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Dipole-dipole-interaction-induced line narrowing in thin-film vibrational-mode spectra

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Under certain circumstances the electric dipole interaction can reduce or eliminate the effects of spectral inhomogeneous broadening on an infrared absorption line of a thin film. The oscillating electric dipole moment must be oriented perpendicular to the film surface, and the dipole interaction, as measured by the frequency shift that it induces, must be larger than the width of the inhomogeneous frequency distribution. An example of this interaction-induced line narrowing is presented for a vibrational mode of a $KReO_4$ film, and the relevance of this mechanism to two-dimensional electron-gas subband transitions and adsorbate vibrational modes is considered.

Infrared-active modes oriented perpendicular ($\perp$) to the plane of a thin film may assume a collective nature due to the long-range (r^{-3}) electric dipole forces within the film. For these perpendicular modes, frequencies tend to be shifted upward and mode intensities do not obey ordinary sum rules. Analogous effects are found in a number of systems including thin films,[1,2] inversion layers in semiconductors,[3,4] and adsorbate systems.[5-8] Recent advances in the spectroscopy of adsorbate vibrational modes at monolayer and submonolayer coverages[9,10] as well as the heightened interest in two-dimensional (2D) electron systems enhance the importance of understanding these effects.

In this paper we study the ν_3 vibrational mode of a $KReO_4$ thin film. This system has a strong dipole-dipole interaction and exhibits unusual nonlinear behavior which has been discussed elsewhere.[11] Here we concentrate on linear properties and, in particular, show that the perpendicular mode linewidth is narrowed considerably due to the electric dipole-dipole interaction. The possibility that this interaction-induced line narrowing, for which there is a direct analogy in magnetic resonance,[12] has been observed previously in the two-dimensional electron gas on helium[13] is also explored briefly.

Let us begin with the experimental result. Noncrystalline or polycrystalline $KReO_4$ films are thermally evaporated from a powder onto various metal or transparent substrates. In Fig. 1 the transmission spectrum of a ≈ 1000 Å $KReO_4$ film on a KCl substrate is shown for TM polarized radiation incident at 45°. The polarization and angular dependencies of these absorption line strengths show clearly that the lower frequency (≈ 908 cm^{-1}) feature is due to parallel modes while the sharper line at ≈ 951 cm^{-1} is associated with the perpendicular modes. As we expect the film to be nominally isotropic, the substantial difference in the width and shape of the perpendicular and parallel mode absorptions is surprising. We will explain this difference without invoking any anisotropy, as a consequence of the collective (i.e., dipole-coupled) nature of the perpendicular mode oscillations in the thin-film system. (An excellent introduction to the properties of the vibrational modes of thin films and other smaller systems is given in Ruppin and Englman.[2])

The system under study consists of a thin film of thickness d, sandwiched between a substrate (index of refraction, n_3) and air ($n_1=1$). As we are interested in obtaining only the $q=0$ (optical) response, we can model the film by a complex dielectric function $\epsilon_2(\omega)$. (To obtain finite q response more sophisticated approaches, such as the one described by Persson and Ryberg,[8] must be used.) For such a three-layer system the linearized equation for the change in the substrate reflectance due to the presence of the film is given in Ref. 14. From the appropriate Fresnel equation[15] one can derive the analogous equation for the change (due to the film presence) in the transmittance of TM polarized radiation

$$\frac{\Delta T}{T}=2\omega\frac{d}{c}C_0\{C_{\parallel}\cos^2\theta\,\mathrm{Im}[\epsilon_2(\omega)] + C_{\perp}\sin^2\theta\,\mathrm{Im}[-\epsilon_2^{-1}(\omega)]\}\ , \quad (1)$$

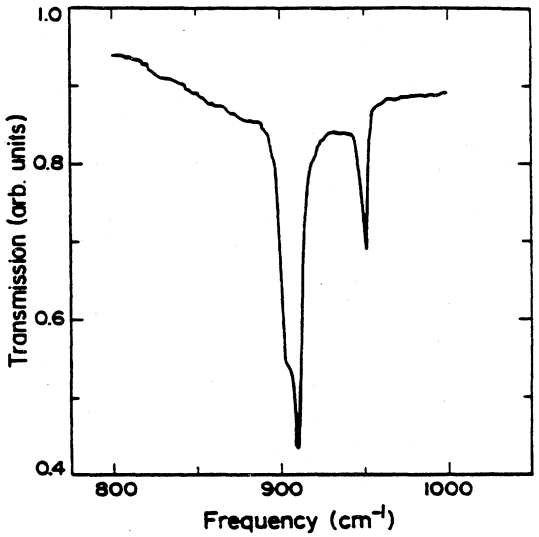

FIG. 1. Absorption lines associated with the ν_3 mode of ReO_4^- in a $KReO_4$ film are shown for $\theta=45°$. The broad resonance near 910 cm^{-1} is due to oscillations polarized in the film plane, while the sharper and weaker line near 950 cm^{-1} is due to perpendicular oscillations.

where ω and θ are the frequency and angle of incidence of the incident radiation, and

$$C_0 = \left[n_1 \left(-\frac{n_1^2}{n_3^2} \sin^2\theta \right)^{1/2} + n_3 \cos\theta \right]^{-1} , \quad (2)$$

$$C_{\parallel} = \left(1 - \frac{n_1^2}{n_3^2} \sin^2\theta \right)^{1/2} / \cos\theta , \quad (3)$$

$$C_{\perp} = n_1^3 n_3 . \quad (4)$$

Although not really necessary for calculation Eq. (1) is heuristically useful since the term containing $\mathrm{Im}[\epsilon_2(\omega)]$ is associated with absorption due to electric dipole oscillations in the plane of the film (parallel modes), while the $\mathrm{Im}[-\epsilon_2^{-1}(\omega)]$ term is due to the perpendicular modes. We will now examine the resonances in these response functions for several simple models.

For a single mode Lorentz oscillator[16] (frequency ω_t, damping γ, mode strength ω_p^2) with static screening ϵ_∞

$$\epsilon_2(\omega) = \epsilon_\infty + \omega_p^2/(\omega_t^2 - \omega^2 - i\gamma\omega) , \quad (5)$$

$\mathrm{Im}[\epsilon_2(\omega)]$ has a resonance at the frequency ω_t of width γ corresponding to the absorption due to the parallel mode. On the other hand, the longitudinal response function

$$\mathrm{Im}[-\epsilon_2^{-1}(\omega)] = \mathrm{Im}\left(\frac{\omega_p^2/\epsilon_\infty^2}{\omega_t^2 + \omega_p^2/\epsilon_\infty - \omega^2 + i\gamma\omega} \right) , \quad (6)$$

which is associated with the perpendicular oscillations, has its resonance at the higher frequency

$$\omega_l = \omega_t + \omega_p^2/\epsilon_\infty . \quad (7)$$

With respect to the parallel mode the perpendicular mode resonance is (1) shifted upward in frequency by approximately

$$\omega_s = \frac{\omega_p^2}{2\epsilon_\infty \omega_T} , \quad (8)$$

(2) weaker in intensity by ϵ_∞^2, and (3) equal in linewidth. (1) and (2) are consistent with the experimental results (Fig. 1); however, (3) is not since in the experiment we find that the parallel mode absorption is significantly broader than that associated with the perpendicular mode.

In order to explain this linewidth discrepancy let us consider the introduction of inhomogeneous broadening to $\epsilon_2(\omega)$, the simplest case of which involves a two oscillator dielectric function:

$$\epsilon_2(\omega) = \epsilon_\infty + \sum_{j=1}^{2} \frac{\omega_{pj}^2}{\omega_{tj}^2 - \omega^2 - i\gamma\omega} . \quad (9)$$

In this case $\mathrm{Im}[\epsilon_2(\omega)]$, as shown in Fig. 2, has a doublet resonance with peaks at ω_{t1} and ω_{t2} corresponding to absorption due to parallel modes. Surprisingly, however, $\mathrm{Im}[-\epsilon_2^{-1}(\omega)]$ does not mimic this doublet structure, but has only a single sharp resonance at a frequency between $\omega_{t1} + (\omega_{p1}^2 + \omega_{p2}^2)/\epsilon_\infty$ and $\omega_{t2} + (\omega_{p1}^2 + \omega_{p2}^2)/\epsilon_\infty$. This tendency of the resonance in $\mathrm{Im}[-\epsilon_2^{-1}(\omega)]$ to remain narrow despite the inhomogeneous broadening in $\epsilon_2(\omega)$ is found to prevail whenever the perpendicular-parallel mode splitting ($\approx \omega_s$) is greater than the separation of the parallel modes ($\omega_{t1} - \omega_{t2}$).

It is now clear why a transmission spectrum calculated using Eqs. (1) and (9) can compare favorably to the data

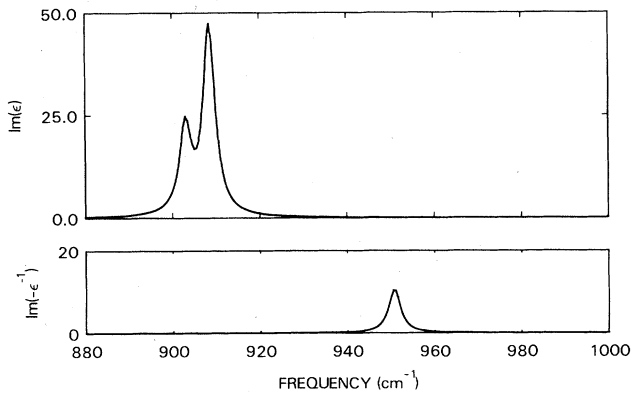

FIG. 2. Resonances of the two mode Lorentz oscillator dielectric function are shown as a function of frequency. In $\mathrm{Im}(-\epsilon^{-1})$ the double resonance put into ϵ has coalesced into a single line.

shown in Fig. 1. The striking point is not that we can fit the data with Lorentz oscillators, but that the (doublet) structure introduced to fit the parallel modes does not produce a corresponding structure in the perpendicular absorption line.

Departing from the data of Fig. 1, we can explore this electric dipole-dipole-interaction narrowing by considering an inhomogeneously broadened line with a Gaussian profile, i.e.,

$$\epsilon_2(\omega) = \epsilon_\infty + \frac{\omega_p^2}{\sqrt{\pi}\Delta} \int_{-\infty}^{\infty} \frac{e^{-(\tilde{\omega}-\omega_t)^2/\Delta^2}}{\tilde{\omega}^2 - \omega^2 - i\gamma\omega} d\tilde{\omega} , \quad (10)$$

Here ω_t is the center frequency of the Gaussian packet and Δ and γ are the inhomogeneous and homogeneous linewidths, respectively. (We assume $\Delta > \gamma$.)

The resonance in $\mathrm{Im}[\epsilon(\omega)]$, which is associated with parallel mode absorption, always exhibits the full inhomo-

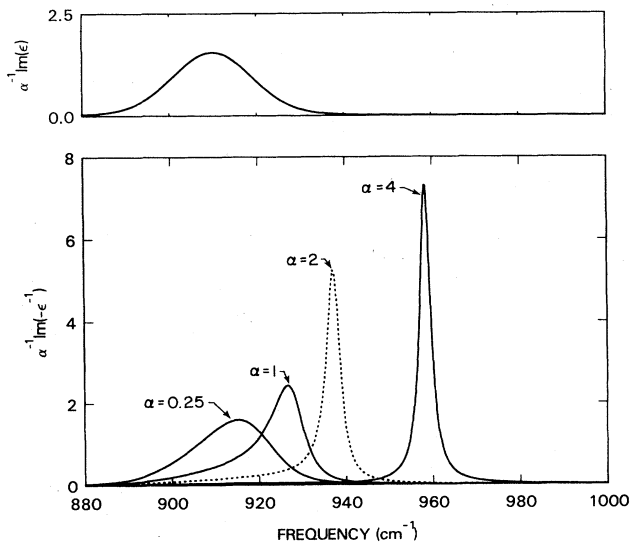

FIG. 3. Resonances of a Gaussian distribution of Lorentz oscillators are shown. The resonance in $\mathrm{Im}(\epsilon)$ is Gaussian for all α. In contrast, the resonance in $\mathrm{Im}(-\epsilon^{-1})$ crosses over from a broad Gaussian to the narrow Lorentzian in the neighborhood of $\alpha = 1$, as illustrated.

geneous width Δ, as shown in Fig. 3. The width and shape of the resonance in $\mathrm{Im}[-\epsilon_2^{-1}(\omega)]$, however, depends on the dimensionless ratio of coupling strength to inhomogeneity:

$$\alpha = \omega_s/\Delta \ .$$

For the strongly coupled system ($\alpha >> 1$) the resonance exhibits the homogeneous width (γ) and shape, while in the weak-coupling regime ($\alpha << 1$) the line is Gaussian of width Δ. An abrupt crossover occurs near $\alpha = 1$. The line shape and width of perpendicular modes thus depend critically on α.

This line narrowing may actually have been observed for the perpendicular (subband) excitations of electrons bound to the surface of He. In this system inhomogeneous broadening can be introduced in a controlled manner via a parallel magnetic field. It has been observed that with increasing areal electron density a remarkable narrowing of the resonant absorption line occurs.[13] Although an explanation in terms of changes in the velocity autocorrelation function has been put forward, dipole-dipole-interaction-induced narrowing should also be considered, especially since the observed line narrowing occurs for increasing α near[17] $\alpha = 1$.

In summary, we have shown that substantial differences observed in the linewidth and shape of parallel and perpendicular modes of $KrReO_4$ film can be accounted for by a dipole-dipole-interaction-induced narrowing of the perpendicular mode. In this collective mode individual molecules oscillate in phase at a single frequency despite having differing natural frequencies and thus the inhomogeneity inherent in the system is obscured. This interaction-induced line narrowing can occur in a wide variety of systems involving two-dimensional arrays of interacting dipole oscillators, including electrons on He, planar arrays of metal particles, inversion layers, and adsorbate layers, as well as in thin films.

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[17]To obtain α from microscopic quantities one can use $\omega_p^2 = 4\pi ne^2/m$ for the multilayer thin-film system, where n is the density of oscillators, e the effective change, and m the effective mass of the vibrational mode. 2D systems, such as electrons on He or adsorbates at monolayer or submonolayer coverage, may be handled somewhat differently. The dipole sum (r_{ij}^{-3}) is more or less independent of structure for close-packed 2D lattices and it is then not a bad approximation to use $\omega_p^2 \cong 8.9 n_s^{3/2} e^2/m$ (see Ref. 6), where n_s is the areal density (coverage). The situation of random partial coverage of such a lattice is treated in Ref. 5; $\omega_p^2 = 8.9\Theta \tilde{n}_s^{3/2} e^2/m$ is a reasonable approximation where $\tilde{n}_s$ is the areal density at full coverage and Θ is the fractional coverage.