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Multiphonon effects in thin organic films

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An interpretation of two recent experiments involving the inelastic scattering of helium atoms from thin films composed of long organic chain molecules is given based on multiphonon-scattering theory. In the semiclassical limit of the experiments, the theory depends only upon the temperature of the film and the effective mass of the molecular end hit by the incoming helium beam. The effective mass of the end group is obtained and suggested experimental directions are given.

I. INTRODUCTION

Langmuir-Blodgett (LB), self-assembly (SA), and free-standing organic thin films have or are expected to have long-range order with two-dimensional crystalline structure.[1-9] Of these three classes of organic films, the LB films are formed on a water surface and then usually transferred to a crystalline metal surface.[1,2] Further, they form dense monolayers with the lattice spacing characteristically determined by their molecular size. They are incommensurate with the substrate, but have large domains. The SA films are formed by chemisorption from the liquid phase onto a metal substrate[3-6] where the SA layers can be commensurate or incommensurate with the substrate. Often a sulfur atom is the chemical link to the metal substrate while the rest of the long molecular chain can be perpendicular or tilted with respect to the substrate. The top layer of the SA film is made by the end groups of the chain pointing away from the substrate, which may be composed of various molecules such as methyl groups. The free-standing films offer an opportunity to examine thin molecular film surfaces which do not have a substrate.[7] None of the latter have yet been examined by helium scattering.

Organic thin films are of considerable interest because a basic knowledge of their preparation and properties should serve as a guide toward understanding biological films, spacer lubrication layers, organic coatings, and possibly new thin film dielectric materials.[8,9] With the continuing development of surface instrumentation, our understanding of the surface structure of organic films has increased considerably,[3-6] but the use of nondestructive surface probes such as helium-atom scattering to study surface dynamics over the whole surface Brillouin zone has lagged the structure developments.[2,10] This paper is written to point out that nondestructive surface instrumentation is already available in the form of helium-atom scattering,[2,10] and that combined with current developments in multiphonon-scattering theory, can provide new methods for interpreting inelastic-scattering information.[11-13]

We briefly discuss He-atom scattering (HAS) used in structural studies first and then we consider the main topic which is an interpretation of two previous inelastic He scattering studies. One of these involved a monolayer film of arachidic acid and methyl sterate (AAMS, in the molar ratio 9:1)[2] and the second was a study of three long chain molecules on LiF surfaces.[10] The interpretation of these two inelastic results by our current multiphonon model gives us confidence that the essential physics is contained in the model and further that it can provide a useful guide to predict what to search for in future experiments on these important materials.[11-14]

II. STRUCTURAL STUDIES

The nondestructive and nonreactive scattering of thermal energy neutral helium atoms from a surface can be used to obtain surface information in two ways: one is to carry out elastic-scattering experiments which gives information on surface structure and corrugation, and the second is to measure the inelastic scattering which provides information on the surface forces.[15,16] The surface structure can be obtained by scattering a monoenergetic beam of He atoms and measuring the elastic-scattering intensity as a function of incident wave vector, angle, target temperature, and crystal preparation method. For crystalline surfaces, the elastic-scattered intensity in the form of specular and Bragg diffraction peaks can be used to determine the cell spacing, the crystal orientation, and the corrugation of the surface. The shapes of the peaks and their dependence on incident wave vector can further give the domain size and the step density on the surface.[15-17]

Some examples of structural studies for the n-alkane thiols $CH_3(CH_2)_nSH$ where n is an integer, including adsorbate studies, were reported in the series of papers of Refs. 3–6. The substrates were Au(111) and Ag(111) surfaces and information on the crystal structure, spacing, domain size, chain length, and end molecular-group dependence was obtained.

This elastic-scattering work demonstrates the promise in He scattering methods. However, the thrust of this paper is the inelastic scattering where the surface forces can be determined. Inelastic experiments use the time-of-flight (TOF) method in which a pulse of He atoms is directed onto the surface where an energy exchange takes place in the collisions. The scattered He atoms then travel a flight path sufficiently long so that the atoms with different energies can spread out spatially and be counted as a function of time as they pass through an ionizer detector. The time differences between the peaks then give the energy losses or gains suffered by the He atoms at the surface.[15,18]

III. DYNAMICAL MEASUREMENTS AND DISCUSSION

The dynamical study of Vogel and Wöll (VW) produced an inelastic-scattering curve for 30-meV monoenergetic He atoms scattered from the AAMS film.[2] The measurements were made on a surface fixed at approximately 130 K and the TOF method was used. They published only the energy-change (loss or gain) spectrum with an explanation that the curve represented multiphonon interactions. The inelastic collision regime was very different than in the usual HAS experiments where one explores the surface dynamics under conditions where single-phonon scattering events dominate the inelastic scattering.[15,18]

The condition for single-phonon collisions is expressed in terms of the exponent of the Debye-Waller factor $\exp(-2W)$, where, in its simplest form $2W$ is proportional to the mean-square surface displacement as shown below. The value of $2W$ gives approximately the average number of quanta exchanged in a scattering event, thus for the single-phonon collision regime, $2W \leq 1$. In the AAMS study, the conditions on $2W$ appeared to be well into the multiphonon regime, as the good agreement of our model below shows that $2W \simeq 15$. It is known[12] that at sufficiently high temperatures where $2W > 6$, the scattering is in the classical multiphonon regime.

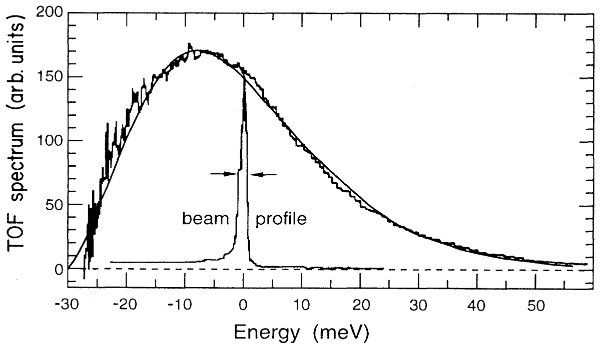

FIG. 1. Plot of a time-of-flight (TOF) spectrum (histogramlike curve) converted to energy gains and losses for a monoenergetic He-atom beam (30 meV) scattered from an AAMS monolayer surface at a temperature of 130 K (Ref. 2). The narrow peak shows the energy width of the incident He beam including all broadening by the instrument. The solid smooth curve is the fit from this theory with a surface temperature of 130 K and an effective end-group mass of M=15 amu.

The results of the VW work are reproduced as a histogramlike curve in Fig. 1. It shows the intensity in the specular direction of the scattered He as a function of energy loss or gain. The former corresponds to He collisions with a net creation of phonons, while the latter is from net annihilation collision events. Note that the net energy shift of the maximum in the spectrum is one of energy loss by the He atoms. Under the extreme inelastic conditions of this experiment, in which $2W$ is substantially greater than 6, the scattered intensity $I(\omega)$ is described by an essentially classical relation which is independent of the Debye temperature of the crystal, and which depends on the dynamics of the crystal only through the effective mass M of the target[12]

$$I(\omega) \sim k_f \mid \tau_{fi} \mid^2 [\hbar\pi/(\omega_0 k_B T)]^{1/2} \times \exp[-\hbar(\omega+\omega_0)^2/(4k_B T\omega_0)], \tag{1}$$

where $\hbar\omega = E_f - E_i$ is the difference between the final and the incident beam energies E_f and E_i. The surface temperature is T, the energy shift is $\hbar\omega_0 = \hbar^2 k^2/2M$, where $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$ is the total momentum exchange in the collision, and $\mid \tau_{fi} \mid^2$ is the scattering form factor. The general form of Eq. (1) has been obtained in a variety of different ways.[19-22] Sometimes it appears with an additional Gaussian-like factor in the parallel momentum transfer.[21,22] The form exhibited in Eq. (1) is applicable to the case of an incident point projectile interacting with a surface of atomic-scattering centers. In the extreme semiclassical limit of large numbers of phonon transfers, the region of coherence for the scattering process becomes small, and the scattering becomes essentially a two-body collision process. A distinctly different case occurs when the incident projectile interacts with many surface atoms, for example in the case of a large incident particle. In this situation the surface can be replaced by a continuum, and Eq. (1) is multiplied by the factor

$$\exp[-2\hbar v_R K^2/4k_B T\omega_0], \tag{2}$$

where v_R is a representative parallel velocity of phonons at the surface.[12,21] Equation (1) is the expression applicable to He scattering under the present conditions.

Characteristic of the classical scattering regime, the Debye-Waller factor $\exp(-2W)$ does not appear explicitly in Eq. (1). In its simplest form the exponent of the Debye-Waller factor is given by the classic expression

$$2W = \langle(\mathbf{k}\cdot\mathbf{u})^2\rangle, \tag{3}$$

which is the mean square surface displacement weighted by the momentum transfer. Under quantum-mechanical conditions, in which $2W \ll 6$, the Debye-Waller factor multiplies each of the various intensity components, such as the specular elastic and diffraction peaks and the single phonon lines. In the classical limit, the Debye-Waller factor is exactly cancelled by a term $\exp(+2W)$ arising from multiphonon contributions,[21] and the scattered intensity takes on the skewed Gaussian behavior of Eq. (1). However, the fact that the Debye-Waller factor does not appear explicitly in Eq. (1) does not preclude it from playing an important role. The exponent $2W(\mathbf{k})$ of Eq. (3) can always be calculated and continues to give an estimate of the number of quanta exchanged in a collision.

The fit shown as the solid smooth curve in Fig. 1 is based on Eq. (1) with the film temperature of T = 130 K as given in the experiment and with an effective mass of M=15 amu, in agreement with the AAMS film which has a methyl group with mass 15 as its end group from which the He scatters. The form factor is chosen to be the square modulus of the hard-wall scattering matrix element

$$\tau_{fi} = 2\hbar^2 k_{fz} k_{iz}/m, \tag{4}$$

where k_{fz} (k_{iz}) is the component of $\mathbf{k}_f$ ($\mathbf{k}_i$) normal to the surface and m is the projectile mass.

What the fit tells us, in terms of the model, is (1) that in the region where $\omega \approx 0$, $2W \approx 15$, or on the average 15 phonon exchanges are incurred by the He. Hence our confirmation of the VW statement that the results are well into the multiphonon regime. (2) For an incident He beam and fixed incident momentum $\mathbf{k}_i$, the theoretical fit to the experiment depends only on T and M. The position of the maximum in the inelastic intensity depends on $1/M$ through the energy shift ω_0, and the width of the inelastic intensity distribution varies as the ratio T/M. Thus, a fit to the experimental data at a known surface temperature gives a value of the effective mass of the end-group molecules from which the He projectile atoms scatter. The end groups can easily be changed over a reasonable mass range.[3-6,10] (3) The inability to find a specular elastic peak in the energy distribution or in the angular distribution (see VW, their Fig. 4) is clearly understood because the Debye-Waller factor is small, of the order 10^{-6}, hence all quantum-mechanical peaks are negligibly small.

The shape of the inelastic-scattering distribution in the extreme semiclassical regime shown in Fig. 1, and the simple form of the theoretical function which explains it, show that although much information can be gained from such experiments, little can be learned about the details of surface dynamics. This requires experiments in the quantum regime, where distinct diffraction and single phonon peaks can be resolved.

We would like to consider the question of feasibility of carrying out experiments in the quantum-mechanical domain with these types of surface systems. It is clear that at sufficiently small incident projectile energies and low temperatures the quantum domain can always be obtained. However, the present theoretical model allows us to address this question quantitatively, and to show that the experiments discussed here can be carried out in the quantum domain with energies and temperatures well within currently feasible ranges. Figure 2 shows theoretical curves for several different initial parameters (crystal temperature, end-group mass, and incident He energy). Clearly, when the incident energy, or crystal temperature is increased, the scattering becomes more classical and the intensity distribution becomes simply a broader, flatter skewed Gaussian. However, if the incident energy is halved and the crystal temperature is reduced to 40 K as in Fig. 2 curve b, it is seen that the multiphonon intensity is greatly reduced; the Debye-Waller exponent at $\omega_0 \approx 0$ is about 3 implying that the scattering is approaching the quantum-mechanical regime. We note that this observation is in agreement with previous work which showed that diffraction peaks could be observed in He scattering from similar surfaces at T = 40 K, but were no longer observable at T = 300 K.[3,4] Figure 2 curve b and the other curves in Fig. 2 were calculated with the fully quantum-mechanical version of the theory[12] using a Debye temperature of 120 K, and only the multiphonon contribution to the intensity is shown. Elastic and single-phonon contributions are not included. The total intensity in the single-phonon contribution for the conditions of Fig. 2 curve b is roughly equal to the total of all multiphonon contributions, implying that the inelastic single-phonon peaks should be readily measurable in such an experiment. Since the surface temperatures and incident beam energies in the range of the conditions of Fig. 2 curve b are routinely available,[11,15,16,23] it should be possible to carry out such experiments. In particular, it has been suggested that LB films may exhibit low-energy Einstein-like modes in the range of 1 meV,[24] and VW have argued that the important vibrational levels would be in the 0.2-meV range.[2] Resolution of such modes is within current experimental capabilities.

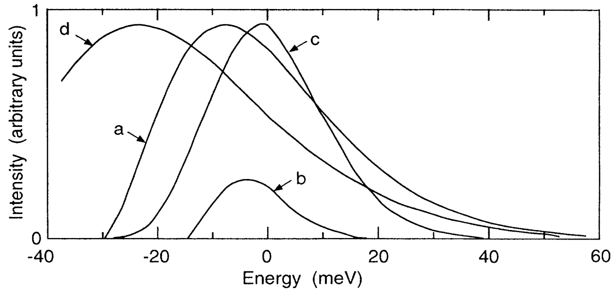

FIG. 2. Calculations of multiphonon intensity vs energy transfer for several selected cases. Curve a, same as in Fig. 1. Curve b, T = 40 K, E_i = 15 meV, M = 15 amu, with intensity in correct relative proportion to a. Curve c, T = 130 K, E_i = 30 meV, M = 60 amu. Curve d, T = 130 K, E_i = 60 meV, M = 15 amu. Curves c and d are normalized to the same maximum as a.

The second inelastic-scattering study was that of Cohen, Naaman, and Sagiv[10] who used a 50-μs-wide pulsed beam (we consider only the He case) and scattered it from three different organic layered films on LiF substrates. The materials were (1) n-octadecyltrichlorosilane (OTS), an 18 carbon chain prepared by the SA method, with a CH_3 tail, (2) Cd(II) arachidate, a 20 carbon chain prepared by the LB method and also with a CH_3 tail, and (3) perfluorinated acid ester (PFAE), a SA chain fluorinated over the outer eight carbons and with a CF_3 terminal group.

This work had much larger experimental uncertainties than that of VW. Further, their interpretation was more *ad hoc* in that an effusive functional form and a nozzle beam form for the speed distribution of the He atoms were used to fit the time-of-flight measurements.[10] The long pulse time and the uncertainty of the energy spread in the incident beam obviates a detailed theoretical comparison as in Fig. 1. However, the physics contained in their measurements can still be interpreted by our model.

From the full width at half maximum (FWHM) of the two films presented in their Fig. 2, we find TOF widths of 0.34 and 0.29 ms for the films with the methyl and trifluoromethyl (TFM) end groups, respectively. The scattering from clean LiF has a time width of 0.22 ms. We consider the FWHM of LiF as representing all of the instrumental uncertainties. We assume a Gaussian addition of the FWHM's and find the increase for the two scattering substrates as 0.26 and 0.19 ms, respectively. If we assume the two cases have similar temperatures then our model says that the ratio of these times should go inversely as the square root of the respective end-group masses. We assume that the methyl group has a mass of 15 amu as in the VW case. With that assumption we find the mass for the TFM end group to be about 28 amu. This is smaller than the value of 69 amu, but in agreement with Cohen, Naaman, and Sagiv[10] who argued that the scattering from the TFM end is much stiffer than for the methyl group. This suggests that the model can be used to extract effective-mass–bond-strength information.

The implications are that the model can now serve as a guide to future experimental directions. Two such goals would be to first explore the experimental conditions where single-phonon events might be used to study organic chain-molecular films and second to further refine the theory. The first goal means that 2W should be considerably less than 6 so that the scattering is in the quantum-mechanical regime where phonon-frequency distribution or phonon spectral density information is obtained.

This goal would allow the surface vibration dynamics to be obtained. Toward this effort, Farnell and Adler[25] have examined thin films on substrates in the continuum limit (long Love interface modes for the thin films). Additionally, Alldredge, Allen, and de Wette[26] and Gibson *et al.*[27] have considered theoretically the surface vibrational properties of thin films from the continuum to the dispersive region. Inelastic He measurements have been used to explore the Rayleigh mode behavior of thin films, interface modes, as well as other vibrational properties of very thin films.[28–30] The two experiments discussed above and the previous He work suggest that HAS can also be used on the very-low-energy modes of organic thin films. Infrared, Raman, and Brillouin probes will also work, but they are less surface sensitive, requiring a number of organic film layers, and generally they can only be used for long-wavelength vibrations at or near the Brillouin-zone center.[1,9,31]

We should point out that organic films attached to substrates are a realization of surface-dynamical systems with rather unusual properties. They have one end of the molecule fixed at the substrate while the rest of the molecule and the other end can move rather freely.[24] The moving ends correspond more to a liquid and may represent a state of matter difficult to achieve with a more conventional solid surface where melting or evaporation might take place before conditions corresponding to those in the film are reached. It is possible that this extreme region might become experimentally accessible by controlling the conditions for HAS. The theory for such scattering could be included in a refinement of the above model.

IV. CONCLUSIONS

We have shown that the available scattered intensity measurements of a He beam incident on several selected substrate layers of long organic chain molecules can be readily explained in terms of a classical multiphonon inelastic-scattering model. Comparison with experiment can give detailed information on the effective end-group mass. Because of the simple expression of Eq. (1) and the hard-wall form factor picked for this analysis in Eq. (4), the suitability of the latter could be further explored by varying the z components of the incident and scattered wave vectors. This could prove very useful in the quantum-scattering region as discussed below.

Much more detailed information about the surface dynamics is available from scattering experiments in the quantum-mechanical regime, and we argue that such experiments are feasible. Vogel and Wöll have concluded that the vibrational energy levels in AAMS could be in the 0.2-meV range, which should not challenge the resolution of He scattering. For He beams, energies near a few meV have been obtained with energy resolution below 0.1 meV.[32,33] It is further clear that cooling of the substrate will greatly aid in surface-dynamical studies,[3–6] where the above substrates were at temperatures of 130 K (Ref. 2) and 300 K,[10] respectively. In addition, other organic films with different tail groups might have higher vibrational energies which could have larger scattering cross sections. For example, short-chain self-assembly molecules might assemble on a gold single-crystal substrate and appear vibrationally very similar to CO on a metal substrate, a system already successfully studied by He scattering.[34]

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