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Influence of a Magnetic Field on Line Intensities in the Optical Spectra of Free Molecules

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Results are derived, by an analysis based on irreducible Cartesian tensors, for the change in line intensities in the optical spectrum of a free molecule under application of a static magnetic field. Consideration is specifically given to the cases of electric dipole-allowed, magnetic dipole-allowed and electric quadrupole-allowed transitions, and distinctions are drawn between their behaviour. Magnetochromic effects are identified in connection with both plane and circularly polarised light. In the case of an electric dipole-forbidden transition excited by application of a plane-polarised beam, the differential absorption signal should be sufficiently large to be readily measurable. Suitable candidates for study are the analogues in chiral systems of magnetic dipole-allowed transitions in parent molecules of higher symmetry.

Introduction

Application of a static magnetic field can influence the optical absorption properties of free molecules in a variety of ways. Many of these are associated with the removal of spin degeneracy known as Zeeman splitting, where the combined gyrotropic effect of the magnetic field and electromagnetic radiation can lead to an apparent chirality manifest for example in magnetic circular dichroism (MCD). However, even where lack of spin degeneracy makes Zeeman splitting impossible, MCD persists through a direct magneto-optical interaction (the Faraday *B*-term).[1] A number of other such magneto-optical effects arise in connection with the transmission of light, principally Faraday rotation and the Voigt effect.[2,3] Magnetic field-induced polarisation effects also occur in Raman scattering.[4,5] The theory of such processes is a very active area of research. Indeed it is only recently that the first definitive calculation of the Verdet constant, which characterises Faraday rotation, has been accomplished[6] even for molecules as simple as H_2 and D_2.

Magneto-optical effects connected with conventional photoabsorption have been the subject of extensive theoretical treatments by other authors.[7,8] Particularly interesting is the magneto-chiral dichroism which can arise, not least in the case of excitation with unpolarised light.[9] In this paper magneto-optical effects are considered with particular reference to transitions which are allowed through multipolar (magnetic dipole and electric quadrupole) interactions with the radiation. Magnetochromic effects are identified through calculations based on the methods of molecular quantum electrodynamics,[5] and explicit expressions for the differential absorption are given in terms of irreducible Cartesian tensors. The results suggest that anomalously large differential absorption signals can be expected in the case of certain electric dipole-forbidden transitions.

Theory

The leading terms in the coupling between radiation and molecules in the presence of a static magnetic field are as follows;

$$H_{\text{int}} = -\varepsilon_0^{-1}\boldsymbol{\mu}\cdot\boldsymbol{d}^{\perp} - \boldsymbol{m}\cdot\boldsymbol{b} - \varepsilon_0^{-1}\boldsymbol{Q}:\nabla\boldsymbol{d}^{\perp} - \boldsymbol{m}\cdot\boldsymbol{B} \quad (1)$$

where $\boldsymbol{\mu}$ is the electric dipole operator, $\boldsymbol{m}$ the magnetic dipole operator and $\boldsymbol{Q}$ is the electric quadrupole operator. The radiation field is characterised by its electric displacement field operator $\boldsymbol{d}^{\perp}$ and magnetic field operator $\boldsymbol{b}$; $\boldsymbol{B}$ is the local static magnetic induction field. Quadrupolar and higher order interactions with the static field are ignored on the reasonable assumption that it is spatially homogeneous over molecular dimensions. It is also assumed that higher orders of the multipolar interaction with the radiation contribute negligibly.

The intensity of any given line in the optical absorption spectrum is as usual obtained from the Fermi rule expression for the absorption rate;

$$\Gamma = \frac{2\pi}{\hbar}\langle|M_{\text{f0}}|^2\rangle\rho \quad (2)$$

where the angular brackets denote the molecular rotational average required for a fluid sample. In eqn. (2), ρ is the density of states and M_{f0} is the matrix element given by the perturbation series expansion;

$$M_{\text{f0}} = \langle \text{f}_\text{s}|H_{\text{int}}|0_\text{s}\rangle + \sum_{\text{r}_\text{s}}\frac{\langle \text{f}_\text{s}|H_{\text{int}}|\text{r}_\text{s}\rangle\langle \text{r}_\text{s}|H_{\text{int}}|0_\text{s}\rangle}{E_{0_\text{s}} - E_{\text{r}_\text{s}}}\cdots$$

$$= M_{\text{f0}}^{(1)} + M_{\text{f0}}^{(2)} \quad (3)$$

Here the subscript s denotes the fact that all states and energies refer to those of the system comprising the molecule and the radiation. The initial state of the system can thus be expressed as $|0_\text{s}\rangle = |0; n\rangle$ and the final state as $|\text{f}_\text{s}\rangle = |\text{f}; n-1\rangle$, where the ket $|a; b\rangle$ designates the molecule in a state $|a\rangle$ and the radiation in a state with b quanta of radiation.

The two terms $M_{\text{f0}}^{(1)}$ and $M_{\text{f0}}^{(2)}$ in eqn. (3) are usefully represented by time-ordered diagrams as shown in Fig. 1. In Fig. 1(*a*) the molecule proceeds directly from its ground state $|0\rangle$ to its final state $|\text{f}\rangle$ by a multipolar interaction with the radiation in which a single photon is annihilated; this corresponds to the static field-independent term $M_{\text{f0}}^{(1)}$. In Fig. 1(*b*), the incorporation of a horizontal line designates an additional interaction with the magnetic field, which may take place either before or after the radiative interaction. The corresponding intermediate states are thus $|\text{r}; n\rangle$ and $|\text{r}; n-1\rangle$. The two diagrams of Fig. 1(*b*) together represent the field-dependent term $M_{\text{f0}}^{(2)}$: the two other second-order possibilities involving either two radiative interactions or two static interactions are excluded on the grounds of the energy conservation requirement $E_{\text{f0}} = \hbar\omega$, where ω is the circular frequency of the radiation.

In order to ascertain any effect upon the absorption intensity due to application of the magnetic field, we need to

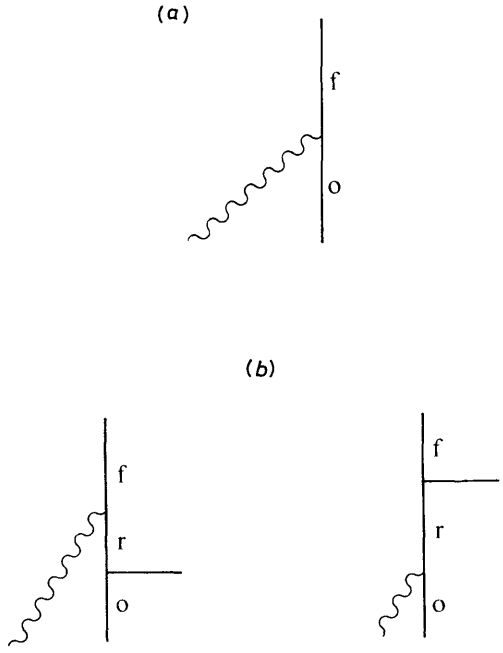

Fig. 1 Time-ordered diagrams for magnetochromism: (*a*) absorption of a photon without perturbation by the magnetic field, (*b*) photoabsorption with linear magnetic field perturbation

evaluate the rate difference $\Delta\Gamma$ given by;

$$\Delta\Gamma = \frac{2\pi}{\hbar}\langle|M_{f0}^{(1)} + M_{f0}^{(2)}|^2\rangle\rho - \frac{2\pi}{\hbar}\langle|M_{f0}^{(1)}|^2\rangle\rho$$

$$\approx \frac{4\pi}{\hbar}\,\mathrm{Re}\langle M_{f0}^{(1)}\bar{M}_{f0}^{(2)}\rangle\rho \qquad (4)$$

Evaluation of the leading correction term is sufficient for our purposes; terms associated with the modulus square of $M_{f0}^{(2)}$ will be of much smaller magnitude. The change in spectral line intensities is most conveniently characterised by the dimensionless parameter $\gamma = \Delta\Gamma/\Gamma$ which is thus given by

$$\gamma = 2\,\mathrm{Re}\langle M_{f0}^{(1)}\bar{M}_{f0}^{(2)}\rangle/\langle|M_{f0}^{(1)}|^2\rangle \qquad (5)$$

To evaluate the numerator and denominator of eqn. (5) based on eqn. (1) and (3) requires application of the following mode expansion for the electromagnetic field at a position $\boldsymbol{r}$:[10]

$$\boldsymbol{d}^{\perp}(\boldsymbol{r}) = \mathrm{i}\sum_{\boldsymbol{k},\lambda}\left(\frac{\hbar ck\varepsilon_0}{2V}\right)^{1/2}[\boldsymbol{e}^{(\lambda)}(\boldsymbol{k})a^{(\lambda)}(\boldsymbol{k}) \times \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) - \bar{\boldsymbol{e}}^{(\lambda)}(\boldsymbol{k})a^{\dagger(\lambda)}(\boldsymbol{k})\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})] \qquad (6)$$

$$\boldsymbol{b}(\boldsymbol{r}) = \mathrm{i}\sum_{\boldsymbol{k},\lambda}\left(\frac{\hbar k}{2\varepsilon_0 cV}\right)^{1/2}[\boldsymbol{b}^{(\lambda)}(\boldsymbol{k})a^{(\lambda)}(\boldsymbol{k}) \times \exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}) - \bar{\boldsymbol{b}}^{(\lambda)}(\boldsymbol{k})a^{\dagger(\lambda)}(\boldsymbol{k})\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r})] \qquad (7)$$

where

$$(\boldsymbol{b})^{(\lambda)}(\boldsymbol{k}) = \hat{\boldsymbol{k}} \times \boldsymbol{e}^{(\lambda)}(\boldsymbol{k}) \qquad (8)$$

Here $\boldsymbol{k}$ denotes the wavevector, $\boldsymbol{e}^{(\lambda)}$ the polarisation vector and $a^{\dagger(\lambda)}(\boldsymbol{k})$, $a^{(\lambda)}(\boldsymbol{k})$, the corresponding creation and annihilation operators. In terms of a right-handed set of unit vectors, $\hat{\boldsymbol{\imath}}$, $\hat{\boldsymbol{\jmath}}$, $\hat{\boldsymbol{k}}$, the polarisation vectors are for plane polarisation;

$$\boldsymbol{e} = \hat{\boldsymbol{\imath}};\ \boldsymbol{b} = \hat{\boldsymbol{\jmath}} \qquad (9)$$

and for circular polarisation;

$$\boldsymbol{e}^{(\mathrm{L})} = \frac{1}{\sqrt{2}}(\hat{\boldsymbol{\imath}} + \mathrm{i}\hat{\boldsymbol{\jmath}});\ \boldsymbol{b}^{(\mathrm{L})} = \frac{1}{\sqrt{2}}(-\mathrm{i}\hat{\boldsymbol{\imath}} + \hat{\boldsymbol{\jmath}})$$

$$\boldsymbol{e}^{(\mathrm{R})} = \bar{\boldsymbol{e}}^{(\mathrm{L})};\ \boldsymbol{b}^{(\mathrm{R})} = \bar{\boldsymbol{b}}^{(\mathrm{L})} \qquad (10)$$

Finally, V in eqn. (6) and (7) represents the quantisation volume, which contains n photons.

In the general case the following results are obtained for the matrix elements $M_{f0}^{(1)}$:

$$M_{f0}^{(1)} = M_{f0}^{(1)}(E1) + M_{f0}^{(1)}(M1) + M_{f0}^{(1)}(E2) \qquad (11)$$

where, adopting the convention of implied summation of repeated indices, we have

$$M_{f0}^{(1)}(E1) = -\mathrm{i}\left(\frac{n\hbar ck}{2\varepsilon_0 V}\right)^{1/2}\mu_i^{f0}e_i^{(\lambda)} \qquad (12)$$

$$M_{f0}^{(1)}(M1) = -\mathrm{i}\left(\frac{n\hbar k}{2\varepsilon_0 cV}\right)^{1/2}m_i^{f0}b_i^{(\lambda)} \qquad (13)$$

$$M_{f0}^{(1)}(E2) = \left(\frac{n\hbar ck^3}{2\varepsilon_0 V}\right)^{1/2}Q_{(ij)}^{f0}\hat{k}_i e_j^{(\lambda)} \qquad (14)$$

for a molecule arbitrarily located at $\boldsymbol{r} = 0$; here and elsewhere brackets enclosing subscripts denote symmetry with respect to index permutation. For $M_{f0}^{(2)}$ we need only consider contributions associated with an $M1$ interaction with the static field. Thus we have

$$M_{f0}^{(2)} = M_{f0}^{(2)}(M1;\,E1) + M_{f0}^{(2)}(M1;\,M1) + M_{f0}^{(2)}(M1;\,E2) \qquad (15)$$

where

$$M_{f0}^{(2)}(M1;\,E1) = \mathrm{i}\left(\frac{n\hbar ck}{2\varepsilon_0 V}\right)^{1/2}G_{ij}^{f0}B_i e_j^{(\lambda)} \qquad (16)$$

$$M_{f0}^{(2)}(M1;\,M1) = \mathrm{i}\left(\frac{n\hbar k}{2\varepsilon_0 cV}\right)^{1/2}H_{ij}^{f0}B_i b_j^{(\lambda)} \qquad (17)$$

$$M_{f0}^{(2)}(M1;\,E2) = -\left(\frac{n\hbar ck^3}{2\varepsilon_0 V}\right)^{1/2}J_{i(jk)}^{f0}B_i\hat{k}_j e_k^{(\lambda)} \qquad (18)$$

The molecular tensors involved here are defined as follows;

$$\boldsymbol{G}_{ij}^{f0} = \sum_{r}{}'\left(\frac{m_i^{fr}\mu_j^{r0}}{E_{0r} + \hbar\omega} + \frac{\mu_j^{fr}m_i^{r0}}{E_{0r}}\right) \qquad (19)$$

$$\boldsymbol{H}_{ij}^{f0} = \sum_{r}{}'\left(\frac{m_i^{fr}m_j^{r0}}{E_{0r} + \hbar\omega} + \frac{m_j^{fr}m_i^{r0}}{E_{0r}}\right) \qquad (20)$$

$$\boldsymbol{J}_{i(jk)}^{f0} = \sum_{r}{}'\left(\frac{m_i^{fr}Q_{(jk)}^{r0}}{E_{0r} + \hbar\omega} + \frac{Q_{(jk)}^{fr}m_i^{r0}}{E_{0r}}\right) \qquad (21)$$

where the prime on each summation denotes exclusion from the sum over virtual states $|\mathrm{r}\rangle$ of the initial and final states $|0\rangle$ and $|\mathrm{f}\rangle$. To simplify subsequent calculations it is worth noting that whilst the tensors $\boldsymbol{G}_{ij}^{f0}$ and $\boldsymbol{H}_{ij}^{f0}$ in general have no index symmetry properties, $\boldsymbol{J}_{i(jk)}^{f0}$ is both symmetric and traceless with respect to its j, k indices by virtue of the transition electric quadrupole moments from which it is constructed. For transitions between non-degenerate states, the tensors $\boldsymbol{G}^{f0}$ and $\boldsymbol{J}^{f0}$ are imaginary, whilst $\boldsymbol{H}^{f0}$ is real. Finally, it is worth noting that $\boldsymbol{H}^{f0}$ and $\boldsymbol{J}^{f0}$ are typically smaller than $\boldsymbol{G}^{f0}$ by a factor of the order of the fine structure constant.

Results

First we give the general result for the case of a $|\mathrm{f}\rangle \leftarrow |0\rangle$ transition which is $E1$, $M1$- and $E2$-allowed; special cases of forbidden transitions are examined subsequently. In general

we have, from eqn. (5) and (11)–(18);

$$\begin{aligned}\gamma = 2B\ \mathrm{Re}\langle & -c^2\mu_i^{f0}\bar{G}_{jk}^{f0}\, e_i^{(\lambda)}\hat{B}_j\bar{e}_k^{(\lambda)} - c\mu_i^{f0}\bar{H}_{jk}^{f0}\, e_i^{(\lambda)}\hat{B}_j\bar{b}_k^{(\lambda)} \\ & + ic^2k\mu_i^{f0}\bar{J}_{j(kl)}^{f0}\,\bar{e}_i^{(\lambda)}\hat{B}_j\hat{k}_k\bar{e}_l^{(\lambda)} - cm_i^{f0}\bar{G}_{jk}^{f0}\, b_i^{(\lambda)}\hat{B}_j\bar{e}_k^{(\lambda)} \\ & - m_i^{f0}\bar{H}_{jk}^{f0}\, b_i^{(\lambda)}\hat{B}_j\bar{b}_k^{(\lambda)} + ickm_i^{f0}\bar{J}_{j(kl)}^{f0}\, b_i^{(\lambda)}\hat{B}_j\hat{k}_k\,\bar{e}_l^{(\lambda)} \\ & - ic^2kQ_{(ij)}^{f0}\bar{G}_{kl}^{f0}\,\hat{k}_i e_j^{(\lambda)}\hat{B}_k\bar{e}_l^{(l)} - ickQ_{(ij)}^{f0}\bar{H}_{kl}^{f0}\,\hat{k}_i e_j^{(\lambda)}\hat{B}_k\bar{b}_l^{(\lambda)} \\ & - c^2k^2Q_{(ij)}^{f0}\bar{J}_{k(lm)}^{f0}\,\hat{k}_i e_j^{(\lambda)}\hat{B}_k\hat{k}_l\bar{e}_m^{(\lambda)}\rangle \\ \times \langle & c^2\mu_i^{f0}\bar{\mu}_j^{f0}e_i^{(\lambda)}\bar{e}_j^{(\lambda)} + c\mu_i^{f0}\bar{m}_j^{f0}e_i^{(\lambda)}\bar{b}_j^{(\lambda)} \\ & + c\bar{\mu}_i^{f0}m_j^{f0}\bar{e}_i^{(\lambda)}b_j^{(\lambda)} - ic^2k\mu_i^{f0}\bar{Q}_{(jk)}^{f0}\, e_i^{(\lambda)}\hat{k}_j\bar{e}_k^{(\lambda)} \\ & + ic^2k\bar{\mu}_i^{f0}Q_{(jk)}^{f0}\,\bar{e}_i^{(\lambda)}\hat{k}_j e_k^{(\lambda)} + m_i^{f0}\bar{m}_j^{f0}b_i^{(\lambda)}\bar{b}_j^{(\lambda)} \\ & - ickm_i^{f0}\bar{Q}_{(jk)}^{f0}\, b_i^{(\lambda)}\hat{k}_j\bar{e}_k^{(\lambda)} + ick\bar{m}_i^{f0}Q_{(jk)}^{f0}\,\bar{b}_i^{(\lambda)}\hat{k}_j e_k^{(\lambda)} \\ & + c^2k^2Q_{(ij)}^{f0}\bar{Q}_{(kl)}^{f0}\,\hat{k}_i e_j^{(\lambda)}\hat{k}_k\bar{e}_l^{(\lambda)}\rangle^{-1} \end{aligned} \tag{22}$$

To evaluate the various terms in eqn. (22) requires application of standard methods for tensor rotational averaging,[11–14] based on the assumption that the quantum structure of rotational motion is not resolved; results will therefore apply to all liquids, matrix-isolated species of random orientation, and gases under low spectral resolution.

It transpires that because of the index symmetry in the electric quadrupole moment, the $E1$–$E2$ and $M1$–$E2$ cross-terms in the denominator of eqn. (22) vanish, and the remaining results are as follows:

$$\langle \mu_i^{f0}\bar{G}_{jk}^{f0}\, e_i^{(\lambda)}\hat{B}_j\bar{e}_k^{(\lambda)}\rangle = \frac{i\theta}{6}\,\mu_\lambda^{f0}\bar{G}_{\mu\nu}^{f0}\varepsilon_{\lambda\mu\nu}\cos\phi \tag{23}$$

$$\langle \mu_i^{f0}\bar{H}_{jk}^{f0}\, e_i^{(\lambda)}\hat{B}_j\bar{b}_k^{(\lambda)}\rangle = -\tfrac{1}{6}\mu_\lambda^{f0}\bar{H}_{\mu\nu}^{f0}\varepsilon_{\lambda\mu\nu}\cos\phi \tag{24}$$

$$\langle \mu_i^{f0}\bar{J}_{j(kl)}^{f0}\, e_i^{(\lambda)}\hat{B}_j\hat{k}_k\bar{e}_l^{(\lambda)}\rangle = \tfrac{1}{10}\mu_\lambda^{f0}\bar{J}_{\mu(\mu\lambda)}^{f0}\cos\phi \tag{25}$$

$$\langle m_i^{f0}\bar{G}_{jk}^{f0}\, b_i^{(\lambda)}\hat{B}_j\bar{e}_k^{(\lambda)}\rangle = \tfrac{1}{6}m_\lambda^{f0}\bar{G}_{\mu\nu}^{f0}\varepsilon_{\lambda\mu\nu}\cos\phi \tag{26}$$

$$\langle m_i^{f0}\bar{H}_{jk}^{f0}\, b_i^{(\lambda)}\hat{B}_j\bar{b}_k^{(\lambda)}\rangle = \frac{i\theta}{6}\, m_\lambda^{f0}\bar{H}_{\mu\nu}^{f0}\varepsilon_{\lambda\mu\nu}\cos\phi \tag{27}$$

$$\langle m_i^{f0}\bar{J}_{j(kl)}^{f0}\, b_i^{(\lambda)}\hat{B}_j\hat{k}_k\bar{e}_l^{(\lambda)}\rangle = -\frac{i\theta}{10}\, m_\lambda^{f0}\bar{J}_{\mu(\mu\lambda)}^{f0}\cos\phi \tag{28}$$

$$\langle Q_{(ij)}^{f0}\bar{G}_{kl}^{f0}\,\hat{k}_i e_j^{(\lambda)}\hat{B}_k\bar{e}_l^{(\lambda)}\rangle = \tfrac{1}{10}Q_{(\lambda\mu)}^{f0}\,\bar{G}_{\lambda\mu}^{f0}\cos\phi \tag{29}$$

$$\langle Q_{(ij)}^{f0}\bar{H}_{kl}^{f0}\,\hat{k}_i e_j^{(\lambda)}\hat{B}_k\bar{b}_l^{(\lambda)}\rangle = \frac{i\theta}{10}\, Q_{(\lambda\mu)}^{f0}\bar{H}_{\lambda\mu}^{f0}\cos\phi \tag{30}$$

$$\langle Q_{(ij)}^{f0}\bar{J}_{k(lm)}^{f0}\,\hat{k}_i e_j^{(\lambda)}\hat{B}_k\hat{k}_l\bar{e}_m^{(\lambda)}\rangle = \frac{i\theta}{30}\, Q_{(\lambda\mu)}^{f0}\bar{J}_{\nu(\mu o)}^{f0}\varepsilon_{\lambda\nu o}\cos\phi \tag{31}$$

$$\langle \mu_i^{f0}\bar{\mu}_j^{f0}e_i^{(\lambda)}\bar{e}_j^{(\lambda)}\rangle = \tfrac{1}{3}\mu_\lambda^{f0}\bar{\mu}_\lambda^{f0} \tag{32}$$

$$\langle \mu_i^{f0}\bar{m}_j^{f0}e_i^{(\lambda)}\bar{b}_j^{(\lambda)} + \text{c.c.}\rangle = \frac{i\theta}{3}\,\mu_\lambda^{f0}\bar{m}_\lambda^{f0} + \text{c.c.} \tag{33}$$

$$\langle m_i^{f0}\bar{m}_j^{f0}b_i^{(\lambda)}\bar{b}_j^{(\lambda)}\rangle = \tfrac{1}{3}m_\lambda^{f0}\bar{m}_\lambda^{f0} \tag{34}$$

$$\langle Q_{(ij)}^{f0}\,\bar{Q}_{(kl)}^{f0}\,\hat{k}_i e_j^{(\lambda)}\hat{k}_k\bar{e}_l^{(\lambda)}\rangle = \tfrac{1}{10}Q_{(\lambda\mu)}^{f0}\bar{Q}_{(\lambda\mu)}^{f0} \tag{35}$$

where

$$\theta = i\hat{\boldsymbol{k}}\cdot(\boldsymbol{e}\times\bar{\boldsymbol{e}}) = \left\{\begin{array}{l}+1\ \text{(left c.p.l.)}\\ =0\ \text{(plane pol.)}\\ =-1\ \text{(right c.p.l.)}\end{array}\right\} \tag{36}$$

and

$$\cos\phi = \hat{\boldsymbol{k}}\cdot\hat{\boldsymbol{B}} \tag{37}$$

In eqn. (36) θ can be identified with $i\xi$ as defined elsewhere.[15]

The final result for γ is most usefully expressed in terms of irreducible cartesian tensor components. In this framework the electric dipole transition component μ_λ^{f0} is expressed as $\mu_\lambda^{(1-)}$, the magnetic component m_λ^{f0} as $m_\lambda^{(1+)}$ and the electric quadrupole component $Q_{(\lambda\mu)}^{f0}$ as $Q_{(\lambda\mu)}^{(2+)}$, the superscripts denoting weight and parity. Decomposing the reducible tensors $\boldsymbol{G}^{f0}$, $\boldsymbol{H}^{f0}$ and $\boldsymbol{J}^{f0}$ using standard formulae of irreducible tensor calculus,[14,16] we thus obtain;

$$\begin{aligned}\gamma = 2B\cos\phi[\mathrm{Re}\{ & 5c\mu_\lambda^{(1-)}\bar{H}_{\mu\nu}^{(1+)}\varepsilon_{\lambda\mu\nu} - 5cm_\lambda^{(1+)}\bar{G}_{\mu\nu}^{(1-)}\varepsilon_{\lambda\mu\nu} \\ & + 3ck\theta m_\lambda^{(1+)}\bar{J}_{\mu(\mu\lambda)}^{(1+)} + 3ck\theta Q_{(\lambda\mu)}^{(2+)}\bar{H}_{\lambda\mu}^{(2+)}\} \\ & + \mathrm{Im}\{5c^2\theta\mu_\lambda^{(1-)}\bar{G}_{\mu\nu}^{(1-)}\varepsilon_{\lambda\mu\nu} - 3c^2k\mu_\lambda^{(1-)}\bar{J}_{\mu(\mu\lambda)}^{(1+)} \\ & + 5\theta m_\lambda^{(1+)}\bar{H}_{\mu\nu}^{(1+)}\varepsilon_{\lambda\mu\nu} + 3c^2kQ_{(\lambda\mu)}^{(2+)}\bar{G}_{\lambda\mu}^{(2-)} \\ & + c^2k^2\theta Q_{(\lambda\mu)}^{(2+)}\bar{J}_{\nu(\mu o)}^{(2+)}\varepsilon_{\lambda\nu o}\}] \\ \times[& 10c^2\mu_\lambda^{(1-)}\bar{\mu}_\lambda^{(1-)} - 20c\theta\ \mathrm{Im}\ \mu_\lambda^{(1-)}\bar{m}_\lambda^{(1+)} \\ & + 10m_\lambda^{(1+)}\bar{m}_\lambda^{(1+)} + 3c^2k^2Q_{(\lambda\mu)}^{(2+)}\bar{Q}_{(\lambda\mu)}^{(2+)}]^{-1} \end{aligned} \tag{38}$$

where

$$H_{\lambda\mu}^{(1+)} = \tfrac{1}{2}\varepsilon_{\lambda\mu\nu}\varepsilon_{\rho\sigma\nu}H_{\rho\sigma}^{f0} \tag{39}$$

$$H_{\lambda\mu}^{(2+)} = \tfrac{1}{2}(H_{\lambda\mu}^{f0} + H_{\mu\lambda}^{f0}) - \tfrac{1}{3}\delta_{\lambda\mu}H_{\nu\nu}^{f0} \tag{40}$$

$$J_{\lambda(\mu\nu)}^{(1+)} = \tfrac{1}{10}[3\delta_{\lambda\mu}J_{\rho(\rho\nu)}^{f0} + 3\delta_{\lambda\nu}J_{\rho(\rho\mu)}^{f0} - 2\delta_{\mu\nu}J_{\rho(\rho\lambda)}^{f0}] \tag{41}$$

$$\begin{aligned}J_{\lambda(\mu\nu)}^{(2+)} = & \tfrac{1}{6}\varepsilon_{\lambda\mu\tau}[2\varepsilon_{\rho\sigma\tau}J_{\rho(\sigma\nu)}^{f0} + 2\varepsilon_{\rho\sigma\nu}J_{\rho(\sigma\tau)}^{f0}] \\ & + \tfrac{1}{6}\varepsilon_{\mu\nu\tau}[\varepsilon_{\rho\sigma\tau}J_{\rho(\sigma\lambda)}^{f0} + \varepsilon_{\rho\sigma\lambda}J_{\rho(\sigma\tau)}^{f0}] \end{aligned} \tag{42}$$

and the expressions for $G_{\lambda\mu}^{(1-)}$, $G_{\lambda\mu}^{(2-)}$ have the same structure as eqn. (39) and (40).

The result of eqn. (38) applies to transitions in molecules of arbitrary symmetry and under arbitrary polarisation conditions. It is, however, worth considering the special results which arise in the cases of excitation with plane and polarised ($\theta = 0$) and circularly polarised light ($\theta = \pm 1$).

Plane-polarised Excitation

E1-allowed

$$\begin{aligned}\gamma \approx \frac{B\cos\phi}{5c\,|\mu^{(1-)}|^2}\,[& 5\ \mathrm{Re}(\mu_\lambda^{(1-)}\bar{H}_{\mu\nu}^{(1+)}\varepsilon_{\lambda\mu\nu} - m_\lambda^{(1+)}\bar{G}_{\mu\nu}^{(1-)}\varepsilon_{\lambda\mu\nu}) \\ & + 3ck\ \mathrm{Im}(Q_{(\lambda\mu)}^{(2+)}\bar{G}_{\lambda\mu}^{(2-)} - \mu_\lambda^{(1-)}\bar{J}_{\mu(\mu\lambda)}^{(1+)})] \end{aligned} \tag{43}$$

E1-forbidden

$$\gamma = 2cB\cos\phi\left(\frac{3ck\ \mathrm{Im}\ Q_{(\lambda\mu)}^{(2+)}\bar{G}_{\lambda\mu}^{(2-)} - 5\ \mathrm{Re}\ m_\lambda^{(1+)}\bar{G}_{\mu\nu}^{(1-)}\varepsilon_{\lambda\mu\nu}}{3c^2k^2\boldsymbol{Q}^{(2+)}:\bar{\boldsymbol{Q}}^{(2+)} + 10\,|\boldsymbol{m}^{(1+)}|^2}\right) \tag{44}$$

The products between tensors of opposite parity in eqn (43) and (44) attest the fact that changes in absorptivity are only to be observed in chiral molecules, where they are enantiomerically specific.[7] However, in such species, there are no symmetry constraints to exclude $E1$ contributions to transitions which are $M1$-allowed. Interest is therefore limited to cases where the $E1$ transition moment is negligible for other reasons (see Discussion). Results precisely equivalent to eqn. (43) and (44) arise in the case of excitation with an unpolarised source.

Circularly Polarised Excitation

The general result here is less simple, but of more general application. Of particular interest are the specific results for

the differential change in absorption associated with reversing the helicity of the beam.

E1-allowed

$$\gamma^{L} - \gamma^{R} \approx \frac{2B \cos \phi}{|\mu^{(1-)}|^2} \text{ Im } \mu_{\lambda}^{(1-)} \bar{G}_{\mu\nu}^{(1-)} \varepsilon_{\lambda\mu\nu} \qquad (45)$$

This result applies rigorously if the transition is $M1$- and $E2$-forbidden, as for example in the case of a transition of A_{1u} symmetry in a $D_{\infty h}$ molecule; it also holds approximately if $M1$- or $E2$-contributions are present.

E1-forbidden

$$\gamma^{L} - \gamma^{R} = 4B \cos \phi \times \left(\frac{3ck \text{ Re } (m_{\lambda}^{(1+)} \bar{J}_{\mu(\mu\lambda)}^{(1+)} + Q_{(\lambda\mu)}^{(2+)} \bar{H}_{\lambda\mu}^{(2+)}) + \text{Im}(5m_{\lambda}^{(1+)} \bar{H}_{\mu\nu}^{(1+)} \varepsilon_{\lambda\mu\nu} + c^2 k^2 Q_{(\lambda\mu)}^{(2+)} \bar{J}_{\nu(\mu 0)}^{(2+)} \varepsilon_{\lambda\nu o})}{10|\boldsymbol{m}^{(1+)}|^2 + 3c^2 k^2 \boldsymbol{Q}^{(2+)} : \boldsymbol{Q}^{(2+)}} \right) \qquad (46)$$

The above equation simplifies further if a transition is (*a*) $M1$-allowed but $E2$-forbidden as for example in an A_{2g} transition in a molecule of $D_{\infty h}$ symmetry, or (*b*) $E2$-allowed but $M1$-forbidden, as in the case of an E_{2g} transition in such a molecule. Results (45) and (46) reflect the Faraday B-term magnetic circular dichroism which is observed in achiral species without any lifting of spin degeneracy.[1] Here the chirality apparently manifest by the molecule results from a gyrotropic dressing by the combined influence of the radiation and the applied magnetic field. This interpretation is attested by the fact that repeating the calculations for the case of an applied electric field yields a vanishing result, a conclusion validated by considerations of parity and time-reversal symmetry.[17,18]

Discussion

The most obvious features of the general result, eqn. (38), are its linear dependence in the leading order of perturbation theory on both the magnetic field and on cos ϕ. The latter shows that application of the field parallel to the irradiation direction produces the largest effect, as in Faraday rotation and MCD, and should therefore be the experimentally prefered configuration.

It is instructive to estimate the size of the effects we have described. It can readily be shown that the values of $\Delta\gamma$ as given by eqn. (45) and (46) are typically given by a factor of the form $(mB/\hbar\,\Delta\omega)$, where m is a typical magnetic transition moment and $\Delta\omega$ a typical detuning from the nearest resonance; $\hbar\,\Delta\omega$ corresponds to a mean of the quantities which appear in the denominator of the tensor $\boldsymbol{G}^{f0}$. For a detuning $\Delta\omega$ of 3×10^{14} Hz and a typical dipole moment of 1 μ_B, we obtain a value for $\Delta\gamma$ of only 3×10^{-4} (B/T). It is clearly appropriate to employ electro-optical polarisation modulation methods in measurements of this kind.

The results for γ as given by eqn. (43) and (44) are typified by values of the order of $\alpha(mB/\hbar\,\Delta\omega)$ and $\alpha^{-1}(mB/\hbar\,\Delta\omega)$, respectively, where α is again the fine structure constant. The former result therefore corresponds to a negligible effect which is unlikely to be experimentally detectable. However, in the latter case, that of an $E1$-forbidden transition excited by application of a plane-polarised beam, the size of the effect is $\gamma \approx 0.04(B/\text{T})$. Thus with a readily attainable field of the order of 1 T (significantly more intense fields being routinely applied in laser magnetic resonance measurements[19]), the influence of the magnetic field should certainly be measurable. It is notable that the technique of measuring polarisation difference is neither necessary nor even helpful in this case. Suitable candidates for study are the analogues in chiral systems of magnetic dipole allowed transitions in parent molecules of higher symmetry, as in the several examples discussed by Barron and Vrbancich.[8]

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