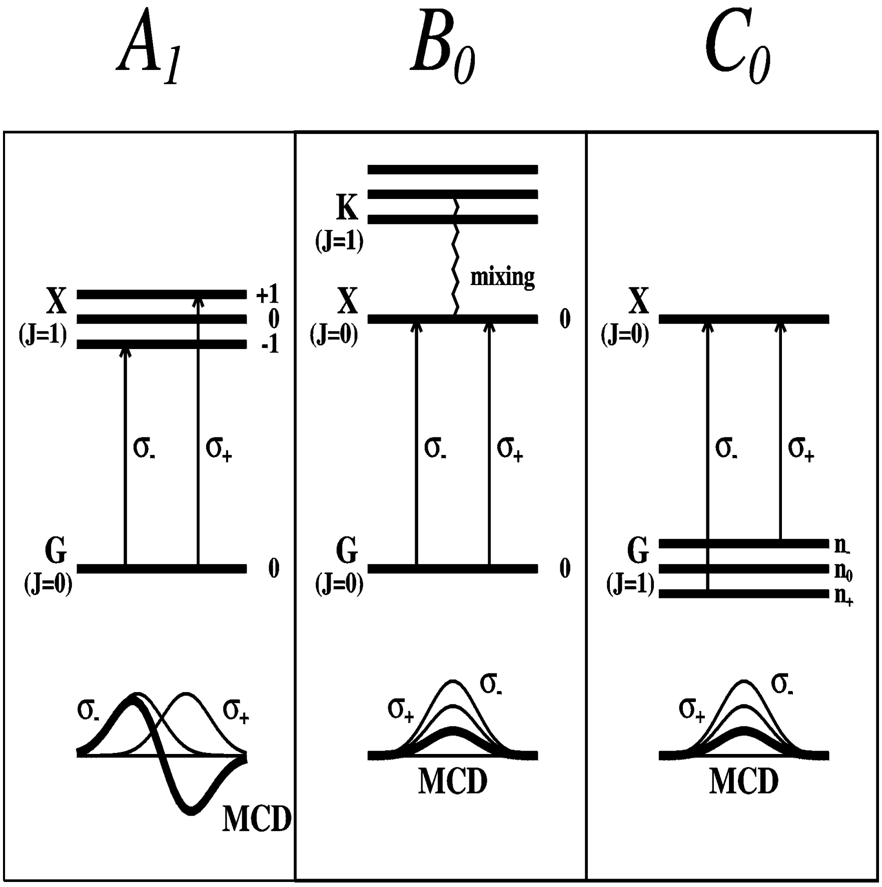
MCD for Dummies

Before you lies the text that I have written when I was staying at the University of California at Berkeley (1995). The text is intended as in introduction into the art of magnetic circular dichroism of absorption, MCD. Although the text should be enough to understand and work with MCD, I recommend reading the article of Stephens. In fact, this text is mainly based on his work.

Peter Stallinga, Faro,2001



Introduction

The purpose of this exercise is to show how MCD works. That is, to derive the form of the three terms in MCD, $\mathbf{A_1}$, $\mathbf{B_0}$ and $\mathbf{C_0}$. This will be done on basis of simple intuitive derivations. First we will analyse the absorption spectra in the absence of magnetic fields where there is no difference between left and right circular polarized light. After that we will apply magnetic fields to the system and see how this will change the difference in absorption between σ^+ and σ^-.

Optical Spectroscopy

In Figure 1 the vibrational and electronic states of a general system are drawn. This is done in a special way in order to visualize it more clearly. First, the energy of the system is drawn as a function of the configurate coordinate. A configurate coordinate can be any combination of the real-space coordinates, for instance the "breathing" of the four atoms in a tetrahedrally surrounded atom, in which case the coordinate Q represents the (equal) distance of all four atoms relative to the central atom. When we have established what this configurate coordinate is the energy of the system can be expressed in it. In Figure 1 two electronic levels are visible, namely the two parabolas,. Each has a different value of Q at the minimum. This indicates that the systems in different electronic levels relax to different nuclear positions, for example a configuration in which the atoms are more separated. In each electronic level parabola the vibrational levels are indicated by horizontal lines. The atom(s) in each electronic level can vibrate around the rest position. The curvature at the minimum of a parabola indicates the ease at which it can do this and therefore this determines the level splitting of the vibrational states, $\Delta E = h\omega$ between two levels n and n+1. The vibrational states are normally closer in energy than the electronic states.

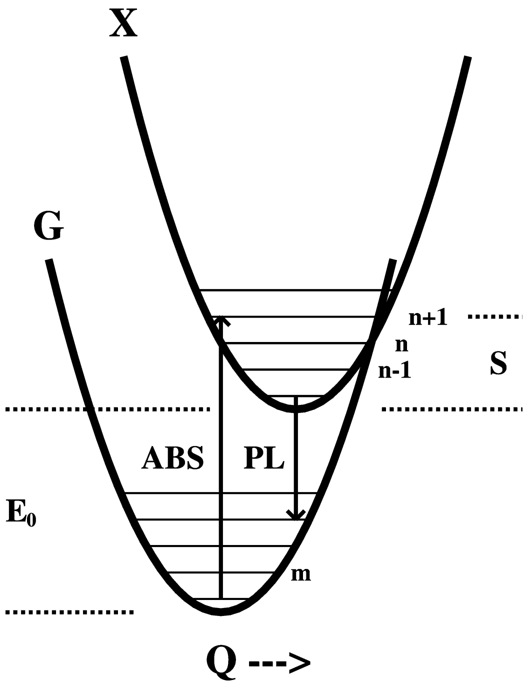


Figure 1: *Electronic ground state (G) and excited state (X) energy as a function of the configurate coordinate Q. E_0 is the splitting between the minima, n and m indicate vibrational sublevels, and S is the Huang-Rhys factor. Absorption (ABS) and luminescence (PL) transitions are indicated.*

In the figure we can see two types of optical electronic transitions, namely from the ground state to the excited state and the reverse. The first type of transitions costs energy and this is what is called absorption. In the other type the opposite happens; when the system relaxes to the ground state energy is released in the form of a photon and this we can detect in luminescence. This can be any type of luminescence: Depending on how the system is brought in excitation this is called electroluminescence (when voltage is applied), cathode ray luminescence (when the system is bombarded with fast electrons) or photoluminescence (when strong light is used to excite). In the following we will assume photoluminescence, although the relevant physics are identical for all types.

Two approximations are made:

1. Born-Oppenheimer. The electronic wave functions are separated from the vibrational wave functions: $\Psi(r,R)=\phi(r,R)\chi(R)$. This also means that the vibrational levels depend only on the curvature and position of the parabola.
2. Franck-Condon: Optical transitions occur with the position of the atoms fixed. In Figure 1 this means that the optical transitions are vertical.

In that case, the energy of a transition is in general

$$E=h\nu=E_0-m\hbar\omega_G+n\hbar\omega_X\,, \tag{1}$$

with h Planck's constant, ν the photon frequency, E_0 the electronic level separation, m and n the vibrational level quantum numbers (1/2, 3/2, ...) and $h\omega$ the vibrational energy where G indicates the ground state and X the excited state.

An important number in optical spectroscopy is the Huang-Rhys factor, *S*. This indicates the displacement of the excited state parabola compared to the ground state parabola. This, in its turn is a measure for the relaxation of the atoms in the two states. A large *S* means that the atoms change position significantly after an optical excitation, while S=0, or aligned parabolas, means no change of the atom positions.

$$S=\frac{k\Delta Q^2}{2h\omega}, \tag{2}$$

with *k* the spring constant or curvature $\mathrm{d}^2E/\mathrm{d}Q^2$ of the parabola, ΔQ the change in configurate coordinate for the two parabolas and hω the vibrational energy quanta. As can be seen in Figure 1, a large value for *S* shifts the absorption (ABS) to higher energy, while it shifts the photoluminescence (PL) to lower energy. This is the Stokes shift. For S=0 the Stokes shift is zero and the ABS and PL coincide in energy, while for increasing S they start differing more and more.

For S=0 there is only one line in the PL and ABS spectra because the transition probabilities from the vibrational states *n* to *m* with $n\neq m$ are zero, because these states are orthogonal. To see why these states are orthogonal we can look at Figure 1 again and realize that for S=0 the parabola are equal in the ground and excited state and, as stated before by the Born-Oppenheimer approximation, then the vibrational levels are the same in the ground and excited states. In the ground state (or excited state) these levels are orthogonal because they are eigenfunctions. Therefore, the intensity from ground sublevel *m* to excited sublevel *n* (or vice verse) in absorption (or luminescence) is 0 unless n=m

$$P_{nm}=\delta(n,m)\quad\text{for}\quad S=0\,, \tag{3}$$

If the Huang-Rhys factor is not equal to zero there can be a substantial contribution to the optical spectrum from transitions with $m \neq n$ as we will see now.

At very low temperatures and in equilibrium only the lowest vibrational state (m=0) of the electronic ground state is occupied. In that case the relative ABS intensities to the various vibrational levels are (without derivation)

$$P_{n0} = \exp(-S)S^n / n! . \tag{4}$$

The zero phonon-line (ZPL), *i.e.*, the transition in which no change of vibrational level occurs is at E_0. From Equation 4 it can be seen that this is not always the highest intensity line. For larger S the peak of the absorption band occurs at higher energy, see Figure 2. For luminescence a similar analysis can be made. Since the non-radiative, vibrational relaxations are much faster than the radiative electronic relaxations, most of the luminescence occurs from the lowest vibrational state (n=0) when the temperature is sufficiently low. In that case the PL mirrors the ABS.

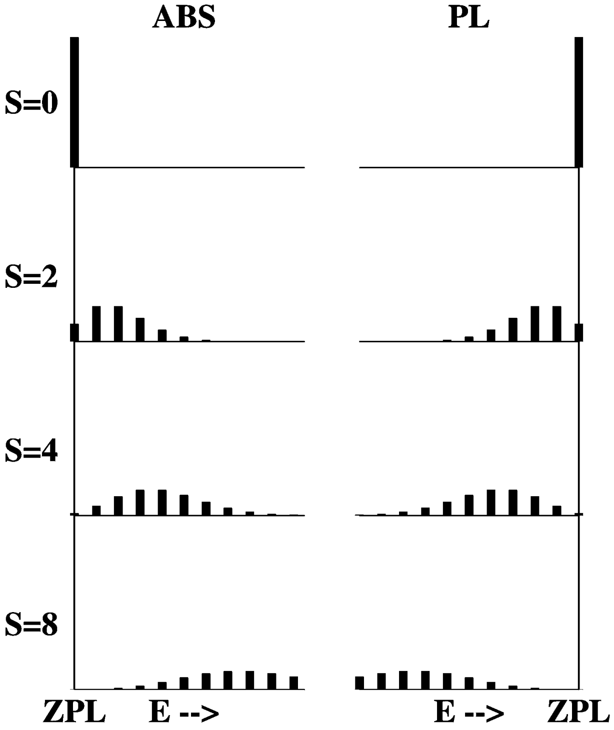


Figure 2: *Stick diagram of the absorption and luminescence spectra (at T=0 K). This shows the effect of an increasing Huang-Rhys factor. For S=0 only the zero phonon line (ZPL) is visible. For increasing S the spectrum broadens rapidly. The Stokes shift is the difference in energy of the maximum of the ABS and PL spectra.*

Quantum Mechanics

Now that we have established the optical spectra we can proceed to calculate the MCD, which is the difference of absorption of left and right polarized light in the presence of a magnetic field. To do this we first have to calculate the absorption without magnetic fields. In weak illumination conditions the absorption of the light per unit of length is linearly proportional to the intensity of the light and the transition probability. We will calculate the absorption by calculating the transition probabilities between all the vibrational levels in the electronic ground state G to an excited state X, *i.e.*, we look at one particular absorption band. The electric dipole operator, ε (ε^+ and ε^- for σ^+ and σ^- circular polarized light respectively), causes a transition from $|Gg\rangle$ to $|Xx\rangle$ (in this scheme, capital characters denote the electronic states and lower case characters denote vibrational states). The transition probability of such an electric dipole induced transition is

$$P_{Gg\to Xx} = \left|\langle Xx|\varepsilon_\pm|Gg\rangle\right|^2 . \tag{5}$$

This occurs at a photon energy $E_{Xx} - E_{Gg} = E_0 + (e_x - e_g)$, where e_x and e_g are the vibrational energies relative to the respective vibrational ground states and E_0 is the zero phonon line energy. If we now sum up the contributions from all transitions to the absorption line A this becomes

$$A_\pm(E) = h\nu\, n_d\, n_{Gg}(1-n_{Xx})\left|\langle Xx|\varepsilon_\pm|Gg\rangle\right|^2 \delta(E-E_0-(e_x-e_g)), \tag{6}$$

with hν the energy of the photon of absorption, n_d the density of the defect, n_{Gg} and n_{Xx} the occupancy of the ground and excited state levels and δ the Kroniger delta function. We can now make some simplifications of this formula:

1) In the Born-Oppenheimer approximation the wave functions can be decomposed into an electronic and a vibrational part

$$|Gg\rangle = |G\rangle|g\rangle$$

$$|Xx\rangle = |X\rangle|x\rangle$$

Moreover, the Franck-Condon approximation tells us that the dipole operator does not work on the vibrational parts:

$$\langle x|\langle X|\varepsilon_\pm|G\rangle|g\rangle = \langle X|\varepsilon_\pm|G\rangle\langle x|g\rangle$$

Note that, although the vibrational states in the ground state (and in the excited state) are orthonormal, $<g_1|g_2> = \delta(g_1,g_2)$, they are not necessarily orthogonal to the excited states: $<x|g> \neq 0$.

2) In Equation 6 the absorptions are assumed to occur at sharp energies. The real absorption lines are broadened by various effects. Therefore, the δ-functions have to be replaced by general line shapes $f(E)$.

3) For low temperatures the excited state X is completely empty (n_{Xx}=0). For finite temperatures there still exists a distribution over the various vibrational levels in the ground state, $n_{Gg} = d_G n_g \neq 0$, with d_G the degeneracy of the ground state.

4) The electronic levels can be degenerate. As we will see later this is essential for MCD spectroscopy. It will be shown that some types of MCD activity are depending on the degeneracy of the ground or excited state. To label these degeneracies we can use χ and γ.

Putting all this in Equation 6 yields

$$A_\pm(E)/h\nu = n_d \left|\langle X\chi|\varepsilon_\pm|G\gamma\rangle\right|^2 \left[\frac{n_g}{d_G}\left|\langle x|g\rangle\right|^2 f(E-(E_0+e_x-e_g))\right]. \tag{7}$$

To get the absorption spectrum now all we have to do is summing up all the possible transitions within the absorption band G→X:

$$A_\pm(E)/h\nu = \frac{1}{d_G} n_d \sum_{\chi,\gamma}\left|\langle X\chi|\varepsilon_\pm|G\gamma\rangle\right|^2 \sum_{x,g}\left[n_g\left|\langle x|g\rangle\right|^2 f(E-(E_0+e_x-e_g))\right], \tag{8}$$

This can be decomposed into two parts, a transition part D_0 and a line shape part $F(E)$. Equation 8 can be written as

$$A/h\nu = D_0 F(E), \tag{9}$$

with

$$D_0 = \frac{1}{d_G} n_d \sum_{\chi,\gamma} \left|\langle X\chi|\varepsilon|G\gamma\rangle\right|^2, \tag{10}$$

$$F(E) = \sum_{x,g}\left[n_g|\langle x|g\rangle|^2 f(E-(E_0+e_x-e_g))\right], \tag{11}$$

Here we have taken the absorption of unpolarized light, where $\varepsilon=\frac{1}{2}(\varepsilon_+ + \varepsilon_-)$. For MCD the difference of left and right circular polarized light is measured, therefore, ε should be replaced with $\varepsilon_{\mathrm{MCD}} = \frac{1}{2}(\varepsilon_+ - \varepsilon_-)$. In its turn, ε_+ and ε_- can be expressed in polarization operators: $\varepsilon_+ = \varepsilon_x + i\varepsilon_y$ and $\varepsilon_- = \varepsilon_x - i\varepsilon_y$. Therefore, $\varepsilon_{\mathrm{MCD}} = i\varepsilon_y$, and we can immediately see from this that without a magnetic field there is no MCD signal: Because all wave functions $|X\chi\rangle$ and $|G\gamma\rangle$ are real (because they are eigenvalues of the real Hamiltonian) and ε is a real operator the overlap of $\langle X\chi|\varepsilon_{MCD}|G\gamma\rangle$ is always zero. In other words, there is no difference in absorption between left and right circular polarized light; no MCD.

Magnetic Field

Now we will introduce a magnetic field into the calculation. This will do three things:

1. Lift degeneracies (γ and χ) of the ground and excited states.
2. Changes the population of the levels via a new Boltzmann distribution.
3. Mixes the levels G and X with other electronic levels.

Each of these will have important consequences to the MCD spectrum. They will be discussed separately:

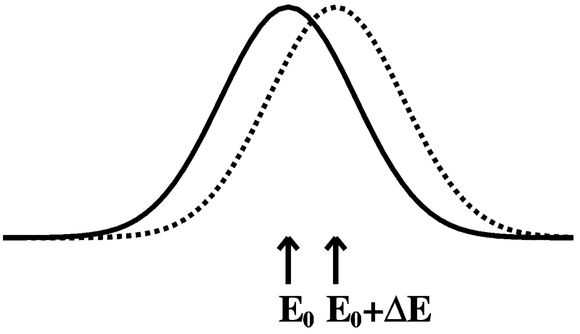


Figure 3: *Shift of the line as caused by a magnetic interaction. In first order the entire line shifts rigidly by ΔE. This shift is exaggerated in the figure; normally it is much less than the line width.*

1. The extra energy gained by the system is $-\boldsymbol{\mu}\cdot\mathbf{B}$, where **B** is the magnetic field vector and **μ** is the magnetic dipole: $\boldsymbol{\mu} = \mu_B(\mathbf{L}+g\mathbf{S})$, or in general $\boldsymbol{\mu} = \mu_B g_J \mathbf{J}$, with **J** the total angular momentum and g_J the (Landé) g-factor and μ_B the Bohr magneton. In this case the energy is $\mu_B g_J J_z B_z$. This is purely an energy effect and it only changes the line positions in the line shape function *f(E)*. This should be replaced by the new absorption function

$$f'(E) = f(E+\Delta E) = f\left(E - \left[E_0 + e_x - e_g\right] + \left[g_J^{X\chi} J_z^{X\chi} - g_J^{G\gamma} J_z^{G\gamma}\right]B_z\right), \tag{12}$$

or

$$f\left(E - \left[E_0 + e_x - e_g\right] + \left[\langle X\chi|\mu_z|X\chi\rangle - \langle G\gamma|\mu_z|G\gamma\rangle\right]B\right), \tag{13}$$

which defines an energy

$$\Delta E = \left[\langle X\chi|\mu_z|X\chi\rangle - \langle G\gamma|\mu_z|G\gamma\rangle\right]B, \tag{14}$$

over which the absorption line is shifted rigidly, see Figure 3. This shift is normally much smaller than the absorption band.

2. For the ground state G this also means a change in distribution over the vibrational sublevels. If the Zeeman energy is small compared to the thermal energy the Boltzmann distribution can be Taylor expanded. Neglecting terms in $(B/kT)^2$ and higher the distribution over the levels becomes

$$n'_{G\gamma g} = n^0_{G\gamma g}\left[1 + \langle G\gamma|\mu_z|X\chi\rangle^0 \frac{B}{kT}\right], \tag{15}$$

3. Intermixing of levels can change the wave functions. In first order perturbation theory it does not change the energies. To apply perturbation theory we have to calculate the new wave functions:

$$|G\gamma\rangle' = |G\gamma\rangle - \sum_{K\lambda}|K\lambda\rangle \frac{\langle K\lambda|\mu_z|G\gamma\rangle}{E_K - E_G}B, \tag{16}$$

$$|X\chi\rangle' = |X\chi\rangle - \sum_{K\lambda}|K\lambda\rangle \frac{\langle K\lambda|\mu_z|X\chi\rangle}{E_K - E_X}B, \tag{17}$$

Then

$$\langle X\chi|\varepsilon_\pm|G\gamma\rangle = \langle X\chi|\varepsilon_\pm|G\gamma\rangle^0 + \langle X\chi|\varepsilon_\pm|G\gamma\rangle' B, \tag{18}$$

These three effects can be substituted into Equation 8 on page 4:

$$\begin{aligned} A_\pm / h\upsilon &= \frac{1}{d_G}\sum_{\chi\gamma} n'_{G\gamma g}\left|\langle G\gamma|'\,\varepsilon_\pm|X\chi\rangle'\right|^2 F(E) \\ &= \sum_{\chi\gamma}\left\{\frac{1}{d_G}\left[1 + \langle G\gamma|\mu_z|X\chi\rangle^0\frac{B}{kT}\right]\cdot\left|\langle X\chi|\varepsilon_\pm|G\gamma\rangle^0 + \langle X\chi|\varepsilon_\pm|G\gamma\rangle' B\right|^2\right\}\cdot \\ &\cdot\sum_{gx} n_g\left|\langle x|g\rangle\right|^2 f\left(E - \left[E_0 + e_x - e_g\right] + \left[\langle X\chi|\mu_z|X\chi\rangle - \langle G\gamma|\mu_z|G\gamma\rangle\right]B\right) \end{aligned} \tag{19}$$

Because the energy corrections in $F(E)$ are small compared to the line width, $F(E)$ can be Taylor expanded around $E-(E_0+e_x-e_g)$. Doing this and collecting terms of zeroth and first order in B gives

$$\begin{aligned} A_\pm / h\nu = A^0_\pm / h\nu + B\cdot&\left\{\sum_{\chi\gamma}\frac{1}{d_G}\left|\langle X\chi|\varepsilon_\pm|G\gamma\rangle^0\right|^2 \Delta E\frac{\partial F(E)}{\partial E} + \right. \\ &+\sum_{\chi\gamma}\frac{2}{d_G}\mathrm{Re}\left[\langle X\chi|\varepsilon_\pm|G\gamma\rangle^0\langle X\chi|\varepsilon_\pm|G\gamma\rangle'^*\right]\cdot F(E) + \\ &\left.+\sum_{\chi\gamma}\frac{1}{d_G}\left|\langle G\gamma|\mu_z|G\gamma\rangle^0\langle X\chi|\varepsilon_\pm|G\gamma\rangle^0\right|^2\cdot\frac{1}{kT}\cdot F(E)\right\} \end{aligned} \tag{20}$$

With the earlier remark that A_0 is equal for σ_+ and σ_- light we can rewrite this while defining the three MCD terms, $\mathbf{A_1}$, $\mathbf{B_0}$ and $\mathbf{C_0}$:

$$\Delta A / h\nu = \left(A_+ - A_-\right) / h\nu = \left(\mathbf{A}_1 + \mathbf{B}_0 + \mathbf{C}_0\right)\cdot B \tag{21}$$

$$\begin{aligned}\mathbf{A}_1 = \sum_{\chi\gamma}\Big\{\Big(\big|\langle X\chi|\varepsilon_+|G\gamma\rangle^0\big|^2 - \big|\langle X\chi|\varepsilon_-|G\gamma\rangle^0\big|^2\Big)\cdot\Big(\langle X\chi|\mu_z|X\chi\rangle^0 - \langle G\gamma|\mu_z|G\gamma\rangle^0\Big)\Big\}\cdot \\ \cdot\frac{1}{d_G}\cdot\frac{\partial F(E)}{\partial E}\end{aligned} \tag{22}$$

$$\begin{aligned}\mathbf{B}_0 = \sum_{\chi\gamma}\mathrm{Re}\Bigg\{\sum_{K\lambda\neq X}\Big[\langle X\chi|\varepsilon_-|G\gamma\rangle^0\langle K\lambda|\varepsilon_+|G\gamma\rangle^0 - \langle X\chi|\varepsilon_+|G\gamma\rangle^0\langle K\lambda|\varepsilon_-|G\gamma\rangle^0\Big]\cdot\frac{\langle X\chi|\mu_z|K\lambda\rangle^0}{E_K^0 - E_X^0} + \\ + \sum_{K\lambda\neq G}\Big[\langle X\chi|\varepsilon_-|G\gamma\rangle^0\langle K\lambda|\varepsilon_+|X\chi\rangle^0 - \langle X\chi|\varepsilon_+|G\gamma\rangle^0\langle K\lambda|\varepsilon_-|X\chi\rangle^0\Big]\cdot\frac{\langle K\lambda|\mu_z|G\gamma\rangle^0}{E_K^0 - E_G^0}\Bigg\}\cdot\frac{2}{d_G}\end{aligned}$$

$$\mathbf{C}_0 = \frac{1}{d_G}\sum_{\chi\gamma}\left\{\left[\big|\langle X\chi|\varepsilon_-|G\gamma\rangle^0\big|^2 - \big|\langle X\chi|\varepsilon_+|G\gamma\rangle^0\big|^2\right]\cdot\frac{\langle G\gamma|\mu_z|G\gamma\rangle}{kT}\right\} \tag{23}$$

Explanation of the MCD Terms

Immediately some remarks can be made about the terms:

1. The necessary degeneracy requirement of some levels for the $\mathbf{A_1}$, $\mathbf{B_0}$ and $\mathbf{C_0}$ terms. For the $\mathbf{C_0}$ term the ground state G has to be degenerate. Here 'degenerate' means 'to be magnetically degenerate', so that the operator μ_z yields a nonzero result when averaged over the wave function, $\langle G\gamma|\mu_z|G\gamma\rangle \neq 0$. In the same way it can be shown that for the $\mathbf{A_1}$ term the ground state *or* the excited state needs to be degenerate, while for the $\mathbf{B_0}$ term the μ_z operator should mix a degenerate level into the ground *or* excited state (it can even be so that this third level is the ground or excited state itself).

2. The temperature dependence: It is clear that only the $\mathbf{C_0}$ term depends on the temperature. This is a way to distinguish it from the other two terms.

3. The $\mathbf{B_0}$ term is diamagnetic, but often also the $\mathbf{A_1}$ term is labelled diamagnetic since it has no paramagnetism in the ground state. Only the $\mathbf{C_0}$ term is purely paramagnetic.

We can look into the three terms more carefully. In Figure 4 the three different sources for MCD are shown.

$\mathbf{A_1}$ This term is caused by the fact that the σ_+ and σ_- absorption occur at different energies. Because this difference is small compared to the absorption band $F(E)$ this can be approximated with

$$\mathrm{MCD} \propto \Delta E \cdot \frac{\partial F}{\partial E} \propto B \cdot \frac{\partial F}{\partial E}, \qquad (24)$$

For example a Gaussian line shape:

$$F(x) = \frac{1}{\Gamma\sqrt{\pi}} \exp\left(-(x - x_0)^2 / \Gamma^2\right), \qquad \mathbf{(25)}$$

$$F'(x) = -\frac{2(x - x_0)}{\Gamma^3\sqrt{\pi}} \exp\left(-(x - x_0)^2 / \Gamma^2\right), \qquad \mathbf{(26)}$$

where Γ is the width of the line. The extremes of this function occur at

$$x_\pm = (x - x_0) = \pm\frac{\Gamma}{\sqrt{2}}. \qquad \mathbf{(27)}$$

At which point the intensity is

$$F'(x_\pm) = \pm\sqrt{\frac{2}{\pi}} \cdot \frac{1}{\Gamma^2} \qquad \mathbf{(28)}$$

The peak-peak intensity of an **A_1** -MCD signal is therefore proportional to the magnetic field and inversely proportional to the square of the line width Γ:

$$\mathrm{MCD} \propto B / \Gamma^2 \qquad \mathbf{(29)}$$

It is also immediately clear that to have a difference in energy of σ_+ and σ_- absorption either the ground or the excited state has to be degenerate.

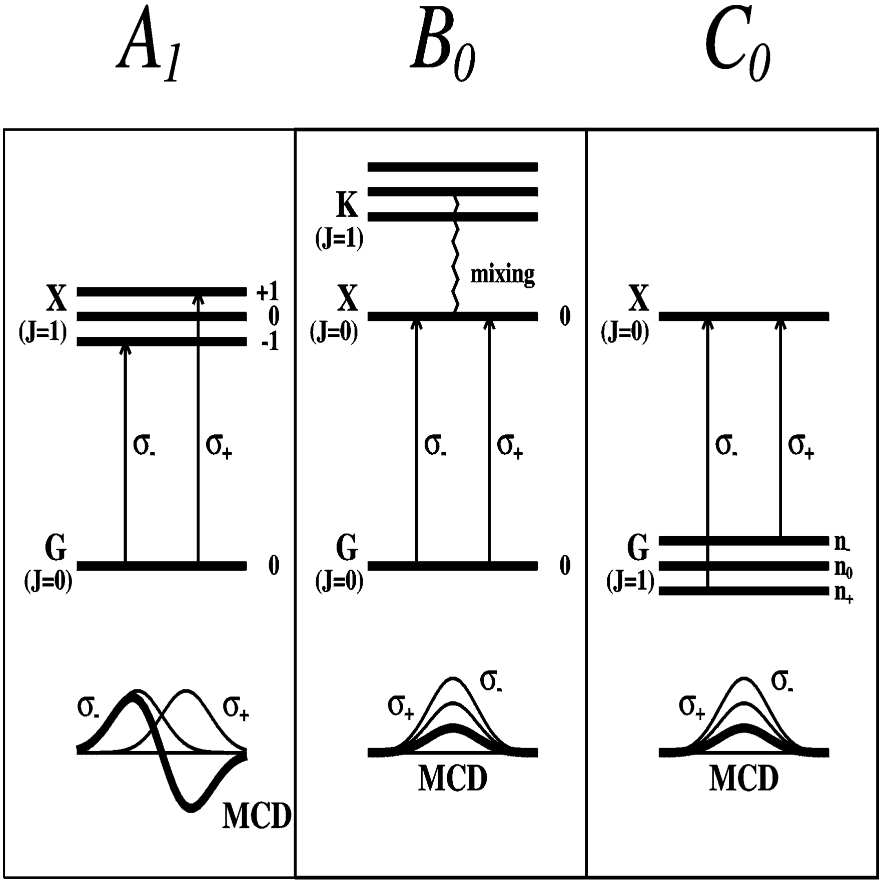


Figure 4: *The three types of MCD activity,* ***A_1*****,** ***B_0*** *and* ***C_0****. The* ***A_1*** *term is caused by a shift in energy of the σ_+ and σ_- absorption and depends on the magnetic field and the line width. The* ***B_0*** *term is caused by a mixing of a level into the ground or excited state and depends on the distance in energy to this level and the magnetic field which the source of the mixing. The* ***C_0*** *term depends on temperature and magnetic field, as it is caused by a Boltzmann distribution over the magnetic sublevels.*

term	*description*	*depends on*	*required degeneracy*	*line shape*
A_1	Zeeman energy splitting	Γ, B	G or X	derivative
B_0	Mixing of electronic states	$\Delta E, B$	G, X, or K	normal
C_0	Zeeman Boltzmann distribution	T, B	G	normal

Table 1: *Description of the three MCD terms, what they depend on, the required degeneracy and line shape.*

C_0 This term is depending on the temperature. This can easily be seen in Figure 4: although the transition probabilities for σ_+ and σ_- are the same, the number of available systems in the appropriate state (n_+ and n_-) is not equal. The MCD is

$$\text{MCD} \propto n_-\sigma_- - n_+\sigma_+ \propto n_- - n_+ . \qquad \textbf{(30)}$$

The population of the levels follows a Boltzmann distribution,

$$\frac{n_-}{n_+} = \exp(-g_J \mu_B B) , \qquad \textbf{(31)}$$

so that

$$\text{MCD} \propto \frac{n_+ - n_-}{n_+ + n_-} = \tanh(g_J \mu_B B / 2kT) . \qquad \textbf{(32)}$$

Of course, to have a splitting in the ground level it had to be degenerate before the presence of a magnetic field.

B_0 This term is most difficult to visualize. The principle is that the magnetic field mixes the higher electronic states into the ground or excited state directly involved into the optical transitions. In this way a little of the degeneracies of these electronic states are introduced into G or X. It is obvious that in this case there are no

requirements about the degeneracies of the ground or excited state, although at least one of the levels that mix in should be degenerate. The **B_0** term can also arise from the mixing of the ground and excited states themselves. Again, then one of these should be degenerate, in which case there also exist **A_0** and **C_0** terms with, probably, higher magnitude.
The mixing of the states is, in first order perturbation theory, linearly proportional to the magnetic field and inversely proportional to the energy separation, ΔE of the levels. In Table 1 a summary of the three MCD terms is given.

As a final remark it has to be pointed out that all types of MCD can result in positive as well as negative line shapes, depending on the sign of the Zeeman splitting. In this way the sign of the g value can be determined.

An Example

In Figure 5 an example is drawn. We start with the situation of just two degenerate levels: the ground state is an s-electron doublet (A_1) and the excited state is a p-electron sextet. Part of the degeneracy of the p-electron is lifted by a spin-orbit coupling $\lambda\mathbf{L}\cdot\mathbf{S}$. This breaks down the validity of the quantum numbers S and L. Instead, **J**=**L**+**S** and **J**=**L**−**S** are good. The remaining 4-fold degeneracy is lifted by the magnetic field, so that all 8 levels are separated. The allowed optical transitions are given by $\Delta L = \pm 1$ and $\Delta m_J = \pm 1$ (+1 for σ_+ and −1 for σ_- polarized light). The first restrictions are caused by the fact that the electric dipole operator has odd parity and should therefore change the parity of the system (ΔL is odd). The second restriction is caused by the fact that the z-component of the angular momentum should change, because the photon carries an angular momentum of +1 (σ_+) or −1 (σ_-). This is because of the special configuration of the magnetic field and the photon (**B** is parallel to **k** or **P**, the propagation vector of the photon).

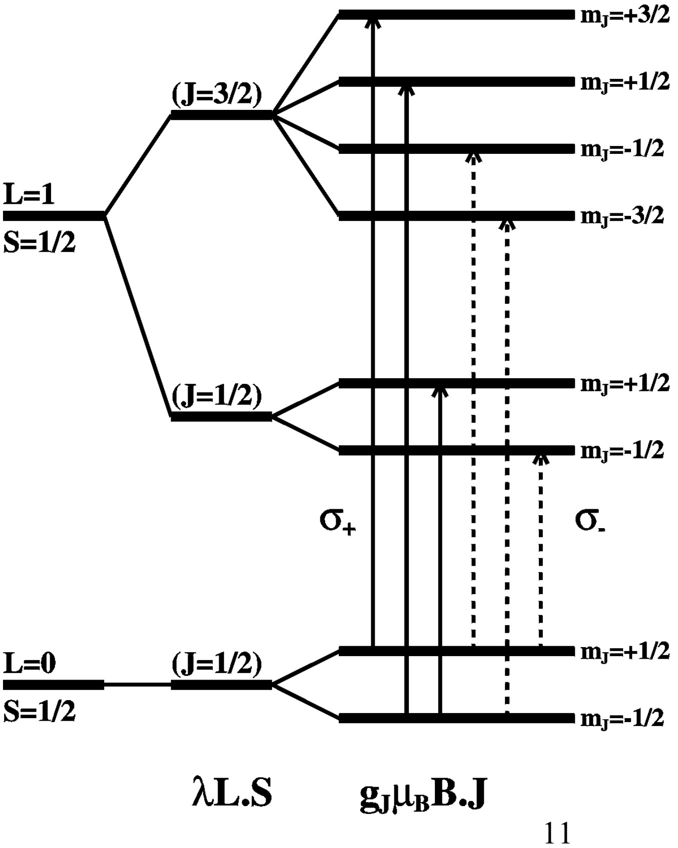


Figure 5: *An example of MCD. In this case the ground state is an L=0, S=1/2 level and the excited state L=1, S=1/2. The excited state is split by spin-orbit coupling ($\lambda L\cdot S$) into a doublet (J=L–S=1/2) and a quartet (J=L+S=3/2). The last degeneracies are removed by a Zeeman interaction $g_J\mu_B B\cdot J$.*

Optical excitations are indicated by lines, solid for σ_+ and dashed for σ_-.

The allowed transitions are indicated in Figure 5. To calculate the relative transition probabilities, first we have to find the eigenfunctions after S.O. coupling, since they are no longer simple.

$$\lambda\mathbf{L}\cdot\mathbf{S} = \lambda\left(L_xS_x + L_yS_y + L_zS_z\right). \tag{33}$$

This can be expressed in creation and annihilation operators.

$$\begin{aligned} L_x &= \frac{1}{2}\left(L_+ + L_-\right), \quad & S_x &= \frac{1}{2}\left(S_+ + S_-\right), \\ L_y &= \frac{1}{2i}\left(L_+ - L_-\right), \quad & S_y &= \frac{1}{2i}\left(S_+ - S_-\right). \end{aligned} \tag{34}$$

Therefore

$$\lambda\mathbf{L}\cdot\mathbf{S} = \lambda\left[\frac{1}{2}\left(L_+S_- + L_-S_+\right) + L_zS_z\right]. \tag{35}$$

The Hamiltonian can then be calculated if we use

$$\begin{aligned} L_+|l\rangle &= \sqrt{L(L+1) - l(l+1)}\,|l+1\rangle \\ L_-|l\rangle &= \sqrt{L(L+1) - l(l-1)}\,|l-1\rangle \\ L_z|l\rangle &= l|l\rangle \\ S_+|s\rangle &= \sqrt{S(S+1) - s(s+1)}\,|s+1\rangle \\ S_-|s\rangle &= \sqrt{S(S+1) - s(s-1)}\,|s-1\rangle \\ S_z|s\rangle &= s|s\rangle \end{aligned} \tag{36}$$

	|+1>|+½>	|+1>|–½>	|0>|+½>	|0>|–½>	|–1>|+½>	|–1>|–½>
|+1>|+½>	λ					
|+1>|–½>		λ	λ/√2			
|0>|+½>		λ/√2	λ			
|0>|–½>				λ	λ/√2	
|–1>|+½>				λ/√2	λ	
|–1>|–½>						λ

From this table it can be seen that |+1>|+½> and |–1>|–½> are still eigenfunctions. The other wave functions can be calculated by solving the above Hamiltonian. In the ground state (G) there is no spin-orbit coupling, since there is no orbital momentum (L=0). Therefore, the eigenfunctions remain unaltered. To summarize, the wave functions in the ground and excited state are as in Table 2.

Now the transition probabilities, or oscillator strengths, can be calculated with the restrictions (selection rules) for optical transitions as described before. The restriction $\Delta L = \pm 1$ means that optical excitations are only from the ground state to the excited state and vice verse, while the restriction $\Delta m_J = \pm 1$ means that for instance the $m_J = -$

1/2 level is linked to the $m_J = -3/2$ level by σ_- light and to the $m_J=+1/2$ by σ_+ light. (NB: it is assumed that we have stimulated absorption transitions and not stimulated emission. In the latter case the same levels would be linked by σ_+ light and σ_- light respectively, *i.e.*, reversed). As an example we can calculate the transition probability between the $m_J=-1/2$ ground state to the $m_J=+1/2$ excited state.

$$P = \left|\left\{\left\langle\sqrt{2/3}\langle 0|\langle +1/2| + \sqrt{1/3}\langle +1|\langle -1/2|\right\}\varepsilon_+|-1/2\rangle\right|^2 = 1/3. \quad \textbf{(37)}$$

The transition probabilities are summarized in Table 3 (for simplicity they have all been multiplied by a factor 3).

Table 2: *Wave functions after spin orbit coupling. The ground state G is unaltered. In the excited state (X, L=1) the sextet is split into a doublet with effective spin J=L–S=1/2 and a quartet with effective spin J=L+S=3/2.*

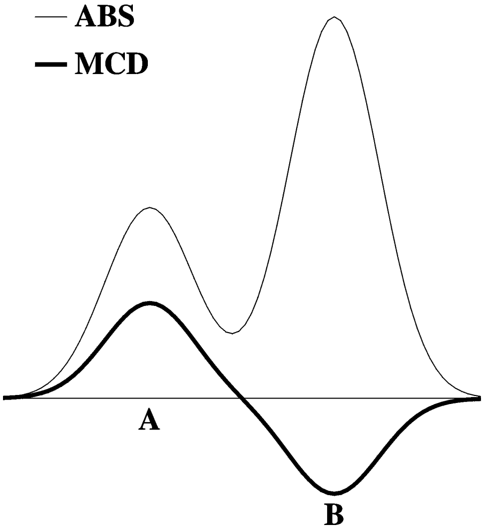
	J	m_J	*wavefunction*
X	3/2	3/2	|+1>|+½>
(L=1)	3/2	1/2	√2/3·|0>|+½>+√1/3·|+1>|–½>
J=3/2	3/2	–1/2	√1/3·|–1>|+½>+√2/3·|0>|–½>
	3/2	–3/2	|–1>|–½>
X (L=1)	1/2	1/2	√1/3·|0>|+½>–√2/3·|+1>|–½>
J=1/2	1/2	–1/2	√2/3·|–1>|+½>–√1/3·|0>|–½>
G (L=0)	1/2	1/2	|+½>
J=1/2	1/2	–1/2	|–½>

Table 3: *Oscillator strengths (transition probabilities) of a L=0, S=1/2 system to a spin-orbit coupled L=1, S=1/2 system. The bold numbers are for σ_+, while the numbers for σ_- are printed in italics. For comparison also the legal EPR transitions are listed.*

	G		X						m_J
G		epr		**2**	*3*		**1**		1/2
	epr		*2*			*1*		**3**	–1/2
		2		epr					1/2
	2		epr						–1/2
X	**3**					epr			3/2
		1			epr		epr		1/2
	1					epr		epr	–1/2
		3					epr		–3/2
m_J	1/2	–1/2	1/2	–1/2	3/2	1/2	–1/2	–3/2	
	(J=1/2)		(J=1/2)			(J=3/2)			

With this table in hand we can reconstruct the MCD spectrum. Figure 5 has actually two absorption bands, one from the ground state to J=1/2 (A) and one to J=3/2 (B). In this way we can expect two $\mathbf{C_0}$ terms with opposite sign as clarified in Table 4. Figure 6 shows such an MCD spectrum. Both these parts of the spectrum depend on temperature via ($n_- - n_+$) one is located at position E_A and one at E_B. The superposition looks exactly like an $\boldsymbol{A_1}$ term, but it is not as can be tested by changing the temperature.

The $\mathbf{A_1}$ term can be found in this case too, if we look more carefully at the transitions. If we look only at the transition to the excited J=1/2 state (band A in Figure 6) and we take $n_- = n_+ = n/2$, then the $\mathbf{A_1}$ term (and the $\mathbf{C_0}$ term) vanishes and there seems to be no MCD activity. Closer examination reveals that the σ_+ and σ_- absorption occur at a slightly different energy. For a positive g_J the σ_- absorption is at a slightly lower energy: $E_{\sigma+} - E_{\sigma-} = 2g\mu_B B$. This causes the $\mathbf{A_1}$ term of MCD.



	σ_+	σ_-	ABS $\sigma_+ + \sigma_-$	MCD $\sigma_+ - \sigma_-$
A	$2n_-$	$2n_+$	$2n$	$2(n_- - n_+)$
B	$n_- + 3n_+$	$3n_- + n_+$	$4n$	$-2(n_- - n_+)$

Figure 6 and Table 4: *Absorption and MCD spectrum (not to scale) of the system of Figure 5. This system has two absorption peaks (at A and B). The combination of the resulting two* $\mathbf{C_0}$ *peaks of opposite sign looks like a derivative peak, but should not be confused with a single* $\mathbf{A_1}$ *peak.*

There will also be a $\mathbf{B_0}$ term, since the ground state as well as the excited state are degenerate and can (and will) mix with each other. The large distance between the levels makes the $\mathbf{B_0}$ term very small, though.

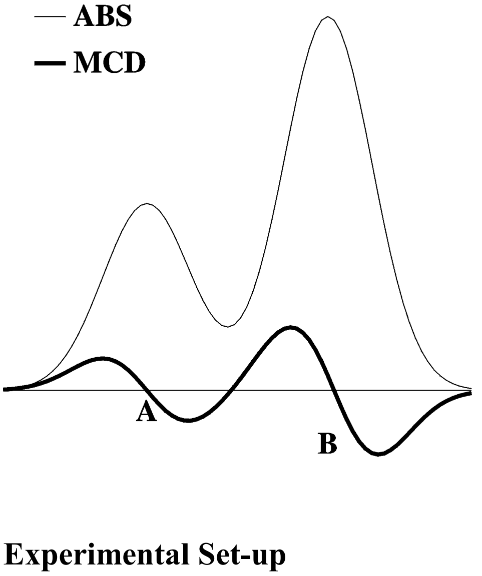


Figure 7: *An example MCD caused by an* $\mathbf{A_1}$ *term. This system has two absorption peaks (at A and B). This results in a complicated spectrum of a combination of two* $\mathbf{A_1}$ *peaks.*

Experimental Set-up

Figure 8 shows a typical experimental set-up. It consists of the following items:

- A light source.
- A monochromator for scanning the wavelength.

- A light chopper. This is only used when measuring the absorption spectrum. For the MCD spectrum this item is removed.
- A circulator. This is the crux of the system. It consists of a linear polarizer and a quarter-wave plate. The quarter wave plate is normally a crystal of Piezo active material, whose fast and slow directions depend on the direction in which the crystal is deformed. Because of its Piezo-electric character the crystal can be deformed by electric field. Applying alternating voltage on the crystal continually changes stretching and shrinking of the crystal in the direction of the electric field. The effect on the outgoing beam is an alternating of the circular polarization direction.
- The sample under study. For some applications (for instance to test the temperature dependence) this can be cooled using a normal cryostat.
- The detector. The frequency range of interest determines the type of the detector.
- A lock-in amplifier. This steers the circulator or light chopper with a reference signal (typically in the order of 40 kHz for the circulator).
- A recorder. In modern equipment this means a computer.

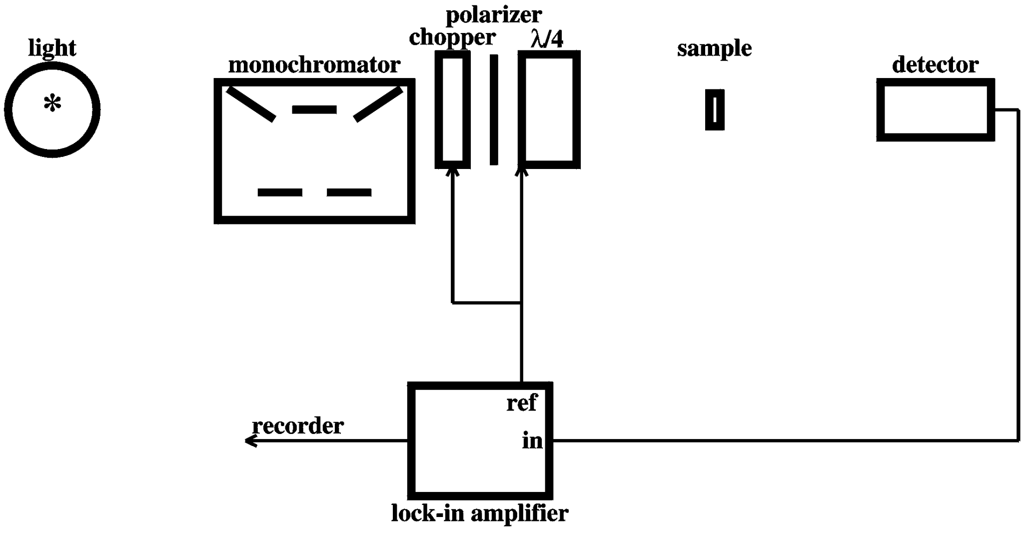


Figure 8: *Typical MCD (of absorption) set-up. It invariably consists of a light source, a circular modulator, a detector and a lock-in amplifier connected to a recorder. For absorption spectra a chopper is used in place of the modulator. In some spectrometers the sample can be cooled or placed in a microwave cavity. The latter for optical detection of magnetic resonance (ODMR).*

Measuring the MCD spectrum consists of first taking the difference signal ($\sigma_+ - \sigma_-$) in the presence of a magnetic field (as high as possible, though typically in the order of 2 T) and then dividing it by the absorption signal without magnetic fields.

The MCD signal can also be used to detect magnetic *resonance* in ODMR. In this case the magnetic field is scanned while also a microwave field is applied to the crystal. Outside resonance the MCD signal is described as before. When the system is in resonance the population difference ($n_+ - n_-$) is annihilated and the MCD signal disappears. Resonance therefore decreases the MCD intensity. See for example the ODMR study of the As_{Ga} defect in GaAs by Meyer et al.

REFERENCES:

1. P.J. Stephens, Advances in Chem. Phys. **35**, 197 (1976).
2. "Optical Properties of the As-Antisite and *EL2* Defects in GaAs", B.K. Meyer, J.-M Speath and M. Scheffler, Phys. Rev. Lett. **52**, 851 (1984).
3. "Magneto-Optic Experiments on the *F* Center and *A* Center in Kcl", C.H. Henry, Phys. Rev. 140, A256 (1965).
4. "As_{Ga}-induced Dichroism in GaAs", U. Kaufmann, Comment Phys. Rev. Lett. **54**, 1332 (1985).
5. "Optical matrix elements and cross sections for deep levels in GaAs: the impurity superlattice model", P. Dzwig, M.G. Burt, J.C. Inkson, and V. Crum, J. Phys. C 15, 1187 (1982).
6. "Hole photoionization cross sections of EL2 in GaAs", P. Silverberg, P. Omling and L. Samuelson, Appl. Phys. Lett. 52, 1689 (1988).
7. "Introduction to Modern Optics", Grant R. Fowles, Dover Publications, New York (1989).