Anomalous Optical Homogeneous Linewidths in Glasses

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The homogeneous linewidth is calculated for resonant optical transitions in glasses. The width is due to modulation of the optical levels caused by coupling to the diagonal as well as off-diagonal elements of the two-level modes. The main contribution arises from diagonal modulation of abundant but weakly coupled two-level modes. For a flat density of states of two-level modes and a dipole-quadrupole coupling a large $T^{1.75}$ behavior is found in good agreement with recent data.

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Recent data of fluorescence homogeneous linewidths in glasses show anomalously large magnitudes and unusual temperature dependence compared with those of crystalline hosts.[1,2] The linewidth is proportional to $T^{\gamma\pm0.2}$ with $\gamma=1.8$ ($7<T<80$ K) for Eu^{3+}-doped silicate glass[1] and $\gamma=1.85$ and $\gamma=1.88$ ($6<T<300$ K) for Pr^{+}-doped BeF_2 and GeO_2 glasses, respectively.[2] The anomaly is believed[1,2] to be due to the so-called two-level modes (TLM) present in amorphous hosts.[3,4] The purpose of this paper is to present a theory for this phenomenon at low temperatures.

Recently the effect of modulation of the optical levels via coupling to the off-diagonal elements of TLM has been studied.[5] The modulation occurs as a result of a rapid phonon-assisted tunneling motion, between two local potential wells, of an atom (or a group of atoms) which is coupled to the optical ion through multipolar interaction. (The frequency is $\Gamma h^{-1}\sim 4\times10^{7}$ Hz for $Ek_B^{-1}=5$ K; E is the two-level energy separation.) A quadratic temperature dependence was obtained. However, a very large density of states was necessary to fit the data.[5] In this paper I examine the effect of the coupling of the optical levels with the diagonal (together with off-diagonal) elements of TLM for arbitrary coupling strengths. I find that the diagonal modulation (DM) is much more important than the off-diagonal modulation (ODM) and that dominant contributions to fluorescence linewidth ($\Delta\omega$) arise from the abundant weakly coupled TLM, the coupling strengths (V) of which lie between the small damping (Γ) of the TLM and two-level separation (i.e., $\Gamma\ll V\ll E$). Each two-level system in this range contributes an amount Γ to $\Delta\omega$ independent of V in contrast to the recent "perturbation" (line narrowing) result of Selzer *et al.*[1] where a contribution V^2/Γ was found. I find the latter behavior only in the true perturbation limit $V\ll\Gamma$. The contribution from these extremely weakly coupled TLM is negligible.

The resonant optical transition occurs between the ground ($n=0$) and excited ($n=1$) levels of an impurity ion. The transition energy, namely, the resonant photon energy $\hbar\omega_0=\epsilon_1-\epsilon_0$ is much larger than the Debye acoustic phonon energy ($\hbar\omega_D$) and the energy (E) of TLM. The Hamiltonian describing an optical ion interacting with a single two-level system in the phonon field is given by

$$H=\sum_{n=0}^{1}\epsilon_n\psi_n^{\dagger}\psi_n+\tfrac{1}{2}E\sigma^{z}+\tfrac{1}{2}\sum_{n=0}^{1}\sum_{\alpha}V_n^{\alpha}\psi_n^{\dagger}\psi_n\sigma^{\alpha}+\sum_q\hbar\omega_q(n_q+\tfrac{1}{2})+\tfrac{1}{2}\sum_{\alpha}f^{\alpha}\epsilon\sigma^{\alpha}, \tag{1}$$

where the fermion creation and annihilation operators $\psi_n^{\dagger}$ and ψ_n describe the electronic states and σ^{α} are the Pauli matrices. The index α is summed over $\alpha=z$, $+$, and $-$, with $\sigma^{\pm}=\sigma^{x}\pm i\sigma^{y}$. The first three terms in (1) describe the ion, the two-level system, and the interaction between them, respectively. The latter contains the DM (V_n^{z}) as well as ODM ($V_n^{\pm}$). The last two terms in (1) describe the phonon energies and the interaction of the two-level system with the strain. Eventually contributions from all TLM will be summed.

The energy E is related to the energy asymmetry Δ of the wells and the overlap energy $t/2$ by $E=(\Delta^2+t^2)^{1/2}$.[3,4] The coefficients f^{α} are given by $f^{z}=B\Delta/E$ and $f^{\pm}=Bt/2E$ where B is the difference in the deformation potential constants for the two unperturbed wells. Similarly, $V_n^{z}=C_n\Delta/E$ and $V_n^{\pm}=C_nt/2E$ where C_n is the difference in the coupling strengths between the nth optical level and the two unperturbed wells. The quantities Δ and t are of the order of E so that $f^{z}\sim f^{\pm}\sim B$ and $V_n^{z}\sim V_n^{\pm}\sim C_n$.

The spectral line shape is given by the imaginary part of the Fourier transform $[F(\omega)]$ of the

retarded Green's function[6]

$$F(t) = -i\,\theta(t)\,\langle[(\psi_1\psi_0{}^\dagger)(t), \psi_0\psi_1{}^\dagger]\rangle,$$

where θ and the angular brackets denote the unit step function and thermal average, respectively, and $(\psi_1\psi_0{}^\dagger)(t)$ is in the Heisenberg representation. The square brackets represent the commutator. The spectral function is evaluated rigorously by employing the equation of motion method for arbitrary coupling strengths $V_n{}^\alpha$ and a small strain. The mathematical details of the calculation are complicated and will be presented elsewhere. However, the results can be interpreted in a simple way as will be shown below.

For this purpose the first three terms in (1) are diagonalized for the occupation of the nth level yielding a doublet $\epsilon_n \pm \frac{1}{2}E_n$ with

$$E_n = [(E + V_n{}^z)^2 + 4(V_n{}^+)^2]^{1/2}. \tag{2}$$

The off-diagonal part of the last term (to be denoted as $H_{\mathrm{TLM-ph}}$) in (1) is then rewritten in terms of these new diagonal bases (to be designated as $|n,\pm\rangle$) as

$$\langle n,\pm|H_{\mathrm{TLM-ph}}|n,\mp\rangle = \frac{\epsilon}{E_n}\{f^z V_n{}^+ - f^+(E + V_n{}^z)\}. \tag{3}$$

The optical line shape is Lorentzian and the width ($\Delta\omega$) equals the sum of the widths of the ground- and excited-state sublevels involved in the transition. The total fluorescence linewidth is then a properly averaged sum of these individual widths arising from four possible optical transitions [cf. (5)]. At this point it is useful to note that the observed inhomogeneous linewidth in a typical glass[1,2,7] is of order of 100 cm^{-1} and the spectral shifts $\pm E_0 \pm E_1$ can be partially responsible.

The widths of the sublevels $|n, \alpha = \pm\rangle$ due to one-phonon-assisted processes are given by

$$\Gamma_n{}^\alpha = 2\pi\sum_q \left\{\frac{f^z V_n{}^+ - f^+(E + V_n{}^z)}{E_n}\right\}^2 |\langle n_q + \alpha|\epsilon|n_q\rangle|^2 \delta(\hbar\omega_q - E_n), \tag{4}$$

where $\alpha = \pm 1$ will be assigned to $\alpha = \pm$ for the strain matrices in (4) for emission and absorption processes, respectively. The ODM [i.e., the first term in the curly brackets in (4)] was obtained by Lyo and Orbach,[5] while the DM (i.e., the second term) is a new effect. The total observed optical homogeneous linewidth equals

$$\Delta\omega = \sum_E \sum_{\alpha=\pm} p_\alpha \sum_{\alpha'=\pm} S_{\alpha'\alpha}(\Gamma_0{}^\alpha + \Gamma_1{}^{\alpha'}), \tag{5}$$

where the first sum denotes summing over all TLM, and

$$p_\alpha = \tfrac{1}{2}\exp(-\alpha\beta E_0/2)/\cosh(\beta E_0/2)$$

($\beta^{-1} = k_B T$) is the thermal occupation probability for the ground-state doublet. The transition probability $S_{\alpha'\alpha}$ is given by

$$S_{\alpha'\alpha} = |\langle 1, \alpha'|0, \alpha\rangle|^2 = \tfrac{1}{2}\{E_0E_1 + \alpha'\alpha[(V_0{}^z + E)(V_1{}^z + E) + 4V_0{}^+V_1{}^+]\}/E_0E_1. \tag{6}$$

Note that the transition vanishes between different "spin" states (i.e., $\alpha\alpha' = -1$) in the limit $V_0{}^+$ (or $V_1{}^+$) = 0.

We expect that only a small number of TLM are close to the optical ion under consideration. Most of them are distant and thus weakly coupled. For these abundant, weakly coupled TLM ($|V^\alpha| < E$), DM is dominant over ODM in view of the fact that $f^z \sim f^\pm$ and $V^z \sim V^\pm$. Because the magnitude of the quantity in the curly brackets of (4) is of the order of f^α for all TLM, the main contribution to $\Delta\omega$ arises from these weakly coupled TLM and the ODM will be neglected (i.e., $V_n{}^+ = 0$) in (4). Even in the opposite limit (i.e., $V_n{}^+ > E$) this approximation yields a rough order-of-magnitude estimate. A quantitative justification of this approximation will be given later.

After we set $V_n{}^z = V_n{}^\pm = 0$ in (4) whereby $S_{\alpha'\alpha} = \delta_{\alpha'\alpha}$ (δ is the Kronecker delta) in (5), the contribution to the width ($\Delta\omega$) from a two-level system then equals the thermal average of the widths of the two levels of the TLM and is, remarkably, independent of V (i.e., the ion-TLM separation)! Of course this cannot be true for an arbitrarily weak modulation. To investigate this question let us evaluate the spectral function for DM ($V^+ \equiv 0$, $V^z \equiv V_1{}^z - V_0{}^z \neq 0$). We find

$$F(\omega) = \frac{\Omega + \frac{1}{2}V^z(p_+ - p_-) - i\hbar\tau^{-1}}{\Omega^2 - \frac{1}{4}(V^z)^2 - i\Omega\hbar\tau^{-1} - \frac{1}{2}iV^z(\Gamma_+ - \Gamma_-)}, \tag{7}$$

where $\Gamma_\pm = \Gamma_0{}^\pm + \Gamma_1{}^\pm$ and $\Omega = \hbar\omega - \hbar\omega_0$. In the lim-

it $|V^z| \gg \hbar\tau^{-1} (\equiv \Gamma_+ + \Gamma_-)$, we find from (7)

$$F(\omega) = \sum_{\pm} \frac{p_{\pm}}{\Omega \mp \frac{1}{2}V^z - i\Gamma_{\pm}}$$

in agreement with the analysis given above. In this regime the levels of the optical ion and TLM are strongly coupled [cf. (2)] and locked together. In the opposite extremely weak-coupling limit $|V^z| \ll \hbar\tau^{-1}$, we find

$$F(\omega) = [\Omega - \tfrac{1}{2}V^z(p_+ - p_-) - \tfrac{1}{4}i(V^z)^2\hbar^{-1}\tau \operatorname{sech}^2(\beta E/2)]^{-1}, \quad (8)$$

which agrees with the recent motional-narrowing result of Selzer *et al.*[1] but disagrees with the result of Reinecke.[8] The interaction is perturbative. The relaxation time τ of TLM is not long enough to form a coherent coupled state [cf. (2)]. Note that the line is shifted by the average amount of modulation. The contribution, however, is negligible because $(V^z)^2$ decays rapidly with range in contrast to the case $V^z > \hbar\tau^{-1}$ where it is independent of V^z.

The linewidth is then given by

$$\Delta\omega = 2\int dE\, \rho(E) \int_{r<r_c} d^3r \sum_\alpha p_\alpha(E) \langle \Gamma^\alpha(E) \rangle_{\mathrm{av}}, \quad (9)$$

where $\rho(E)$ is the density of states per volume of TLM. The E dependence is specifically shown for p_α and $\Gamma^\alpha (\equiv \Gamma_n{}^\alpha)$ in connection with Eqs. (4) and (5). The width of TLM averaged over the random parameters Δ and t is given by[3]

$$\langle \Gamma^\alpha \rangle_{\mathrm{av}} = \tfrac{1}{4}\pi(E/\hbar\omega_{\mathrm{D}})^3 D[n_E + (\alpha+1)/2],$$

where n_E is the boson function and

$$D = \frac{1}{\lambda_{\max}} \left(\frac{\lambda_{\min}}{\lambda_{\max}}\right)^{\eta} \frac{3\pi\langle B^2\rangle_{\mathrm{av}}}{M v_s{}^2}. \quad (10)$$

Here η, M, and v_s are respectively a constant of order unity, the mass of the unit cell, and sound velocity. The quantities $\lambda_{\min} < \lambda < \lambda_{\max}$ determine the upper and lower bounds[3] of the overlap integral $t \propto e^{-\lambda}$. For typical parameters[3] $\eta = 1$, $\langle B^2\rangle_{\mathrm{av}} = 1$ (eV)^2, $\lambda_{\min} = 5$, $\lambda_{\max} = 15$, $M = 100$ amu (GeO_2), and $v_s = 3\times10^5$ cm/sec, I estimate $D = 2\times10^{-2}$ eV. The final result Eq. (11) does not depend on the value of D sensitively.

For a multipolar form of interaction, the maximum cutoff range (r_c) of the spatial integration in (9) is a decreasing function of E and is determined by the condition $|V^z| = b/r_c{}^s = \langle \Gamma^+(E) + \Gamma^-(E) \rangle_{\mathrm{av}}$. Assuming a flat density of states for TLM, we find at temperatures much below the cutoff energy of TLM

$$\Delta\omega = \tfrac{4}{3}\pi^2 D\rho\hbar\omega_D I_s (4b/\pi D)^{3/s} (T/\theta_{\mathrm{D}})^{4-9/s}, \quad (11)$$

where θ_{D} is the Debye temperature and

$$I_s = \int_0^\infty \frac{e^x x^{3-9/s}\, dx}{(e^x+1)^{1+3/s}(e^x-1)^{1-3/s}}.$$

For a general $\rho(E) \propto E^\mu$, the temperature dependence is $\Delta\omega \propto T^{\mu+4-9/s}$. It is seen that dipole-quadrupole interaction ($s = 4$) yields $\Delta\omega \propto T^{1.75}$ with $\mu = 0$ as compared to the observed behavior[1,2] $\Delta\omega \propto T^{(1.8-1.88\pm0.2)}$. At temperatures above the cutoff energy of TLM, the width increases much more slowly, as $T^{0.25}$. I fit the data at 20 K ($\Delta\omega = 0.15$ cm^{-1}) for the $^3P_0$-$^3H_4$ resonant transition in Pr^+-doped GeO_2 glass,[2] using $\theta_{\mathrm{D}} = 300$ K and $\rho = 2.0\times10^{20}$/eV cm^3 (deduced from Anderson, Halperin, and Varma[3] and the specific-heat data of Zeller and Pohl[9]) and choosing $b = 5.1\times10^2$ eV Å (Ref. 4):

$$\Delta\omega = 7.9\times10^{-4}\, T^{1.75} \text{ cm}^{-1} \quad (12)$$

for T in kelvins. Defining a to be the approximate molecular dimensions of TLM and the optical ion and e the unit electronic charge, and setting $b = e^2a^3$, we find $a = 3.3$ Å. The result in (12) also explains roughly the $^3P_0$-$^3H_4$ resonant transition in Pr^+-doped BeF_2 glass[2] and the $^5D_0$-$^7F_0$ resonant transition in Eu^+-doped silicate glass[1] at low temperatures. At high temperatures ($T > 50$ K), the theoretical values deviate gradually from the data, yielding, for example, $\Delta\omega = 17.2$ cm^{-1} compared to the observed value $\Delta\omega = 40$ cm^{-1} at 300 K for GeO_2 glass. In this temperature range, a two-phonon Raman contribution ($\propto T^2$) seems to be sufficient to explain the data.[2] At high temperatures, contributions from strongly coupled TLM are not negligible and the Debye approximation is poor. Also, the validity of a constant density of states of TLM is unclear.

The relative contribution from strongly coupled TLM ($V > E$) is small at low temperatures because of their scarcity; for the parameters used above, the cutoff radius for the spatial integration in (9) is given by $r_c = 102$ Å at 20 K ($\equiv E/k_{\mathrm{B}}$), while the strongly coupled TLM (i.e., $|V^z| > E$) lie within the radius $r = 24$ Å. The relative

fraction of the contribution from the strongly coupled TLM is then 0.8%, justifying the weak-coupling approximation. This argument is further strengthened by the fact that the approximate magnitude of the integrand for the spatial integration in (9) is smaller in the strong-coupling region than in the weak-coupling region because of the Boltzmann factors, except for the S_{+-} transition to be considered below.

A good feature of the present theory is that the optical linewidth is explained in terms of the weakly coupled, nearly isolated TLM, for which the model is well understood. Nevertheless, I mention here an interesting problem that the strongly coupled TLM may introduce to (5). Of particular interest therein is the contribution of the transition from $|0,-\rangle$ to $|1,+\rangle$ which becomes significant (i.e., $s_{+-}\sim 1$) for strongly coupled TLM at all temperatures. For the other processes, the Boltzmann factors cut off the contributions from the strongly coupled TLM (with $E_n \gg k_B T$). The quantity Γ_1^+ in (5) contains a spontaneous part and makes a temperature-independent contribution to $\Delta\omega$ at the wings of the inhomogeneously broadened line. This contribution is difficult to calculate because we do not have a reliable model for these distorted TLM. I mention here merely that the data show no appreciable temperature-independent part,[1,2] indicating that it is a small effect.

For a general density of states ($\propto E^{\mu}$) of TLM and coupling ($\propto r^{-s}$), the present result predicts $\Delta\omega \propto T^{4+\mu-9/s}$ and can only determine the relationship between μ and s from the optical data. The density of states of the low-energy (below 1 cm^{-1}) TLM is known to be constant.[9] There exists, however, a large uncertainty as to its nature for higher energy TLM. I have determined $s=4$ for the case $\mu=0$. This conclusion is further supported by the recent low-temperature data of Macfarlane and Shelby[10] who obtained $\Delta\omega = 20$ MHz at 1.6 K in a Eu-doped silicate glass using a hole-burning technique. This datum point lies on the line extrapolated from the data of Selzer *et al.*[1] in a $\log\Delta\omega$-$\log T$ plot, indicating that the power-law behavior continues down to 1.6 K. An interesting way of testing the theory is to alter the nature of the coupling by polarizing (depolarizing) the TLM by doping (undoping) the sample with donor impurities such as OH^- ions.[11] A more detailed account of this work will be published elsewhere.

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