

HOLE BURNING LINE SHAPES IN A TWO-DIMENSIONAL GLASS: A MODEL FOR HOLE BURNING LINE SHAPES OF MOLECULES ON SURFACES

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A method for calculating the low temperature, hole burning line shapes of molecules in a two-dimensional glass is presented. An extension of the standard dynamic model for three-dimensional glasses is employed. A calculation of the 2-D spatial average with the proper correlation function description predicts non-Lorentzian hole profiles (narrower near the peak, broader in the wings) due to the reduction in dimensionality. A steeper power law, $\Delta\nu = aT^b$, is predicted for two-dimensional linewidths, compared to standard three-dimensional results. These results are in qualitative agreement with recent experiments of molecules on surfaces.

1. Introduction

Persistent spectral hole burning has become a widely used method for uncovering dynamic information from inhomogeneously broadened bands of chromophores in complex systems such as glasses, polymers, and biological hosts [1-6]. Optical probe molecules doped into these hosts characteristically exhibit wide, inhomogeneously broadened spectra due to the distribution of environments they inhabit. Recently, molecules on surfaces have begun to be studied with the technique [7-11]. Like bulk systems, the spectra of surface species are also inhomogeneously broadened. One recent result of these efforts has been the observation of glass-like thermal broadening of the hole width at low temperatures: $\Delta\nu = aT^b$, where $1.6 < b < 2.1$ [11]. This type of power law has been linked to low energy degrees of freedom unique to amorphous systems that are describable as tunneling states or two-level systems (TLSs) [1]. The new surface data indicate the existence of glass-like degrees of freedom [11].

Since all but the most carefully prepared surfaces are inherently disordered, it is natural to consider

modeling their low temperature properties through analogies to glasses. Some measurements of low temperature properties, known to be anomalous in amorphous materials, such as heat capacity, thermal conductivity and the attenuation of acoustic waves, are difficult to measure for surfaces. Optical measurements such as spectral hole burning, however, have been proven capable of measuring the anomalous low temperature degrees of freedom in glasses [1,12,13], and can readily be applied to various surface systems.

In a recent series of papers Berg et al. [14], and Bai and Fayer [15,16] have demonstrated that the correct description of a hole burning experiment in complex systems is achieved through the use of a four-point correlation function formalism. This is because materials such as glasses, or paramagnetic impurities in crystals with unpaired spins, possess wide distributions of rate processes which perturb the probe chromophores [16-18]. This leads to time evolution of the hole width, termed spectral diffusion in accord with the analogous spin resonance phenomenon. Comparison of two-pulse photon echo and optical hole burning measurements on organic dye/glass systems show that the techniques measure linewidths differing by factors of 6 to 9 [14,19,20]. The hole burning measurements, which typically take seconds to minutes to perform, are dominated by

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spectral diffusion. The processes termed spectral diffusion are merely the TLS jumps with rates slow enough to be rephased by the echo method, but fast relative to the time required to burn and read a hole. The time scale of the experiment, i.e. the pulse separation for a stimulated echo, or the wait between burning and reading for hole burning, must be explicitly accounted for in a correct correlation function treatment. For many surfaces, just as in glasses, a wide distribution of relaxation rates is very likely to exist. In particular, surface systems exhibiting a $\Delta\nu = aT^b$ linewidth signature are expected to possess a wide, glassy distribution of relaxation rates. Thus, the method of ref. [16] for calculating time dependent hole burning linewidths resulting from spectral diffusion, should also be applicable to glass-like surfaces.

This Letter focuses on the influence of dimensionality on the correlation function, which comes into play through the average over the spatial distribution of perturbing TLSs. The four-point correlation function formalism is applied to a model surface system and the appropriate two-dimensional (2-D) integral over surface TLS positions is treated. This leads to non-Lorentzian hole profiles with consequences for the TLS concentration, time, and temperature dependences of the linewidth.

The tunneling two-level system model for glasses has been the most successful at explaining low temperature experimental measurements. To uncover the subtle effects of low temperature TLS behavior in bulk glasses, line narrowing techniques such as the two pulse photon echo [14,18,21], accumulated grating echo [21,22], fluorescence line narrowing [23] and spectral hole burning [1,14,18] have been employed. One of the results of these experiments has been the consistent observation of Lorentzian line shapes for the frequency domain experiments [1,14], and exponential decay functions for the time domain measurements [12,14]. Calculations show that the perturbation of the optical probes by the TLS modes must be of a dipole-dipole nature to obtain Lorentzian lines [14] or exponential echo decays [12,14]. Then, when one averages over the spatial, tunneling rate and energy distributions of the ensemble of TLSs, a Lorentzian line shape which varies with time and temperature, is obtained [16]. (The calculation of a Lorentzian line shape caused by a ran-

dom distribution of dipolar perturbers in 3-D is a well known result [24]. A concise discussion of how this comes about and why the central limit theorem does not apply to long range perturbations is given on p. 1581 of ref. [14].)

In this Letter, we extend the averaging technique to surfaces, changing the spatial average to that appropriate for a two-dimensional case. We find, that *based on reduction of dimensionality alone*, the standard TLS model predicts a non-Lorentzian line shape and a steeper temperature dependence in 2-D than in 3-D for a given distribution of TLS energies.

2. The four-point correlation function formalism for hole burning

The spectral profile of the hole is proportional to the Fourier transform of the four-point, or stimulated echo, correlation function, $C(\tau, T_w, \tau)$ [15,16],

$$I_H(\nu) = \int_{-\infty}^{\infty} d\tau \exp(i\omega\tau) C(\tau, T_w, \tau), \quad (1)$$

where $C(\tau, T_w, \tau)$ is

$$C(\tau, T_w, \tau) = \left\langle \exp\left(i \sum_j^N \phi_j(\tau, T_w)\right) \right\rangle_{H,r,E,\lambda}. \quad (2)$$

The averages for each TLS, j , are over the stochastic history path, H , the spatial distribution, r , and the microscopic parameters of a TLS, the splitting energy E , and the tunneling parameter $\lambda = d(2MV/\hbar)^{1/2}$ [15,16]. Adopting the sudden jump model to describe the perturbation caused by TLSs, $\phi_j(\tau, T_w)$ is the function [15,16,25,26]

$$\phi_j(\tau, T_w) = \Delta\omega_j \left(\int_0^\tau h(t) dt - \int_{T_w+\tau}^{T_w+2\tau} h(t) dt \right), \quad (3)$$

where $\Delta\omega_j$ is the perturbation of the chromophore's optical frequency by the j th TLS. $h(t)$ is a random telegraph function that takes on the values $+1$ or -1 depending on the state of the TLS. The time dependence of the frequency, here, arises from the sudden jumps between the levels of the perturbers. The time limits in the integrals of eq. (3) are straightforward for stimulated echoes. τ and T_w are defined as the

delays between the first and second pulses, and the second and third pulses, respectively. The stimulated echo is generated at time $T_w + 2\tau$ later. For a hole burning experiment, τ is the lifetime of the coherent polarization induced during the burning and reading pulses, essentially the T_2' that a two-pulse echo would measure [16]. T_w is basically the time required to perform the experiment, from burning through reading the hole [16]. In hole burning, T_w is typically many orders of magnitude longer than τ .

The correlation function is set up in eq. (2) as an average over path histories, spatial positions and internal parameters of the perturbation of N TLSs on the frequency of a single reference chromophore. This is valid for a low concentration sample [24–28]. The sum, \sum_j , corresponds to a particular configuration of N TLSs around a chromophore. The exponential in eq. (2) can be factored into a product of terms corresponding to a fixed reference chromophore and all N TLSs

$$C(\tau, T_w, \tau) = \prod_{j=1}^N \langle \exp[i\phi_j(\tau, T_w)] \rangle_{H,r,E,\lambda}. \quad (4)$$

The product of N similar terms may be further simplified to give

$$C(\tau, T_w, \tau) = \langle \exp[i\phi(\tau, T_w)] \rangle_{H,r,E,\lambda}^N \quad (5)$$

and the subscript, j , dropped as the averages will be the same for all N TLSs.

These, and the following manipulations used to reduce the N -body problem to a two-body problem calculated N times, are quite well known [24–28]. Here, we follow Bai and Fayer [15,16], who perform the path history average first, along with the usual rearrangements made possible by assuming each of the N perturbers are non-interacting. The spatial average is postponed until after the average over path histories is taken [16]. This has been shown to aid in the evaluation of systems with non-uniform distributions of perturbers and keeps the treatment more general [16]. Also, the complex part of the calculation cancels naturally in the history average [16], avoiding the need to introduce approximations eliminating it [27,29]. Using

$$\langle \exp[i\phi(\tau, T_w)] \rangle^N = 1 - \langle 1 - \exp[i\phi(\tau, T_w)] \rangle^N \quad (6)$$

and

$$\lim_{N \rightarrow \infty} (1 + y/N)^N = \exp y, \quad (7)$$

eq. (5) becomes

$$C(\tau, T_w, \tau) = \exp\{-n_0 \langle 1 - \exp[i\phi(\tau, T_w)] \rangle_{H,r,E,\lambda}\}, \quad (8)$$

where the density of TLS, $n_0 = N/A$ for a 2-D system, has been explicitly included, after separating the $1/A$ area factor from the spatial average,

$$\langle \rangle_r = \frac{1}{A} \int_0^{\infty} dA. \quad (9)$$

The history average may now be performed. In the long time limit, $T_w \gg \tau$, the result is [16]

$$C(\tau, T_w, \tau) = \exp\{-n_0 \langle \sin^2(\Delta\omega\tau) \operatorname{sech}^2(E/2kT) \times [1 - \exp(-RT_w)] \rangle_{r,E,\lambda}\}. \quad (10)$$

In deriving eq. (10), the dynamics of the two-level perturbers are modeled as one-phonon-induced sudden jumps, each characterized by a relaxation rate, R . The distribution of energy splitting, E and tunneling parameters, λ , leads naturally to a distribution of rates $P(R)$. The average over E and λ can be converted to one over E and R [15,16]

$$C(\tau, T_w, \tau) = \exp\{-n_0 \langle \sin^2(\Delta\omega\tau) \operatorname{sech}^2(E/2kT) \times [1 - \exp(-RT_w)] \rangle_{r,E,R}\}. \quad (11)$$

When the optical center has no significant effect on the TLSs behavior the average over spatial position can be separated from the E and R averages to give [16]

$$\langle \sin^2[\Delta\omega(r)\tau] \rangle_r \times \langle \operatorname{sech}^2(E/2kT) [1 - \exp(-RT_w)] \rangle_{E,R}. \quad (12)$$

The correlation function has now been split into two parts, the spatial average $\langle \rangle_r$, and the temperature and time-dependent part that determines the number of TLS systems that have flipped, in an interval T_w , $\langle \rangle_{E,R}$ [13,16,30]. This essentially gives a line shape function times a number. The shape function, i.e. the spatial average, is dependent on the

chromophore-TLS interaction and the spatial distribution of TLS, for its functional form. For dipole-dipole interactions, with a random distribution of perturbers, this leads to a Lorentzian line in three-dimensional systems [24]. For a two-dimensional distribution of perturbers, the line shape is more complex and must be numerically evaluated.

3. The two-dimensional spatial average

Our problem is now to solve the spatial average in eq. (12) for a molecule surrounded by a two-dimensional distribution of perturbing TLSs. The functional form of the chromophore-perturber interaction, $\Delta\omega(r)$, and the spatial distribution, $P(r)$, must be specified. A uniform surface distribution of TLSs is chosen: $P(r) dr = dA/A$. The frequency perturbation, $\Delta\omega(r)$, is assumed to be of a dipole-dipole nature. This is consistent with several different types of experimental results [12,14] for three-dimensional systems. The dipoles involved could be either electric, or elastic, strain dipoles [30]. $\Delta\omega(r)$ is

$$\Delta\omega(r, \Omega) = \frac{\Delta\mu_M \Delta\mu_{\text{TLS}} \kappa(\Omega)}{r^3} = \frac{D\kappa(\Omega)}{r^3}. \quad (13)$$

r is the distance between a TLS and the chromophore. $\kappa(\Omega)$ is the orientational factor for the dipolar coupling. D is the dipolar coupling constant, $D = \Delta\mu_M \Delta\mu_{\text{TLS}}$. It is the change in dipole moments, $\Delta\mu$, between the TLS states and the ground and excited levels of the optical center that determines the coupling strength.

A model surface is depicted in fig. 1. The $\Delta\mu$ dipole vectors are centered on the surface plane, but are allowed to point in any direction. Both the chromophores and the perturbers are confined to the plane. This type of model would still apply to a layer of finite thickness if the disorder modes were found mainly on the interface. The substrate is assumed not to possess tunneling states, or at least, to have only weakly coupled ones, or low concentrations of them.

The spatial average from eq. (12) is

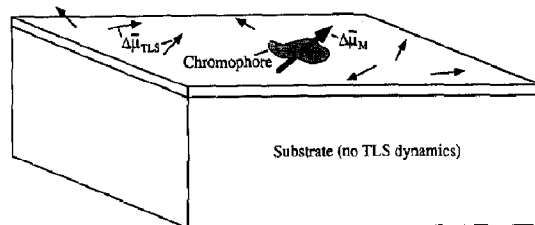


Fig. 1. Picture of a model surface. A chromophore with a ground-excited state dipole moment change $\Delta\mu_M$ is surrounded by a random distribution of surface TLSs with dipolar changes $\Delta\mu_{\text{TLS}}$ associated with jumps between the two states. TLSs are present only on the surface. The bulk substrate is presumed not to possess TLS modes, or equivalently, that their concentrations and/or coupling strengths are small enough that they may be ignored.

$$\langle \sin^2(\Delta\omega\tau) \rangle_{r,\Omega} = \int_0^{2\pi} d\theta \int_0^\infty r dr \sin^2\left(\frac{D}{r^3} \tau \langle \kappa(\Omega) \rangle_\Omega\right), \quad (14)$$

$$= \frac{2}{3}\pi \langle |\kappa(\Omega)| \rangle_\Omega^{2/3} (D\tau)^{2/3} \int_0^\infty \frac{\sin^2(x) dx}{x^{5/3}}, \quad (14a)$$

$$= 3.343 \langle |\kappa(\Omega)| \rangle_\Omega^{2/3} (D\tau)^{2/3}. \quad (14b)$$

It follows that the correlation function, eq. (11), will be non-exponential for a two-dimensional system, proportional to $\exp(-c\tau^{2/3})$, where c is a constant. In evaluating eq. (14) the spatial angle θ , and the dipolar orientational angles, referred to collectively as Ω , have been kept separate. The $1/A$ normalization factor is already contained in the surface concentration factor. After the variable change, the numerically evaluated expression

$$\int_0^\infty \frac{\sin^2(x) dx}{x^{5/3}} = 1.596 \quad (15)$$

has been used. The dipolar orientational average, $\langle |\kappa(\Omega)| \rangle_\Omega$, is a term on the order of one [31]. It has been explicitly calculated for electric dipoles for a variety of orientational models and found to be between 0.574 and 0.920 in two-dimensional systems [31]. For elastic dipolar interactions $\langle |\kappa(\Omega)| \rangle_\Omega$ is a more complex function involving the strain tensors of the medium [30]. For a three-dimensional system, an approximate calculation gave the value 0.87 [30]. In what follows this term is combined with the dipolar coupling constant, D . It does not influence

the hole shape or temperature dependence. Note that the lower limit of the spatial integral in eq. (14) may be set equal to zero without significant error, despite the probe molecule's finite size. The effect of this finite dimension (termed r_c in a spherical approximation) is to introduce a cutoff in the far wings of the line shape at $\omega_c = D/r_c^3$ [27]. This is discussed further in ref. [20] for 3-D systems with intrinsically confined geometries.

This treatment is similar to that for three-dimensional systems. In the three-dimensional expression, $r dr$ is replaced with $r^2 dr$, and the integral (with $x = 1/r^3$, and c a constant) then becomes [24–28]

$$\frac{1}{3} \int_0^{\infty} dx \frac{\sin^2(\tau cx)}{x^2} = \frac{1}{6} \pi |\tau c|. \quad (16)$$

This result leads to the exponential decay of the correlation function, and the line shape, eq. (1), is Lorentzian. Eq. (14) is the proper description for a two-dimensional distribution of dipolar perturbers. Differing orientational models such as fixing the dipole vectors in the plane, versus allowing them to point freely in space, will only cause changes in the value of $\kappa(\Omega)$ [31], and will not affect the final line shape function. Distributing the perturbers in a surface layer, thin with respect to the coupling strength, will give a correlation function between the $\exp(-c\tau^{2/3})$ and $\exp(-c\tau^1)$ limits. As a layer's thickness increases, the spatial average rapidly approaches the exponential three-dimensional limit, leading to Lorentzian line shapes. A completely analogous calculation for a one-dimensional distribution of dipolar perturbers, leads to a correlation function proportional to $\exp(-c\tau^{1/3})$, although such a system is physically unlikely. These stretched exponential correlation functions, used here to calculate line shapes, resemble other types of decay laws involving excitation transport discussed by Blumen et al. for fractal lattices of varying dimension [32].

4. Calculation of the 2-D line shape

The average over E and R in eq. (12) selects out only the active TLSs, those which have changed state and perturbed the chromophore at a given temperature, T , by the experimental waiting time, T_w . This

effectively changes the density of TLSs, n_0 , into a weighted density, dependent on temperature and time, $n(T, T_w)$. The expression which must be evaluated to generate a model hole burning line shape is

$$I_H(\nu) = \int_{-\infty}^{\infty} d\tau \exp(i\omega\tau) \times \exp[-3.343n(T, T_w)(D\tau)^{2/3}]. \quad (17)$$

The non-exponential temporal function is transformed with a fast Fourier transform algorithm to generate the line profile. An array of several thousand time points is used ranging, typically, from picoseconds to nanoseconds.

Values must be chosen for the active TLS density, $n(T, T_w)$, and the dipolar coupling constant, D . We choose these parameters to give linewidths comparable to the data of Orrit, Bernard and Möbius on resorufin on a Langmuir–Blodgett monolayer [11]. They observed non-Lorentzian holes with fwhm of about 2.7 GHz at 2.0 K. They also observed a linewidth versus temperature dependence of the form, $\Delta\nu = aT^b$, where the b values were in the range 1.6–2.1. This is a steeper power law than usually observed in bulk glasses for which the value $b = 1.3$ is surprisingly common [1,33]. The function, eq. (17), is able to produce line shapes similar to those reported in ref. [11]. In addition, the 2-D linewidth from eq. (17) has a steeper temperature dependence than a 3-D width for identical distributions of TLS splitting energies.

Fig. 2 plots the two-dimensional hole profile from eq. (17) with the product $n(T, T_w)D^{2/3} = 2.1 \times 10^6 \text{ Hz}^{2/3}$. Physically realistic concentrations and coupling strengths can give this value, i.e. $n(T, T_w) = 5.0 \times 10^{-3} \text{ TLS}/\text{\AA}^2$ (≈ 1 TLS in a circle of $r = 8 \text{ \AA}$), $\Delta\mu_M \approx 1 D$, and $\Delta\mu_{\text{TLS}} \approx 0.06 D$ ($1 D^2 = 1.509 \times 10^{14} \text{ Hz } \text{\AA}^3 = 1 \times 10^{36} \text{ erg cm}^3$). Also shown in fig. 2 are Lorentzian functions fit to the data. The model hole shape is sharper than the least-squares-fit Lorentzian, fig. 2a, similar to the observations of Orrit et al. in their monolayer study [11]. The comparison to a fwhm and peak height matching Lorentzian, fig. 2b, shows that the 2-D hole profile is sharper around the maximum and broader in the wings. Orrit et al. attributed their non-Lorentzian hole profiles to dispersive kinetics of the hole burning process

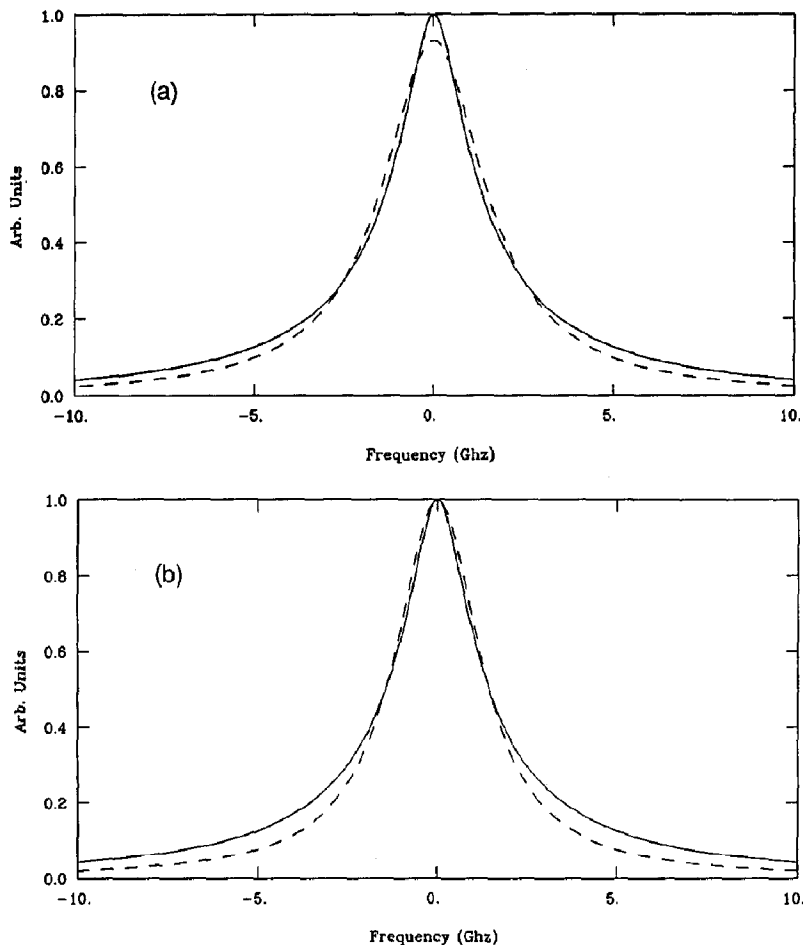


Fig. 2. The 2-D line shape compared to Lorentzian fits. (a) The 2-D line shape from eq. (12) is plotted with the solid line. A Lorentzian least-squares fit to the ± 10 GHz points is plotted with the dashed line. (b) The 2-D line shape from eq. (12) is plotted with the solid line. A Lorentzian matching the fwhm and peak height is plotted with the dashed line. Holes for systems exhibiting 2-D glassy behavior are inherently non-Lorentzian. The lines are narrower near the peak. This is consistent with experiment (see text).

[11,34]. This is certainly a possible explanation. The calculations presented here, however, show that strictly two-dimensional glass-like systems will inevitably have non-Lorentzian line shapes, with no assumptions other than the standard TLS model.

Using the standard TLS model distribution functions for E and λ , and their relationship to the relaxation rate, R , the function $n(T, T_w)$ can be obtained. Briefly, the standard model in its simplest form assumes that the distribution functions for the microscopic tunneling state parameters are constant, at least within some range. This leads to a constant low-energy density of states, $P(E) = P_E$. This con-

stant energy distribution model dates back to the effort to explain the anomalous linear term in the low temperature heat capacity [35,36]. For a given experimental waiting time T_w , the $\langle \rangle_{E,R}$ average in eq. (12) becomes

$$\langle \text{sech}^2(E/2kT) [1 - \exp(-RT_w)] \rangle_{E,R}$$

$$\propto P_E \int_{E_{\min}}^{E_{\max}} dE \text{sech}^2(E/2kT), \quad (18)$$

$$\propto (T/2k) \tanh(E/2kT) \Big|_{E_{\min}}^{E_{\max}}, \quad (18a)$$

$$\propto T^{-1} \quad (E_{\min}/2k \ll T, E_{\max}/2k \gg T). \quad (18b)$$

$n(T, T_w)$ is then proportional to T and, in 3-D, the Lorentzian hole width widens as T^1 . In 2-D glassy systems, the non-Lorentzian line shape of eq. (17) leads to an altered temperature dependence. The fwhm of the hole increases as $T^{1.5}$, which is significantly more rapid than the 3-D linear dependence. Choosing a slowly varying energy density of states ($P(E) \propto E^{0.3}$), which has been used to model observed temperature dependences, leads to $T^{1.3}$ in 3-D [1]. For this case, the 2-D linewidth increases even more steeply, as $T^{1.9}$. Similar temperature dependences were observed in the surface monolayer study of Orrit and coworkers [11]. Plots for both cases are shown in fig. 3 (the same concentration and coupling strength values used to generate fig. 2 are employed). The same consideration of line shape that

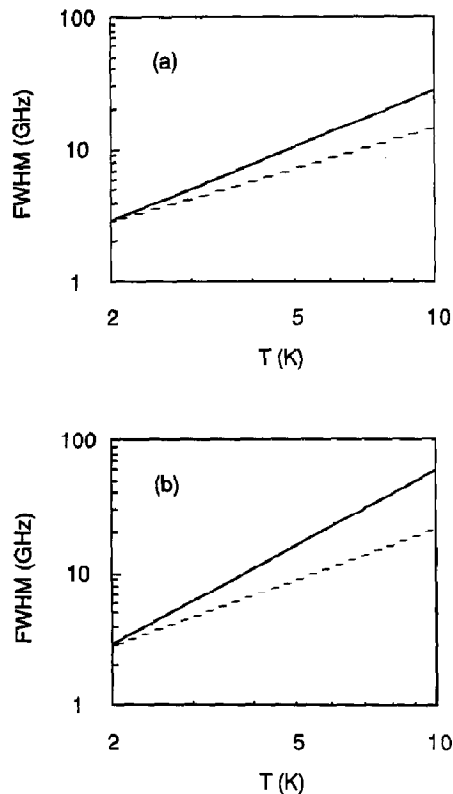


Fig. 3. fwhm versus temperature for 2-D linewidths compared to 3-D linewidths. Solid lines are 2-D linewidths, dashed lines are 3-D linewidths. Reducing the dimensionality of the system increases the steepness of the temperature dependence. This is consistent with experiment. (a) 3-D, T^1 ; 2-D, $T^{1.5}$. (b) 3-D, $T^{1.3}$; 2-D, $T^{1.9}$.

leads to different temperature behavior of the fwhm will also alter the time dependence of the width. A simple $1/R$ distribution of TLS relaxation rates yields a logarithmic time dependence for the 3-D $n(T, T_w)$ [16,37]. A somewhat faster increase of linewidth from spectral diffusion is expected for the 2-D fwhm from eq. (17), all relevant parameters, such as the TLS tunneling rate distribution, being identical, except for the dimension.

5. Conclusions

Modeling a surface as a two-dimensional glass predicts non-Lorentzian line shapes for optical hole burning of adsorbates. The hole profile is the Fourier transform of the stretched exponential correlation function, $C(\tau, T_w, \tau) \propto \exp(-c\tau^{2/3})$. The dimensional arguments leading to this result will also apply to other experiments properly described by the four-point correlation function formalism [15,16], such as fluorescence line narrowing [8,10], and the calculations are similar. While the model presented is for an ideal two-dimensional system, it is still appropriate when the perturbing TLS modes are confined primarily to a flat interface containing the optical probes. When the widths of 2-D line profiles are considered, rather than their detailed shapes, increases in their time and temperature growth rates are expected, relative to three-dimensional cases.

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