (40)
and from thus \( f_{q1} = f_{q2} = 1 \). Then Drude’s term vanishes in eq. (10) and we get Chandrasekhar’s formula. Of course, in real molecules \( f_{q1} = f_{q2} \leq n \), where \( n \) is a number of oscillating electrons. In Heitler - London approximation one may write \( \langle 1n|q_1|0\rangle = \langle 2n|q_2|0\rangle \) and therefore
\[ \frac{f_{q1}}{\omega_{1n0}} = \frac{f_{q2}}{\omega_{2n0}} = \frac{f_0}{\omega_{n0}} . \] (41)

Here \( f_0 \) is, as before, average value of both oscillator strengths, that is oscillator strength of single oscillator. Further \( \omega_{n0} \) is characteristic frequency of uncoupled oscillator. Using eq. (37) we get from eq. (14)
\[ f_{q1} + f_{q2} = 2f_0, \quad f_{q2} - f_{q1} = -\frac{2\pi^2f_0\epsilon}{\omega_{n0}^2} = -\frac{\epsilon f_0\lambda_0^2}{2c^2} \] (42)
and substituting these expressions into eq. (10) one has

$$
\rho(\lambda) = \frac{\pi Ne^2 d (\alpha^2 + \beta^2) \epsilon f_0 \lambda_0^4 \sin \theta}{mc^4} \cdot \frac{\lambda^2 + \lambda_0^2}{(\lambda^2 - \lambda_0^2)^2} \quad (43)
$$

or

$$
\rho(\lambda) = \frac{K^{(3)} (\lambda^2 + \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^2}. \quad (44)
$$

This formula is identical with that obtained by Agranovich [10, 11] and by Tsvirko [12]. We see that formula (44) is nothing but the special case of our combined formula (3).

Kato et alii [24] have derived ORD formula from the exciton dispersion theory. Their formula is

$$
\rho(\lambda) = \frac{K^{(4)} (3\lambda^2 - \lambda_0^2)}{(\lambda^2 - \lambda_0^2)^2}. \quad (45)
$$

Without entering into the details of the microscopic theory it is interesting that when $K^{(2)} = 2K^{(1)}$ in our formula (3) this formula reduces to formula (45). On the other hand formula (4) may be formally obtained from formula (3) when $2K^{(1)} = -K^{(2)}$ but it is nothing but Heitler - London approximation discussed in eqs. (11) - (14).

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