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D.Q. Feng
University of Nebraska-Lincoln, nkfdq@bigred.unl.edu

Peter A. Dowben
University of Nebraska-Lincoln, pdowben@unl.edu

R. Rajesh
University of Nebraska-Lincoln

Jody G. Redepenning
University of Nebraska-Lincoln, jredepenning1@unl.edu

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The anomalous “stiffness” of biphenyldimethyldithiol

D. Q. Feng and P. A. Dowben
Department of Physics and Astronomy, Behlen Laboratory of Physics and Center for Materials Research and Analysis, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0111

R. Rajesh and J. Redepenning
Department of Chemistry, Hamilton Hall, and Center for Materials Research and Analysis, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0304

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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 $\theta_D$ 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 ($\theta_D$) of annealed alkyl halide $\text{BrCH}_2(\text{CH}_2)_n\text{CH}_3$ has been determined to be about 95 K, 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. Self-assembly systems can “pack” well ordered and quite dense, with more rigid thiophene rings including pendant sulfur, to poly(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. on the gold substrates and was undertaken in prior studies, 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. The combined resolution of the system was about 500 meV using an Mg K$_\alpha$ line (1253.6 eV) monochromated 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, is difficult to measure in most surface spectroscopies, the effective surface Debye temperature can be readily obtained using XPS and ultraviolet photoemission, low energy electron diffraction (LEED), electron energy loss spectroscopy (EELS), inverse photoemission spectroscopy (IPES), and other surface sensitive techniques. 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

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

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

$$W = \frac{2}{3} \frac{\hbar^2}{m k_B^5} \frac{V^2}{k_B T}.$$

One such system is biphenyldimethyldithiol (HS-CH$_2$-C$_6$H$_5$-C$_6$H$_5$-CH$_2$-SH) which is found to form a dense and regular packing with the planes of benzene rings oriented normal to the surface. 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(hexylthiophene) (P3HT), with pendant carbon chains but with a more rigid thiophene (sulfur containing arene ring).

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$\text{BrCH}_2(\text{CH}_2)_n\text{CH}_3$

$\text{BrCH}_2(\text{CH}_2)_n\text{CH}_3$
DMT and P3HT match expectations. The logarithm of the peak integral intensities, after background subtraction, for the core level photoemission suggests that the mean-square displacement is rather high values for the Debye temperature abstracted from the absolute values and accuracy of the derived Debye temperature.

As is expected, the core level photoemission intensities decrease with increasing temperature, as shown in Fig. 1. For BPDMT films, the effective Debye temperatures are among the thiol aromatic films given in Refs. 23 and 24, while the valence band photoemission for both BPDMT and P3HT match expectations. While a similar high value for the sulfur in the 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 suggest 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. 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 \( \theta_D \approx 1600 \) K (reflecting the a-b plane) and a value for Debye temperature \( \theta_D \approx 200 \) K (reflecting motion normal to the a-b plane). The latter value reflects the weaker, largely van der Waals, bonding between sheets. 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 the relative differences in the measured effective Debye temperatures between carbon and sulfur provides an indication as to the origin of the high Debye temperature values.
temperatures of 1397±110 K from the C 1s photoemission process, even when given a number of BPDMT films, are anomalously high on the time scale of the photoemission process, even when given a number of BPDMT films, this preferential alignment is considered in comparing the intra-arene ring effective Debye temperature25,26 is one of several complications that must be taken into account for the intramolecular ring plane orientation where the measurements here were taken. Although we expect that the thiophene ring plane, for highly regioregular poly(3-hexylthiophene), to be aligned along the surface normal,30 similar to the “benzene” ring orientation for benzene27,28, the mean-square displacement 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 compared to the effective Debye temperatures of 1397±110 K from the C 1s core level intensity for the BPDMT films.

In summary, despite exceptions 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 description is appropriate for the more rigid “close packed” molecular orientations.

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