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MOLECULAR PHYSICS, 1992, VOL. 75, NO. 1, 99–125

Optically induced static magnetization near optical resonances in molecular systems. 2. Inverse magnetochiral birefringence

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(*Received 26 June 1991; accepted 3 September 1991*)

The static magnetization induced by unpolarized (or arbitrarily polarized) light in an isotropic medium composed of chiral molecules increases significantly in absolute magnitude near optical resonances. The magnetic dipole as well as electric quadrupole interaction with the radiation field have been taken into consideration to obtain analytical expressions for and numerical calculations of the effect. Dispersion curves of diamagnetic and paramagnetic contributions to the inverse magnetochiral birefringence are shown. Complete theoretical expressions for the nonlinear polarizabilities involved in the effect are presented and their properties discussed.

1. Introduction

The multipolar theory of electromagnetic polarization states that the optical properties of a molecular system undergo modification when an external electric or magnetic field is applied [1–5]. Thus, a static magnetic field directed along the propagation direction of circularly polarized light in an optically active isotropic medium induces a linear magnetorefractive effect [1, 6, 7]. The molecular theory of this effect, which describes the variation of the refractive index and the absorption coefficient, has been formulated for molecules with a nondegenerate or degenerate electronic ground state [8, 9]. It has been shown [9, 10] that the change in refractive index and in absorption coefficient in the presence of a static magnetic field applied along the direction of light propagation is not a circular differential effect, and that it can occur in optically active media for circularly, linearly, and unpolarized light, leading to magneto-chiral birefringence (MCHB) and magnetochiral dichroism (MCHD) [11, 12]. The molecular theory of MCHB and MCHD has been extended to the case of additional external static electric [13] or optical [14] fields for media composed of diamagnetic as well as paramagnetic molecules [15]. Both effects have also been considered in connection with parity violation in atoms [16].

As was recently shown [17], a coherent beam of light of arbitrary polarization travelling in a medium composed of randomly orientated chiral molecules induces a static magnetization parallel or antiparallel to the direction of propagation. The sign of the magnetization depends on the direction of propagation of the light as well as on the particular enantiomer of the chiral molecules, and changes by either reversing the propagation direction or replacing the chiral molecules by their enantiomers. This

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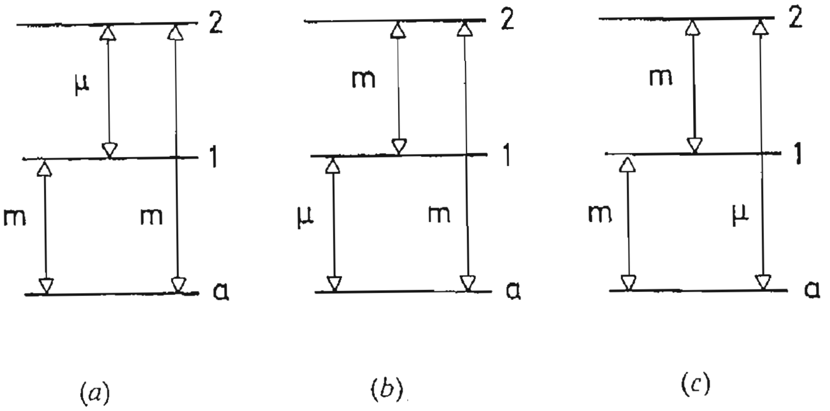


Figure 1. Diagrams for three level systems exhibiting magnetic dipole interaction with the radiation (equation (20)). The effect related to transitions (*a*), (*b*) and (*c*) is described by the functions $g_1(\omega)$, $g_2(\omega)$ and $g_3(\omega)$, respectively; μ denotes electric dipole and m magnetic dipole transitions.

nonlinear optical effect, in analogy to the inverse Faraday effect (IFE) [18–22], is named inverse magnetochiral birefringence (IMCHB). The role of molecular symmetry in IMCHB in nonabsorbing molecular systems has been discussed recently [23].

2. Diamagnetic contribution to the static magnetization

2.1. *Polarizability description*

A coherent beam of arbitrarily polarized light within electric and magnetic fields

$$\boldsymbol{E} = \hat{\boldsymbol{E}}^- + \hat{\boldsymbol{E}}^+ \equiv \boldsymbol{E}^- \mathrm{e}^{-i(\omega t - \boldsymbol{k}.\boldsymbol{r})} + \boldsymbol{E}^+ \mathrm{e}^{i(\omega t - \boldsymbol{k}.\boldsymbol{r})}, \tag{1}$$

$$\boldsymbol{B} = \hat{\boldsymbol{B}}^- + \hat{\boldsymbol{B}}^+ \equiv \boldsymbol{B}^- \mathrm{e}^{-i(\omega t - \boldsymbol{k}.\boldsymbol{r})} + \boldsymbol{B}^+ \mathrm{e}^{i(\omega t - \boldsymbol{k}.\boldsymbol{r})} \tag{2}$$

propagating in a molecular system induces electric and magnetic multipole moments [1–5, 24]. Since we are interested in the static magnetization induced in the medium by the nonlinear interaction with the radiation, it is sufficient to consider only the following terms for the induced magnetic dipole moment:

$$\begin{aligned} m_i(0) = {} & {}^{\mathrm{m}}\alpha^{\mathrm{em}}_{ijk}(0;\ \omega,\ -\omega)\hat{E}^-_j \hat{B}^+_k \\ & + {}^{\mathrm{m}}\alpha^{\mathrm{em}}_{ijk}(0;\ -\omega,\ \omega)\hat{E}^+_j \hat{B}^-_k + \tfrac{1}{3}{}^{\mathrm{m}}\alpha^{\mathrm{ee}}_{ijkl}(0;\ \omega,\ -\omega)\hat{E}^-_j \nabla_l \hat{E}^+_k \\ & + \tfrac{1}{3}{}^{\mathrm{m}}\alpha^{\mathrm{ee}}_{ijkl}(0;\ -\omega,\ \omega)\hat{E}^+_j \nabla_l \hat{E}^-_k , \end{aligned} \tag{3}$$

where ${}^{\mathrm{m}}\alpha^{\mathrm{em}}_{ijk}$ and ${}^{\mathrm{m}}\alpha^{\mathrm{ee}}_{ijkl}$ are the dipolar magnetic polarizabilities related to the electric dipole and magnetic dipole transitions (the former) or electric dipole and electric quadrupole transitions (the latter). The quantum mechanical form of these polarizabilities in the presence of damping can be calculated using a density matrix formalism (double Feynman diagrams) [25, 26] or an energy perturbation technique (single diagrams) [27]. In general, the polarizabilities ${}^{\mathrm{m}}\boldsymbol{\alpha}^{\mathrm{em}}$ and ${}^{\mathrm{m}}\boldsymbol{\alpha}^{\mathrm{ee}}$ may be split

$${}^{\mathrm{m}}\boldsymbol{\alpha}^{\mathrm{em}} = {}^{\mathrm{m}}\hat{\boldsymbol{\beta}}^{\mathrm{em}} + i\,{}^{\mathrm{m}}\hat{\boldsymbol{\gamma}}^{\mathrm{em}}, \tag{4}$$

$${}^{\mathrm{m}}\boldsymbol{\alpha}^{\mathrm{ee}} = {}^{\mathrm{m}}\hat{\boldsymbol{\beta}}^{\mathrm{ee}} + i\,{}^{\mathrm{m}}\hat{\boldsymbol{\gamma}}^{\mathrm{ee}}, \tag{5}$$

where ${}^{\mathrm{m}}\hat{\boldsymbol{\beta}}^{\mathrm{em}}$, ${}^{\mathrm{m}}\hat{\boldsymbol{\gamma}}^{\mathrm{em}}$, ${}^{\mathrm{m}}\hat{\boldsymbol{\beta}}^{\mathrm{ee}}$ and ${}^{\mathrm{m}}\hat{\boldsymbol{\gamma}}^{\mathrm{ee}}$ are all complex in the presence of damping, with the quantum mechanical forms given by equations (A1–A4) in appendix A. The electric quadrupole moment operator $\boldsymbol{Q}$ is traceless ($Q_{ii} = 0$) and symmetrical with respect to permutation of the indices ($Q_{ij} = Q_{ji}$); therefore, the coordinates of ${}^{\mathrm{m}}\boldsymbol{\alpha}^{\mathrm{ee}}$ fulfil the relations

$$\left.\begin{aligned} {}^{\mathrm{m}}\hat{\beta}^{\mathrm{cc}}_{ijkl} &= {}^{\mathrm{m}}\hat{\beta}^{\mathrm{cc}}_{ijlk} \\ {}^{\mathrm{m}}\hat{\gamma}^{\mathrm{cc}}_{ijkl} &= {}^{\mathrm{m}}\hat{\gamma}^{\mathrm{ce}}_{ijlk} \end{aligned}\right\}, \tag{6}$$

$${}^{\mathrm{m}}\hat{\beta}^{\mathrm{cc}}_{ijkk} = {}^{\mathrm{m}}\hat{\gamma}^{\mathrm{ee}}_{ijkk} = 0. \tag{7}$$

Since the operators $\boldsymbol{\mu}$, $\boldsymbol{m}$ and $\boldsymbol{Q}$ in equations (A1–A4) in appendix A are Hermitian operators, we have the very important relations

$${}^{\mathrm{m}}\alpha^{\mathrm{em}}_{ijk}(0;\, \omega, -\omega) = {}^{\mathrm{m}}\alpha^{\mathrm{em}*}_{ijk}(0;\, -\omega, \omega), \tag{8}$$

$${}^{\mathrm{m}}\alpha^{\mathrm{ee}}_{ijkl}(0;\, \omega, -\omega) = {}^{\mathrm{m}}\alpha^{\mathrm{ee}*}_{ijkl}(0;\, -\omega, \omega), \tag{9}$$

from which in particular we find (${}^{\mathrm{m}}\beta^{\mathrm{em}} \equiv \mathrm{Re}\,{}^{\mathrm{m}}\hat{\boldsymbol{\beta}}^{\mathrm{em}}$, ${}^{\mathrm{m}}\gamma^{\mathrm{cc}} \equiv \mathrm{Re}\,{}^{\mathrm{m}}\hat{\gamma}^{\mathrm{ce}}$)

$${}^{\mathrm{m}}\beta^{\mathrm{em}}_{ijk}(0;\, \omega, -\omega) = {}^{\mathrm{m}}\beta^{\mathrm{em}}_{ijk}(0;\, -\omega, \omega), \tag{10}$$

$${}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{ijkl}(0;\, \omega, -\omega) = -{}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{ijkl}(0;\, -\omega, \omega). \tag{11}$$

These relations are important for the calculation of the inverse magnetochiral birefringence.

For a macroscopic molecular system we express the magnetization as

$$\boldsymbol{M} = N\langle \boldsymbol{m}(\boldsymbol{E}, \boldsymbol{B})\rangle, \tag{12}$$

where N is the number of molecules per unit volume; $\langle\ \rangle$ stands for the statistical average. After space-averaging equation (12), taking into account equations (3–11), we have

$$M_{\mathrm{D}}(0) = \frac{N}{3c}\left[\varepsilon_{\alpha\beta\gamma}\,{}^{\mathrm{m}}\beta^{\mathrm{em}}_{\alpha\beta\gamma}(0;\, \omega, -\omega) + \frac{\omega}{5}\,{}^{\mathrm{m}}\gamma^{\mathrm{ee}}_{\alpha\beta\beta\alpha}(0;\, \omega, -\omega)\right](\boldsymbol{E}^{-}.\boldsymbol{E}^{+})\boldsymbol{s} \tag{13}$$

with $\boldsymbol{s}$ designating a unit vector along the propagation direction of the light. Furthermore, we have used the well known relations:

$$\nabla\hat{\boldsymbol{E}}^{\pm} = \mp i\frac{\omega}{c}\boldsymbol{s}\hat{\boldsymbol{E}}^{\pm}, \qquad \boldsymbol{E}^{-}\times\boldsymbol{B}^{+} = \boldsymbol{E}^{+}\times\boldsymbol{B}^{-} = \frac{1}{c}(\boldsymbol{E}^{-}.\boldsymbol{E}^{+})\boldsymbol{s}; \tag{14}$$

subscript D in (13) stands for 'diamagnetic contribution'. This effect occurs for chiral molecules only. Point group symmetry implies:

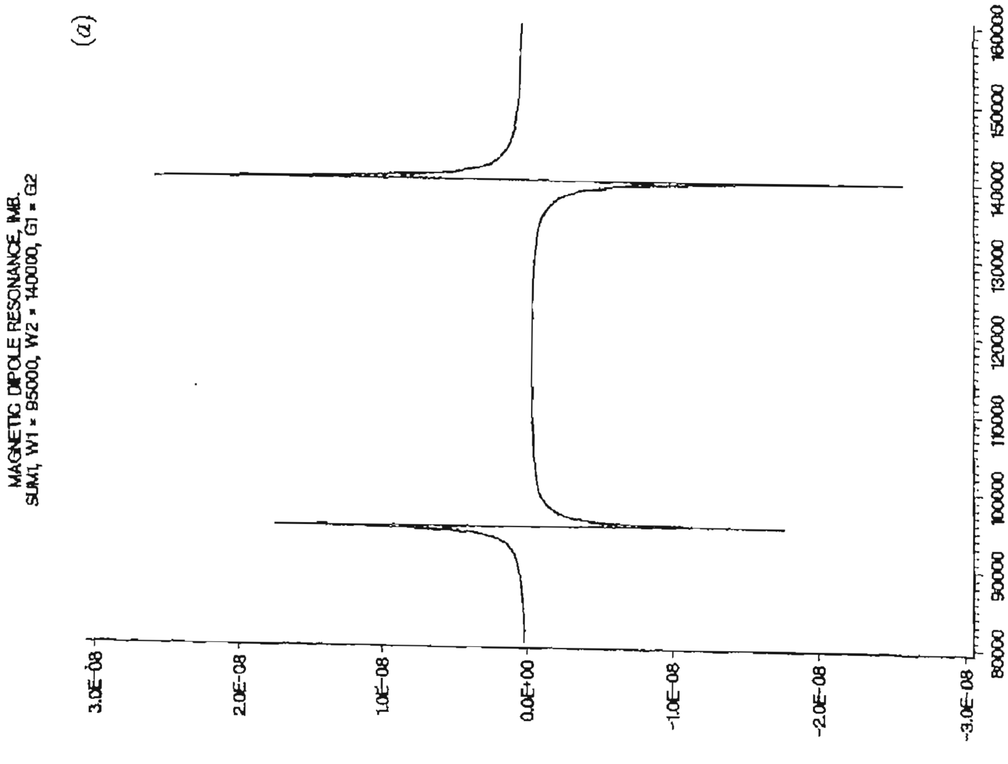
$$M_{\mathrm{D}} = 2\frac{N}{c}\left[{}^{\mathrm{m}}\beta^{\mathrm{em}}_{123} + \frac{\omega}{10}({}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{1111} + 2\,{}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{1221})\right](\boldsymbol{E}^{-}.\boldsymbol{E}^{+}) \tag{15a}$$

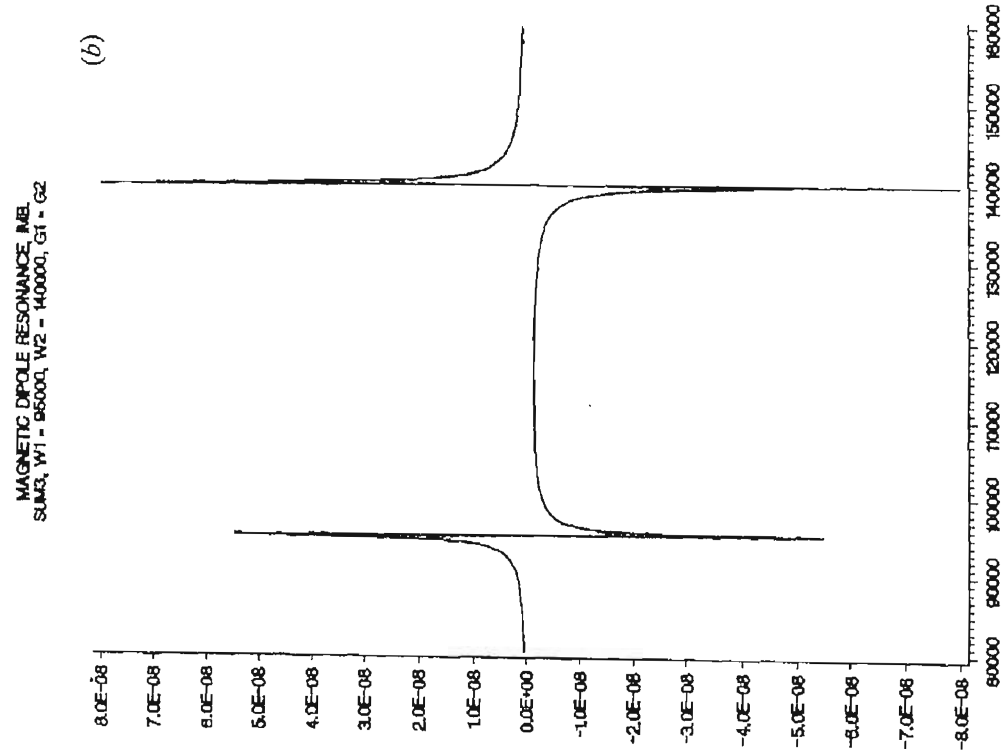
for molecules with the symmetries O, Y and K;

$$M_{\mathrm{D}} = \frac{N}{c}\left[{}^{\mathrm{m}}\beta^{\mathrm{cm}}_{123} - {}^{\mathrm{m}}\beta^{\mathrm{cm}}_{213} + \frac{\omega}{5}({}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{1111} + {}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{1221} + {}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{1331})\right](\boldsymbol{E}^{-}.\boldsymbol{E}^{+}) \tag{15b}$$

for molecules with the point group symmetry T;

$$\begin{aligned} M_{\mathrm{D}} = \frac{2N}{3c}\Big[&{}^{\mathrm{m}}\beta^{\mathrm{em}}_{123} + {}^{\mathrm{m}}\beta^{\mathrm{em}}_{231} + {}^{\mathrm{m}}\beta^{\mathrm{em}}_{312} \\ &+ \frac{\omega}{5}({}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{3333} + 2\,{}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{1111} + 2\,{}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{1221} + 2\,{}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{1331} + 2\,{}^{\mathrm{m}}\gamma^{\mathrm{cc}}_{3113})\Big](\boldsymbol{E}^{-}.\boldsymbol{E}^{+}) \end{aligned} \tag{15c}$$


MAGNETIC DIPOLE RESONANCE, IMB.
SUM1, W1 = 95000, W2 = 140000, G1 = G2


MAGNETIC DIPOLE RESONANCE, IMB.
SUM3, W1 = 95000, W2 = 140000, G1 = G2

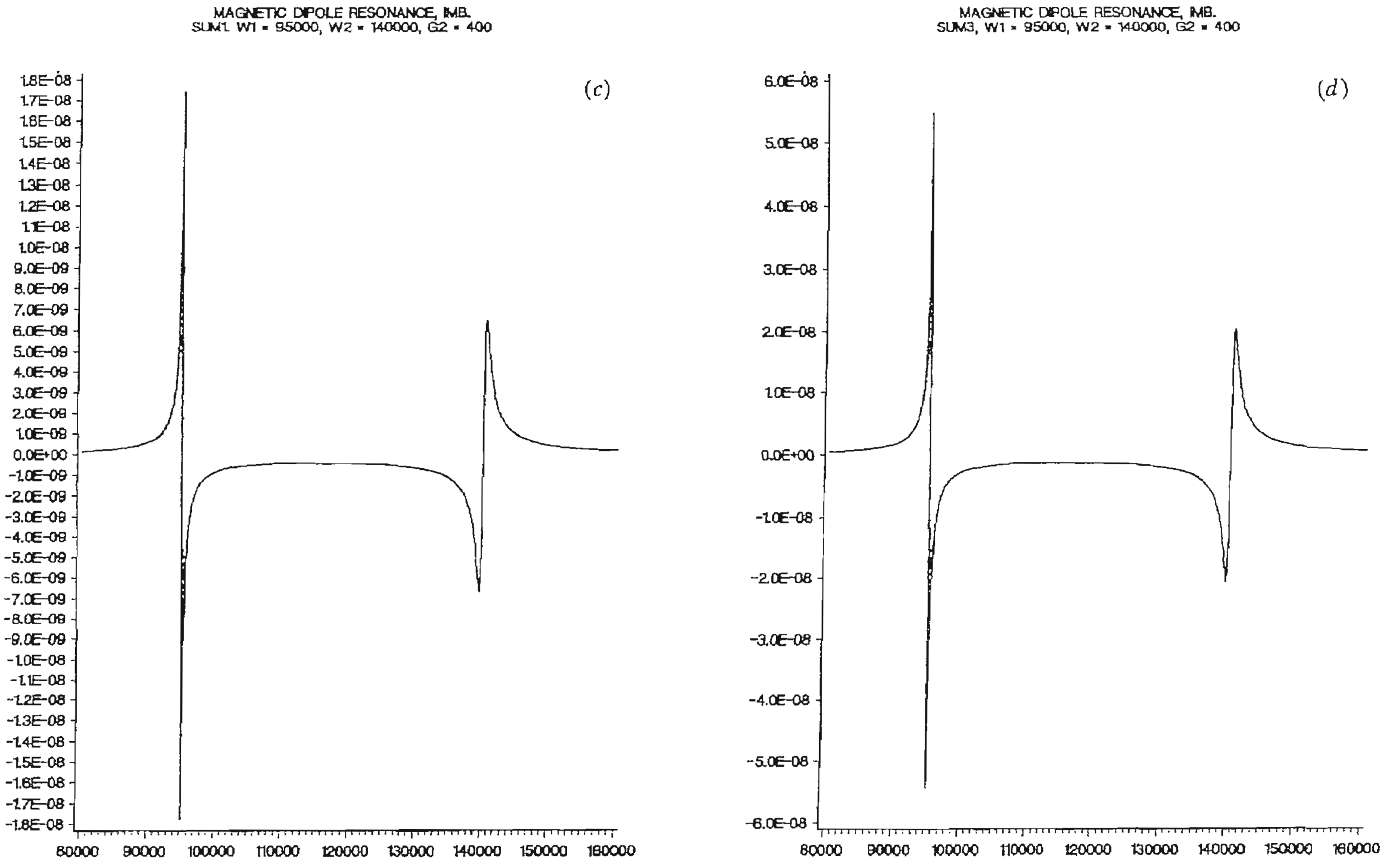
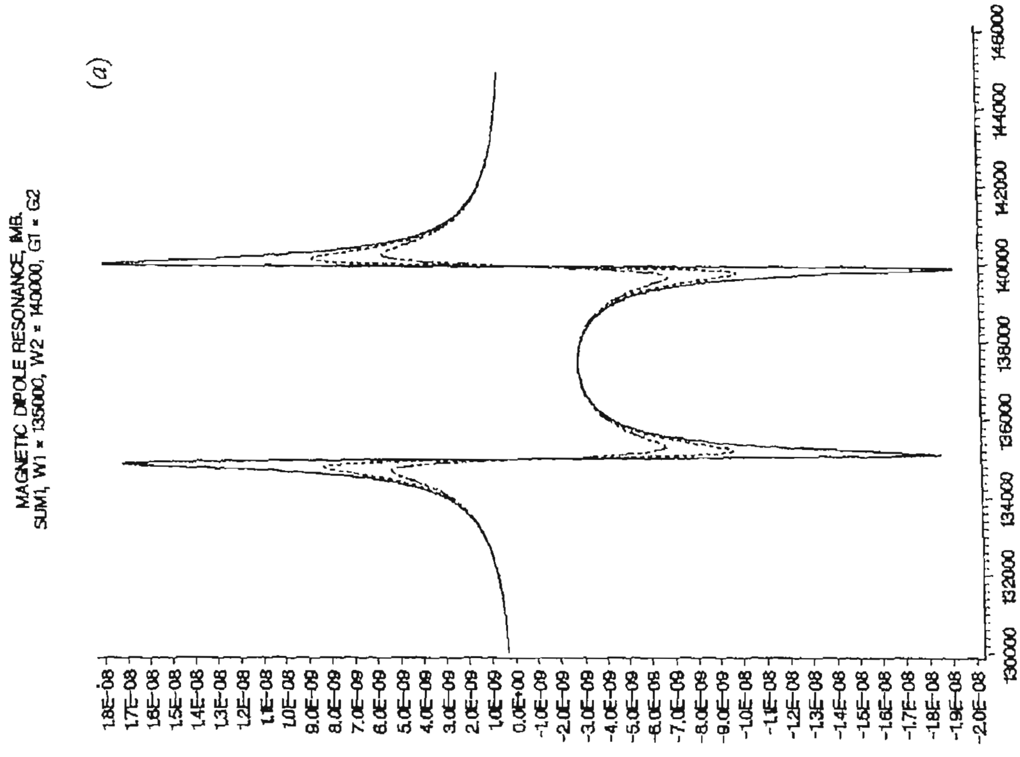


Figure 2. The function $\tilde{g}_n(\tilde{\omega})$ (in cm^2) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) for a three level system with resonances at $\tilde{\omega}_1 = 95\,000\,\mathrm{cm}^{-1}$ and $\tilde{\omega}_2 = 140\,000\,\mathrm{cm}^{-1}$. (*a*) $\tilde{g}_1(\tilde{\omega})$ for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


(a)
MAGNETIC DIPOLE RESONANCE, IMB.
SUM1, W1 = 135000, W2 = 140000, G1 = G2
1.8E-08
1.7E-08
1.6E-08
1.5E-08
1.4E-08
1.3E-08
1.2E-08
1.1E-08
1.0E-08
9.0E-09
8.0E-09
7.0E-09
6.0E-09
5.0E-09
4.0E-09
3.0E-09
2.0E-09
1.0E-09
0.0E+00
-1.0E-09
-2.0E-09
-3.0E-09
-4.0E-09
-5.0E-09
-6.0E-09
-7.0E-09
-8.0E-09
-9.0E-09
-1.0E-08
-1.1E-08
-1.2E-08
-1.3E-08
-1.4E-08
-1.5E-08
-1.6E-08
-1.7E-08
-1.8E-08
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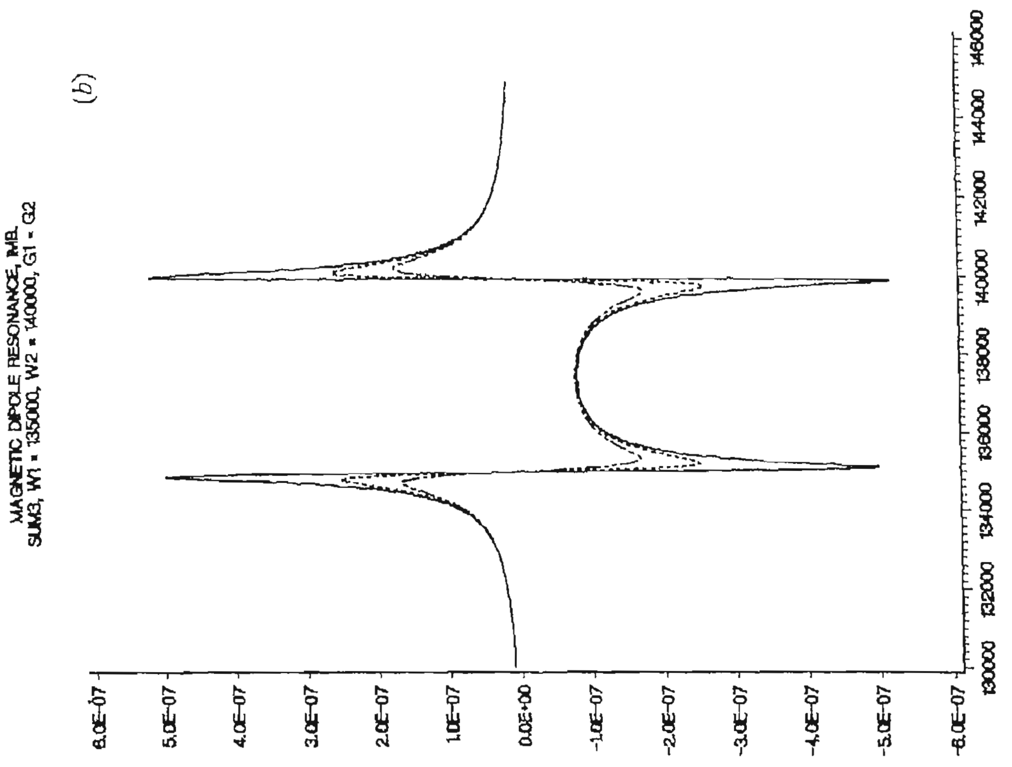
136000
138000
140000
142000
144000
146000


(b)
MAGNETIC DIPOLE RESONANCE, IMB.
SUM3, W1 = 135000, W2 = 140000, G1 - G2
6.0E-07
5.0E-07
4.0E-07
3.0E-07
2.0E-07
1.0E-07
0.0E+00
-1.0E-07
-2.0E-07
-3.0E-07
-4.0E-07
-5.0E-07
-6.0E-07
130000
132000
134000
136000
138000
140000
142000
144000
146000

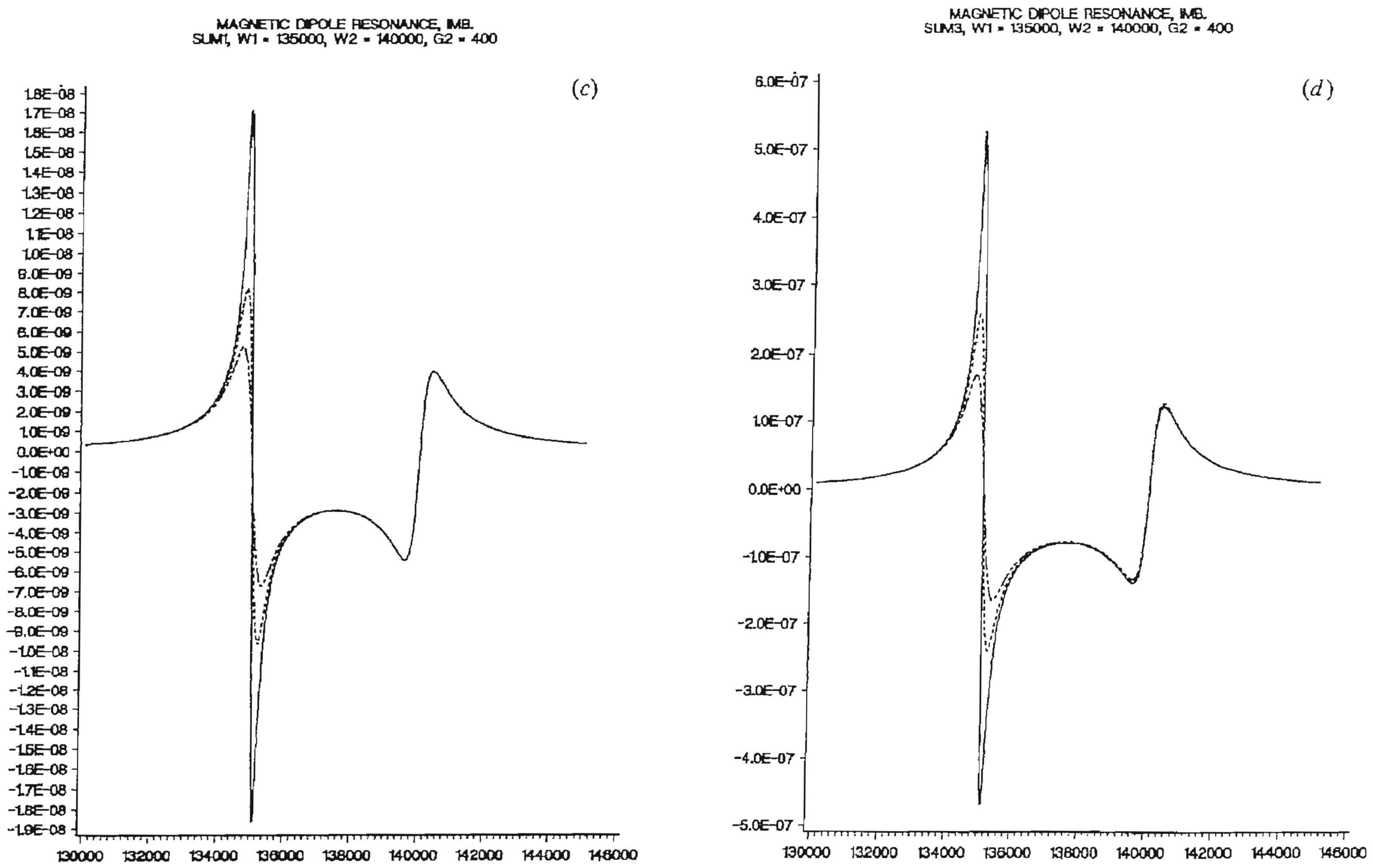
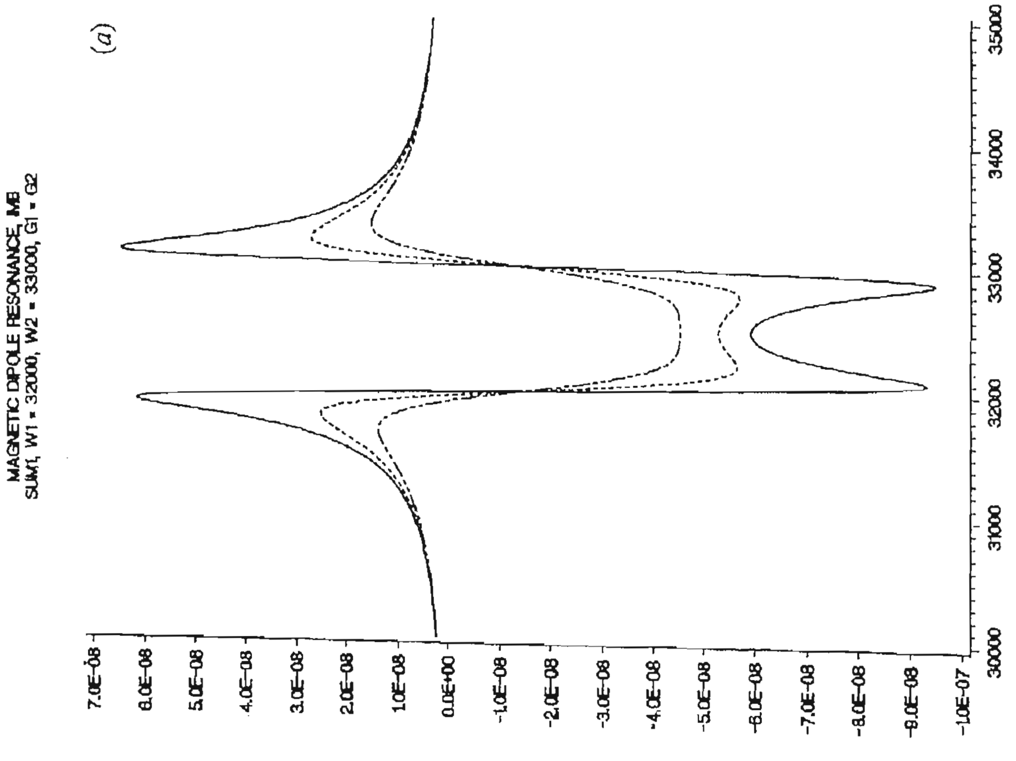
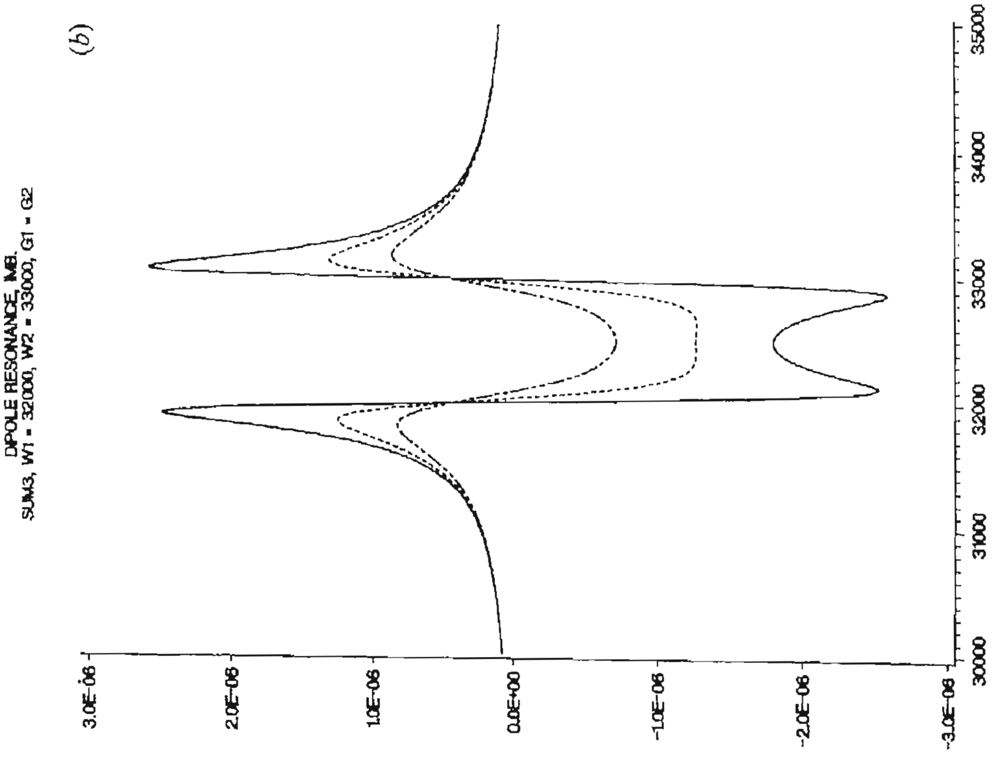


Figure 3. The functions $\tilde{g}_{n}(\tilde{\omega})$ (in cm^2) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) for a three level system with resonances at $\tilde{\omega}_1 = 135\,000\,\mathrm{cm}^{-1}$ and $\tilde{\omega}_2 = 140\,000\,\mathrm{cm}^{-1}$. (*a*) $\tilde{g}_1(\tilde{\omega})$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


(a)
MAGNETIC DIPOLE RESONANCE, MB
SUM1, W1 = 32000, W2 = 33000, G1 = G2
7.0E-08
6.0E-08
5.0E-08
4.0E-08
3.0E-08
2.0E-08
1.0E-08
0.0E+00
-1.0E-08
-2.0E-08
-3.0E-08
-4.0E-08
-5.0E-08
-6.0E-08
-7.0E-08
-8.0E-08
-9.0E-08
-1.0E-07
30000
31000
32000
33000
34000
35000


(b)
DIPOLE RESONANCE, MB.
SUM3, W1 = 32000, W2 = 33000, G1 = G2
3.0E-06
2.0E-06
1.0E-06
0.0E+00
-1.0E-06
-2.0E-06
-3.0E-06
30000
31000
32000
33000
34000
35000

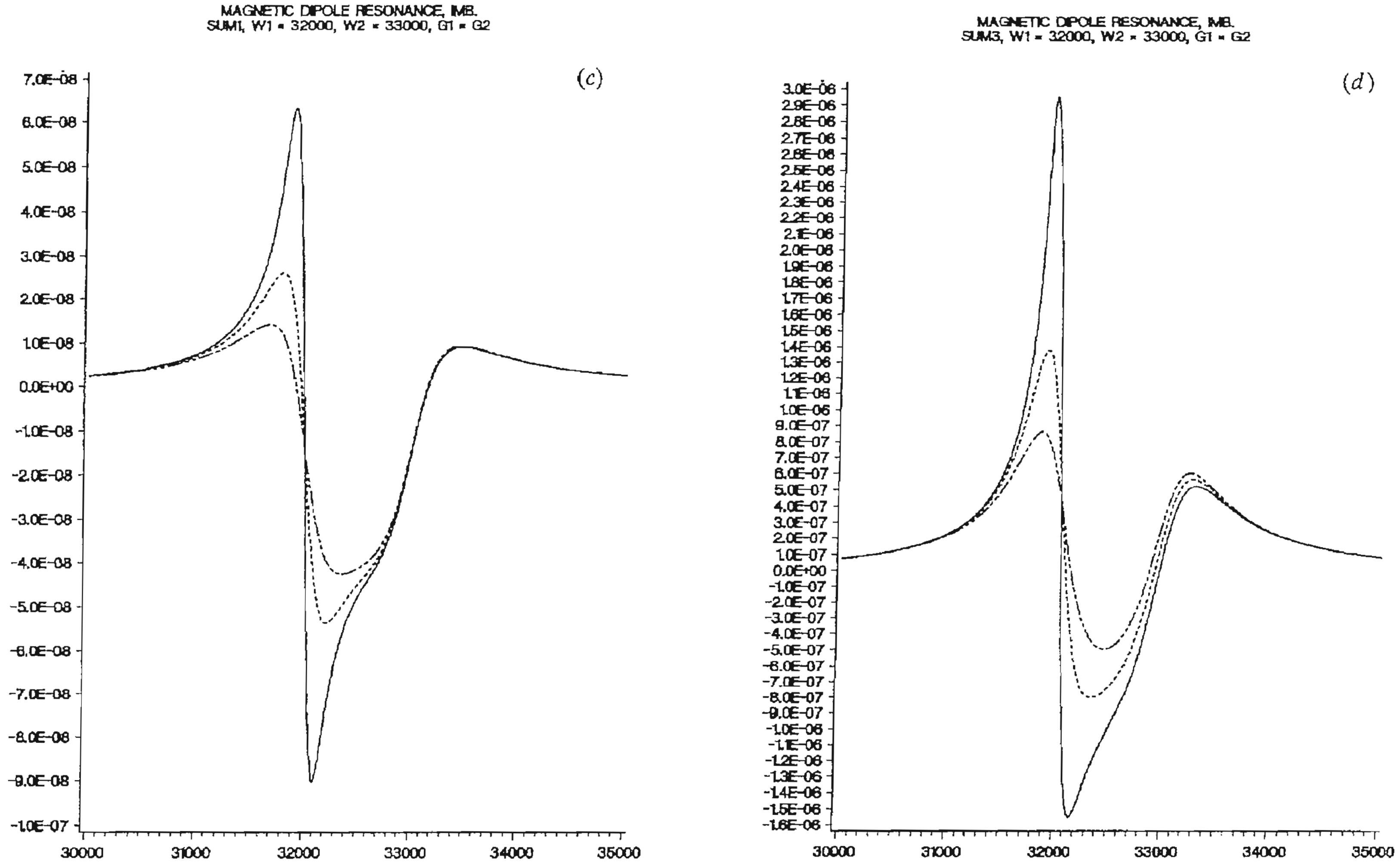
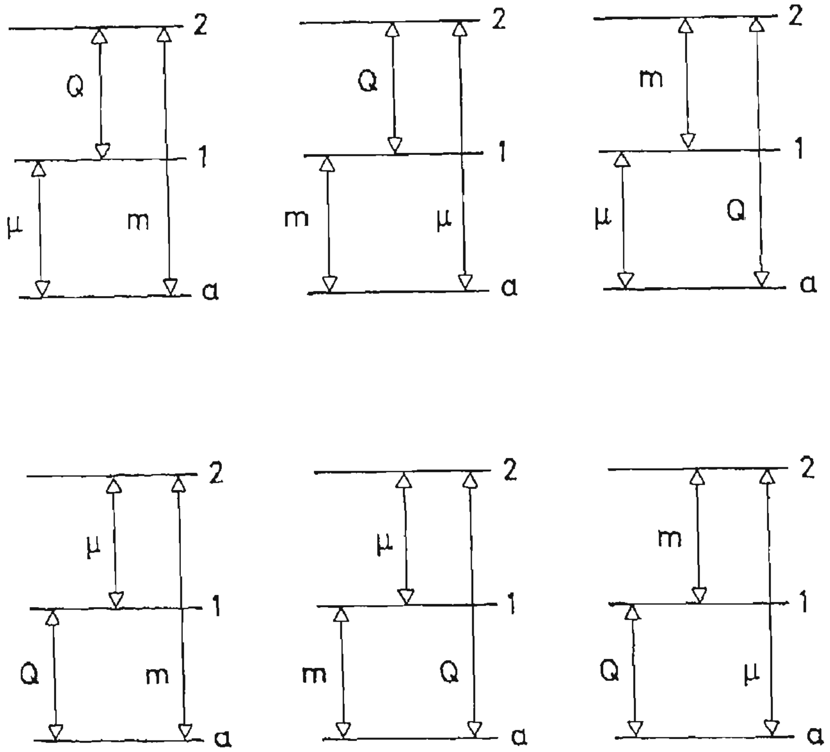


Figure 4. The functions $\tilde{g}_n(\tilde{\omega})$ (in cm^2) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) for a three level system with resonances at $\tilde{\omega}_1 = 32\,000\,\mathrm{cm}^{-1}$ and $\tilde{\omega}_2 = 33\,000\,\mathrm{cm}^{-1}$. (*a*) $\tilde{g}_1(\tilde{\omega})$ for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



(*a*) (*b*) (*c*)

Figure 5. Diagrams for three level systems exhibiting electric quadrupole interaction with the radiation (equation (24)). The effect related to transitions (*a*), (*b*) and (*c*) is described by the functions $h_1(\omega)$, $h_2(\omega)$ and $h_3(\omega)$, respectively; μ, m and Q denote electric dipole, magnetic dipole and electric quadrupole transitions, respectively.

for molecules with the symmetries C_3, C_4, C_6, C_∞, D_3, D_4 and D_6;

$$M_D = \frac{N}{3c}\Big[{}^{m}\beta^{em}_{123} + {}^{m}\beta^{em}_{231} + {}^{m}\beta^{em}_{312} - {}^{m}\beta^{em}_{132} - {}^{m}\beta^{em}_{213} - {}^{m}\beta^{em}_{321} + \frac{\omega}{5}\big({}^{m}\gamma^{ee}_{1111} + {}^{m}\gamma^{ee}_{2222} + {}^{m}\gamma^{ee}_{3333} + {}^{m}\gamma^{ee}_{1221} + {}^{m}\gamma^{ee}_{1331} + {}^{m}\gamma^{ee}_{2112} + {}^{m}\gamma^{ee}_{2332} + {}^{m}\gamma^{ee}_{3113} + {}^{m}\gamma^{ee}_{3223}\big)\Big](\boldsymbol{E}^{-}\cdot\boldsymbol{E}^{+}) \qquad (15d)$$

for the symmetries C_1, C_2 and D_2.

In reference [23], the magnetization induced by the inverse magnetochiral birefringence is described by the polarizabilities ${}^{e}\beta^{mm}_{ijk}(-\omega;\ \omega,\ 0)$ and ${}^{e}\gamma^{em}_{ijkl}(-\omega;\ \omega,\ 0)$ which, in the absence of damping, give results equivalent to equations (13–15). Since $(\boldsymbol{E}^{-}\cdot\boldsymbol{E}^{+})$ does not depend on the polarization of light but on the intensity of light only, effect (13) is independent of the polarization, in contrast to the inverse Faraday effect [22].

3. Frequency dependence of the diamagnetic contribution

3.1. *Magnetic dipole interaction with the radiation*

In this section we analyse the first term of equation (13) only: that means, the term related to the magnetic dipole interaction with the radiation described by the tensor

${}^{\mathrm{m}}\beta^{\mathrm{em}}(0;\,\omega,\,-\omega)$ and denoted now by $M_{\mathrm{D}}^{\mathrm{m}}(0)$:

$$M_{\mathrm{D}}^{\mathrm{m}}(0) = \frac{N}{3c}\,\varepsilon_{\alpha\beta\gamma}\,{}^{\mathrm{m}}\beta^{\mathrm{em}}_{\alpha\beta\gamma}(0;\,\omega,\,-\omega)\,(\boldsymbol{E}^-\,.\,\boldsymbol{E}^+)s \tag{16}$$

which, taking into account equation (A1) in appendix A, can be written in the form (see appendix B):

$$M_{\mathrm{D}}^{\mathrm{m}} = \frac{N}{3\hbar^2 c}\sum_{\mathrm{abc}}\rho^{(0)}_{\mathrm{aa}}\{(B_1 + B_2)\,[\mathrm{Re}(\boldsymbol{m}_{\mathrm{ac}}\,.\,\boldsymbol{\mu}_{\mathrm{cb}} \times \boldsymbol{m}_{\mathrm{ba}}) - \mathrm{Re}(\boldsymbol{m}_{\mathrm{ac}}\,.\,\boldsymbol{m}_{\mathrm{cb}} \times \boldsymbol{\mu}_{\mathrm{ba}})]$$
$$+ [(B_3 + B_4)\,(1 + K') + B_5 K'']\mathrm{Re}(\boldsymbol{m}_{\mathrm{ac}}\,.\,\boldsymbol{m}_{\mathrm{cb}} \times \boldsymbol{\mu}_{\mathrm{ba}})\}\,(\boldsymbol{E}^-\,.\,\boldsymbol{E}^+)s. \tag{17}$$

The coefficients B_n are even in ω, and their analytical form is given by equations (B3–B7) in appendix B; K' and K'' are the real and imaginary part of the correction term, equation (A5) in appendix A. For the effect without damping ($B_2 = B_4 = B_5 = K' = K'' = 0$)

$$M_{\mathrm{D}}^{\mathrm{m}} = \frac{N}{3\hbar^2 c}\sum_{\mathrm{abc}}\rho^{(0)}_{\mathrm{aa}}\left\{\frac{\omega^2(\omega_{\mathrm{ba}} + \omega_{\mathrm{ca}})}{\omega_{\mathrm{ca}}(\omega_{\mathrm{ba}}^2 - \omega^2)\,(\omega_{\mathrm{ca}}^2 - \omega^2)}\,\mathrm{Re}(\boldsymbol{m}_{\mathrm{ac}}\,.\,\boldsymbol{m}_{\mathrm{cb}} \times \boldsymbol{\mu}_{\mathrm{ba}})\right.$$
$$\left. + \frac{\omega_{\mathrm{ba}}}{\omega_{\mathrm{ca}}(\omega_{\mathrm{ba}}^2 - \omega^2)}\,\mathrm{Re}(\boldsymbol{m}_{\mathrm{ac}}\,.\,\boldsymbol{\mu}_{\mathrm{cb}} \times \boldsymbol{m}_{\mathrm{ba}})\right\}(\boldsymbol{E}^-\,.\,\boldsymbol{E}^+)s. \tag{18}$$

If, moreover, we assume that all molecules are in their ground state and we use the relation

$$2\sum_{\mathrm{bc}}\mathrm{Re}(\boldsymbol{m}_{\mathrm{ac}}\,.\,\boldsymbol{\mu}_{\mathrm{cb}} \times \boldsymbol{m}_{\mathrm{ba}})\,\frac{\omega_{\mathrm{ba}}}{\omega_{\mathrm{ca}}(\omega_{\mathrm{ba}}^2 - \omega^2)}$$
$$\equiv -\sum_{\mathrm{bc}}\frac{\omega(\omega_{\mathrm{ba}} + \omega_{\mathrm{ca}})}{\omega_{\mathrm{ba}}\omega_{\mathrm{ca}}(\omega_{\mathrm{ba}} + \omega)\,(\omega_{\mathrm{ca}} - \omega)}\,\mathrm{Re}(\boldsymbol{m}_{\mathrm{ac}}\,.\,\boldsymbol{\mu}_{\mathrm{cb}} \times \boldsymbol{m}_{\mathrm{ba}}), \tag{19}$$

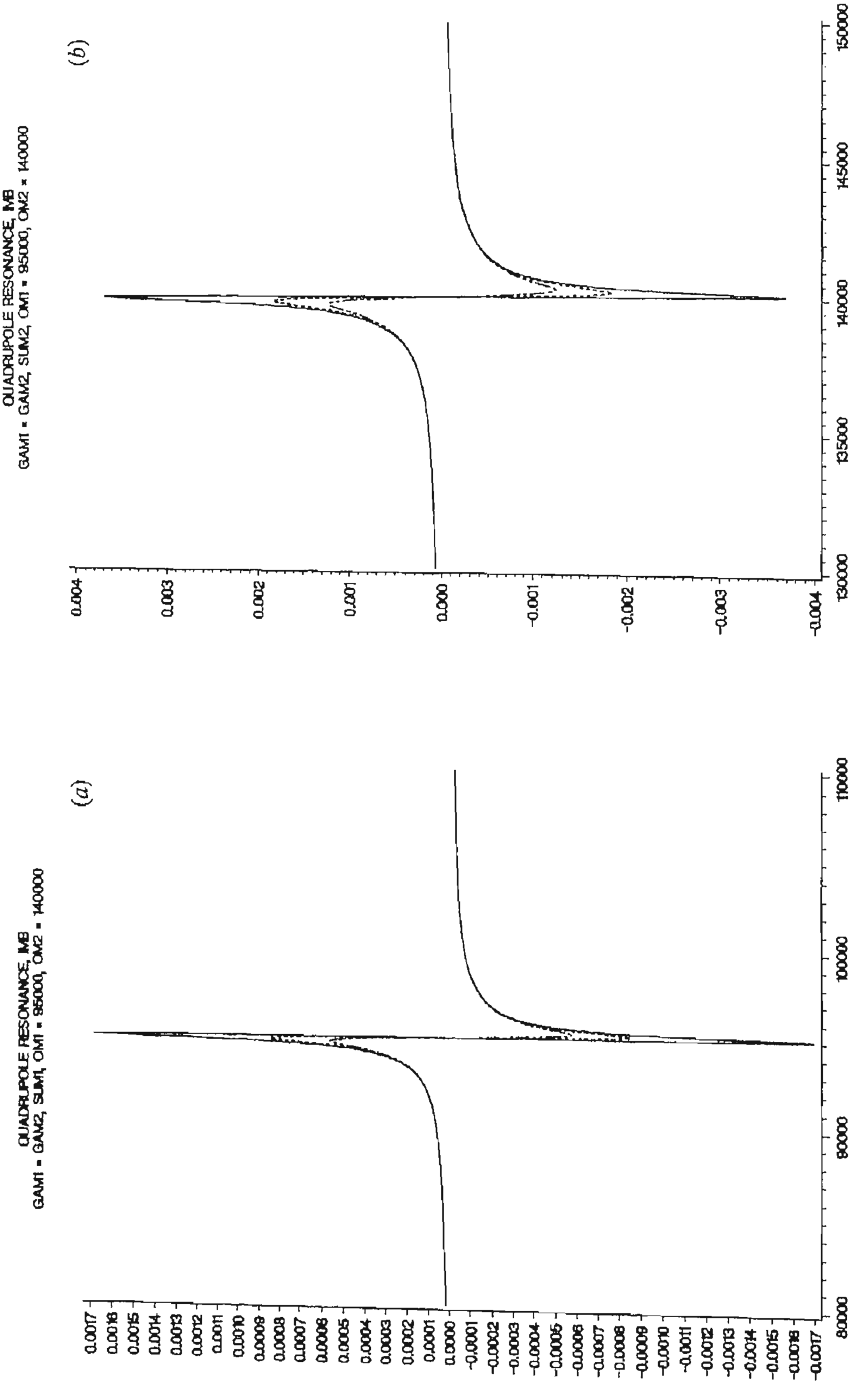
we have equation (18) in the form of equation (12) in [17].

Now we apply the general equation (17) to a three-level molecular system (a, the ground state; 1 and 2, the excited states) and we neglect the correction term K (see the discussion in appendix A). Assuming that all molecules are in their ground states, the static magnetization induced by arbitrarily polarized light is given by the following expression (for the contribution to $\boldsymbol{M}(0)$ from the diagonal transition matrix elements, see appendix D).

$$M_{\mathrm{D}}^{\mathrm{m}} = \frac{N}{3\hbar^2 c}\{g_1(\omega)\mathrm{Re}(\boldsymbol{m}_{\mathrm{a}2}\,.\,\boldsymbol{\mu}_{21} \times \boldsymbol{m}_{1\mathrm{a}}) + g_2(\omega)\mathrm{Re}(\boldsymbol{m}_{\mathrm{a}2}\,.\,\boldsymbol{m}_{21} \times \boldsymbol{\mu}_{1\mathrm{a}})$$
$$+ g_3(\omega)\mathrm{Re}(\boldsymbol{m}_{\mathrm{a}1}\,.\,\boldsymbol{m}_{12} \times \boldsymbol{\mu}_{2\mathrm{a}})\}\,(\boldsymbol{E}^-\,.\,\boldsymbol{E}^+)s, \tag{20}$$

where all frequency-dependent functions $g_n(\omega)$ are even in ω and their analytical forms are presented in appendix C. Figure 1 shows diagrams related to equation (20). We note that the first term in (20), (figure 1(*a*)) described by the function $g_1(\omega)$, is related to electric dipole transition moments between two excited states (and magnetic dipole transition moments between the ground state and the excited states), but the second and the third term, described by the functions $g_2(\omega)$ and $g_3(\omega)$, respectively, are related to magnetic dipole transition moments between two excited states.

As in the first part of this work [22], we have calculated and plotted the functions $\tilde{g}_n(\tilde{\omega}) = c^2 g_n(\omega)$ (with the dimension cm^2 if $\tilde{\omega} = \omega/c = 2\pi\tilde{\nu}$ is given in cm^{-1}, where c is the velocity of light) in absorption regions for different resonance frequencies ω_n and relaxation times Γ_n^{-1}.


(a)
QUADRUPOLE RESONANCE, MB
GAM1 = GAM2, SUM1, OM1 = 95000, OM2 = 140000
0.0017
0.0016
0.0015
0.0014
0.0013
0.0012
0.0011
0.0010
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
-0.0001
-0.0002
-0.0003
-0.0004
-0.0005
-0.0006
-0.0007
-0.0008
-0.0009
-0.0010
-0.0011
-0.0012
-0.0013
-0.0014
-0.0015
-0.0016
-0.0017
80000
80000
80000
100000
110000
(b)
QUADRUPOLE RESONANCE, MB
GAM1 = GAM2, SUM2, OM1 = 95000, OM2 = 140000
0.004
0.003
0.002
0.001
0.000
-0.001
-0.002
-0.003
-0.004
130000
135000
140000
145000
150000

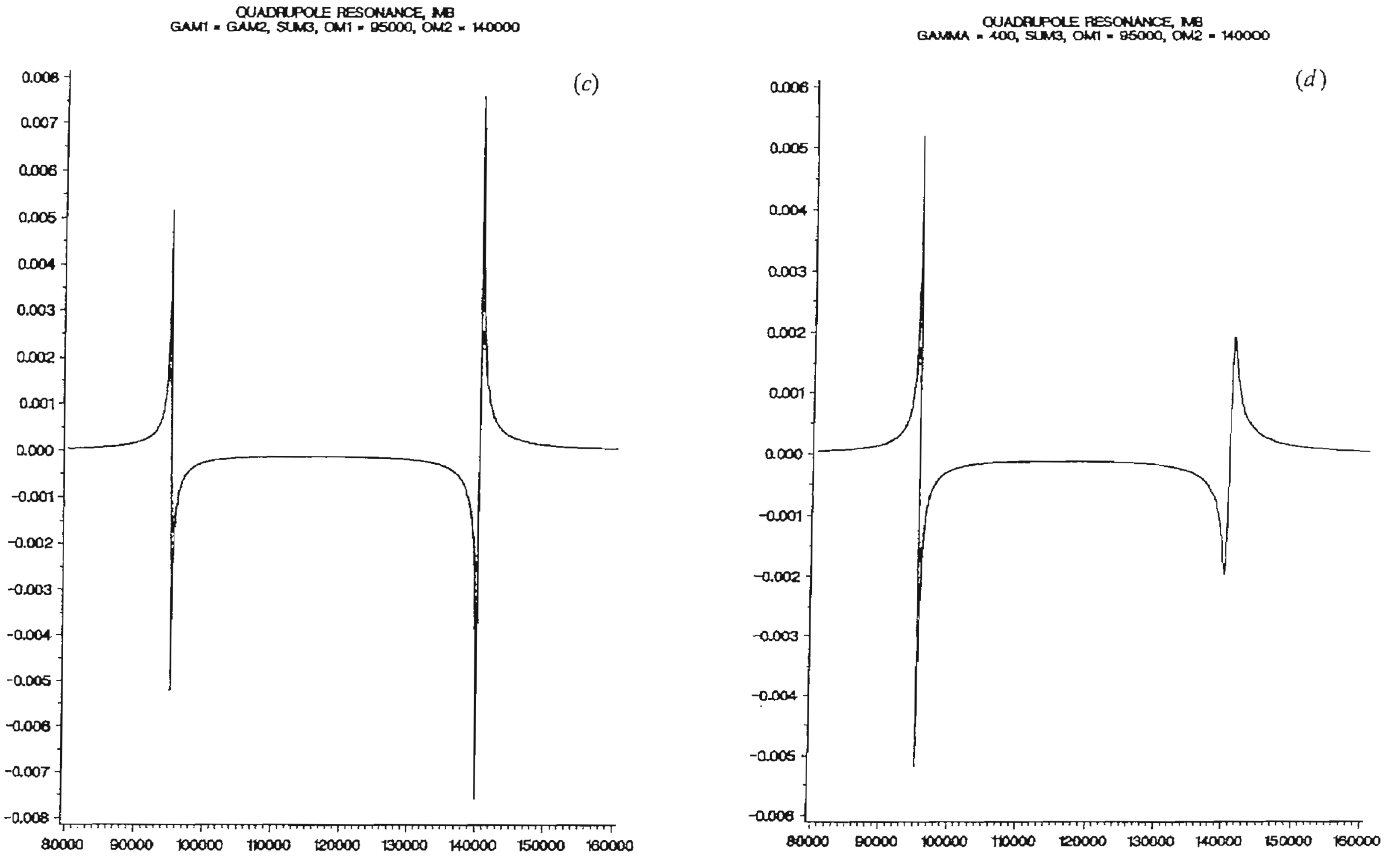
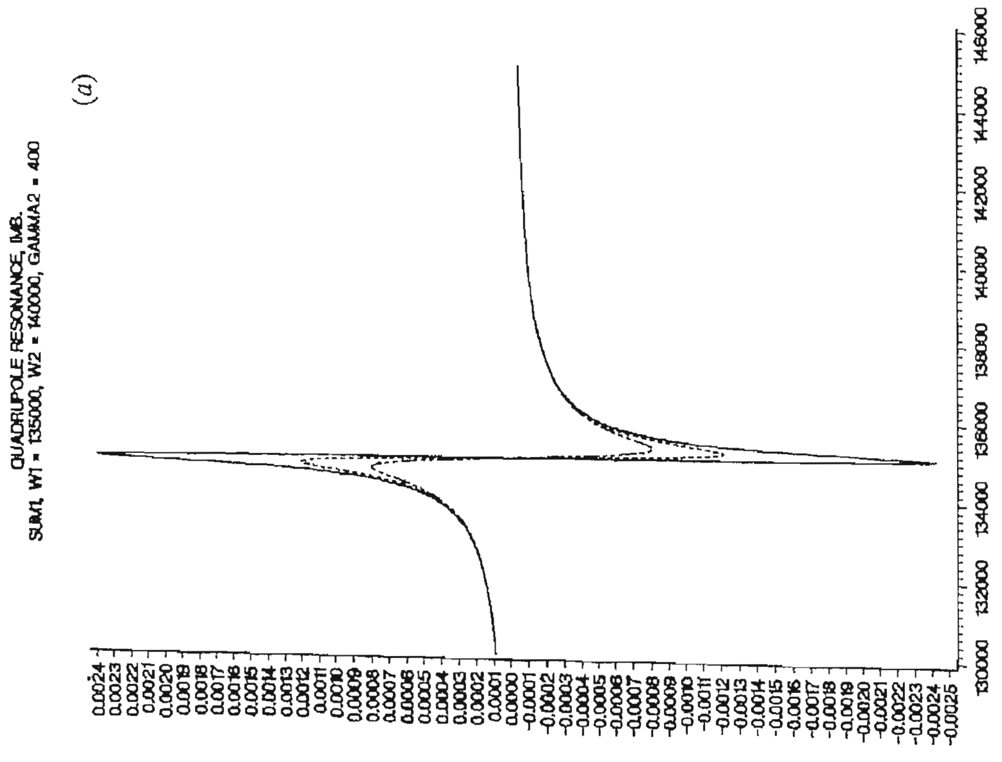
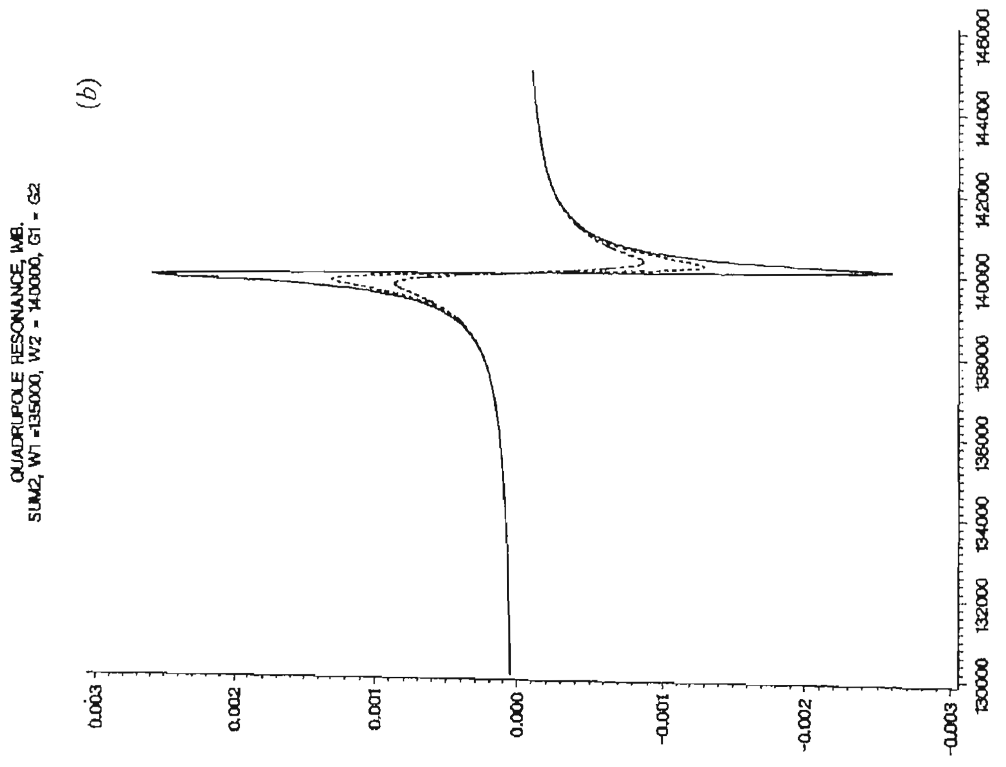


Figure 6. The functions $\tilde{h}_n(\tilde{\omega})$ (in cm) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) for a three level system with resonances at $\tilde{\omega}_1 = 95\,000\,\mathrm{cm}^{-1}$ and $\tilde{\omega}_2 = 140\,000\,\mathrm{cm}^{-1}$. (*a*) $\tilde{h}_1(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\,\mathrm{cm}^{-1}$; (*b*) $\tilde{h}_2(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\,\mathrm{cm}^{-1}$; (*c*) $\tilde{h}_3(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\,\mathrm{cm}^{-1}$; (*d*) $\tilde{h}_3(\tilde{\omega})$ for $\Gamma_1 = 100, 200, 300\,\mathrm{cm}^{-1}$, $\Gamma_2 = 400\,\mathrm{cm}^{-1}$.



QUADRUPOLE RESONANCE, IMB.
SUM1, W1 = 135000, W2 = 140000, GAMMA2 = 400
0.0024
0.0000
-0.0025
130000
132000
134000
136000
138000
140000
142000
144000
146000

(*a*)



QUADRUPOLE RESONANCE, WB.
SUM2, W1 =135000, W2 = 140000, G1 = G2
0.003
0.002
0.001
0.000
-0.001
-0.002
-0.003
130000
132000
134000
136000
138000
140000
142000
144000
146000

(*b*)

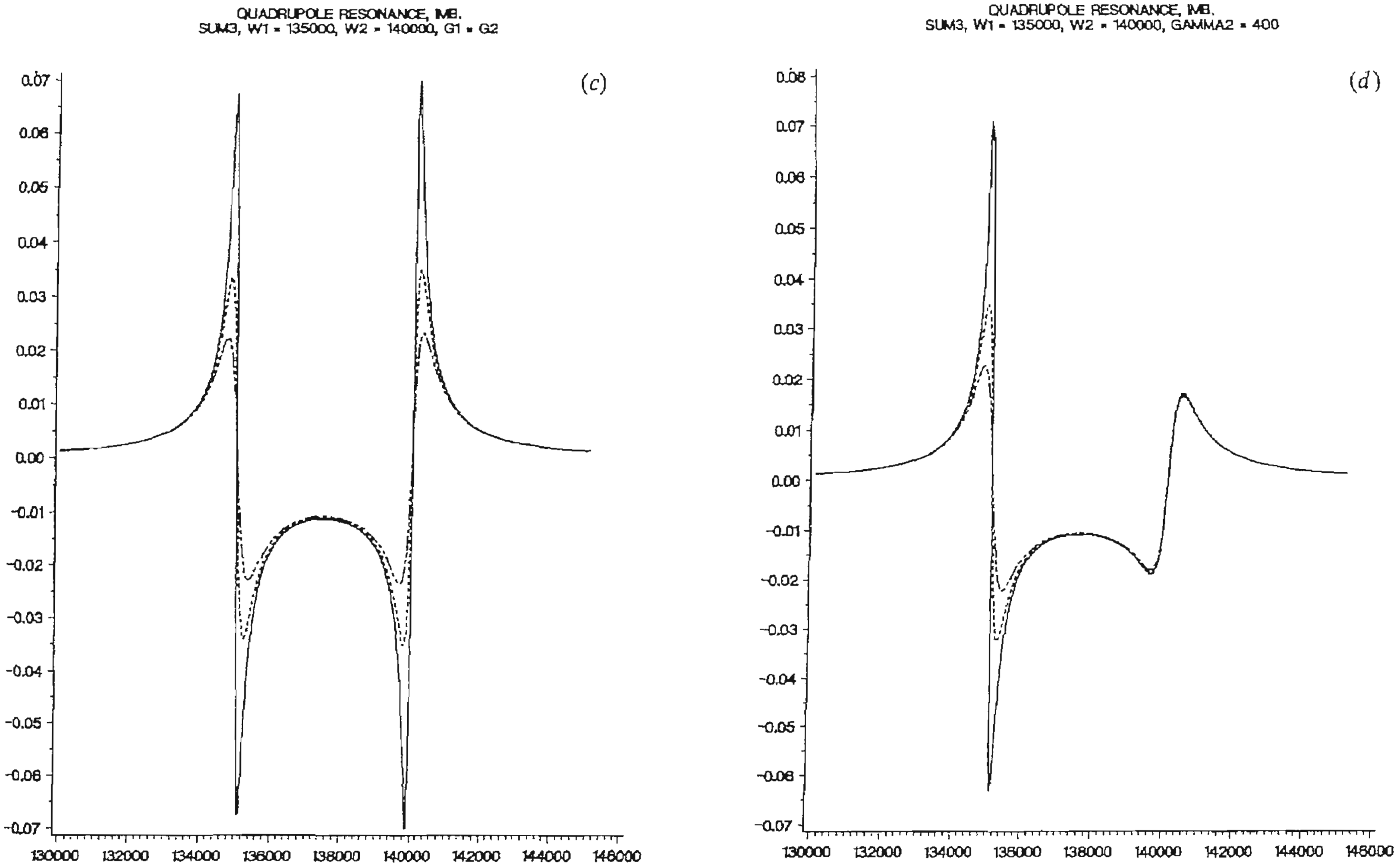
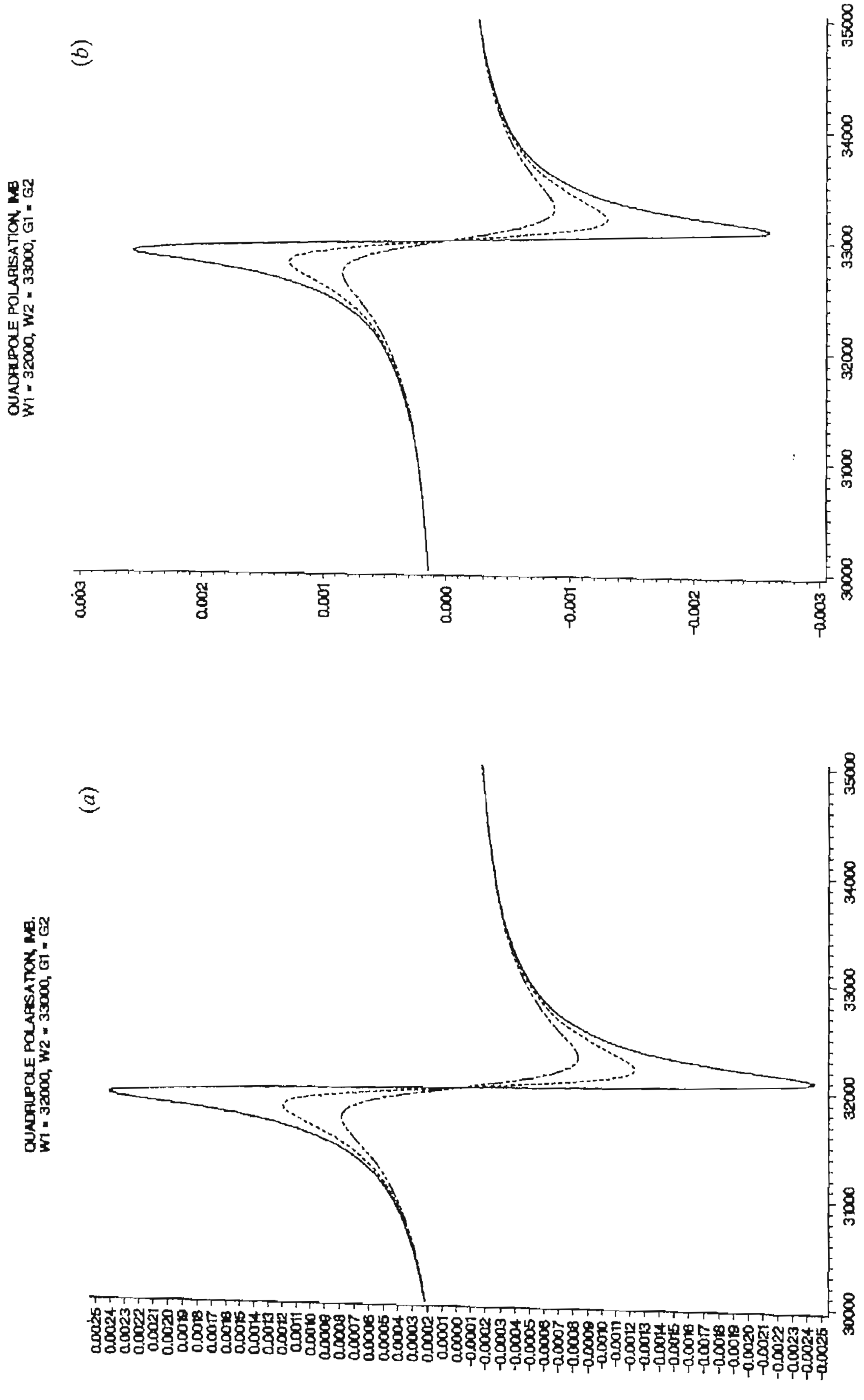


Figure 7. The functions $\tilde{h}_n(\tilde{\omega})$ (in cm) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) for a three level system with resonances at $\tilde{\omega}_1 = 135\,000\,\text{cm}^{-1}$ and $\tilde{\omega}_2 = 140\,000\,\text{cm}^{-1}$. (*a*) $\tilde{h}_1(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\,\text{cm}^{-1}$; (*b*) $\tilde{h}_2(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\,\text{cm}^{-1}$; (*c*) $\tilde{h}_3(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100\ 200, 300\,\text{cm}^{-1}$; (*d*) $\tilde{h}_3(\tilde{\omega})$ for $\Gamma_1 = 100, 200, 300\,\text{cm}^{-1}$, $\Gamma_2 = 400\,\text{cm}^{-1}$.


(b)
QUADRUPOLE POLARISATION, MB
W1 = 32000, W2 = 33000, G1 = G2
0.003
0.002
0.001
0.000
-0.001
-0.002
-0.003
30000
31000
32000
33000
34000
35000
(a)
QUADRUPOLE POLARISATION, MB.
W1 = 32000, W2 = 33000, G1 = G2
0.0025
0.0024
0.0023
0.0022
0.0021
0.0020
0.0019
0.0018
0.0017
0.0016
0.0015
0.0014
0.0013
0.0012
0.0011
0.0010
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0.0000
-0.0001
-0.0002
-0.0003
-0.0004
-0.0005
-0.0006
-0.0007
-0.0008
-0.0009
-0.0010
-0.0011
-0.0012
-0.0013
-0.0014
-0.0015
-0.0016
-0.0017
-0.0018
-0.0019
-0.0020
-0.0021
-0.0022
-0.0023
-0.0024
-0.0025
30000
31000
32000
33000
34000
35000

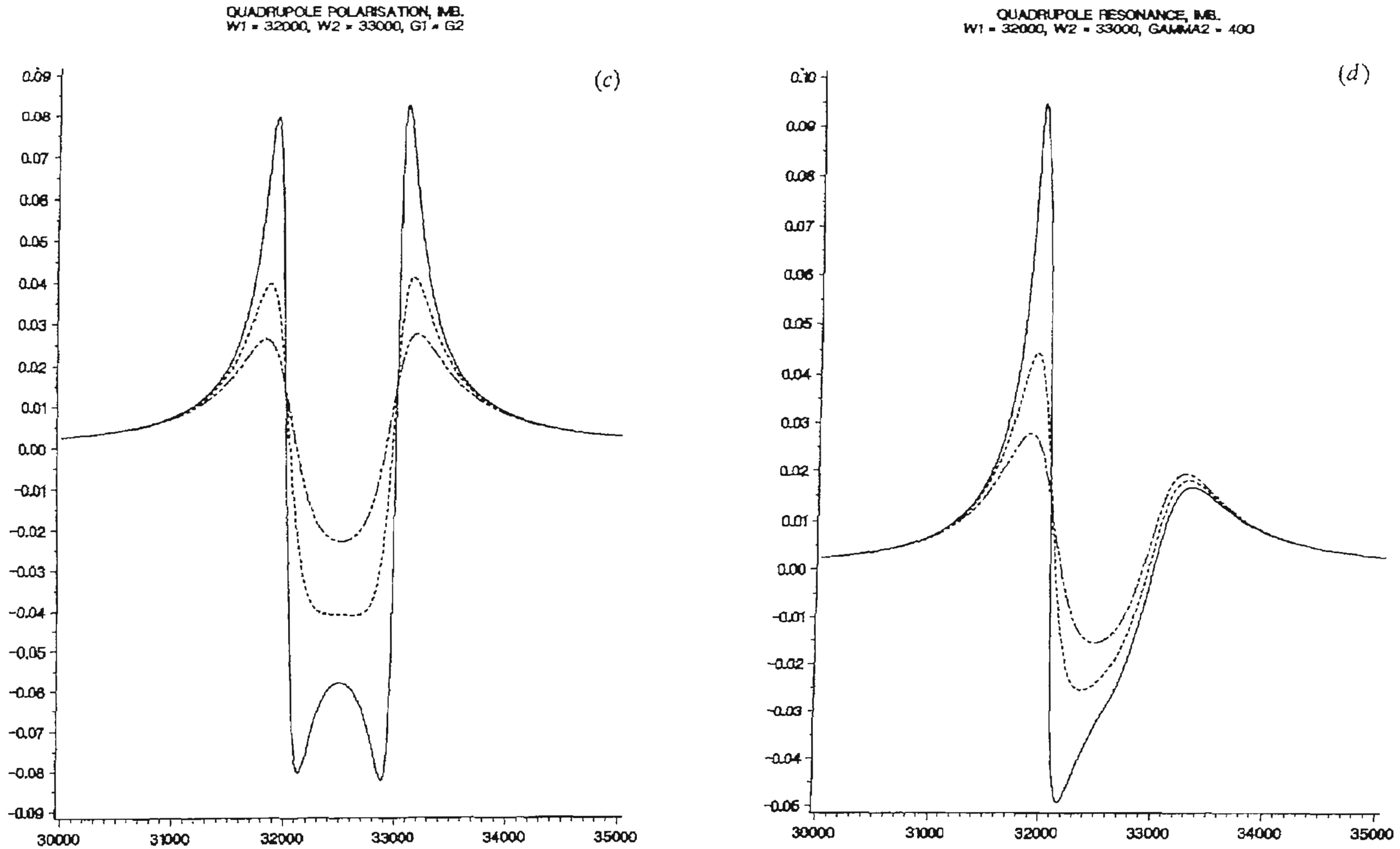


Figure 8. The functions $\tilde{h}_n(\tilde{\omega})$ (in cm) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) for a three level system with resonances at $\tilde{\omega}_1 = 32\,000\,\mathrm{cm}^{-1}$ and $\tilde{\omega}_2 = 33\,000\,\mathrm{cm}^{-1}$. (*a*) $\tilde{h}_1(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\,\mathrm{cm}^{-1}$; (*b*) $\tilde{h}_2(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\,\mathrm{cm}^{-1}$; (*c*) $\tilde{h}_3(\tilde{\omega})$ for $\Gamma_1 = \Gamma_2 = 100, 200, 300\,\mathrm{cm}^{-1}$; (*d*) $\tilde{h}_3(\tilde{\omega})$ for $\Gamma_1 = 100, 200, 300\,\mathrm{cm}^{-1}$, $\Gamma_2 = 400\,\mathrm{cm}^{-1}$.

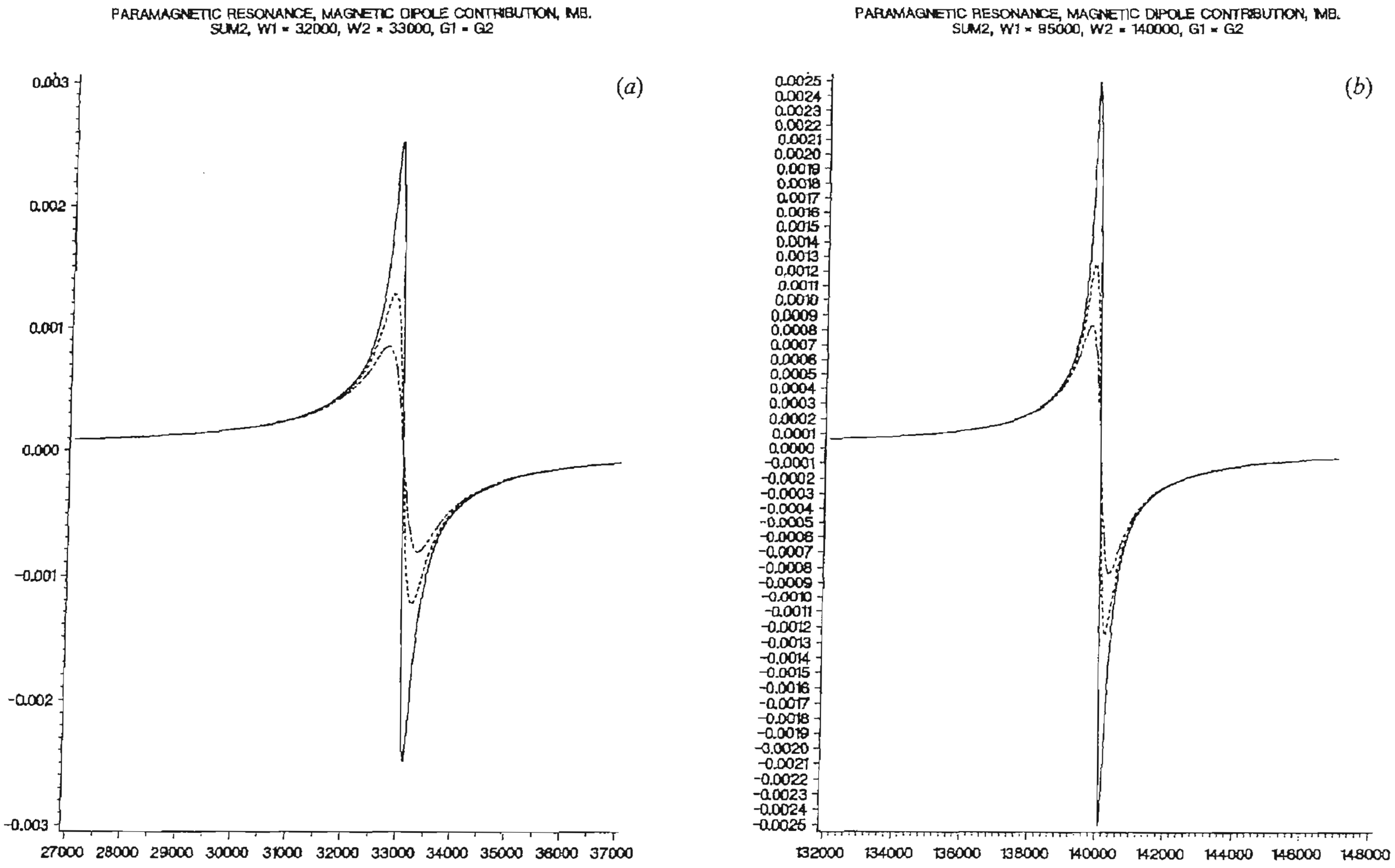


Figure 9. The function $\tilde{u}_2(\tilde{\omega})$ (in cm) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) (*a*) for $\tilde{\omega}_2 = 33\,000\,\mathrm{cm}^{-1}$ and $\Gamma_2 = 100, 200, 300\,\mathrm{cm}^{-1}$; (*b*) for $\tilde{\omega}_2 = 140\,000\,\mathrm{cm}^{-1}$ and $\Gamma_2 = 100, 200, 300\,\mathrm{cm}^{-1}$.

As for the inverse Faraday effect [22], we observe an enhancement of the order of 10–10^2 of the static magnetization near resonance frequencies, depending on the damping factors Γ_n, and the main contribution comes from the functions $g_2(\omega)$ and $g_3(\omega)$ (figure 1(*b*, *c*)), if the magnetic dipole transition between excited states is strongly favoured. Moreover, the closer together are the excited states in energy, the greater is the ratio of the contributions from the transition illustrated in figure 1(*b* or *c*) and (*a*). In figures 2–4 we show the functions $\tilde{g}_1(\tilde{\omega})$ and $\tilde{g}_3(\tilde{\omega})$ only; the function $\tilde{g}_2(\tilde{\omega})$ has the same shape as $\tilde{g}_3(\tilde{\omega})$ and its value is about 5% less than $\tilde{g}_3(\tilde{\omega})$ for the cases presented in figures 3 and 4, and about 30% less than $\tilde{g}_3(\tilde{\omega})$ in the case shown in figure 2. The static magnetization does not vanish inside the reasonances ($\omega = \omega_1$ or $\omega = \omega_2$) (there the effect is of the same order of magnitude as far from the resonance) because of damping, and the change of sign is shifted.

3.2. *Electric quadrupole interaction with the radiation*

The contribution M_D^Q to the static magnetization related to the electric quadrupole interaction with the radiation is given by the second term of equation (13) with the tensor ${}^{m}\gamma^{ee}(0;\,\omega,\,-\omega)$:

$$M_D^Q(0) = \frac{N\omega}{15c}\,{}^{m}\gamma^{ee}_{\alpha\beta\beta\alpha}(0;\,\omega,\,-\omega)\,(E^-\,.\,E^+)s, \tag{21}$$

which, taking into account equation (A4) in appendix A, can be written in the form (see appendix B)

$$M_D^Q = \frac{N}{15\hbar^2 c}\sum_{abc}\rho^{(0)}_{aa}\{(C_1 + C_2)\,[\mathrm{Im}(\boldsymbol{m}_{ac}\cdot\boldsymbol{Q}_{cb}\cdot\boldsymbol{\mu}_{ba}) + \mathrm{Im}(\boldsymbol{m}_{ca}\cdot\boldsymbol{Q}_{ab}\cdot\boldsymbol{\mu}_{bc})]$$
$$+ [(C_3 + C_4)\,(1 + K') + C_5K'']\mathrm{Im}(\boldsymbol{\mu}_{ba}\cdot\boldsymbol{Q}_{ac}\cdot\boldsymbol{m}_{cb})\}\,(E^-\,.\,E^+)s. \tag{22}$$

The coefficients C_n are related directly to the coefficients A_n describing the inverse Faraday effect with damping [22], see equation (B16) in appendix B. If we neglect damping (e.g., far from resonances),

$$C_2 = C_4 = C_5 = K' = K'' = 0$$

and

$$M_D^Q = \frac{N\omega^2}{15\hbar^2 c}\sum_{abc}\rho^{(0)}_{aa}\left\{\frac{1}{\omega_{ca}(\omega_{ba}^2 - \omega^2)}\,[\mathrm{Im}(\boldsymbol{m}_{ac}\cdot\boldsymbol{Q}_{cb}\cdot\boldsymbol{\mu}_{ba}) + \mathrm{Im}(\boldsymbol{m}_{ca}\cdot\boldsymbol{Q}_{ab}\cdot\boldsymbol{\mu}_{bc})]\right.$$
$$\left. + \frac{\omega_{ba} + \omega_{ca}}{(\omega_{ba}^2 - \omega^2)\,(\omega_{ca}^2 - \omega^2)}\,\mathrm{Im}(\boldsymbol{\mu}_{ba}\cdot\boldsymbol{Q}_{ac}\cdot\boldsymbol{m}_{cb})\right\}(E^-\,.\,E^+)s. \tag{23}$$

Applying general expression (22) to the case of a three level system (with the same assumptions as in section 3.1), we have

$$M_D^Q = \frac{N}{15\hbar^2 c}\{h_1(\omega)\,[\mathrm{Im}(\boldsymbol{m}_{a2}\cdot\boldsymbol{Q}_{21}\cdot\boldsymbol{\mu}_{1a}) + \mathrm{Im}(\boldsymbol{m}_{2a}\cdot\boldsymbol{Q}_{a1}\cdot\boldsymbol{\mu}_{12})]$$
$$+ h_2(\omega)\,[\mathrm{Im}(\boldsymbol{m}_{a1}\cdot\boldsymbol{Q}_{12}\cdot\boldsymbol{\mu}_{2a}) + \mathrm{Im}(\boldsymbol{m}_{1a}\cdot\boldsymbol{Q}_{a2}\cdot\boldsymbol{\mu}_{21})]$$
$$+ h_3(\omega)\,[\mathrm{Im}(\boldsymbol{\mu}_{1a}\cdot\boldsymbol{Q}_{a2}\cdot\boldsymbol{m}_{21}) + \mathrm{Im}(\boldsymbol{\mu}_{2a}\cdot\boldsymbol{Q}_{a1}\cdot\boldsymbol{m}_{12})]\}\,(E^-\,.\,E^+)s, \tag{24}$$

where

$$h_n(\omega) = \omega f_n(\omega) \tag{25}$$

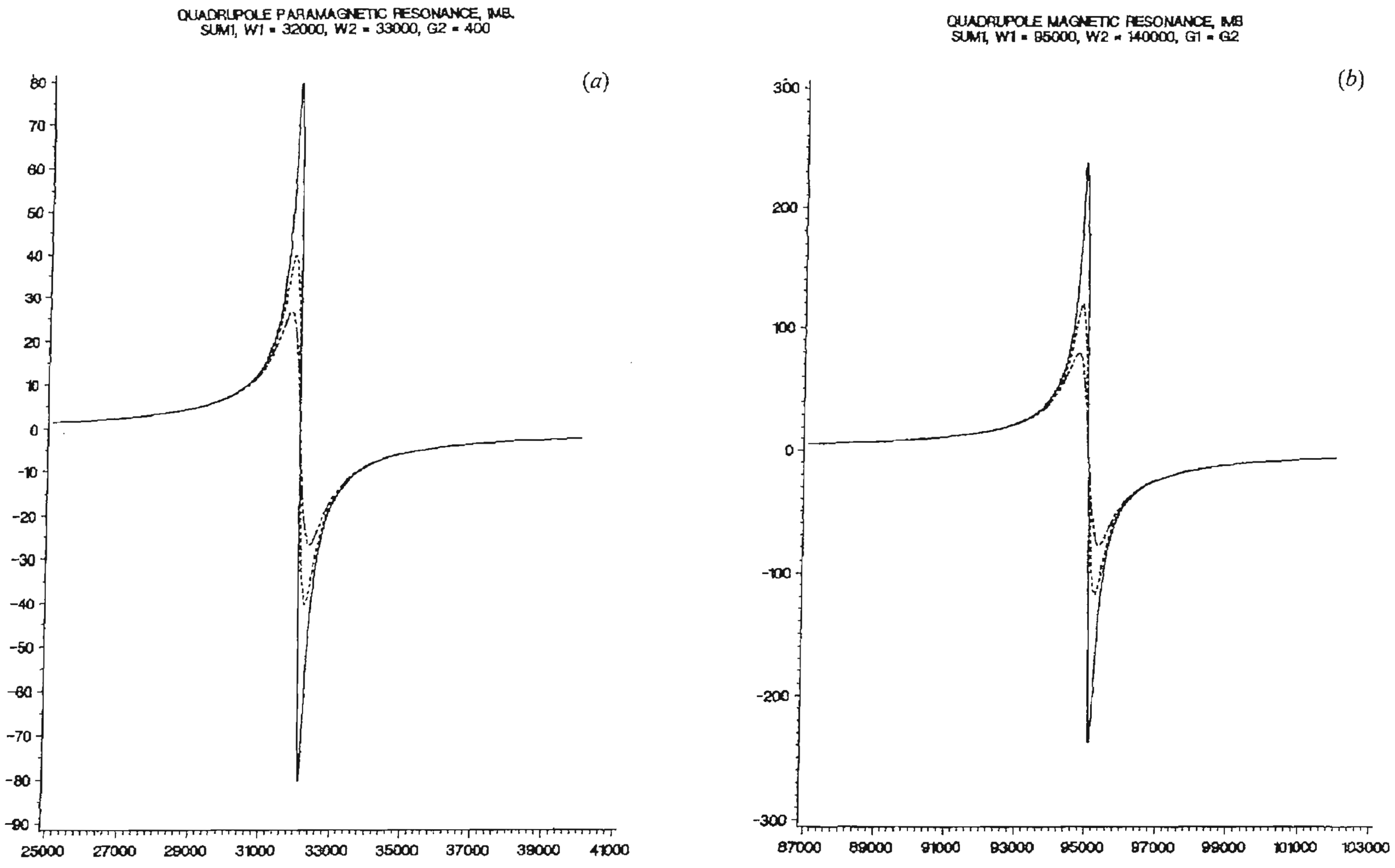


Figure 10. The functions $\tilde{w}_n(\tilde{\omega})$ (dimensionless) versus $\tilde{\omega} = 2\pi\tilde{\nu}$ (in cm^{-1}) (*a*) $\tilde{w}_1(\tilde{\omega})$ for $\tilde{\omega}_1 = 32\,000\,\mathrm{cm}^{-1}$ and $\Gamma_1 = 100, 200, 300\,\mathrm{cm}^{-1}$; (*b*) $\tilde{w}_1(\tilde{\omega})$ for $\tilde{\omega}_1 = 95\,000\,\mathrm{cm}^{-1}$ and $\Gamma_1 = 100, 200, 300\,\mathrm{cm}^{-1}$; (*c*) $\tilde{w}_2(\tilde{\omega})$ for $\tilde{\omega}_2 = 140\,000\,\mathrm{cm}^{-1}$ and $\Gamma_1 = 100, 200, 300\,\mathrm{cm}^{-1}$.

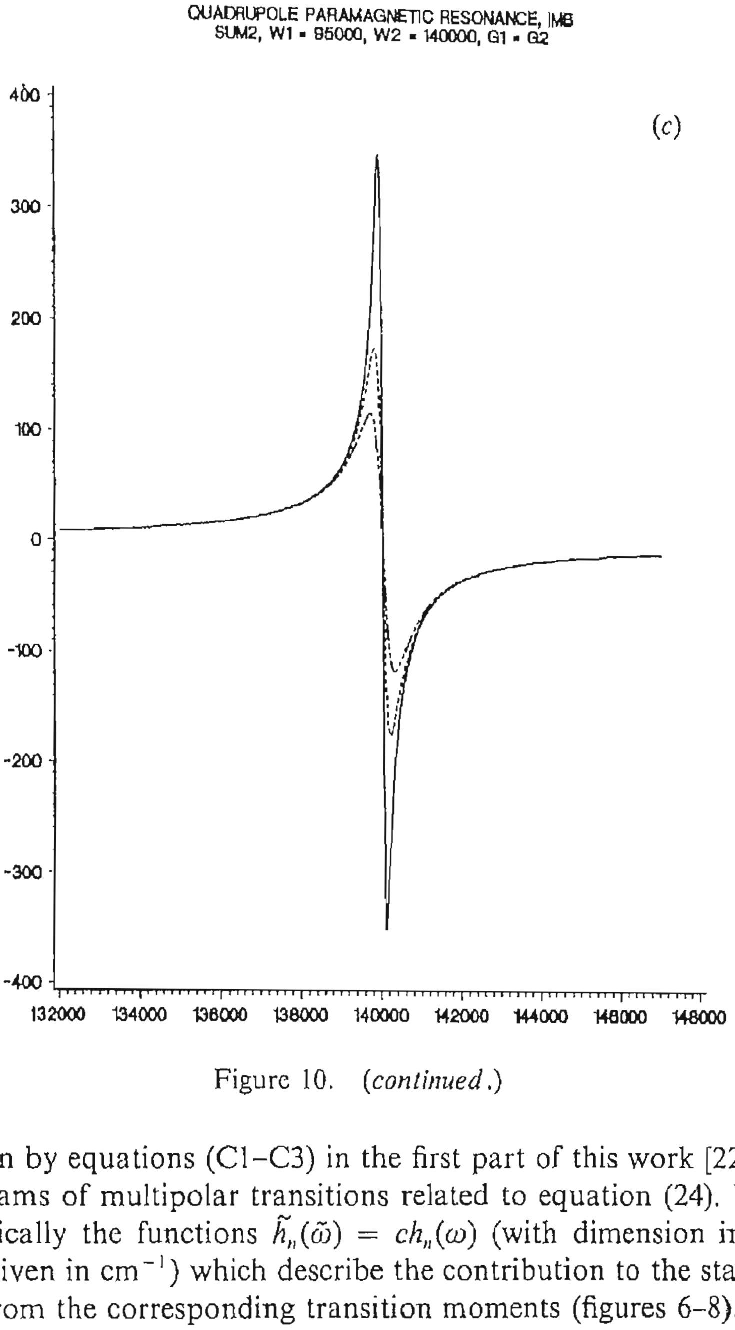


Figure 10. (*continued*.)

with $f_n(\omega)$ given by equations (C1–C3) in the first part of this work [22]. In figure 5 we show diagrams of multipolar transitions related to equation (24). We have calculated numerically the functions $\tilde{h}_n(\tilde{\omega}) = ch_n(\omega)$ (with dimension in cm if $\tilde{\omega} = \omega/c = 2\pi\tilde{\nu}$ is given in cm^{-1}) which describe the contribution to the static magnetization arising from the corresponding transition moments (figures 6–8).

One can see that in the case where all multipolar transitions are allowed as indicated, the main contribution to the static magnetization comes from the situation shown in figure 5(*c*). The magnetization induced by such transitions near the resonance frequencies $\tilde{\omega}_1 = 95\,000\,\mathrm{cm}^{-1}$ and $\tilde{\omega}_2 = 140\,000\,\mathrm{cm}^{-1}$ is about 2 to 3 times greater than the magnetization caused by the transitions of figure 5(*a*, *b*), respectively (see figure 6). If the excited states are close together in energy, that contribution is even more significant (e.g., for $\tilde{\omega}_1 = 135\,000\,\mathrm{cm}^{-1}$ and $\tilde{\omega}_2 = 140\,000\,\mathrm{cm}^{-1}$, it exceeds 28 and 27 times the contributions from the situations in figure 5(*a*, *b*) (see figure 7)). Numerical calculations show that the function $\tilde{h}_1(\tilde{\omega})$ depends very slightly on the damping parameter Γ_2 (and $\tilde{h}_2(\tilde{\omega})$ on Γ_1), and its shape and magnitude are the same in parts (*d*) in figures 6–8 as in part (*a*).

We conclude that, in addition to the magnetic dipole interaction, the electric quadrupole interaction with the radiation field also causes an enhancement of the optically induced static magnetization in the resonance regions (figures 6–8).

4. Paramagnetic contributions to IMCHB

Following the procedure in reference [17], we also find paramagnetic contributions to the static magnetization, in the cases of both magnetic dipole $M_{\mathrm{p}}^{\mathrm{m}}$, and electric quadrupole $M_{\mathrm{p}}^{\mathrm{Q}}$ interaction with the radiation:

$$M_{\mathrm{p}}^{\mathrm{m}} = \frac{2N}{3\hbar kTc} \sum_{\mathrm{ab}} \rho_{\mathrm{aa}}^{(0)} \frac{\omega_{\mathrm{ba}}(\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2)}{(\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2)^2 + 4\omega^2\Gamma_{\mathrm{ba}}^2} \mathrm{Re}(\boldsymbol{\mu}_{\mathrm{ab}} \times \boldsymbol{m}_{\mathrm{ba}}) \,.\, \boldsymbol{m}_{\mathrm{aa}}(\boldsymbol{E}^- \,.\, \boldsymbol{E}^+)s, \tag{26}$$

$$M_{\mathrm{p}}^{\mathrm{Q}} = \frac{2N}{15\hbar kTc} \sum_{\mathrm{ab}} \rho_{\mathrm{aa}}^{(0)} \frac{\omega^2(\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2)}{(\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2)^2 + 4\omega^2\Gamma_{\mathrm{ba}}^2} \mathrm{Im}(\boldsymbol{\mu}_{\mathrm{ab}} \times \boldsymbol{Q}_{\mathrm{ba}}) \,.\, \boldsymbol{m}_{\mathrm{aa}}(\boldsymbol{E}^- \,.\, \boldsymbol{E}^+)s, \tag{27}$$

where $\boldsymbol{m}_{\mathrm{aa}} = \langle \mathrm{a}|\boldsymbol{m}|\mathrm{a}\rangle$ is the magnetic dipole moment of the molecule in the ground state a, k is the Boltzmann constant, and T is the temperature. For the three level system introduced in section 3, we have

$$M_{\mathrm{p}}^{\mathrm{m}} = \frac{2N}{3\hbar kTc} [u_1(\omega)\mathrm{Re}(\boldsymbol{\mu}_{\mathrm{a1}} \times \boldsymbol{m}_{\mathrm{1a}}) \,.\, \boldsymbol{m}_{\mathrm{aa}} + u_2(\omega)\mathrm{Re}(\boldsymbol{\mu}_{\mathrm{a2}} \times \boldsymbol{m}_{\mathrm{2a}}) \,.\, \boldsymbol{m}_{\mathrm{aa}}]\,(\boldsymbol{E}^- \,.\, \boldsymbol{E}^+)s, \tag{28}$$

$$M_{\mathrm{p}}^{\mathrm{Q}} = \frac{2N}{15\hbar kTc} [w_1(\omega)\mathrm{Im}(\boldsymbol{\mu}_{\mathrm{a1}} \cdot \boldsymbol{Q}_{\mathrm{1a}}) \,.\, \boldsymbol{m}_{\mathrm{aa}} + w_2(\omega)\mathrm{Im}(\boldsymbol{\mu}_{\mathrm{a2}} \cdot \boldsymbol{Q}_{\mathrm{2a}}) \,.\, \boldsymbol{m}_{\mathrm{aa}}]\,(\boldsymbol{E}^- \,.\, \boldsymbol{E}^+)s, \tag{29}$$

with

$$u_n(\omega) = \frac{\omega_n(\omega_n^2 - \omega^2 + \Gamma_n^2)}{(\omega_n^2 - \omega^2 + \Gamma_n^2)^2 + 4\omega^2\Gamma_n^2}, \tag{30}$$

$$w_n(\omega) = \frac{\omega^2(\omega_n^2 - \omega^2 - \Gamma_n^2)}{(\omega_n^2 - \omega^2 + \Gamma_n^2)^2 + 4\omega^2\Gamma_n^2}, \tag{31}$$

and where we use the notation $\omega_n \equiv \omega_{n\mathrm{a}}$, $\Gamma_n \equiv \Gamma_{n\mathrm{a}}$. We have calculated the functions $\tilde{u}(\tilde{\omega}) = cu(\omega)$ (given in cm if $\tilde{\omega} = 2\pi\tilde{\nu}$ is in cm^{-1}) and $\tilde{w}_n(\tilde{\omega}) \equiv w_n(\omega)$ (which are dimensionless) for different resonance frequencies and different relaxation times Γ_n^{-1}. As can be seen from figure 9, the shape and the magnitude of $\tilde{u}_n(\tilde{\omega})$ do not depend on the resonance frequency but on damping (we present the function $\tilde{u}_2(\tilde{\omega})$ only; the function $\tilde{u}_1(\tilde{\omega})$ looks exactly the same but it correspondingly depends on the frequency ω_1). On the other hand, the values of the functions $\tilde{w}_n(\tilde{\omega})$ depend both on damping as well as on resonance frequency (figure 10), giving an additional cause for the increase of the effect.

Appendix A

Nonlinear polarizabilities in IMCHB

The polarizabilities describing the static magnetic dipole moment (equation (3)) induced in a molecule by the optical field given by equations (1) and (2) have the form of equations (4) and (5) with

$${}^{\mathrm{m}}\tilde{\beta}_{ijk}^{\mathrm{em}}(0;\, \omega,\, -\omega) = \frac{1}{\hbar^2} \sum_{\mathrm{abc}} \rho_{\mathrm{aa}}^{(0)} \left\{ \frac{\mathrm{Re}[(m_i)_{\mathrm{ac}}(m_k)_{\mathrm{cb}}(\mu_j)_{\mathrm{ba}}]}{(\omega_{\mathrm{ca}} - i\Gamma_{\mathrm{ca}})\,(\omega_{\mathrm{ba}} - \omega - i\Gamma_{\mathrm{ba}})} \right.$$

$$
\begin{aligned}
&+ \frac{\mathrm{Re}[(m_i)_{\mathrm{ac}}(\mu_j)_{\mathrm{cb}}(m_k)_{\mathrm{ba}}]}{(\omega_{\mathrm{ca}} - i\Gamma_{\mathrm{ca}})\,(\omega_{\mathrm{ba}} + \omega - i\Gamma_{\mathrm{ba}})} \\
&+ \frac{\mathrm{Re}[(\mu_j)_{\mathrm{ac}}(m_k)_{\mathrm{cb}}(m_i)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} + i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} + \omega + i\Gamma_{\mathrm{ca}})} \\
&+ \frac{\mathrm{Re}[(m_k)_{\mathrm{ac}}(\mu_j)_{\mathrm{cb}}(m_i)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} + i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} - \omega + i\Gamma_{\mathrm{ca}})} \\
&+ \frac{\mathrm{Re}[(\mu_j)_{\mathrm{ac}}(m_i)_{\mathrm{cb}}(m_k)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} + \omega - i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} + \omega + i\Gamma_{\mathrm{ca}})}(1 + K) \\
&+ \left.\frac{\mathrm{Re}[(m_k)_{\mathrm{ac}}(m_i)_{\mathrm{cb}}(\mu_j)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} - \omega - i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} - \omega + i\Gamma_{\mathrm{ca}})}(1 + K)\right\}, \qquad \text{(A1)}
\end{aligned}
$$

$$
\begin{aligned}
{}^{\mathrm{m}}\hat{\gamma}^{\mathrm{em}}_{ijk}(0;\,\omega,\,-\omega) = \frac{1}{\hbar^2}\sum_{\mathrm{abc}} \rho^{(0)}_{\mathrm{aa}} \Bigg\{ &\frac{\mathrm{Im}[(m_i)_{\mathrm{ac}}(m_k)_{\mathrm{cb}}(\mu_j)_{\mathrm{ba}}]}{(\omega_{\mathrm{ca}} - i\Gamma_{\mathrm{ca}})\,(\omega_{\mathrm{ba}} - \omega - i\Gamma_{\mathrm{ba}})} \\
&+ \frac{\mathrm{Im}[(m_i)_{\mathrm{ac}}(\mu_j)_{\mathrm{cb}}(m_k)_{\mathrm{ba}}]}{(\omega_{\mathrm{ca}} - i\Gamma_{\mathrm{ca}})\,(\omega_{\mathrm{ba}} + \omega - i\Gamma_{\mathrm{ba}})} \\
&+ \frac{\mathrm{Im}[(\mu_j)_{\mathrm{ac}}(m_k)_{\mathrm{cb}}(m_i)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} + i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} + \omega + i\Gamma_{\mathrm{ca}})} \\
&+ \frac{\mathrm{Im}[(m_k)_{\mathrm{ac}}(\mu_j)_{\mathrm{cb}}(m_i)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} + i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} - \omega + i\Gamma_{\mathrm{ca}})} \\
&+ \frac{\mathrm{Im}[(\mu_j)_{\mathrm{ac}}(m_i)_{\mathrm{cb}}(m_k)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} + \omega - i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} + \omega + i\Gamma_{\mathrm{ca}})}(1 + K) \\
&+ \frac{\mathrm{Im}[(m_k)_{\mathrm{ac}}(m_i)_{\mathrm{cb}}(\mu_j)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} - \omega - i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} - \omega + i\Gamma_{\mathrm{ca}})}(1 + K)\Bigg\}, \qquad \text{(A2)}
\end{aligned}
$$

$$
\begin{aligned}
{}^{\mathrm{m}}\hat{\beta}^{\mathrm{ee}}_{ijkl}(0;\,\omega,\,-\omega) = \frac{1}{\hbar^2}\sum_{\mathrm{abc}} \rho^{(0)}_{\mathrm{aa}} \Bigg\{ &\frac{\mathrm{Re}[(m_i)_{\mathrm{ac}}(Q_{kl})_{\mathrm{cb}}(\mu_j)_{\mathrm{ba}}]}{(\omega_{\mathrm{ca}} - i\Gamma_{\mathrm{ca}})\,(\omega_{\mathrm{ba}} - \omega - i\Gamma_{\mathrm{ba}})} \\
&+ \frac{\mathrm{Re}[(m_i)_{\mathrm{ac}}(\mu_j)_{\mathrm{cb}}(Q_{kl})_{\mathrm{ba}}]}{(\omega_{\mathrm{ca}} - i\Gamma_{\mathrm{ca}})\,(\omega_{\mathrm{ba}} + \omega - i\Gamma_{\mathrm{ba}})} \\
&+ \frac{\mathrm{Re}[(\mu_j)_{\mathrm{ac}}(Q_{kl})_{\mathrm{cb}}(m_i)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} + i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} + \omega + i\Gamma_{\mathrm{ca}})} \\
&+ \frac{\mathrm{Re}[(Q_{kl})_{\mathrm{ac}}(\mu_j)_{\mathrm{cb}}(m_i)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} + i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} - \omega + i\Gamma_{\mathrm{ca}})} \\
&+ \frac{\mathrm{Re}[(\mu_j)_{\mathrm{ac}}(m_i)_{\mathrm{cb}}(Q_{kl})_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} + \omega - i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} + \omega + i\Gamma_{\mathrm{ca}})}(1 + K) \\
&+ \frac{\mathrm{Re}[(Q_{kl})_{\mathrm{ac}}(m_i)_{\mathrm{cb}}(\mu_j)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}} - \omega - i\Gamma_{\mathrm{ba}})\,(\omega_{\mathrm{ca}} - \omega + i\Gamma_{\mathrm{ca}})}(1 + K)\Bigg\}, \qquad \text{(A3)}
\end{aligned}
$$

$$
\begin{aligned}
{}^{\mathrm{m}}\hat{\gamma}^{\mathrm{ee}}_{ijkl}(0;\,\omega,\,-\omega) = \frac{1}{\hbar^2}\sum_{\mathrm{abc}} \rho^{(0)}_{\mathrm{aa}} \Bigg\{ &\frac{\mathrm{Im}[(m_i)_{\mathrm{ac}}(Q_{kl})_{\mathrm{cb}}(\mu_j)_{\mathrm{ba}}]}{(\omega_{\mathrm{ca}} - i\Gamma_{\mathrm{ca}})\,(\omega_{\mathrm{ba}} - \omega - i\Gamma_{\mathrm{ba}})} \\
&+ \frac{\mathrm{Im}[(m_i)_{\mathrm{ac}}(\mu_j)_{\mathrm{cb}}(Q_{kl})_{\mathrm{ba}}]}{(\omega_{\mathrm{ca}} - i\Gamma_{\mathrm{ca}})\,(\omega_{\mathrm{ba}} + \omega - i\Gamma_{\mathrm{ba}})}
\end{aligned}
$$

$$+\frac{\mathrm{Im}[(\mu_j)_{\mathrm{ac}}(Q_{kl})_{\mathrm{cb}}(m_i)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}}+i\Gamma_{\mathrm{ba}})(\omega_{\mathrm{ca}}+\omega+i\Gamma_{\mathrm{ca}})}$$
$$+\frac{\mathrm{Im}[(Q_{kl})_{\mathrm{ac}}(\mu_j)_{\mathrm{cb}}(m_i)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}}+i\Gamma_{\mathrm{ba}})(\omega_{\mathrm{ca}}-\omega+i\Gamma_{\mathrm{ca}})}$$
$$+\frac{\mathrm{Im}[(\mu_j)_{\mathrm{ac}}(m_i)_{\mathrm{cb}}(Q_{kl})_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}}+\omega-i\Gamma_{\mathrm{ba}})(\omega_{\mathrm{ca}}+\omega+i\Gamma_{\mathrm{ca}})}(1+K)$$
$$\left.+\frac{\mathrm{Im}[(Q_{kl})_{\mathrm{ac}}(m_i)_{\mathrm{cb}}(\mu_j)_{\mathrm{ba}}]}{(\omega_{\mathrm{ba}}-\omega-i\Gamma_{\mathrm{ba}})(\omega_{\mathrm{ca}}-\omega+i\Gamma_{\mathrm{ca}})}(1+K)\right\}, \qquad \text{(A4)}$$

where $(m_i)_{\mathrm{ba}} \equiv \langle \mathrm{b}|m_i|\mathrm{a}\rangle$, $(\mu_j)_{\mathrm{ba}} \equiv \langle \mathrm{b}|\mu_j|\mathrm{a}\rangle$ and $(Q_{kl})_{\mathrm{ba}} \equiv \langle \mathrm{b}|Q_{kl}|\mathrm{a}\rangle$ denote magnetic dipole, electric dipole and electric quadrupole transitions between the states $|\mathrm{a}\rangle$ and $\langle \mathrm{b}|$, respectively (Q_{kl} is the traceless electric quadrupole moment operator), with the frequency $\omega_{\mathrm{ba}} = \omega_{\mathrm{b}} - \omega_{\mathrm{a}} = (E_{\mathrm{b}} - E_{\mathrm{a}})/\hbar$, $\rho_{\mathrm{aa}}^{(0)}$ is the population of the system in the stationary state $|\mathrm{a}\rangle$, $\Gamma_{\mathrm{ba}}^{-1}$ is a characteristic relaxation time between the states $|\mathrm{b}\rangle$ and $|\mathrm{a}\rangle$, and

$$K = \frac{i(\Gamma_{\mathrm{bc}} - \Gamma_{\mathrm{ba}} - \Gamma_{\mathrm{ca}})}{\omega_{\mathrm{bc}} - i\Gamma_{\mathrm{bc}}} \qquad \text{(A5)}$$

is the correction term [22, 28]. Using simple perturbation theory [27] for the calculation of the polarizabilities ${}^{\mathrm{m}}\alpha_{ijk}^{\mathrm{cm}}(0;\ \omega,\ -\omega)$ and ${}^{\mathrm{m}}\alpha_{ijkl}^{\mathrm{cc}}(0;\ \omega,\ -\omega)$, one obtains expressions (A1–A4) without the correction term K. The quantum mechanical forms of the polarizabilities ${}^{\mathrm{m}}\alpha_{ijk}^{\mathrm{cm}}(0;\ -\omega,\ \omega)$ and ${}^{\mathrm{m}}\alpha_{ijkl}^{\mathrm{cc}}(0;\ -\omega,\omega)$ in equations (3–5, 8–11) are given by equations (A1–A4) if one replaces ω by $-\omega$.

Appendix B

Coefficients $\mathbf{B_n}$ and $\mathbf{C_n}$ of equations (17) and (22)

Taking into consideration that the electric dipole moment, magnetic dipole moment and electric quadrupole moment operators $\boldsymbol{\mu}$, $\boldsymbol{m}$ and $\boldsymbol{Q}$, respectively, are Hermitian, we have

$$\mathrm{Re}(\boldsymbol{\mu}_{\mathrm{bc}} \cdot \boldsymbol{m}_{\mathrm{ab}} \times \boldsymbol{m}_{\mathrm{ca}}) = \mathrm{Re}(\boldsymbol{\mu}_{\mathrm{cb}} \cdot \boldsymbol{m}_{\mathrm{ba}} \times \boldsymbol{m}_{\mathrm{ac}}), \qquad \text{(B1)}$$
$$\mathrm{Im}(\boldsymbol{\mu}_{\mathrm{ab}} \cdot \boldsymbol{Q}_{\mathrm{ca}} \cdot \boldsymbol{m}_{\mathrm{bc}}) = -\mathrm{Im}(\boldsymbol{\mu}_{\mathrm{ba}} \cdot \boldsymbol{Q}_{\mathrm{ac}} \cdot \boldsymbol{m}_{\mathrm{cb}}). \qquad \text{(B2)}$$

Equation (12), taking into account equations (A1) and (A4) in appendix A, can then be written in the form of equations (17) and (22), with coefficients B_n and C_n, as follows:

$$B_1 = \omega_{\mathrm{ba}}\omega_{\mathrm{ca}}q_{\mathrm{c}}^0 q_{\mathrm{b}}, \qquad \text{(B3)}$$
$$B_2 = [\omega_{\mathrm{ba}}\omega_{\mathrm{ca}}\Gamma_{\mathrm{ba}}^2 - \Gamma_{\mathrm{ba}}\Gamma_{\mathrm{ca}}(\omega_{\mathrm{ba}}^2 + \omega^2 + \Gamma_{\mathrm{ba}}^2)]q_{\mathrm{c}}^0 q_{\mathrm{b}}, \qquad \text{(B4)}$$
$$B_3 = (\omega_{\mathrm{ba}}^2 - \omega^2)(\omega_{\mathrm{ca}}^2 - \omega^2)(\omega_{\mathrm{ba}}\omega_{\mathrm{ca}} + \omega^2)q_{\mathrm{b}}q_{\mathrm{c}}, \qquad \text{(B5)}$$
$$\begin{aligned} B_4 = {} & \{\Gamma_{\mathrm{ba}}\Gamma_{\mathrm{ca}}[(\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2)(\omega_{\mathrm{ca}}^2 - \omega^2 + \Gamma_{\mathrm{ca}}^2) + 4\omega^2\Gamma_{\mathrm{ba}}\Gamma_{\mathrm{ca}}] \\ & + (\omega_{\mathrm{ba}}\omega_{\mathrm{ca}} + \omega^2)[\Gamma_{\mathrm{ba}}^2(\omega_{\mathrm{ca}}^2 - \omega^2) + \Gamma_{\mathrm{ca}}^2(\omega_{\mathrm{ba}}^2 - \omega^2) + 4\omega^2\Gamma_{\mathrm{ba}}\Gamma_{\mathrm{ca}} + \Gamma_{\mathrm{ba}}^2\Gamma_{\mathrm{ca}}^2] \\ & + 2\omega^2(\Gamma_{\mathrm{ca}} - \Gamma_{\mathrm{ba}})[\Gamma_{\mathrm{ba}}(\omega_{\mathrm{ca}}^2 - \omega^2 + \Gamma_{\mathrm{ca}}^2) - \Gamma_{\mathrm{ca}}(\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2)]\}q_{\mathrm{b}}q_{\mathrm{c}}, \end{aligned} \qquad \text{(B6)}$$
$$\begin{aligned} B_5 = {} & \{(\omega_{\mathrm{ba}}\Gamma_{\mathrm{ca}} - \omega_{\mathrm{ca}}\Gamma_{\mathrm{ba}})[(\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2)(\omega_{\mathrm{ca}}^2 - \omega^2 + \Gamma_{\mathrm{ca}}^2) + 4\omega^2\Gamma_{\mathrm{ba}}\Gamma_{\mathrm{ca}}] \\ & + 2\omega^2(\omega_{\mathrm{ba}} + \omega_{\mathrm{ca}})[\Gamma_{\mathrm{ca}}(\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2) - \Gamma_{\mathrm{ba}}(\omega_{\mathrm{ca}}^2 - \omega^2 + \Gamma_{\mathrm{ca}}^2)]\}q_{\mathrm{b}}q_{\mathrm{c}}, \end{aligned} \qquad \text{(B7)}$$

$$C_1 = \omega^2 \omega_{\mathrm{ca}} (\omega_{\mathrm{ba}}^2 - \omega^2) q_{\mathrm{c}}^0 q_{\mathrm{b}}, \tag{B8}$$

$$C_2 = -\omega^2 \Gamma_{\mathrm{ba}} (\omega_{\mathrm{ca}} \Gamma_{\mathrm{ba}} + 2\omega_{\mathrm{ba}} \Gamma_{\mathrm{ca}}) q_{\mathrm{c}}^0 q_{\mathrm{b}}, \tag{B9}$$

$$C_3 = \omega^2 (\omega_{\mathrm{ba}} + \omega_{\mathrm{ca}})\, (\omega_{\mathrm{ba}}^2 - \omega^2) q_{\mathrm{b}} q_{\mathrm{c}}, \tag{B10}$$

$$\begin{aligned} C_4 = {} & \omega^2 \{ (\omega_{\mathrm{ba}} + \omega_{\mathrm{ca}})\, [(\Gamma_{\mathrm{ba}}^2 (\omega_{\mathrm{ca}}^2 - \omega^2) + \Gamma_{\mathrm{ca}}^2 (\omega_{\mathrm{ba}}^2 - \omega^2) + 4\omega^2 \Gamma_{\mathrm{ba}} \Gamma_{\mathrm{ca}} + \Gamma_{\mathrm{ba}}^2 \Gamma_{\mathrm{ca}}^2] \\ & + 2(\omega_{\mathrm{ba}} \Gamma_{\mathrm{ca}} - \omega_{\mathrm{ca}} \Gamma_{\mathrm{ba}})\, [\Gamma_{\mathrm{ba}} (\omega_{\mathrm{ca}}^2 - \omega^2 + \Gamma_{\mathrm{ca}}^2) - \Gamma_{\mathrm{ca}} (\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2)] \} q_{\mathrm{b}} q_{\mathrm{c}}, \end{aligned} \tag{B11}$$

$$\begin{aligned} C_5 = {} & \omega^2 \{ (\Gamma_{\mathrm{ca}} - \Gamma_{\mathrm{ba}})\, [(\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2)\, (\omega_{\mathrm{ca}}^2 - \omega^2 + \Gamma_{\mathrm{ca}}^2) + 4\omega^2 \Gamma_{\mathrm{ba}} \Gamma_{\mathrm{ca}}] \\ & + 2(\omega_{\mathrm{ba}} \omega_{\mathrm{ca}} + \omega^2 + \Gamma_{\mathrm{ba}} \Gamma_{\mathrm{ca}})\, [\Gamma_{\mathrm{ca}} (\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2) \\ & - \Gamma_{\mathrm{ba}} (\omega_{\mathrm{ca}}^2 - \omega^2 + \Gamma_{\mathrm{ca}}^2)] \} q_{\mathrm{b}} q_{\mathrm{c}}, \end{aligned} \tag{B12}$$

where

$$q_{\mathrm{c}}^0 = (\omega_{\mathrm{ca}}^2 + \Gamma_{\mathrm{ca}}^2)^{-1}, \tag{B13}$$

$$q_{\mathrm{b}} = [(\omega_{\mathrm{ba}}^2 - \omega^2 + \Gamma_{\mathrm{ba}}^2)^2 + 4\omega^2 \Gamma_{\mathrm{ba}}^2]^{-1}, \tag{B14}$$

$$q_{\mathrm{c}} = [(\omega_{\mathrm{ca}}^2 - \omega^2 + \Gamma_{\mathrm{ca}}^2)^2 + 4\omega^2 \Gamma_{\mathrm{ca}}^2]^{-1}, \tag{B15}$$

$$C_n = \omega A_n, \tag{B16}$$

with A_n given by equations (B3–B7) of the first part of this investigation [22].

Appendix C

Frequency dependent functions $g_n(\omega)$ for three-level systems

If in equation (17) for a three level system we take into consideration the relation

$$\mathrm{Re}(\boldsymbol{m}_{a2} \cdot \boldsymbol{\mu}_{21} \times \boldsymbol{m}_{1a}) = -\mathrm{Re}(\boldsymbol{m}_{a1} \cdot \boldsymbol{\mu}_{12} \times \boldsymbol{m}_{2a}), \tag{C1}$$

which follows from the Hermitian properties of the operators, we can obtain equation (20) with the frequency dependent functions

$$g_1(\omega) = g_1^{(1)}(\omega) - g_1^{(2)}(\omega), \tag{C2}$$

$$g_2(\omega) = g(\omega) - g_1^{(1)}(\omega), \tag{C3}$$

$$g_3(\omega) = g(\omega) - g_1^{(2)}(\omega), \tag{C4}$$

given by

$$g_1^{(1)}(\omega) = [\omega_1 \omega_2 (\omega_1^2 - \omega^2 + \Gamma_1^2) - \Gamma_1 \Gamma_2 (\omega_1^2 + \omega^2 + \Gamma_1^2)] q_2^0 q_1, \tag{C5}$$

$$g_1^{(2)}(\omega) = [\omega_1 \omega_2 (\omega_2^2 - \omega^2 + \Gamma_2^2) - \Gamma_1 \Gamma_2 (\omega_2^2 + \omega^2 + \Gamma_2^2)] q_1^0 q_2, \tag{C6}$$

$$\begin{aligned} g(\omega) = {} & \tfrac{1}{2} \sum_{i \neq j = 1,2} \{ (\omega_i^2 - \omega^2)\, (\omega_j^2 - \omega^2)\, (\omega_i \omega_j + \omega^2 + \Gamma_i \Gamma_j) \\ & + 2(\omega_i^2 - \omega^2) \Gamma_j [\Gamma_i \Gamma_j^2 + \Gamma_j (\omega_i \omega_j + \omega^2) + 2\omega^2 (\Gamma_i - \Gamma_j)] \\ & + \Gamma_i \Gamma_j [\Gamma_i^2 \Gamma_j^2 + (\omega_i \omega_j + \omega^2)\, (4\omega^2 + \Gamma_i \Gamma_j) + 2\omega^2 (\Gamma_i^2 + \Gamma_j^2)] \} q_i q_j, \end{aligned} \tag{C7}$$

where $\omega_i \equiv \omega_{ia}$, $\Gamma_i \equiv \Gamma_{ia}$, and q_i^0 and q_i are given by equations (B13) and (B14) in appendix B, respectively.

Appendix D

Diagonal transition matrix element contributon to $M_D(0)$

The sum Σ_{abc} in general expressions (17) and (22) contains two parts

$$\sum_{abc} = \sum_{\substack{a\neq b\\ b\neq c\\ c\neq a}} + \sum_{\substack{a\neq b\\ b=c}} . \tag{D1}$$

The first term of expression (D1) applied to the three level system considered in this paper leads directly to equations (20) and (24), respectively. The contributions to M_D^m and M_D^Q from the second term of expression (D1) depend, in contrast to the contribution from the first term, on the off-diagonal as well as the diagonal transition matrix elements, and have the following form:

$$M_D^m = \frac{N}{3\hbar^2 c} \sum_{\substack{a\\ b\neq a}} \rho_{aa}^{(0)} \kappa_b(\omega) \boldsymbol{m}_{bb} \cdot \mathrm{Re}(\boldsymbol{\mu}_{ab} \times \boldsymbol{m}_{ba})\, (\boldsymbol{E}^- \cdot \boldsymbol{E}^+) s, \tag{D2}$$

$$M_D^Q = \frac{N}{15\hbar^2 c} \sum_{\substack{a\\ b\neq a}} \rho_{aa}^{(0)} \{\eta_b(\omega)\, [\boldsymbol{Q}_{bb} : \mathrm{Im}(\boldsymbol{\mu}_{ab}\boldsymbol{m}_{ba}) + \boldsymbol{\mu}_{bb} \cdot \mathrm{Im}(\boldsymbol{Q}_{ba} \cdot \boldsymbol{m}_{ab})]$$

$$+ \zeta_b(\omega) \boldsymbol{m}_{bb} \cdot \mathrm{Im}(\boldsymbol{Q}_{ba} \cdot \boldsymbol{\mu}_{ab})\}\, (\boldsymbol{E}^- \cdot \boldsymbol{E}^+) s, \tag{D3}$$

where

$$\kappa_b(\omega) = \frac{2(\omega^2 + \Gamma_{ba}^2)}{(\omega_{ba}^2 - \omega^2 + \Gamma_{ba}^2)^2 + 4\omega^2\Gamma_{ba}^2}, \tag{D4}$$

$$\eta_b(\omega) = \frac{\omega^2 \omega_{ba}(\omega_{ba}^2 - \omega^2 - 3\Gamma_{ba}^2)}{(\omega_{ba}^2 + \Gamma_{ba}^2)\, [(\omega_{ba}^2 - \omega^2 + \Gamma_{ba}^2)^2 + 4\omega^2\Gamma_{ba}^2]}, \tag{D5}$$

$$\zeta_b(\omega) = \frac{2\omega^2 \omega_{ba}^2}{(\omega_{ba}^2 - \omega^2 + \Gamma_{ba}^2)^2 + 4\omega^2\Gamma_{ba}^2}. \tag{D6}$$

The function $\eta_n(\omega)$ has a shape similar to that of the function $w_n(\omega)$ (equation (31) and figure 10) with $\eta_b(\omega = \omega_{ba}) \cong -3/4\omega_{ba}$. However, the functions $\kappa_b(\omega)$ and $\zeta_b(\omega)$ have quite different shapes resembling absorption curves, with the maximum at the resonance $\omega = \omega_{ba}$; and

$$\kappa_b(\omega = \omega_{ba}) \cong \frac{1}{2\Gamma_{ba}^2}, \tag{D7}$$

$$\zeta_b(\omega = \omega_{ba}) \cong \frac{\omega_{ba}}{2\Gamma_{ba}^2} = \omega_{ba} \kappa_b(\omega = \omega_{ba}). \tag{D8}$$

Equations (D2–D8) 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 (as in section 4). In this case, one can see from equations (D2) and (D3) that the contributions to $\boldsymbol{M}_D$ considered depend on the off-diagonal as well as the diagonal elements of the multipole transition matrix for the excited states ($\boldsymbol{\mu}_{bb}$, $\boldsymbol{m}_{bb}$, $\boldsymbol{Q}_{bb}$). Moreover, we have simple relations between the functions $\eta_b(\omega)$, $\zeta_b(\omega)$ and $d_b(\omega)$, $r_b(\omega)$, respectively; the latter two describe the contribution to the magnetization $\boldsymbol{M}(0)$ from diagonal elements of the electric dipole and magnetic dipole transition matrices in the inverse Faraday effect

[22]:

$$\left.\begin{aligned}\eta_{\mathrm{b}}(\omega) &= \omega d_{\mathrm{b}}(\omega),\\ \zeta_{\mathrm{b}}(\omega) &= \omega r_{\mathrm{b}}(\omega).\end{aligned}\right\} \qquad \text{(D9)}$$

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