

## Damping corrections and the calculation of optical nonlinearities in organic molecules

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Damping, the effects of uncertainty, Doppler, collisional, and other mechanisms that lead to the broadening of electronic transitions are rarely accounted for in the calculation of optical nonlinearities. Using the two-level model as an illustration, this work points out that damping corrections can be substantial for organic compounds, even for two- or three-photon resonances, and that these corrections are dependent on molecular symmetry. Comparisons of calculated and measured susceptibilities need to take this into account. Results are presented for the quadratic electro-optic, third-harmonic, and electric-field-induced second-harmonic-generation processes.

There is extensive calculational study of nonlinear-optical susceptibilities of organic compounds using quantum-mechanical methods<sup>1-5</sup> and sum over states (SOS) perturbative expressions.<sup>6</sup> Reasonable accuracy has been achieved for  $\text{Re}(\beta)$ ,<sup>3</sup> the real part of the microscopic second-order susceptibility, and less frequently for  $\text{Re}(\gamma)$ ,<sup>7</sup> the real part of the microscopic third-order susceptibility. While it is probably well recognized by researchers that damping can be important in calculating either  $\text{Re}(\beta)$  or  $\text{Re}(\gamma)$ , it has become customary to ignore the complex damping corrections ( $i\Gamma/2$  as defined by Orr and Ward<sup>6</sup>) which arise from the various broadening mechanisms. We report here results for the two-level model<sup>8-10</sup> of  $\gamma$  which suggest that complex damping corrections often cannot be ignored.

Using the expressions from Orr and Ward,<sup>6</sup> the two-level model for  $\gamma$ ,

$$\gamma = -K[(\mu_{01})^4 D_{11} - (\mu_{01})^2 (\Delta\mu_{01})^2 D_{111}] , \quad (1)$$

can be obtained by carrying the summation over one excited state, where  $K$  is a constant that depends on the frequencies and degeneracies of a given optical process,  $\mu_{01}$  is a vector component of the transition moment [ $\int \psi_0(e \cdot \mathbf{r})\psi_1 d\tau$ ] between the state wave functions  $\psi_0, \psi_1$ , and  $\Delta\mu_{01} = \mu_{11} - \mu_{00}$ . The two-level dispersion terms  $D_{111}$  and  $D_{11}$  represent, respectively, the triple and double sums of the four (each) damped dispersion terms of Eq. (43c) of Orr and Ward,<sup>6</sup>

$$D_{111}(-\omega_\sigma, \omega_1, \omega_2, \omega_3) = \hat{\mathbf{I}}_{1,2,3} \{ [(\Omega_{1g} - \omega_\sigma)(\Omega_{1g} - \omega_1 - \omega_2)(\Omega_{1g} - \omega_1)]^{-1} + [(\Omega_{1g}^* + \omega_3)(\Omega_{1g} - \omega_1 - \omega_2)(\Omega_{1g} - \omega_1)]^{-1} \\ + [(\Omega_{1g}^* + \omega_1)(\Omega_{1g}^* + \omega_1 + \omega_2)(\Omega_{1g} - \omega_3)]^{-1} \\ + [(\Omega_{1g}^* + \omega_1)(\Omega_{1g}^* + \omega_1 + \omega_2)(\Omega_{1g}^* + \omega_\sigma)]^{-1} \} , \quad (2)$$

$$D_{11}(-\omega_\sigma, \omega_1, \omega_2, \omega_3) = \hat{\mathbf{I}}_{1,2,3} \{ [(\Omega_{1g} - \omega_\sigma)(\Omega_{1g} - \omega_3)(\Omega_{1g} - \omega_1)]^{-1} + [(\Omega_{1g} - \omega_3)(\Omega_{1g}^* + \omega_2)(\Omega_{1g} - \omega_1)]^{-1} \\ + [(\Omega_{1g}^* + \omega_\sigma)(\Omega_{1g}^* + \omega_3)(\Omega_{1g}^* + \omega_1)]^{-1} + [(\Omega_{1g}^* + \omega_3)(\Omega_{1g} - \omega_2)(\Omega_{1g}^* + \omega_1)]^{-1} \} , \quad (3)$$

where  $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$ ,  $\Omega_{1g} = \omega_{1g} + i\Gamma/2$ , and  $\Omega_{1g}^* = \omega_{1g} - i\Gamma/2$ . The frequency of the first molecular excitation is given by  $\omega_{1g}$ , and  $\Gamma$  is given by  $\Gamma_1 - \Gamma_g$ , where  $\Gamma_g$  and  $\Gamma_1$  are the ground- and first-excited-state inverse radiative lifetimes,<sup>6</sup> respectively. The inverse radiative lifetime  $\Gamma_j$  for any given state  $j$  is difficult to ascertain. However, when the transition occurs between the ground state  $g$  and any given excited state  $j$ , the difference,  $\Gamma = \Gamma_j - \Gamma_g$ , is related to the peak widths measured in simple electronic absorption spectra. Thus the  $\Gamma$  used here refers, in some way (*vide infra*), to the peak width of the lowest energy excitation, as measured in an electronic absorption spectrum.

For each of the sets of four terms for  $D_{111}$  or  $D_{11}$ , the frequencies  $\omega_1, \omega_2, \omega_3$  must be permuted, using the operator  $\hat{\mathbf{I}}_{1,2,3}$ , giving 24 terms. For the most commonly used off-resonant measurement processes—degenerate four-wave mixing (DFWM), quadratic electro-optic modulation (QEO), electric-field-induced second-harmonic generation (EFISH), and third harmonic generation (THG)—these two-level dispersion factors for  $\gamma$  are generally among the largest as long as the fundamental frequency  $\omega_0$  is less than the frequency of the first molecular excitation,  $\omega_{1g}$ , for QEO,  $2\omega_0 < \omega_{1g}$  for EFISH and DFWM and  $3\omega_0 < \omega_{1g}$  for THG. For QEO, EFISH, and THG, these are the common “off-resonant” measurement

TABLE I. Results for QEO.  $\omega_{1g} = 16\,667\text{ cm}^{-1}$ .

$\Gamma\text{ (cm}^{-1}\text{)}$	$\omega_0\text{ (cm}^{-1}\text{)}$	$\omega_{1g}-\omega_0\text{ (cm}^{-1}\text{)}$	$\zeta_{111}$	$\zeta_{11}$	$D_{111}/D_{11}$
350	10 000	6667	1.000	1.000	1.494
1750	10 000	6667	0.94	0.963	1.463
350	11 111	5556	0.996	0.997	1.711
1750	11 111	5556	0.906	0.937	1.650
350	12 500	4167	0.992	0.994	2.162
1750	12 500	4167	0.821	0.891	1.994
350	14 286	2381	0.973	0.985	3.561
1750	14 286	2381	0.486	0.699	3.511
350	15 385	1282	0.902	0.949	6.234
1750	15 385	1282	-0.064	0.281	-1.491

and calculation conditions; thus, examination of the effect of damping on the two-level dispersion terms will reveal the importance of the damping correction. For DFWM it is common to operate closer to resonance, thus a near-resonant damping analysis derived from a two-level model will not be useful. It is recognized that higher states could also be significant for QEO, EFISH, and THG, though the corresponding dispersion terms (e.g.,  $D_{11n}$ ,  $n \neq 1$ ) will usually be smaller than the two-level dispersion terms, given the conditions defined above. In other words, if the correction is significant in  $D_{111}$  and  $D_{11}$ , it can often be ignored for higher states. The generality of this statement fails when two-photon absorptions are not allowed to the first excited state, but are allowed to a low-lying higher state  $m$  [i.e.,  $(\mu_{01})^1(\Delta\mu_{01})^2D_{111} \approx 0$ , but  $D_{1m1} \neq 0$ ]. Under these circumstances,  $D_{1m1}$  could be larger than  $D_{11}$ , because the two-photon frequency could be close to resonance with state  $m$ . In contrast to EFISH and THG, this is not a problem for the QEO process where the two-photon frequency is nearly the same as the fundamental,  $\omega_0$ . For EFISH and THG, damping effects of higher excited states may need to be included.

Using the expressions from Orr and Ward,<sup>6</sup> we have calculated  $D_{111}$  and  $D_{11}$  for the QEO, EFISH, and THG processes, with  $\Gamma=0$  (no damping),  $\Gamma=350\text{ cm}^{-1}$  (weak damping as seen in the most narrow absorption bands), and  $\Gamma=1750\text{ cm}^{-1}$  (moderate damping as seen in absorp-

tions of average width). These quantities represent the peak *half-widths* at half-height (HWHH), and will be relevant regardless of the broadening mechanism, homogeneous or inhomogeneous, since the observed damping is the effect which controls the measured value of  $\chi^{(3)}$  to which calculations are compared. These values of  $\Gamma$  presume Lorentzian peak shapes,<sup>11</sup> though when broadening is inhomogeneous (the usual case for liquids and solids near room temperature) peak shapes will normally be Gaussian, and are somewhat more narrow than implied by the Lorentzian peak HWHH. Thus, the  $350\text{ cm}^{-1}$  HWHH of a Lorentzian peak will behave more like a Gaussian of  $450\text{--}550\text{ cm}^{-1}$  HWHH, while a Lorentzian of  $1750\text{ cm}^{-1}$  HWHH will look like a Gaussian of  $2200\text{--}2450\text{ cm}^{-1}$  HWHH.

For QEO,  $\omega_{1g}$  is fixed at  $16\,667\text{ cm}^{-1}$  ( $\lambda_{\text{max}}=600\text{ nm}$ ), while  $\omega_0$  is varied from  $10\,000\text{ cm}^{-1}$  to  $15\,385\text{ cm}^{-1}$ . For EFISH and THG,  $\omega_0$  is set at  $5263\text{ cm}^{-1}$  ( $\lambda=1.9\text{ }\mu\text{m}$ , a common wavelength for far-off-resonant measurements), while the molecular excitation frequency  $\omega_{1g}$  is varied. For the purpose of analyzing and presenting the data, we define the quantity  $\zeta_q^\Gamma = D_q^\Gamma/D_q^{\Gamma=0}$ , where  $D_q^\Gamma$  is the dispersion ( $q$  either equal to 11 or 111) including damping of  $\Gamma$ , while  $D_q^{\Gamma=0}$  is the term with  $\Gamma=0$ . When the effect of damping is negligible,  $\zeta_q^\Gamma$  will be equal to or near unity. Results are presented in Tables I–III and can be used to judge when damping could be an important con-

TABLE II. Results for EFISH. Note that  $\omega_0=5263\text{ cm}^{-1}$ .

$\Gamma\text{ (cm}^{-1}\text{)}$	$\omega_{1g}\text{ (cm}^{-1}\text{)}$	$\omega_{1g}-2\omega_0\text{ (cm}^{-1}\text{)}$	$\zeta_{111}$	$\zeta_{11}$
350	25 000	14474	1.000	0.999
1750	25 000	14474	0.990	0.992
350	20 000	9474	0.999	0.999
1750	20 000	9474	0.977	0.983
350	16 667	6140	0.998	0.999
1750	16 667	6140	0.947	0.964
350	14 286	3759	0.994	0.997
1750	14 286	3759	0.867	0.918
350	12 500	1974	0.979	0.989
1750	12 500	1974	0.601	0.776

TABLE III. Results for THG. Note that  $\omega_0 = 5263 \text{ cm}^{-1}$ .

$\Gamma \text{ (cm}^{-1}\text{)}$	$\omega_{1g} \text{ (cm}^{-1}\text{)}$	$\omega_{1g}-3\omega_0 \text{ (cm}^{-1}\text{)}$	$\zeta_{111}$	$\zeta_{11}$
350	25 000	9211	1.000	1.000
1750	25 000	9211	0.980	0.984
350	20 000	4211	0.997	0.998
1750	20 000	4211	0.927	0.941
350	16 667	877	0.954	0.958
1750	16 667	877	0.406	0.453

cern and when it can be ignored entirely. Note that for  $\Gamma=0$ , the  $\zeta_q^0$  equal unity and are not listed.

For all processes shown here it is clear that for  $\Gamma=350 \text{ cm}^{-1}$ , damping corrections can be small as long as the difference between  $\omega_{1g}$  and the appropriate one-, two-, or three-photon absorption is large. The frequency probe  $\omega_0$  of QEO can be adjusted as necessary to do this, and for EFISH, even a red to near-ir dye would be sufficiently far from  $1.9 \mu\text{m}$ . However, for THG, a blue dye (wavelength of the absorption maximum  $\lambda_{\text{max}}=600 \text{ nm}$ ) would show noticeable effects from damping. Note that this result assumes a narrow electronic absorption peak only *infrequently* encountered in organic molecules.

When a more realistic  $\Gamma$  of  $1750 \text{ cm}^{-1}$  is used, damping corrections will often be mandatory for many QEO calculations. For  $\approx 99\%$  (Ref. 12) accuracy in THG, damping can only be ignored when  $\omega_{1g} > 25\,000 \text{ cm}^{-1}$ , and for EFISH when  $\omega_{1g} > 20\,000 \text{ cm}^{-1}$ . There is a particular problem with THG, since many of the most interesting molecules with the largest  $\gamma$ 's absorb at wavelengths greater than  $500 \text{ nm}$ . At  $600 \text{ nm}$ , corrections of  $\approx 250\%$  will be necessary. It should be noted that it is possible for  $\Gamma$  to be *greater* than  $1750 \text{ cm}^{-1}$  for molecular electronic excitations.

Far from resonance, the two-level dispersion of  $\gamma$  in a noncentrosymmetric system (the sum of the effects of both  $D_{11}$  and  $D_{111}$ ) will look much like that in a centrosymmetric system ( $D_{11}$  alone) regardless of damping. However, closer to resonance, the tables reveal that  $\zeta_{111} < \zeta_{11}$  for any given set of conditions. Since  $\zeta_{111}$  is only present when  $\Delta\mu_{01} \neq 0$  (i.e., noncentrosymmetry), it is clear that noncentrosymmetric molecules should require larger damping corrections than centrosymmetric molecules. Table I also shows that for QEO (the general trend is also seen in EFISH and THG) the ratio  $D_{111}/D_{11} > 1$  can greatly increase this particular sensitivity as one approaches resonance. This would also be true for DFWM in a regime defined by  $2\omega_0 < \omega_{1g}$ , though this result is of dubious value since most DFWM mea-

surements are far closer to resonance than this, and are influenced by multiphoton resonances with higher states. The sensitivity to symmetry occurs because the enhancement in  $D_{111}$  as one approaches resonance increases faster than for  $D_{11}$ , such that  $D_{111}$  becomes dominant in controlling the overall dispersion. This can be grasped intuitively by examining the first terms of Eqs. (2) and (3), always the largest under the conditions defined above, and noticing that the term for Eq. (2) has an explicit two-photon resonance that is not present in the analogous term in Eq. (3). In contrast to  $D_{11}$ ,  $D_{111}$  will always feel an extra near-resonant influence owing to multiphoton resonances.

Apart from the effects on calculations, there is also an experimental concern regarding the measurement of  $\text{Re}(\beta)$  by EFISH. Even for a fundamental wavelength  $\omega_0 = 1.9 \mu\text{m}$ , measurements of dyes with  $\lambda_{\text{max}} > 500 \text{ nm}$  could require significant damping corrections to accurately compare the  $\beta$  [or the damping uncorrected "dispersionless"  $\beta_0$  (Refs. 13 and 14)] to those of dyes that absorb further to the blue. This correction is less a concern for the  $\mu\beta$  term itself than it is for the smaller electronic third-order correction  $\gamma_e$  that is necessary to extract  $\mu\beta$  from the total EFISH signal. Correcting the second harmonic intensity for the linear absorbance will partly, but not completely, account for the effect of damping in the nonlinear susceptibility.

We have shown that damping corrections will often be significant when calculating third-order nonlinear-optical susceptibilities, the sensitivity of which depend on  $\Gamma$ , the optical process, the relationship between  $\omega_0$  and  $\omega_{1g}$ , and molecular symmetry.

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<sup>11</sup>Presuming a first-order rate decay with lifetime  $\tau$  ( $1/\Gamma$ ), one arrives at, via Fourier transform, the Lorentzian peak shape with the half width at half maximum being given by  $1/\tau$  ( $\Gamma$ ). See W. H. Flygare, *Molecular Structure and Dynamics*

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<sup>12</sup>This presumes the two-level model; the contribution of higher excited states will *reduce* this "confidence" level.

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