

Optically induced static magnetization near optical resonances in molecular systems. 1. Inverse Faraday effect

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The static magnetization induced in molecular systems in second order by circularly polarized light shows anomalous dispersion inside the optical resonance regions. The general analytical expressions describing the effect are presented, and numerical calculations have been made for three-level systems. Dispersion curves of diamagnetic as well as paramagnetic contributions to the inverse Faraday effect are shown. Complete quantum mechanical expressions for the nonlinear polarizabilities involved in the effect are presented, and their properties and orders of magnitude discussed.

1. Introduction

Studies of optical effects in gases and liquids exposed to external electric, magnetic or electromagnetic fields increase our knowledge of molecular properties and intermolecular correlations [1-4]. One of the effects of a static magnetic field B^0 acting on a medium in which a linearly polarized beam of monochromatic light propagates in the direction of B^0 consists in the rotation of the plane of polarization discovered by Faraday [5]. Extensive lists of the papers on the Faraday effect in nonconducting liquid and gaseous, dia- and paramagnetic media may be found in the reviews by Buckingham and Stephens [6] and by Palik and Menvis [7]. Kielich [8] has proposed a general theory of nonlinear electromagneto-optical effects in media with spatial dispersion.

Van der Ziel, Pershan and Malmstrom [9] have shown experimentally that circularly polarized light induces in a medium a static magnetization, and they have called this the inverse Faraday effect (IFE). The effect outside of resonances (without absorption) has been analysed theoretically by these same authors [10], and by Atkins and Miller [11], Shen [4] and Wagnière [12]. The role of molecular symmetry in the IFE has been discussed recently by Woźniak *et al.* [13].

The spectral consequences of the analogy between a static magnetic field and circularly polarized light include the inverse Zeeman effect [14] and possible detection of the magnetization in an NMR or ESR spectrometer, the prototype theory [15] and experiment [16] of which have been initiated recently, and laser induced forward-backward birefringence [17] as well as laser induced dynamic polarization [18], the latter being sustained in chiral, paramagnetic molecules. In the present paper, we analyse the inverse Faraday effect in the optical resonance regions of molecular systems. The magnetization induced by nonpolarized light (or light of any polariz-

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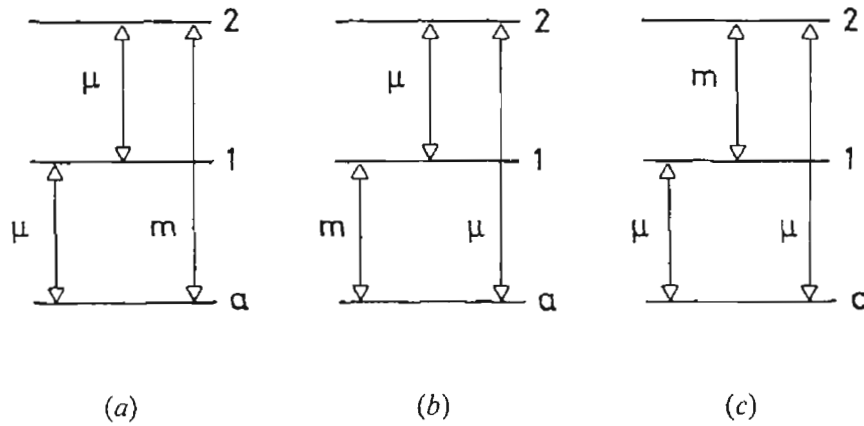


Figure 1. Energy diagrams for a three-level system (equation (28)). Depending on which transitions are allowed, cases (a), (b) and (c) are described by the functions $f_1(\omega)$, $f_2(\omega)$ and $f_3(\omega)$, respectively; μ denotes an electric dipole and m a magnetic dipole allowed transition. Notice that, in molecules without S_n symmetry elements, transitions may be both μ and m allowed.

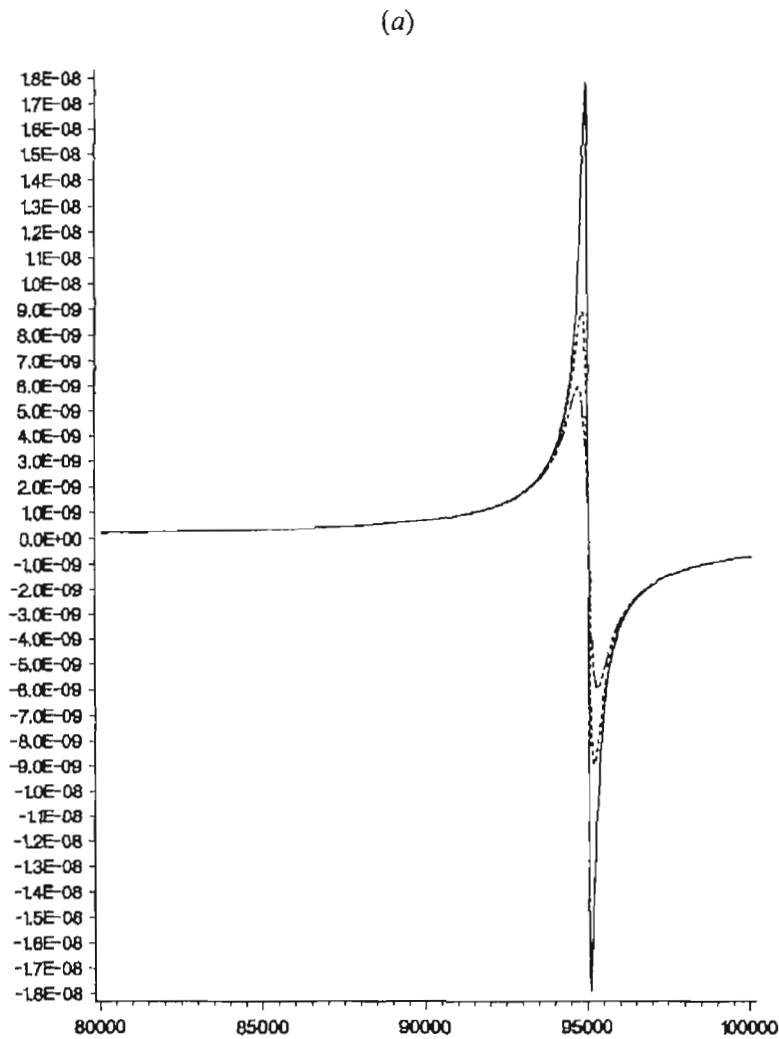


Figure 2. The functions $\tilde{f}_i(\tilde{\omega})$ (in cm^2) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) for a three-level system with resonances at $\tilde{\omega}_1 = 95\,000\text{ cm}^{-1}$ and $\tilde{\omega}_2 = 140\,000\text{ cm}^{-1}$: (a) $\tilde{f}_1(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\text{ cm}^{-1}$; (b) $\tilde{f}_2(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\text{ cm}^{-1}$; (c) $\tilde{f}_3(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\text{ cm}^{-1}$; (d) $\tilde{f}_3(\tilde{\omega})$ for $\Gamma_1 = 100, 200, 300\text{ cm}^{-1}$, $\Gamma_2 = 400\text{ cm}^{-1}$.

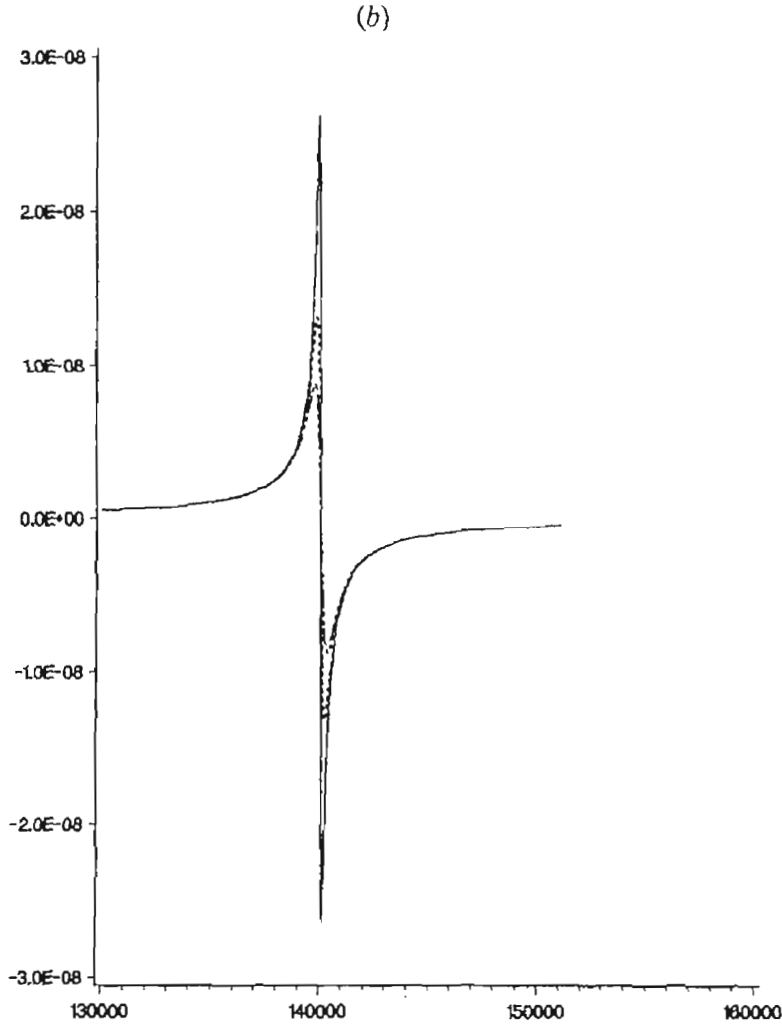


Figure 2 (continued).

ation)—inverse magnetochiral birefringence [12, 13]—in the regions of resonance will be discussed in a later report on this investigation.

2. Nonlinear magnetoelectric polarizabilities of IFE

The CP electric field

$$\mathbf{E} = \mathbf{E}^- e^{-i(\omega t - \mathbf{k} \cdot \mathbf{r})} + \mathbf{E}^+ e^{i(\omega t - \mathbf{k} \cdot \mathbf{r})} \quad (1)$$

of an electromagnetic wave acting on a molecule induces in it a static magnetic dipole moment (in this paper we apply the Einstein convention),

$$m_i(0) = \frac{1}{2} {}^m\alpha_{ijk}^{cc}(0; \omega, -\omega) E_j^- E_k^+ + \frac{1}{2} {}^m\alpha_{ijk}^{cc}(0; -\omega, \omega) E_j^+ E_k^-. \quad (2)$$

Using density matrix formalism (double Feynman diagrams) [4, 19] one can obtain the quantum mechanical form of the tensor ${}^m\alpha^{cc}$ (see appendix A). In general, for molecules with complex wavefunctions, the polarizabilities ${}^m\alpha^{cc}(0; \omega, -\omega)$ and ${}^m\alpha^{cc}(0; -\omega, \omega)$ can be represented as follows,

$$\begin{aligned} {}^m\alpha^{cc}(0; \omega, -\omega) &= {}^m\hat{\beta}^{cc}(0; \omega, -\omega) + i {}^m\hat{\gamma}^{cc}(0; \omega, -\omega), \\ {}^m\alpha^{cc}(0; -\omega, \omega) &= {}^m\hat{\beta}^{cc}(0; -\omega, \omega) + i {}^m\hat{\gamma}^{cc}(0; -\omega, \omega) \end{aligned} \quad (3)$$

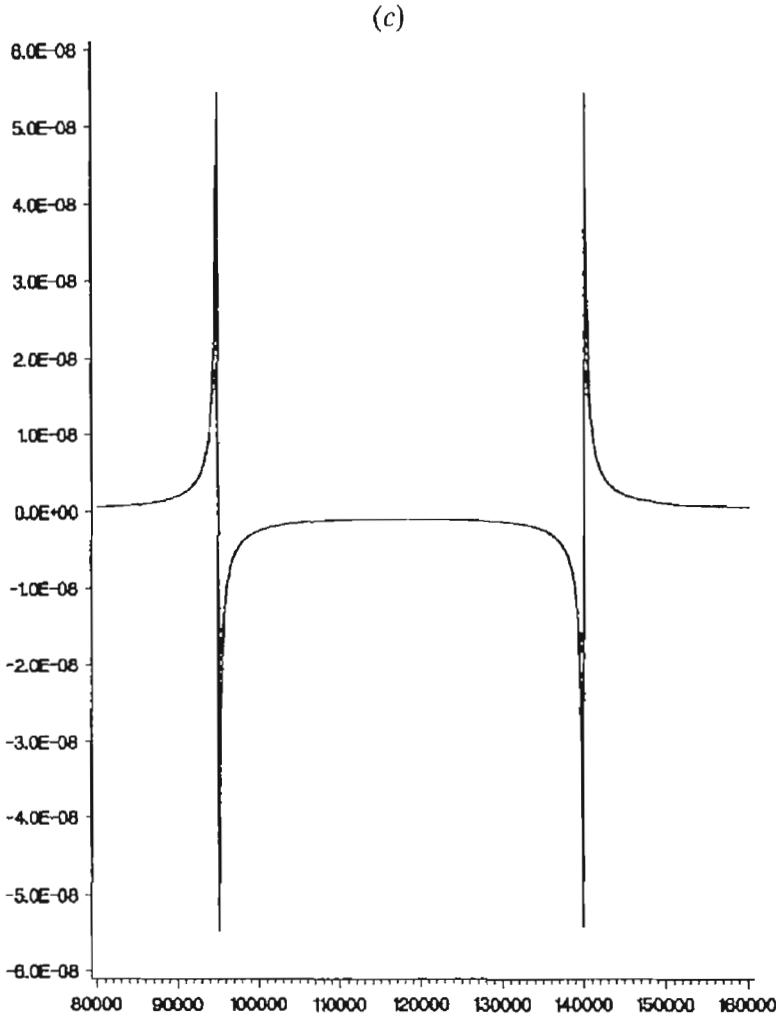


Figure 2 (continued).

and, in the presence of damping, the tensors ${}^m\hat{\beta}^{ec}$ and ${}^m\hat{\gamma}^{ec}$ are complex

$$\begin{aligned} {}^m\hat{\beta}^{ec} &= {}^m\beta^{ec} + i {}^m\beta'^{ec} \\ {}^m\hat{\gamma}^{ec} &= {}^m\gamma^{ec} + i {}^m\gamma'^{ec}, \end{aligned} \quad (4)$$

with quantum mechanical expressions given in appendix A. From equation (A.1) we have

$$\begin{aligned} {}^m\alpha_{ijk}^{cc}(0; \omega, -\omega) &= {}^m\alpha_{ikj}^{cc*}(0; \omega, -\omega), \\ {}^m\alpha_{ijk}^{cc}(0; -\omega, \omega) &= {}^m\alpha_{ikj}^{cc*}(0; -\omega, \omega); \end{aligned} \quad (5)$$

that means that the coordinates of the tensor ${}^m\alpha^{cc}(0; \omega, -\omega)$ fulfil the following relations

$${}^m\beta_{ijk}^{cc}(0; \omega, -\omega) = {}^m\beta_{ikj}^{cc}(0; \omega, -\omega), \quad (6)$$

$${}^m\gamma_{ijk}^{cc}(0; \omega, -\omega) = -{}^m\gamma_{ikj}^{cc}(0; \omega, -\omega), \quad (7)$$

$$\left. \begin{aligned} {}^m\beta'_{ijk}(0; \omega, -\omega) &= -{}^m\beta'_{ikj}(0; \omega, -\omega), \\ {}^m\gamma'_{ijk}(0; \omega, -\omega) &= {}^m\gamma'_{ikj}(0; \omega, -\omega), \end{aligned} \right\} \quad (8)$$

and the same relations are valid for components of ${}^m\alpha^{cc}(0; -\omega, \omega)$. Moreover, there

(d)

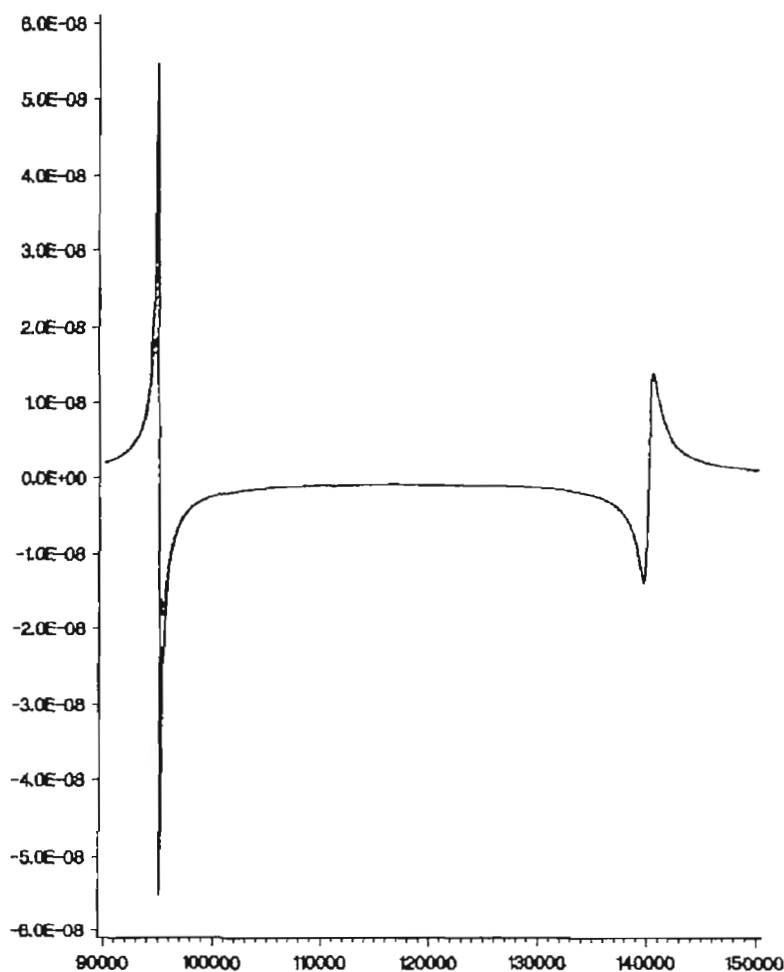


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is the very important relation between ${}^m\alpha^{cc}(0; \omega, -\omega)$ and ${}^m\alpha^{cc}(0; -\omega, \omega)$, viz.,

$${}^m\alpha^{cc}(0; \omega, -\omega) = {}^m\alpha^{cc*}(0; -\omega, \omega) \quad (9)$$

which leads to

$${}^m\beta_{ijk}^{cc}(0; \omega, -\omega) = {}^m\beta_{ijk}^{cc}(0; -\omega, \omega), \quad (10)$$

$${}^m\gamma_{ijk}^{cc}(0; \omega, -\omega) = -{}^m\gamma_{ijk}^{cc}(0; -\omega, \omega), \quad (11)$$

$$\left. \begin{aligned} {}^m\beta'_{ijk}(0; \omega, -\omega) &= -{}^m\beta'_{ijk}(0; -\omega, \omega), \\ {}^m\gamma'_{ijk}(0; \omega, -\omega) &= {}^m\gamma'_{ijk}(0; -\omega, \omega). \end{aligned} \right\} \quad (12)$$

From equations (6–8) and (10–12) we similarly obtain

$${}^m\beta_{ijk}^{cc}(0; \omega, -\omega) = {}^m\beta_{ikj}^{cc}(0; -\omega, \omega), \quad (10a)$$

$${}^m\gamma_{ijk}^{cc}(0; \omega, -\omega) = {}^m\gamma_{ikj}^{cc}(0; -\omega, \omega), \quad (11a)$$

$$\left. \begin{aligned} {}^m\beta'_{ijk}(0; \omega, -\omega) &= {}^m\beta'_{ikj}(0; -\omega, \omega), \\ {}^m\gamma'_{ijk}(0; \omega, -\omega) &= {}^m\gamma'_{ikj}(0; -\omega, \omega). \end{aligned} \right\} \quad (12a)$$

It is obvious (see appendix A) that the polarizability ${}^m\beta^{cc}$ is different from zero for molecules with complex wavefunctions only, but that ${}^m\gamma^{cc}$ is different from zero for all molecules.

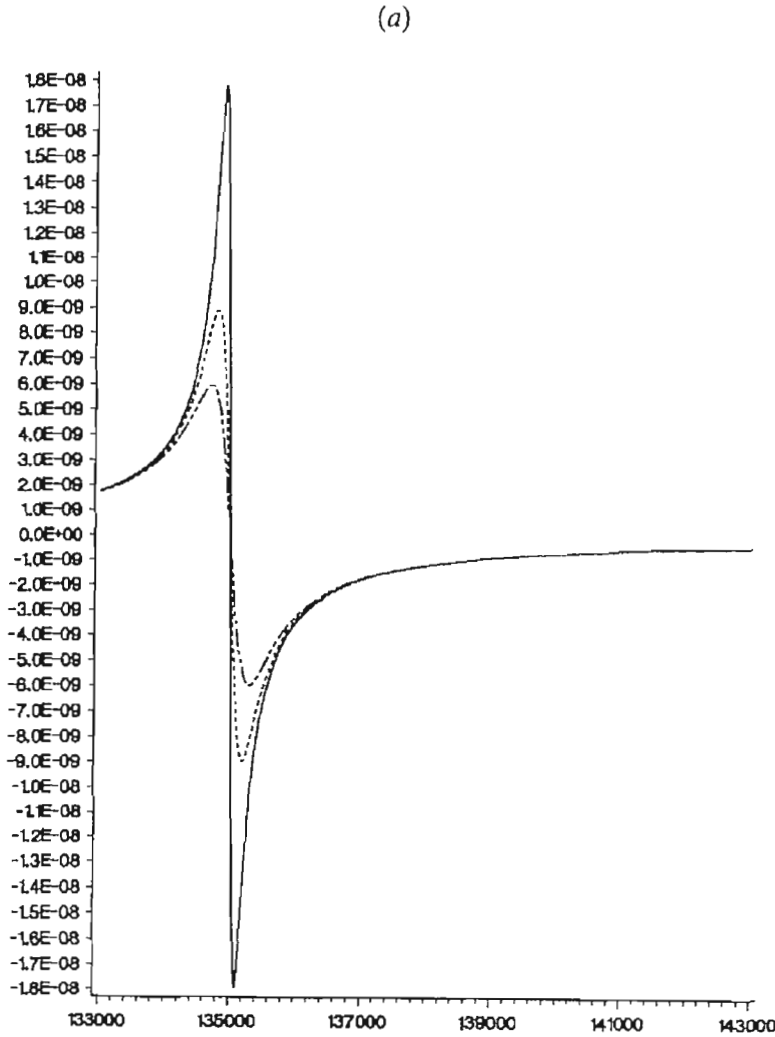


Figure 3. The functions $\tilde{f}_i(\tilde{\omega})$ (in cm^2) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) for a three-level system with resonances at $\tilde{\omega}_1 = 135\,000\text{ cm}^{-1}$ and $\tilde{\omega}_2 = 140\,000\text{ cm}^{-1}$: (a) $\tilde{f}_1(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\text{ cm}^{-1}$; (b) $\tilde{f}_2(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\text{ cm}^{-1}$; (c) $\tilde{f}_3(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\text{ cm}^{-1}$; (d) $\tilde{f}_3(\tilde{\omega})$ for $\Gamma_1 = 100, 200, 300\text{ cm}^{-1}, \Gamma_2 = 400\text{ cm}^{-1}$.

3. The static magnetization of a molecular system: diamagnetic contribution

3.1. Polarizability description

We consider a transparent isotropic medium composed of like molecules in which a left circularly polarized light wave (equation (1)) with electric field

$$\mathbf{E}^\mp = \frac{\sqrt{2}}{2} E_0 (\mathbf{e}_x \pm i\mathbf{e}_y) \quad (13)$$

propagates in the Z direction of the laboratory frame $\{X, Y, Z\}$ and $\mathbf{e}_x, \mathbf{e}_y$ are unit vectors along the X and Y axes, respectively. Since the product $E_j^- E_k^+$ can be split into a symmetric and an antisymmetric part

$$E_j^- E_k^+ \equiv \Pi_{jk}^S + \Pi_{jk}^A \quad (14)$$

with

$$\Pi_{jk}^S = \frac{1}{2}(E_j^- E_k^+ + E_k^- E_j^+), \quad (15)$$

$$\Pi_{jk}^A = \frac{1}{2}(E_j^- E_k^+ - E_k^- E_j^+). \quad (16)$$

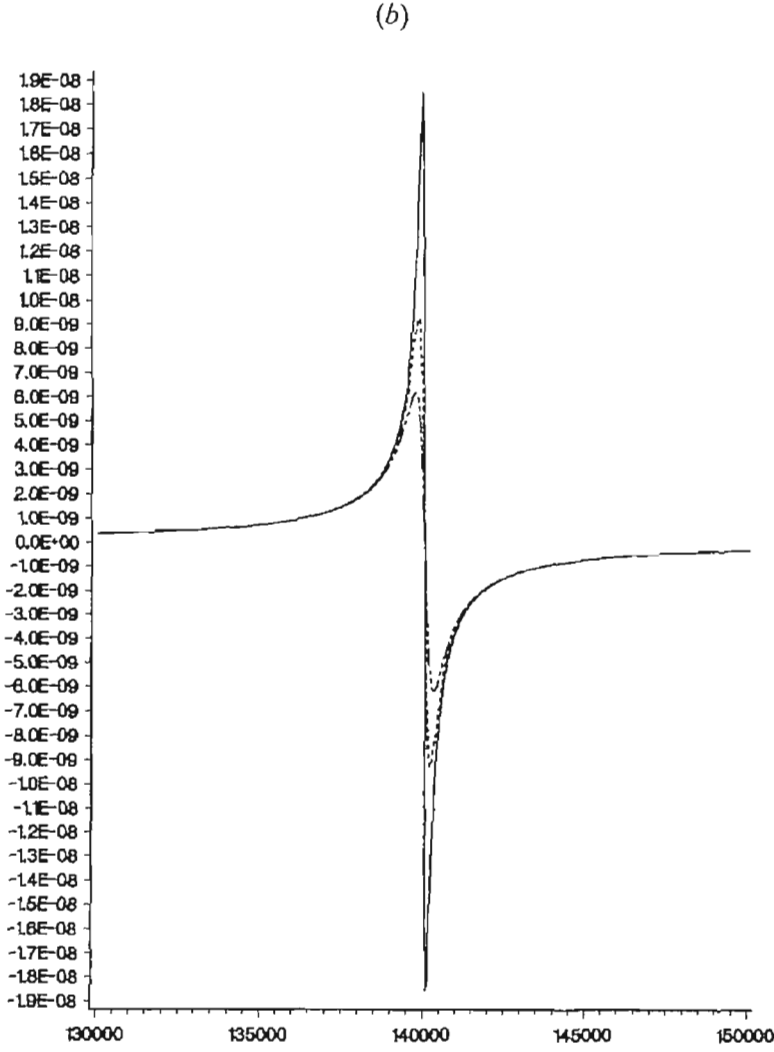


Figure 3 (continued).

Equation (2), taking into account equations (3–12), can be written in the form

$$m_i(0) = {}^m\beta_{ijk}^{cc}(0; \omega, -\omega)\Pi_{jk}^S + i{}^m\gamma_{ijk}^{cc}(0; \omega, -\omega)\Pi_{jk}^A. \quad (17)$$

From equation (17) we obtain for the static magnetization $\mathbf{M}(0)$ of the molecular system the expression

$$M_i(0) = N[\langle {}^m\beta_{ijk}^{cc}(0; \omega, -\omega) \rangle \Pi_{jk}^S + i\langle {}^m\gamma_{ijk}^{cc}(0; \omega, -\omega) \rangle \Pi_{jk}^A], \quad (18)$$

where the symbol $\langle \dots \rangle$ stands for the statistical average, and N is the number of molecules per unit volume. Denoting by $e_{i\alpha}$ the cosines of the angle between the α axis of the molecular system of coordinates $\{1, 2, 3\}$ and i axis of the laboratory frame $\{X, Y, Z\}$, we have

$$\langle {}^m\gamma_{ijk}^{cc} \rangle = \langle e_{i\alpha} e_{j\beta} e_{k\gamma} \rangle {}^m\gamma_{\alpha\beta\gamma}^{cc}, \quad (19)$$

with [20]

$$\langle e_{i\alpha} e_{j\beta} e_{k\gamma} \rangle = \frac{1}{6} \epsilon_{ijk} \epsilon_{\alpha\beta\gamma},$$

where ${}^m\gamma_{\alpha\beta\gamma}^{cc}$ denotes the coordinates of the tensor ${}^m\gamma^{cc}$ given in the molecular frame, and $\epsilon_{\alpha\beta\gamma}$ the Levi-Civita third-rank antisymmetric unit tensor. The first term of equation (18) vanishes after averaging because of symmetry with respect to permutation of the

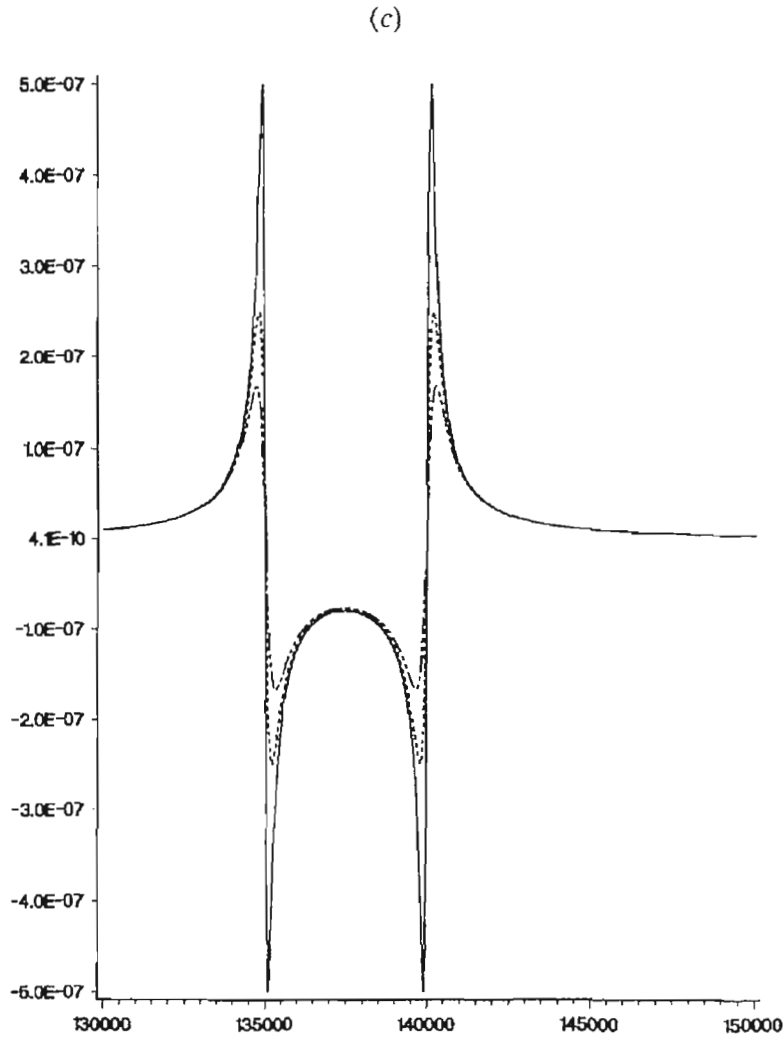


Figure 3 (continued).

last two indices in ${}^m\beta_{\alpha\beta}^{cc}$, and symmetry of Π_{jk}^S , and we have

$$M_i(0) = \frac{N}{6} i \varepsilon_{\alpha\beta\gamma} {}^m\gamma_{\alpha\beta}^{cc}(0; \omega, -\omega) \Pi_i, \quad (20)$$

with

$$\Pi_i = \varepsilon_{ijk} \Pi_{jk}^A \quad (21)$$

or, in vector notation,

$$\boldsymbol{\Pi} = \mathbf{E}^- \times \mathbf{E}^+. \quad (22)$$

From equation (20) one can see that the effect occurs for a circularly polarized beam only, for which product (22) is imaginary [11].

Since, for an optical wave (equation (13))

$$\boldsymbol{\Pi} = \mathbf{E}^- \times \mathbf{E}^+ = -iE_0^2 \mathbf{e}_z, \quad (23)$$

with \mathbf{e}_z the unit vector along the Z axis of the frame $\{X, Y, Z\}$, we have the Z component of the magnetization only,

$$M_Z = \frac{N}{3} ({}^m\gamma_{123}^{cc} + {}^m\gamma_{231}^{cc} + {}^m\gamma_{312}^{cc}) E_0^2 \quad (24)$$

(d)

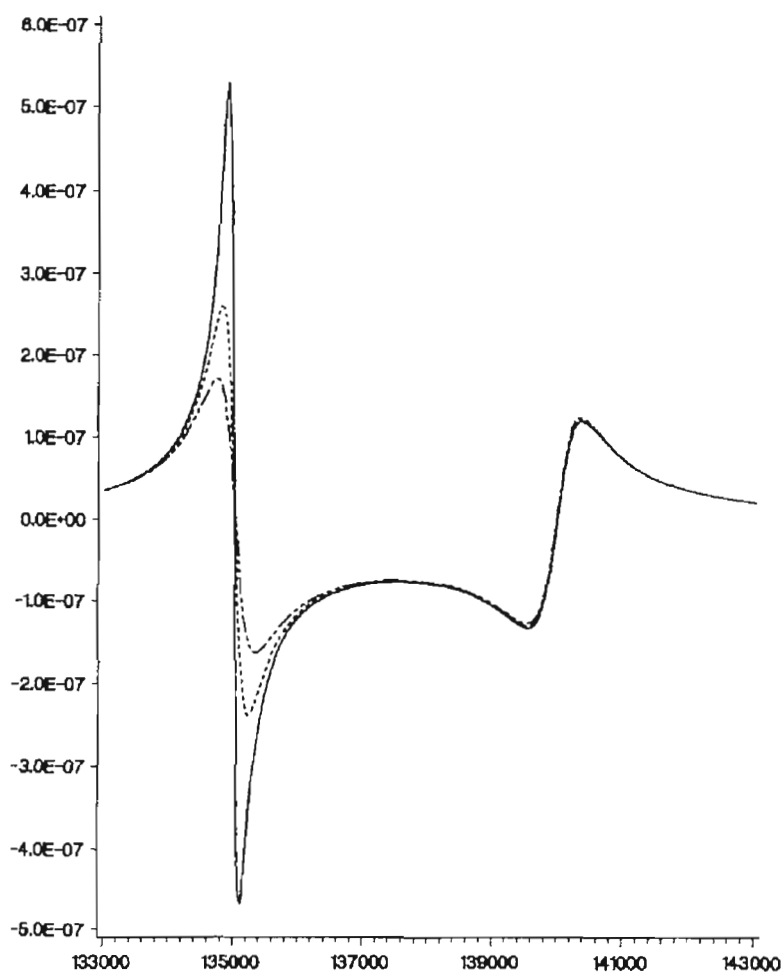


Figure 3 (continued).

for molecules with the symmetry C_1 , C_2 , S_2 , C_{1h} , C_{2h} , C_{2v} , D_2 , and D_{2h} ;

$$M_Z = \frac{N}{3} ({}^m\gamma_{123}^{cc} + 2 {}^m\gamma_{231}^{cc}) E_0^2 \quad (25)$$

for molecules with the symmetry C_3 , D_3 , C_4 , S_4 , D_4 , D_{2d} , C_6 , S_6 , D_6 , C_{3h} , C_{3v} , D_{3h} , D_{3d} , C_{4h} , C_{4v} , D_{4h} , C_{6v} and C_{6h} ; and

$$M_Z = N {}^m\gamma_{123}^{cc} E_0^2 \quad (26)$$

for molecules with higher symmetries. The role of molecular symmetry in the effect without absorption has been discussed in reference [13].

3.2. Frequency dependence

For a quantitative analysis of the frequency dependence of the inverse Faraday effect it is convenient to rewrite equation (20) in quite different form. Keeping in mind that the electric dipole moment and magnetic dipole moment operators are

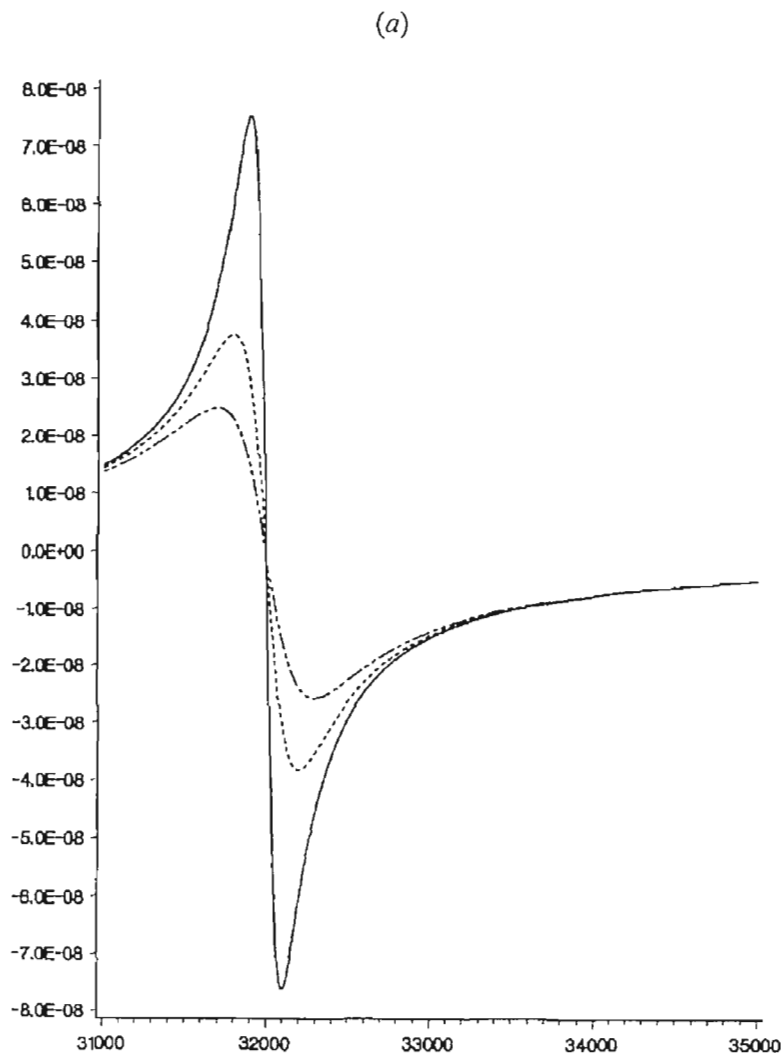


Figure 4. The functions $\tilde{f}_i(\tilde{\omega})$ (in cm^2) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) for a three-level system with resonances at $\tilde{\omega}_1 = 32\,000\text{ cm}^{-1}$ and $\tilde{\omega}_2 = 33\,000\text{ cm}^{-1}$: (a) $\tilde{f}_1^r(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\text{ cm}^{-1}$; (b) $\tilde{f}_2^r(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\text{ cm}^{-1}$; (c) $\tilde{f}_3^r(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\text{ cm}^{-1}$; (d) $\tilde{f}_3^r(\tilde{\omega})$ for $\Gamma_1 = 100, 200, 300\text{ cm}^{-1}$, $\Gamma_2 = 400\text{ cm}^{-1}$.

Hermitian, we have (see appendix B):

$$\begin{aligned}
 \mathbf{M}(0) = & -\frac{N}{3\hbar^2} \sum_{abc} \rho_{aa}^{(0)} \{2(A_1 + A_2) \text{Im}(\mathbf{m}_{ac} \cdot \boldsymbol{\mu}_{cb} \times \boldsymbol{\mu}_{ba}) \\
 & - [(A_3 + A_4)(1 + K') + A_5 K''] \text{Im}(\boldsymbol{\mu}_{ac} \cdot \mathbf{m}_{cb} \times \boldsymbol{\mu}_{ba})\} (i\mathbf{E}^- \times \mathbf{E}^+),
 \end{aligned}
 \tag{27}$$

with coefficients A_n given by equations (B.3–B.7) (appendix B); K' and K'' are the real and imaginary part of the correction term (equation (A.2)), respectively.

If we neglect damping ($A_2 = A_4 = A_5 = K' = K'' = 0$) and assume that all molecules are in their ground states, equation (27) has the form of equation (13) in reference [12]. The general equation (27) can be applied to specific cases.

We consider now a molecule represented by three levels (a, the ground state; 1 and 2, the excited states) for which the correction term K can be neglected (see appendix A). If we assume, moreover, that all molecules are in their ground states, we obtain the static magnetization induced by circularly polarized light in the form (the contribution to $\mathbf{M}(0)$ from the diagonal elements of the electric dipole and magnetic

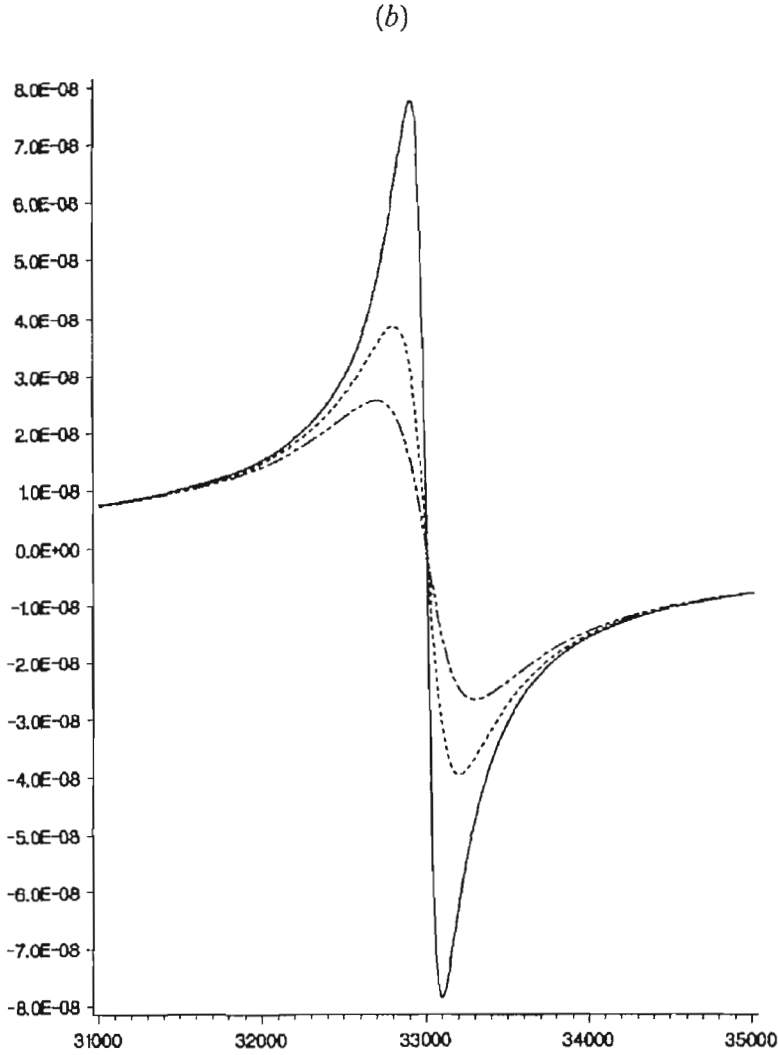


Figure 4 (continued).

dipole transition matrices is discussed in appendix D)

$$\begin{aligned}
 M(0) = & -\frac{2N}{3\hbar^2} \{ f_1(\omega) \operatorname{Im} (\mathbf{m}_{a2} \cdot \boldsymbol{\mu}_{21} \times \boldsymbol{\mu}_{1a}) + f_2(\omega) \operatorname{Im} (\mathbf{m}_{a1} \cdot \boldsymbol{\mu}_{12} \times \boldsymbol{\mu}_{2a}) \\
 & - f_3(\omega) \operatorname{Im} (\boldsymbol{\mu}_{a1} \cdot \mathbf{m}_{12} \times \boldsymbol{\mu}_{2a}) \} (i\mathbf{E}^- \times \mathbf{E}^+), \quad (28)
 \end{aligned}$$

where the functions $f_n(\omega)$ are given by equations (C.1–C.3) (see appendix C).

In figure 1 we present diagrams related to equation (28). Note that the first and the second terms of equation (28) depend on magnetic dipole and electric dipole transitions between the ground state and the excited states (figure 1(a, b)). On the other hand, the third one—a magnetic transition between two excited states (figure 1(c))—leads to quite different contributions to the induced static magnetization. We have calculated and plotted the functions $\tilde{f}_1(\tilde{\omega}) = c^2 f_1(\omega)$, $\tilde{f}_2(\tilde{\omega}) = c^2 f_2(\omega)$ and $\tilde{f}_3(\tilde{\omega}) = c^2 f_3(\omega)$ (with dimension in cm^2 if $\tilde{\omega} = \omega/c = 2\pi\tilde{\nu}$ is given in cm^{-1} ; c is the velocity of light) in absorption regions for molecules with different resonance frequencies and different relaxation times Γ_{ba}^{-1} (figures 2–4).

Our results show that in all cases the IFE increases rapidly when close to a resonance frequency, and the enhancement can be of the order of 10 – 10^2 or even higher, depending on the damping factor Γ_{ba}^{-1} . When magnetic dipole transitions between all molecular levels are allowed, the main contribution to the magnetization

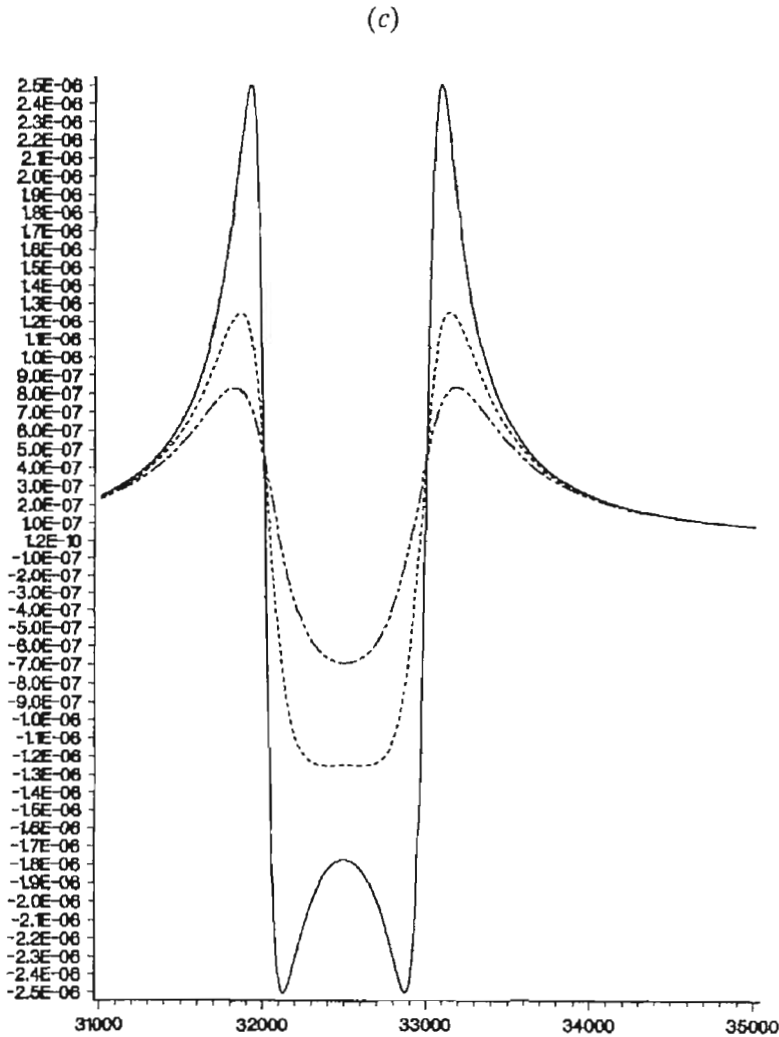


Figure 4 (continued).

comes from the third term of equation (28) (transitions in figure 1(c)). The closer together the excited levels are, the larger are the contributions from the transitions in figure 1(c). Moreover, the function $f_3(\omega)$ gives the enhancement near both resonance frequencies as well as between them (opposed sign) (figures 2(c, d), 3(c, d), 4(c, d)). The functions $f_1(\omega)$ and $f_2(\omega)$, on the other hand, cause increase of the static magnetization near resonance frequencies ω_1 and ω_2 only (figures 2(a, b), 3(a, b), 4(a, b)). If the excited states are close together there is a contribution from $f_1(\omega)$ to the effect near resonance at ω_2 , and from $f_2(\omega)$ to the effect near the resonance at ω_1 (if the transitions of figure 1(a, b) are active), but they have the opposite signs in the region between ω_1 and ω_2 . For $\omega_{12} \gg \Gamma_1$ and $\omega_{12} \gg \Gamma_2$, such contributions are negligible. We would like to emphasize that at exact resonance $\omega = \omega_1$, as well as at $\omega = \omega_2$, the magnetization still occurs because of damping and its magnitude is of the order of the effect far from resonance. The change of sign does not occur exactly at the points $\omega = \omega_1$, or $\omega = \omega_2$.

4. Paramagnetic contributions

To obtain the paramagnetic contribution to the static magnetization induced by circularly polarized light in the presence of damping we follow the procedure of

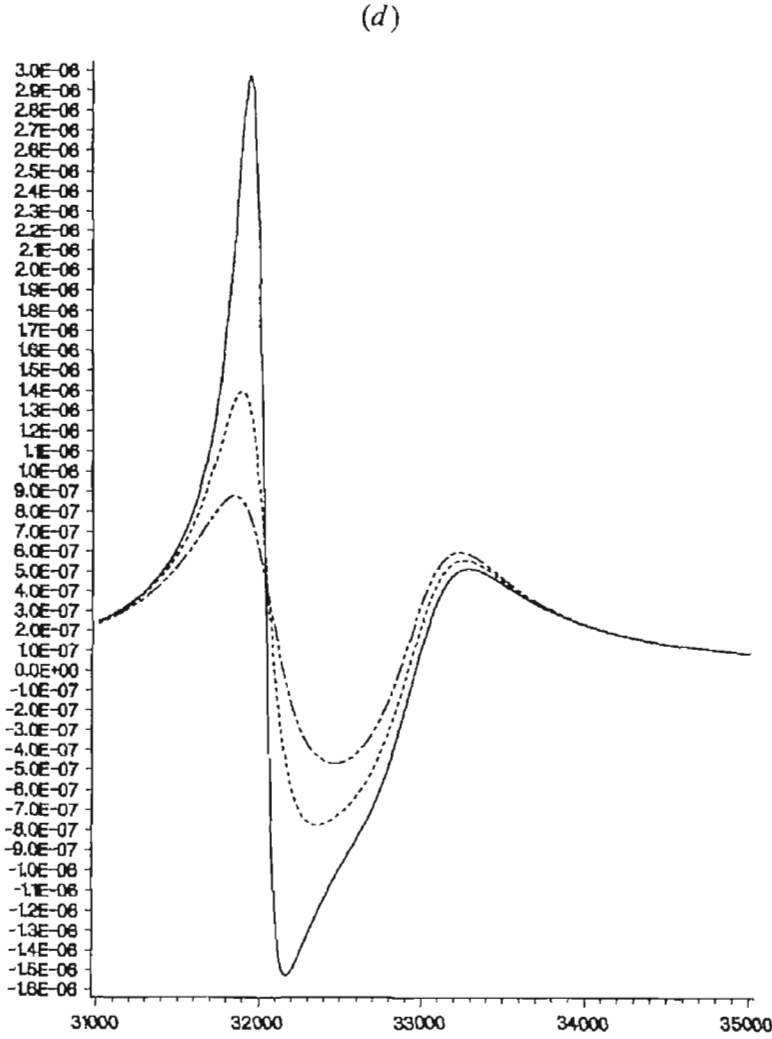


Figure 4 (continued).

reference [12], which leads directly to the result

$$M(0) = -\frac{N}{3\hbar kT} \sum_{ab} \rho_{aa}^{(0)} \frac{\omega(\omega_{ba}^2 - \omega^2 - \Gamma_{ba}^2)}{(\omega_{ba}^2 - \omega^2 + \Gamma_{ba}^2)^2 + 4\omega^2 \Gamma_{ba}^2} \mathbf{m}_{aa} \cdot \text{Im}(\boldsymbol{\mu}_{ab} \times \boldsymbol{\mu}_{ba})(i\mathbf{E}^- \times \mathbf{E}^+), \quad (29)$$

where $\mathbf{m}_{aa} = \langle a|\mathbf{m}|a\rangle$ is the magnetic dipole moment of the molecule in the state a , k is the Boltzmann constant, and T is the temperature. The above equation without damping has been discussed for different molecular symmetries in [13]. For three-level molecules (as in section 3.3) we have

$$M(0) = -\frac{N}{3\hbar kT} [p_1(\omega)\mathbf{m}_{aa} \cdot \text{Im}(\boldsymbol{\mu}_{a1} \times \boldsymbol{\mu}_{1a}) + p_2(\omega)\mathbf{m}_{aa} \cdot \text{Im}(\boldsymbol{\mu}_{a2} \times \boldsymbol{\mu}_{2a})](i\mathbf{E}^- \times \mathbf{E}^+) \quad (30)$$

with

$$p_1(\omega) = \frac{\omega(\omega_1^2 - \omega^2 - \Gamma_1^2)}{(\omega_1^2 - \omega^2 + \Gamma_1^2)^2 + 4\omega^2 \Gamma_1^2} \quad (31)$$

$$p_2(\omega) = \frac{\omega(\omega_2^2 - \omega^2 - \Gamma_2^2)}{(\omega_2^2 - \omega^2 + \Gamma_2^2)^2 + 4\omega^2 \Gamma_2^2}. \quad (32)$$

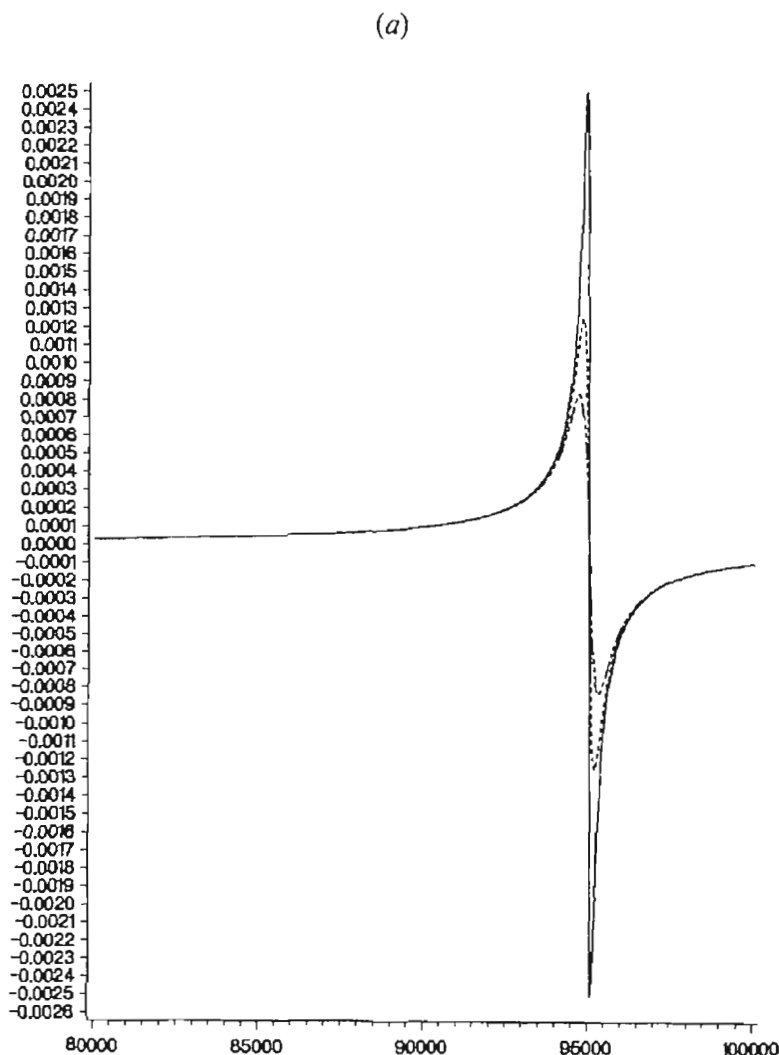


Figure 5. The function $\tilde{p}_i(\tilde{\omega})$ (in cm) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}): (a) $\tilde{p}_1(\tilde{\omega})$ for $\tilde{\omega}_1 = 95\,000\text{ cm}^{-1}$ and $\Gamma_1 = 100, 200, 300\text{ cm}^{-1}$; (b) $\tilde{p}_2(\tilde{\omega})$ for $\tilde{\omega}_2 = 140\,000\text{ cm}^{-1}$ and $\Gamma_2 = 100, 200, 300\text{ cm}^{-1}$.

We notice that $p_1(\omega)$ depends only on ω_1 and Γ_1 , $p_2(\omega)$ only on ω_2 and Γ_2 . This contrasts with the situation shown by the functions $f_1(\omega)$, $f_2(\omega)$, $f_3(\omega)$ (equations (C.1–C.3)), of which each depends both on ω_1 , Γ_1 and ω_2 , Γ_2 . The frequency dependence is illustrated in figure 5(a, b) (instead of $p_1(\omega)$ and $p_2(\omega)$ we have calculated and plotted $\tilde{p}_1(\tilde{\omega}) = cp_1(\omega)$ and $\tilde{p}_2(\tilde{\omega}) = cp_2(\omega)$ given in cm if $\tilde{\omega} = \omega/c$ is in cm^{-1}).

As in the diamagnetic case, there are nonzero paramagnetic contributions for both resonance conditions ($\omega = \omega_1$ and $\omega = \omega_2$), and they are of the order of the effect (paramagnetic part) far from resonances.

From figure 5(a, b) one can see that functions $\tilde{p}_i(\tilde{\omega})$ (and correspondingly $p_i(\omega)$) are largely insensitive to resonance frequency but depend strongly on the damping factor Γ . The calculation, for example, for a resonance frequency $\tilde{\omega} = 32\,000\text{ cm}^{-1}$ gives the same curves as presented in figure 5 (the difference is imperceptible on the graphs, and amounts to about 0.4%).

5. Conclusion

Our results represent an extension of the molecular theory of the inverse Faraday effect to the region of optical resonance. We have shown that the diamagnetic as well

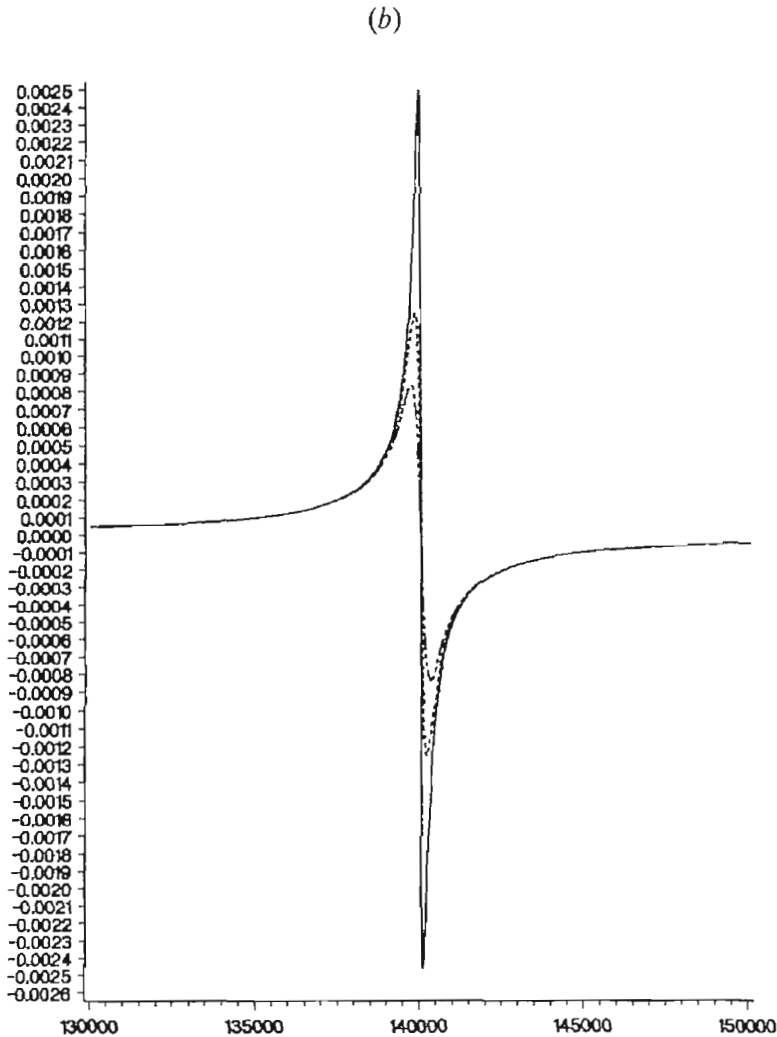


Figure 5 (continued).

as the paramagnetic contributions increase rapidly close to the optical resonance and that their frequency dependences are anomalous in that region.

Since far from an optical resonance (when damping may be neglected) the tensor for the inverse Faraday effect is analogous to that for the ordinary Faraday effect, which for diamagnetic molecules like benzene or carbon disulfide is of the order of $10^{-45} \text{ Am}^4 \text{ V}^{-2}$ [21] (the density number $N \sim 10^{28} \text{ m}^{-3}$) we obtain the magnetization $M \sim 10^{-17} E_0^2$ (given in Am^{-1} if E_0 is in Vm^{-1}). In the present case a Q-switched ruby laser producing a beam of intensity $I \sim 10^{11} - 10^{12} \text{ Wm}^{-2}$ ($E_0^2 \sim 10^{14} - 10^{15} \text{ V}^2 \text{ m}^{-2}$) induces the magnetization $10^{-3} - 10^{-2} \text{ Am}^{-1}$. Pershan *et al.* [9] observed a magnetization of a maximum magnitude of 0.01 Am^{-1} (using a laser with a pulse intensity of the order of 10^{11} Wm^{-2}) in doped glasses and in diamagnetic liquids at room temperature.

Our results show that the experiment should be much more promising if the laser frequency is tuned close to the optical resonance of the molecular system. It may also be of interest to detect the change of the sign of the contribution to the magnetization inside a particular resonance.

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Appendix A

From the equation for the density matrix or from the corresponding diagrams [4, 19, 23] we have:

$$\begin{aligned}
 {}^m\alpha_{ijk}^{cc}(0; \omega, -\omega) = & \frac{1}{\hbar^2} \sum_{abc} \rho_{aa}^{(0)} \left\{ \frac{(m_i)_{ac}(\mu_k)_{cb}(\mu_j)_{ba}}{(\omega_{ca} - i\Gamma_{ca})(\omega_{ba} - \omega - i\Gamma_{ba})} \right. \\
 & + \frac{(m_i)_{ac}(\mu_j)_{cb}(\mu_k)_{ba}}{(\omega_{ca} - i\Gamma_{ca})(\omega_{ba} + \omega - i\Gamma_{ba})} + \frac{(\mu_j)_{ac}(\mu_k)_{cb}(m_i)_{ba}}{(\omega_{ba} + i\Gamma_{ba})(\omega_{ca} + \omega + i\Gamma_{ca})} \\
 & + \frac{(\mu_k)_{ac}(\mu_j)_{cb}(m_i)_{ba}}{(\omega_{ba} + i\Gamma_{ba})(\omega_{ca} - \omega + i\Gamma_{ca})} + \frac{(\mu_j)_{ac}(m_i)_{cb}(\mu_k)_{ba}}{(\omega_{ba} + \omega - i\Gamma_{ba})(\omega_{ca} + \omega + i\Gamma_{ca})} (1 + K) \\
 & \left. + \frac{(\mu_k)_{ac}(m_i)_{cb}(\mu_j)_{ba}}{(\omega_{ba} - \omega - i\Gamma_{ba})(\omega_{ca} - \omega + i\Gamma_{ca})} (1 + K) \right\}, \quad (A 1)
 \end{aligned}$$

where $(m_i)_{ba} = \langle b|m_i|a\rangle$ and $(\mu_j)_{cb} = \langle c|\mu_j|b\rangle$ denote magnetic dipole and electric dipole transitions between the states $|a\rangle$ and $\langle b|$ or $|b\rangle$ and $\langle c|$, respectively, $\rho_{aa}^{(0)}$ is the quantum mean value of the unperturbed density matrix in the stationary state $|a\rangle$, Γ_{ba}^{-1} a characteristic relaxation time between the states $|b\rangle$ and $|a\rangle$, and

$$K = \frac{i(\Gamma_{bc} - \Gamma_{ba} - \Gamma_{ca})}{\omega_{bc} - i\Gamma_{bc}} \quad (A 2)$$

is a correction term which can be neglected in cases where the damping terms are small relative to the frequency ω_{bc} , and which vanishes in the absence of damping, or if $\Gamma_{bc} = \Gamma_{ba} + \Gamma_{ca}$. We can also use the energy perturbation technique [22] for calculation of the polarizability ${}^m\alpha^{cc}(0; \omega, -\omega)$, which leads to equation (A 1) but without the correction term K (as in the case of other hyperpolarizabilities [23]).

For molecules with complex wavefunctions, expression (A 1) can be written in the

form of equation (3) with

$$\begin{aligned}
{}^m\hat{\gamma}_{ijk}^{ec}(0; \omega, -\omega) &= \frac{1}{\hbar^2} \sum_{abc} \rho_{aa}^{(0)} \left\{ \frac{\text{Im} [(m_i)_{ac}(\mu_k)_{cb}(\mu_j)_{ba}]}{(\omega_{ca} - i\Gamma_{ca})(\omega_{ba} - \omega - i\Gamma_{ba})} \right. \\
&+ \frac{\text{Im} [(m_i)_{ac}(\mu_j)_{cb}(\mu_k)_{ba}]}{(\omega_{ca} - i\Gamma_{ca})(\omega_{ba} + \omega - i\Gamma_{ba})} + \frac{\text{Im} [(\mu_j)_{ac}(\mu_k)_{cb}(m_i)_{ba}]}{(\omega_{ba} + i\Gamma_{ba})(\omega_{ca} + \omega + i\Gamma_{ca})} \\
&+ \frac{\text{Im} [(\mu_k)_{ac}(\mu_j)_{cb}(m_i)_{ba}]}{(\omega_{ba} + i\Gamma_{ba})(\omega_{ca} - \omega + i\Gamma_{ca})} + \frac{\text{Im} [(\mu_j)_{ac}(m_i)_{cb}(\mu_k)_{ba}]}{(\omega_{ba} + \omega - i\Gamma_{ba})(\omega_{ca} + \omega + i\Gamma_{ca})} (1 + K) \\
&\left. + \frac{\text{Im} [(\mu_k)_{ac}(m_i)_{cb}(\mu_j)_{ba}]}{(\omega_{ba} - \omega - i\Gamma_{ba})(\omega_{ca} - \omega + i\Gamma_{ca})} (1 + K) \right\}. \quad (\text{A } 3)
\end{aligned}$$

Corresponding, ${}^m\hat{\beta}_{ijk}^{ec}(0; \omega, -\omega)$ is given by equation (A 3) after replacing the imaginary part of the product of matrix elements in the numerators by the real part.

For molecules with real wavefunctions, the polarizability ${}^m\hat{\gamma}^{ec}$ is given by equation (A 3) but ${}^m\hat{\beta}^{ec} = 0$. (In this case the product of matrix elements of the type $[(\mu)_{ac}(\mu)_{cb}(m)_{ba}]$ is purely imaginary.)

The quantum mechanical expression for the susceptibility ${}^m\alpha^{ec}(0; -\omega, \omega)$ is obtained from equations (A 1) and (A 3) if one replaces ω by $-\omega$.

Appendix B

Since the electric dipole moment and magnetic dipole moment operators are Hermitian operators, we have

$$\text{Im} (\mathbf{m}_{ca} \cdot \boldsymbol{\mu}_{ab} \times \boldsymbol{\mu}_{bc}) = \text{Im} (\mathbf{m}_{ac} \cdot \boldsymbol{\mu}_{cb} \times \boldsymbol{\mu}_{ba}), \quad (\text{B } 1)$$

$$\text{Im} (\mathbf{m}_{bc} \cdot \boldsymbol{\mu}_{ca} \times \boldsymbol{\mu}_{ab}) = \text{Im} (\mathbf{m}_{cb} \cdot \boldsymbol{\mu}_{ba} \times \boldsymbol{\mu}_{ac}), \quad (\text{B } 2)$$

and equation (20) can be written in the form of equation (27) with

$$A_1 = \omega\omega_{ca}(\omega_{ba}^2 - \omega^2)q_c^0q_b, \quad (\text{B } 3)$$

$$A_2 = -\omega\Gamma_{ba}(\omega_{ca}\Gamma_{ba} + 2\omega_{ba}\Gamma_{ca})q_c^0q_b, \quad (\text{B } 4)$$

$$A_3 = \omega(\omega_{ba} + \omega_{ca})(\omega_{ba}^2 - \omega^2)(\omega_{ca}^2 - \omega^2)q_bq_c, \quad (\text{B } 5)$$

$$\begin{aligned}
A_4 &= \omega\{(\omega_{ba} + \omega_{ca})[\Gamma_{ba}^2(\omega_{ca}^2 - \omega^2) + \Gamma_{ca}^2(\omega_{ba}^2 - \omega^2) + 4\omega^2\Gamma_{ba}\Gamma_{ca} + \Gamma_{ba}^2\Gamma_{ca}^2] \\
&+ 2(\omega_{ba}\Gamma_{ca} - \omega_{ca}\Gamma_{ba})[\Gamma_{ba}(\omega_{ca}^2 - \omega^2 + \Gamma_{ca}^2) - \Gamma_{ca}(\omega_{ba}^2 - \omega^2 + \Gamma_{ba}^2)]\}q_bq_c, \\
\end{aligned} \quad (\text{B } 6)$$

$$\begin{aligned}
A_5 &= \omega\{(\Gamma_{ca} - \Gamma_{ba})[(\omega_{ba}^2 - \omega^2 + \Gamma_{ba}^2)(\omega_{ca}^2 - \omega^2 + \Gamma_{ca}^2) + 4\omega^2\Gamma_{ba}\Gamma_{ca}] \\
&+ 2(\omega_{ba}\omega_{ca} + \omega^2 + \Gamma_{ba}\Gamma_{ca})[\Gamma_{ca}(\omega_{ba}^2 - \omega^2 + \Gamma_{ba}^2) - \Gamma_{ba}(\omega_{ca}^2 - \omega^2 + \Gamma_{ca}^2)]\}q_bq_c, \\
\end{aligned} \quad (\text{B } 7)$$

and where

$$q_c^0 = (\omega_{ca}^c + \Gamma_{ca}^2)^{-1}, \quad (\text{B } 8)$$

$$q_b = [(\omega_{ba}^2 - \omega^2 + \Gamma_{ba}^2)^2 + 4\omega^2\Gamma_{ba}^2]^{-1}, \quad (\text{B } 9)$$

$$q_c = [(\omega_{ca}^2 - \omega^2 + \Gamma_{ca}^2)^2 + 4\omega^2\Gamma_{ca}^2]^{-1}. \quad (\text{B } 10)$$

Appendix C

If we apply relation (B 2) to a three-level system, we may write equation (27) in the

form of equation (28) with the frequency dependent functions

$$f_1(\omega) = \omega[\omega_2(\omega_1^2 - \omega^2) - \Gamma_1(\omega_2\Gamma_1 + 2\omega_1\Gamma_2)]q_2^0q_1, \quad (\text{C } 1)$$

$$f_2(\omega) = \omega[\omega_1(\omega_2^2 - \omega^2) - \Gamma_2(\omega_1\Gamma_2 + 2\omega_2\Gamma_1)]q_1^0q_2, \quad (\text{C } 2)$$

$$f_3(\omega) = \omega \sum_{i \neq j=1,2} \{(\omega_i - \omega)^2[\omega_i(\omega_j^2 - \omega^2) + \Gamma_j^2(\omega_i + \omega_j) + 2\Gamma_j(\omega_j\Gamma_i - \omega_i\Gamma_j)] \\ + \Gamma_i\Gamma_j[\omega_i(4\omega^2 + \Gamma_i\Gamma_j) + 2\Gamma_j(\omega_i\Gamma_j - \omega_j\Gamma_i)]\}q_iq_j, \quad (\text{C } 3)$$

where q_i^0 and q_i are given by equations (B 8–B 10), and the simplified notation is used: $\omega_i \equiv \omega_{i_a}$, $\Gamma_i \equiv \Gamma_{i_a}$.

Appendix D

The general summation Σ_{abc} in equation (27) contains the triple sum $\Sigma_{(a \neq b)/(b \neq c)/(c \neq a)}$ and the double sum $\Sigma_{(a \neq b)/(b=c)}$. The first sum leads for the three-level system to equation (28). The contribution to $M(0)$ from the latter has the form

$$M = \frac{N}{3\hbar^2} \sum_{a,b \neq a} \rho_{aa}^{(0)} [2d_b(\omega)\mu_{bb} \cdot \text{Im}(\mu_{ab} \times m_{ba}) \\ + r_b(\omega)m_{bb} \cdot \text{Im}(\mu_{ba} \times \mu_{ab})](iE^- \times E^+) \quad (\text{D } 1)$$

where

$$d_b(\omega) = \frac{\omega\omega_{ba}(\omega_{ba}^2 - \omega^2 - 3\Gamma_{ba}^2)}{(\omega_{ba}^2 + \Gamma_{ba}^2)[(\omega_{ba}^2 - \omega^2 + \Gamma_{ba}^2)^2 + 4\omega^2\Gamma_{ba}^2]}, \quad (\text{D } 2)$$

$$r_b(\omega) = \frac{2\omega\omega_{ba}}{(\omega_{ba}^2 - \omega^2 + \Gamma_{ba}^2)^2 + 4\omega^2\Gamma_{ba}^2}. \quad (\text{D } 3)$$

The function $d_b(\omega)$ has a shape similar to that of $p_b(\omega)$ given by equations (31) and (32) and shown in figure 5. At the resonance

$$d_b(\omega = \omega_{ba}) \cong -\frac{3}{4\omega_{ba}^2}.$$

The function $r_b(\omega)$ exhibits the shape of an absorption curve with the maximum at the resonance $\omega = \omega_{ba}$

$$r_b(\omega = \omega_{ba}) = \frac{1}{2\Gamma_{ba}^2}.$$

Equations (D 1–D 3) can be adapted to the three-level system considered in this paper if we put $\rho_{aa}^{(0)} = 1$ and sum over excited states 1 and 2 ($b = 1, 2$). Contribution (D 1) depends, in this case, on off-diagonal elements of the electric dipole and magnetic dipole transition matrices between the ground state and excited states, and on the diagonal elements of these matrices for the excited states.