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The anomalous “stiffness” of biphenyldimethyldithiol

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Although organic adsorbates and thin films are generally regarded as “soft” materials, the effective Debye temperature, indicative of the dynamic motion of lattice normal to the surface, can be very high. For biphenyldimethyldithiol, the effective Debye temperature, determined from core level photoemission from the all carbon arene rings, is comparable to that of graphite. We associate this rigidity to the stiffness of the benzene rings, and the ordering in the molecular thin film. Measurements on the sulfur of poly(hexylthiophene) show that sulfur in an arene ring is less dominated by soft modes than the pendant sulfur of biphenyldimethyldithiol on the time scale of photoemission. © 2005 American Institute of Physics. [DOI: 10.1063/1.2120918]

The study of the surface Debye temperatures now has decades of history, but there are only a few studies of the dynamical motion of organic adlayers and self-assembled organic layers (SAMs). Studies of the Debye temperature θ_D generally confirm that organic adlayers and thin films are indeed soft, that is to say that the effective Debye temperature (characteristics of motion along the surface normal) is very small, or that the mean square displacement, due to thermal motion, is quite large. For example, the Debye temperature (θ_D) of annealed alkyl halide $\text{BrCH}_2(\text{CH}_2)_4\text{CH}_3$ has been determined to be about 95 K,¹ while the effective Debye temperature of copolymer films of vinylidene fluoride (70%) with trifluoroethylene (30%) is 48 K above 200 K and 250 K below 100 K.^{2,3} Strictly speaking, C_{60} and C_{70} are inorganic (not organic), but both exhibit low Debye temperatures. The Debye temperature of C_{70} was calculated to be 45 K, compared to a value of 53 K for C_{60} .⁴ The latter value is in good agreement with the experimentally determined Debye temperature (θ_D) for fullerite C_{60} of about 56 K.^{5,6} Self-assembled monolayers (SAMs) are also generally “soft” organic layers. For *n*-alkane thiols self-assembled monolayers, the relative mean square displacements perpendicular to the surface, on the order of $10^{-4} \text{ \AA}^2/\text{K}$,⁷ have been calculated from the temperature dependence of diffraction peak intensities using Debye-Waller formalism, with similar experimental values obtained for *n*-alkane thiols using helium atom scattering techniques.^{8,9}

It is possible for organic materials to be mechanically quite soft with respect to very low frequency motion but stiff on the time scale dominated by electron phonon coupling. Such rigidity on the short time scale of 10^{-14} to 10^{-16} s would manifest itself as a very high Debye temperature when measured by electron spectroscopy. In addition, thiol molecules that are often a part of self-assembled monolayers (SAMs) systems can “pack” well ordered and quite dense, limiting the possible relative mean square displacements.

One such system is biphenyldimethyldithiol ($\text{HS-CH}_2\text{-C}_6\text{H}_4\text{-C}_6\text{H}_4\text{-CH}_2\text{-SH}$) which is found to form a dense and regular packing with the planes of benzene rings oriented normal to the surface.¹⁰ To test that local properties establish the effective Debye temperature measured in photoemission, we compare biphenyldimethyldithiol (BPDMT) with the more rigid phenyl groups but with pendant sulfur, to poly(3-hexylthiophene) (P3HT), with pendant carbon chains but with a more rigid thiophene (sulfur containing arene ring).

Deposition of BPDMT was undertaken by a solution method described by Eck *et al.*¹¹ on the gold substrates and was undertaken in prior studies,¹⁰ while the regioregular P3HT were prepared on gold by spin-coating techniques. The x-ray photoemission spectroscopy (XPS) studies were performed in an ultrahigh vacuum (UHV) chamber with a large hemispherical analyzer (Perkin Elmer 5000C ESCA) system.¹⁰ The combined resolution of the system was about 500 meV using an Mg K_α line (1253.6 eV) unmonochromated x-ray source. The photoemission spectra were taken with a 60° incidence angle and normal emission, and binding energies are referenced to the Fermi level of the gold substrate. No noticeable x-ray damage of our organic films was observed during the course of our measurements.

While the true surface Debye temperature, containing the in-plane and anharmonic motions,¹² is difficult to measure in most surface spectroscopies, the effective surface Debye temperature can be readily obtained using XPS and ultraviolet photoemission,^{3,13–20} low energy electron diffraction (LEED),^{21,22} electron energy loss spectroscopy (EELS), inverse photoemission spectroscopy (IPES), and other surface sensitive techniques.^{7,8,13} The experimentally derived effective surface Debye temperature is a signature of the dynamic motion of vibrational modes normal to the surface. Due to increased thermal vibrations, the intensity of an emitted or scattered electron beam exponentially decays with increasing temperature as^{3,13–22}

$$I = I_0 \exp(-2W), \quad (1)$$

where W is the Debye-Waller factor and is given by

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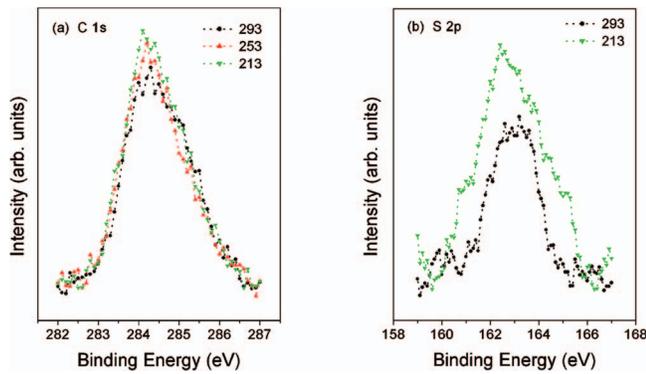


FIG. 1. (Color) X-ray photoemission spectra of the C 1s (a) and S 2p (b) core levels after background subtraction.

$$2W = |\Delta k|^2 \langle u_0 \rangle^2, \quad (2)$$

where Δk is the wave vector transfer and $\langle u_0 \rangle^2$ is the mean-square displacement of the atoms. Within the Debye model of thermal vibrations, in the case of isotropic vibrations, W is described as

$$2W = \frac{3\hbar^2 T (\Delta k)^2}{m k_B \theta_D^2}, \quad (3)$$

where T is the temperature of the sample (in Kelvin), m is the mass of the scattering center, and again θ_D is the Debye temperature. When undertaken using photoemission, the momentum transfer is the momentum of the emitted photoelectron,^{3,13–20} and the mass of the scattering center is the mass of the specific element which is the origin of the emitted photoelectron.¹⁸

As is expected, the core level photoemission intensities decrease with increasing temperature, as shown in Fig. 1. The C 1s and S 2p core level photoemission intensities are a function of temperature for multilayer biphenyldimethyldithiol (BPDMT) films. The core level photoemission spectra from biphenyldimethyldithiol (BPDMT) are consistent with those of the thiol aromatic films given in Refs. 23 and 24, while the valence band photoemission for both BPDMT and P3HT match expectations.^{10,25,26} The log of the core level peak intensities, after background subtraction, for the C 1s [Fig. 2(a)] and the S 2p [Fig. 2(b)] for BPDMT have been plotted against the temperature. Qualitatively similar results were obtained for P3HT as summarized in Fig. 3.

Because the temperatures cannot be accurately measured at the polymer thin films surface, there is some uncertainty in the absolute values and accuracy of the derived Debye temperatures. In spite of the experimental uncertainties, the results are, nonetheless, surprising. What is unexpected are the rather high values for the Debye temperature abstracted from the photoemission intensities (Figs. 2 and 3) using Eq. (3). For BPDMT films, the effective Debye temperatures are 1397 ± 110 K from the C 1s core level intensity and 456 ± 50 K from the S 2p, while for P3HT a Debye temperature of 645 ± 50 K is derived from the S 2p core level intensity. C 1s core level intensity for P3HT is not part of our comparison because this core level contains contributions from both the alkane pendant group and the thiophene rings, so it cannot be easily compared to the measurements from biphenyldimethyldithiol. The relative differences in the mea-

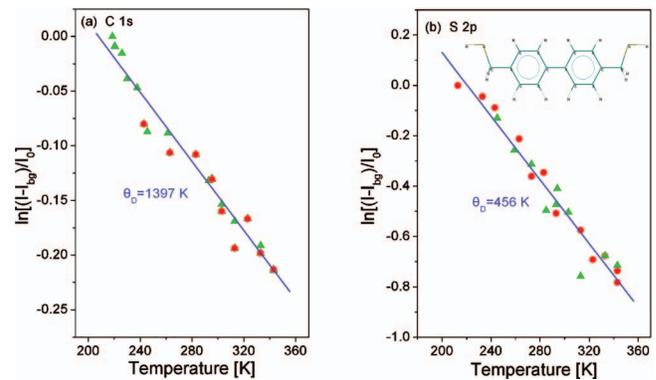


FIG. 2. (Color) Logarithm of the C 1s (a) and S 2p (b) peak integral photoemission intensities for biphenyldimethyldithiol (BPDMT) as a function of temperature, after background (I_{bg}) subtraction and normalization to the peak integral intensity at the lowest temperature I_0 . Two representative sets of data (dots and triangles) are shown. The experimental values were fitted (solid lines) with the Debye-Waller factor using Eqs. (1) and (3). The inset to (b) is a schematic of biphenyldimethyldithiol.

sured effective Debye temperatures between carbon and sulfur provides an indication as to the origin of the high Debye temperature values.

The lower value of the Debye temperature abstracted from the BPDMT S 2p core level, when compared with the value obtained from the C 1s core level intensity, can be understood from the structure of the biphenyldimethyldithiol molecule. The sulfur atoms are pendant to the molecule [as indicated in the inset to Fig. 2(b)] and thus are “less rigid.” This conclusion is supported by the higher value for “sulfur” Debye temperature obtained for P3HT, where the sulfur in a thiophene ring and a carbon chain is pendant, as schematically shown in Fig. 3(b). The fact that the effective Debye temperature is so different for sulfur and carbon in a biphenyldimethyldithiol molecule indicates that the effective Debye temperature is strongly influenced by the local environment, not just the overall rigidity of the molecule within the film. The high effective Debye temperatures abstracted from photoemission suggests that the mean-square displacement is anomalously small for BPDMT and P3HT on the time scale of the photoemission process. We believe this rigidity of BPDMT is due to the stiffness of the benzene rings and the ordering in the molecular thin film.

For multilayer BPDMT films on gold, the molecular axis is parallel to the surface with the benzene plane oriented normal to the surface for BPDMT.¹⁰ With this orientation of the BPDMT molecule, the higher effective Debye temperature for carbon reflects rigidity of benzene and should be comparable to the “stiff” lattice for carbon in the a - b plane of graphite, moderated by π - π interactions between molecules. The Debye temperature of graphite depends strongly on the crystal direction, with a Debye temperature (θ_D) ≈ 1600 K (reflecting the a - b plane) and a value for Debye temperature (θ_D) ≈ 200 K (reflecting motion normal to the a - b plane).²⁷ The latter value reflects the weaker, largely van der Waals, bonding between sheets.^{27–29} Indeed, our value for the effective “carbon” Debye temperature for BPDMT of 1397 ± 110 K is consistent with the higher value Debye temperature of graphite.

While a similar high value for the sulfur in the thiophene rings of P3HT to that for carbon in BPDMT might be expected, the changing polymer molecular geometry with

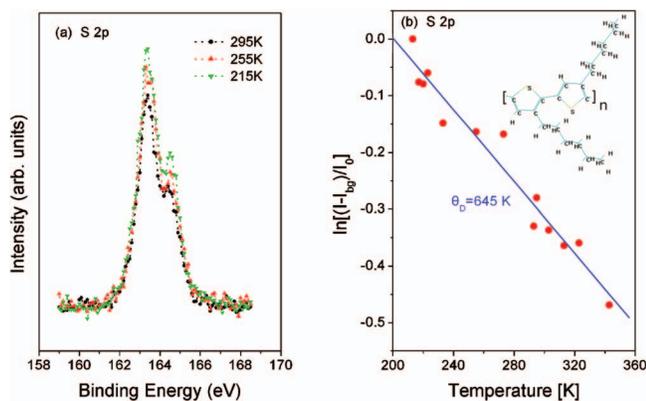


FIG. 3. (Color) Normal emission S 2p x-ray photoemission spectra for poly(3-hexylthiophene) (P3HT) shown in (a) and the intensity is plotted in (b) as a function of temperature after background subtraction. The inset (b) is a schematic of one unit of the poly(hexylthiophene).

temperature^{25,26} is one of several complications that must be considered in comparing the intra-arene ring effective Debye temperatures. In fact the orientations of the thiophene rings change dramatically^{25,26} with respect to one another with increasing temperature, particularly in the vicinity of room temperature where the measurements here were taken. Although we expect that the thiophene ring plane(s), for highly regioregular poly(3-hexylthiophene), to be aligned along the surface normal,³⁰ similar to the “benzene” ring orientation for BPDMT multilayer films, this preferential alignment is lost with increasing temperature. The mean-square displacement for benzene (or thiophene) bending vibrational modes is much larger than for the carbon ring “breathing” modes, consequently a misorientation of the thiophene ring plane away from the surface normal should lead to a decrease in the effective Debye temperature (measured along the surface normal). This factor, combined with the associated weaker intermolecular interactions,^{25,26} may provide a partial explanation for the lower “sulfur” Debye temperature of 645 ± 50 K for P3HT compare to the effective Debye temperatures of 1397 ± 110 K from the C 1s core level intensity for the BPDMT films.

In summary, despite expectations to the contrary, the effective Debye temperatures for some “soft materials,” such as BPDMT films, are anomalously high on the time scale of the photoemission process, even when given a number of experimental uncertainties. This behavior is due, in part, to the structural rigidity of benzene (graphite) in the plane (*a-b* plane). Although many organic materials are considered to be “soft,” a distinctly different depiction is appropriate for the more rigid “close packed” molecular orientations.

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