Solid state effects in the NEXAFS spectra of alkane-based van der Waals crystals: Breakdown of molecular model

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Abstract

Experimental data conclusively shows that the weak van der Waals interactions between alkane molecules, <1.5% the strength of covalent bonding on a per carbon atom basis, modify the carbon 1s near edge X-ray absorption fine structure (NEXAFS) spectrum significantly in ordered solids, both in intensity, spectral shape, peak position, and dichroic signature. This constitutes a further breakdown of the ‘building block’ model, or, more precisely, even a molecular model in interpreting NEXAFS spectra. These observations have significant implications for the interpretation and use of NEXAFS spectra from any crystalline or semi-crystalline macromolecules, small molecules, or other weakly interacting systems.

Over the last two decades, near edge X-ray absorption fine structure spectroscopy (NEXAFS) has evolved into a powerful characterization tool for a number of materials and systems. The NEXAFS of the carbon 1s absorption edge is particularly rich in spectroscopic features [1–3], a result of the many different bonding configurations carbon can have with itself and with heteroatoms such as nitrogen, oxygen, and other elements. The interpretation and use of NEXAFS for polymers and large molecules in the condensed phase are generally based on small-molecule analogues and calculations based on isolated small molecules [1,2]. Implicit in this approach is the assumption that the character of the bonding and antibonding orbitals in molecules are dominating the NEXAFS spectra and that intermolecular interactions and matrix effects are negligible. Indeed, the relative strength of covalent C–H orbitals and van der Waals forces in alkane crystals is ~98.5% covalent. It is thus not surprising that the small-molecule analogue approach (‘building-block principle’) in combination with calculations has yielded considerable insight for the interpretation of NEXAFS spectra of complex and large molecules, including polymers [4–7].

In the case of completely saturated molecules such as alkanes and related materials, the originally envisioned building block was the C–C unit with a single bond between carbon atoms [8]. However, analysis of the angular dependence in self assembled alkyl monolayers showed that the transition dipole moment (TDM) is not along the individual bond direction, but along the backbone direction [9]. A breakdown of the ‘building block’ model was pronounced. For extensive delocalized orbitals in π-conjugated systems, the ‘building block’ necessary to properly describe the NEXAFS spectrum was also shown to be much larger than the individual bonds, requiring a chemical moiety large enough to comprise and properly represent any delocalized orbital [10]. For polymers and weakly interacting molecules in the solid state, intermolecular interactions were generally not observed or expected and hence neglected.

Only few theoretical and experimental studies examined the influence of van der Waals forces and intermolecular interactions on NEXAFS spectra of organic materials. Theoretical consideration by Weiss et al. suggested small energy shifts, but no intensity changes, as a function of

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molecular separation [11]. No effect on conformation was observed in theory and thus spectral changes between ordered and disordered Langmuir–Blodgett (LB) films of Ca-archidate were interpreted to arise from density, i.e. intermolecular, changes rather than conformational, i.e. intramolecular, changes [11]. A study of ethylene-1-alkene copolymers with controlled composition showed relatively large changes in intensity that correlated with the crystallinity of the ethylene-1-alkene copolymer. In contrast to the prediction of Weiss et al., no discernable energy shifts could be observed in these ethylene-1-alkene copolymers. Theoretical calculations by Schöll et al. suggested that the observed changes in intensity are due to intermolecular interaction rather than difference in conformations of a polymer chain [12]. Although solid state effects have thus previously been observed [11–13], the extent and control of order in the materials investigated was insufficient to allow complete understanding. We thus used NEXAFS microscopy to study exceptionally well defined materials in the form of single alkane crystals with defined orientations. The experiments show that even just fractional changes in the weak van der Waals interactions, <1.5% the strength of covalent bonding on a per carbon atom basis, modify the NEXAFS spectrum of organic van der Waals solids significantly in intensity, spectral shape, peak position, and dichroic signature.

Thin crystals of $n$-tetracontane $C_{40}H_{82}$ (TC, $T_m = 80 \, ^{\circ}C$) and $n$-nonadecane $C_{19}H_{40}$ (ND, $T_m = 33 \, ^{\circ}C$) were prepared by solution-casting. TC (98.8%, Supelco) and ND (99%, Aldrich) were dissolved in toluene and acetonitrile (99%, Fluka), respectively, with a mass/volume ratio of 0.5 mg/ml and stirred at 50 °C. A drop of the solution was placed onto a 100 nm thin silicon nitride ($Si_3N_4$) window. The crystallization during the rapid solvent evaporation took place at room temperature for TC. The ND solution was cast at 8 °C. The crystallites produced were characterized with a Nikon Labophot II visual light microscope (VLM) equipped with a SPOT CCD attachment. Although some irregular crystallites formed, numerous crystallites with straight edges and well defined angles and shapes could be found for both alkanes. Acute and obtuse angles of $\sim 68^\circ$ and $\sim 112^\circ$, respectively, were measured for crystallites with regular diamond or parallelogram shapes and even thickness (see Fig. 1a). These angles are in complete accordance with {110} terminated orthorhombic unit cells (see Fig. 1b) derived from X-ray diffraction studies [14].

Well formed, 100–200 nm thick crystals were investigated with scanning transmission X-ray microscopes (STXM) at advanced light source (ALS) beamlines 5.3.2 (BL5.3.2) and 11.0.2 (BL11.0.2), respectively, with a spatial resolution of $\approx 40 \, \text{nm}$ and energy resolution $R > 2000$ [15]. With proper optics alignment, the BL5.3.2 STXM delivers X-rays linearly polarized in the horizontal plane. At the BL11.0.2-STXM, an elliptical undulator provides complete control over the polarization of the X-ray beam. Images and spectra were recorded with the $Si_3N_4$ membrane mounted perpendicular to the optical axis [15]. At BL5.3.2, this sample geometry puts the polarization direction in the plane of the membrane. The spectra from crystallites of different thickness were compared to exclude the possibility of any thickness related effect. Additionally, the

Fig. 1. (a) VLM image of crystallites from $n$-tetracontane (top) and $n$-nonadecane (bottom) after casting from solution. (b) Orthorhombic unit cell of crystalline alkanes and polyethylene as viewed from the [001] direction. The obtuse angle spanned by [110] planes is labeled as $\alpha$. The angle $\theta_0$ of the C–C backbone plane with the $a$-axis is indicated. $\theta_0 \approx 48^\circ$, based on crystalline structure shown in [25]. (c) Symmetry plane of propylene unit, which contains the carbon–carbon backbone.
samples were rotated in the plane of the Si₃N₄ membrane in small angular steps to acquire dichroic spectra from the same crystal. The radiation damage was monitored after the acquisition of spectra by checking for mass loss and for the occurrence of a 285.1 eV resonance that is due to formation of C–C double bonds caused by X-ray radiation damage [16]. The X-ray beam was defocused for the acquisition of spectra to effectively eliminate the possibility of radiation damage. The spectra were carefully normalized to the incident intensity. In order to remove any sensitivity to orientation and acquire average reference spectra, circularly polarized light at the BL11.0.2-STXM was utilized. The energy scale for all the spectra was calibrated using characteristic vibronic peaks of gaseous CO₂ [17].

Fig. 2 shows the carbon 1s NEXAFS spectra of typical TC crystallites and STXM images of such crystals acquired at a photon energy of 288.0 eV. Crystallites imaged with STXM are also well-defined parallelograms with obtuse angles of the images recorded by STXM at a photon energy of 288 eV. Crystallites imaged with conventional NEXAFS dichroism spectra that would distort the DR of the low energy doublet. The agreement recorded with circular polarized light at BL11.0.2 (solid line), compared to the orientation and acquire average reference spectra, circularly polarized light at the BL11.0.2-STXM was utilized. The energy scale for all the spectra was calibrated using characteristic vibronic peaks of gaseous CO₂ [17].

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Table 1 Properties of the first two unoccupied molecular orbitals and their projection onto lattice coordinates

<table>
<thead>
<tr>
<th>Property</th>
<th>n-tetracontane (HTC)</th>
<th>2,6-hexatriacontane (26HTC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orbital symmetry</td>
<td>( \sigma_{c-c} )</td>
<td>( \sigma_{c-c} )</td>
</tr>
<tr>
<td>Local reference</td>
<td>( \parallel ) to ( C-C-C ) plane</td>
<td>( \parallel ) to ( C-C-C ) plane</td>
</tr>
<tr>
<td>Projection onto a-axis</td>
<td>( \cos^2 \theta_0 )</td>
<td>( \cos^2 \theta_0 )</td>
</tr>
<tr>
<td>Projection onto b-axis</td>
<td>( \sin^2 \theta_0 )</td>
<td>( \sin^2 \theta_0 )</td>
</tr>
</tbody>
</table>

* The symmetry labels have been adopted from Ref. [22].
temperatures approaching melting \[25\], accompanied by a

The average in-plane NEXAFS spectra of TC and ND
crystallites are compared in Fig. 3. A low intensity of the

C 1s $\rightarrow \sigma^*_C$ bands was consistently observed for all ND
samples investigated (data not shown), indicating that the
carbon–carbon chains are perpendicular to the Si$_3$N$_4$
windows for ND as well. Somewhat surprisingly, the NEXAFS
spectra of the two alkane crystals differ significantly in
the C 1s $\rightarrow \sigma^*_C$/Rydberg region. The spectrum of TC
has a doublet splitting of $\sim 0.6$ eV, whereas the splitting
of the doublet increases to $\sim 0.9$ eV in the spectrum of
ND with a third component developing into a recognizable
feature at intermediate energy. For short chain alkanes \[26\]
in the gas phase, the energy separation of the doublet
remains constant at $\sim 0.6$ eV beyond hexane. Hence, the
difference in length for the relatively long alkanes used in
the present study should not be a source for the spectral
changes observed. We also note that the number of gauche
conformation defects is about one defect per 190 or 400 C–C
bonds in ND and TC, respectively \[27\]. Even if ND were
to be in the hexagonal R-II phase, the number of defects
would be at most one in 70 C–C bonds. Gauche defects
can thus not directly cause the observed changes.

The comparison of our data to existing NEXAFS theory
is unsatisfactory. A blue shift has been theoretically pre-
dicted \[11\] for increasing intermolecular interaction
between Rydberg states of the molecules. However, a
substantial blue shift of the $\sim 288.3$ eV peak is observed for
the lower density material, which is difficult to reconcile with
Rydberg matrix effects as described by Weiss et al. \[11\].
The results of the calculations of Scholl et al. for parallel
orientation of butane dimers at two different separation

- $b$-axis of the crystals, respectively, the NEXAFS of any
orbital with its TDM along the $z$-axis of the molecular
coordinate system, such as $\phi_1$, will show a Dichroic Ratio
(DR), defined as $(I_a - I_b)/(I_a + I_b)$, of $\text{DR}_z = \cos^2\theta_0 - 
\sin^2\theta_0 = \cos 2\theta_0$. For TC, $\theta_0 \approx 48^\circ$ and $\text{DR}_z = -0.10$
and we would expect higher intensity for polarization align-
ment along the $b$-axis. Any orbital with its TDM along
the $x$-axis would result in $\text{DR}_x = \cos^2(\theta_0 + 90^\circ) - 
\sin^2(\theta_0 + 90^\circ) = -\cos 2\theta_0 = +0.10$. Hence, if the
underlying symmetry is that of the molecule, any spectral
feature that has only one underlying orbital with its
TDM along the $z$ or $x$ axis should have a DR with the same
absolute value, $|\text{DR}|$, irrespective of the value for $\theta_0$. Any
contribution of more than one orbital at a given photon
energy decreases $|\text{DR}|$. The experimental values are
$\text{DR}_{287.6} = -0.06$ and $\text{DR}_{288.2} = +0.11$, respectively. From
a molecular perspective, we should not observe a DR at
288.2 eV larger than at 287.6 eV, yet $\text{DR}_{288.2}$ is almost
2 $\times \text{DR}_{287.6}$. This discrepancy must arise from an interac-
tion of the molecular orbitals with the periodic lattice,
and subsequently, the underlying symmetry of the observed
dichroism cannot be that of the molecule, but has to be
that of the solid, i.e. the alkane crystal. We note that our
overall argument does not depend on the precise value
for $\theta_0$, or other crystal parameters. The DR at 288.2 eV
should never be larger than that observed at 287.6 eV.
Furthermore, any gauche defect and any accompanying disor-
der would also disproportionately reduce $\text{DR}_{288.2}$ over
$\text{DR}_{287.6}$.

In order to exclude any systematic error in the DR due
to imperfect normalization, the sum of the two linear
NEXAFS spectra for the same crystallite rotated by 90\(^\circ\)
(Fig. 2a) was checked against a spectrum acquired with cir-
cular polarized radiation at BL11.0.2. The latter is equiva-
 lent to the average from randomly oriented crystallites. The
sum spectrum of the linear dichroic spectra is virtually
identical to the spectrum with circularly polarized light
from BL11.0.2 over the energy range that covers the low
energy doublet (Fig. 2b), excluding any normalization
artifacts.

The strong influences of the periodic solid can also be
seen by comparison of the NEXAFS spectra of TC and
ND. ND has a significantly lower melting temperature than
TC. Investigating the ordered structure of ND can approx-
imate the temperature dependence of TC, corresponding to
a fixed $\Delta T$\[14,25\]. Use of a shorter alkane is more conve-
nient than temperature control, as both measurements can
be carried out at room temperature. $\theta_0$ approaches 45\(^\circ\)
for temperatures approaching melting \[25\], accompanied by a
non-isotropic thermal expansion of the lattice, with the $a$-
axis expanding faster than the $b$-axis. At room temperature,
ND seems to still form crystals with a corresponding ortho-
rhombic unit cell (see VLM images in Fig. 1), yet the mean
distances between alkane molecules in ND crystals are lar-
ger than those in TC crystals.

The average in-plane NEXAFS spectra of TC and ND
crystallites are compared in Fig. 3. Low intensity of the

Fig. 3. In-plane averaged NEXAFS spectra of two n-alkane crystallites measured by STXM (Solid line for n-tetracontane, dotted line for n-
nonadecane). Overall, the peak intensities for ND is somewhat lower than
for TC, as the integrated intensity is spread over a larger energy range.
Theoretically calculated energy positions and intensities of NEXAFS
resonance \[12\] of butane-dimmers at two different separation distances are
plotted as bar diagrams, with spacing $d = 3.2$ Å in black, and $d = 3.8$ Å in
grey, respectively.
distances are schematically included in Fig. 3 [12]. Again, no clear correlation exists, presumably on account of the crudeness of the model. Disorder reduces the observable dichroism [20], which is not the case in our data, and melted high-density polyethylene looses the double peak structure altogether [12]. This suggests that the NEXAFS spectra of condensed alkane molecules with long-range order along the van der Waals directions have a unique electronic structure that depends on the details of the crystal parameters. The crystal lattice parameters, which are governed by the balance of the van der Waals forces as a primary factor, seem to be the proximal factor of these spectral changes. The proper way to think about the electronic structure of organic van der Waals crystals might therefore be more in terms of band structure rather than in terms of molecular orbitals, similar to other van der Waals solids, such as those of rare-gases [28,29]. A clear indication that this might be a fruitful perspective is the bandstructure calculation for polyethylene (PE) by Serra et al., [30] who have shown that ‘the wave function of the conduction-band edge is of interchain character, as opposed to the intrachain character of all the filled valence-band states’. Furthermore, ‘an electron added in PE will mostly reside between the chains, and far from the existing bonds’ [30]. Our work would indicate that the bandstructure of the valence-band is sensitive to the details of the crystalline structure. Alternatively, Rydberg – valence mixing in a molecular picture including near neighbors that takes the core hole and the full crystallographic nature of ordered alkanes might provide an improved theoretical understanding. Only future calculations that take into account the core hole and the full crystallographic nature of ordered alkanes might provide the required theoretical insight. One of the immediate implications of the present work is that the double peak observed in polyethylene is indeed directly related to the crystalllites in these materials [12].

In summary, the observed dichroism in single crystals of tetraccontane shows that the underlying fundamental symmetry planes are those of the orthorhombic unit cell of the crystal and not the symmetry plane of the molecule. This constitutes a further breakdown of the building block model, or, more precisely, even the molecular model typically used for the interpretation of NEXAFS spectra of polymers and molecules. In addition, the NEXAFS spectra of alkanes of different length depend strongly on subtle structural changes of the respective crystal. Two well ordered solids were compared, rather than spectra from ordered and disordered materials. This provides an improved delineation of the underlying causes of the observed spectral changes. The NEXAFS spectra of ordered alkanes can only be understood from the perspective of a solid, even in the two directions in which these materials are weakly interacting van der Waals solids. This important qualitative conclusion does not depend on the precise values of the crystal lattice parameters, nor on whether ND is orthorhombic or hexagonal. These observations have significant implications for the interpretation and use of NEXAFS spectroscopy of any crystalline or semi-crystalline macromolecules or small molecules [31]. The NEXAFS spectra and dichroism could be used, for example, to investigate a number of self-assembled monolayers used to modify and understand cell and protein adsorption properties of surfaces [32,33], to determine the presence of domains and their local (with NEXAF microscopy [34]) orientation, as well as their packing density [35].

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