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Differences in NEXAFS of odd/even long chain *n*-alkane crystals

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ABSTRACT

We present the near edge X-ray absorption fine structure (NEXAFS) spectra of several long chain *n*-alkanes crystallites formed on Silicon nitride (Si_3N_4) windows. Dichroic signature was investigated with the C—C backbone aligned perpendicular to the substrate. Significant changes in the dichroic signature of spectral intensities at energies below the ionization edge (287.5 and 288.1 eV) have been observed. While the dichroic ratio corresponding to the spectral feature at 287.5 eV remains relatively unaffected by the overall length of C—C backbone, it is noticeably affected by the parity (odd or even) of the number of Carbon atoms in the *n*-alkane backbone. Data obtained provide evidence of the influence of interaction of molecular orbitals with periodic lattice structure.

1. Introduction

Near edge X-ray absorption fine structure spectroscopy (NEXAFS) is increasingly playing an important role in the chemical characterization of several different kinds of materials including polymers [1]. It has been customary to analysis NEXAFS spectra with focus on intramolecular effects, such as bonding and electronic structure. Small-molecule analogs have been routinely used for calculations of NEXAFS spectra of polymers and other large molecules. Intermolecular interactions and matrix effects are generally neglected in these interpretations. This approach has successfully provided considerable insight into the interpretation of NEXAFS spectra of large molecules such as polymers [2–5]. This is also true for alkane crystals since the relative strength of covalent C—H orbitals and van der Waals forces is ~98.5% covalent. However, alkanes have been repeatedly used as test materials for understanding solid-state effects on the NEXAFS spectra. This is especially due to large differences between their gas and condensed phase spectra. With the development of third generation synchrotron sources and better optics, very higher energy resolution spectroscopy can now be performed to detect subtle changes in NEXAFS spectra in alkane single crystals of different lengths [6]. Zou et al. [6] have shown that even fractional changes in the weak van der Waals interactions modify the spectral intensity and shape of the NEXAFS spectrum and the dichroic signature. Previously, theoretical studies by Weiss et al. suggested small energy shifts, but no intensity changes, as a function of molecular separation and conformation [7]. A study of ethylene-1-alkene copolymers has shown large changes in intensity with crystallinity but no energy shifts. Theoretical calculations by Schöll suggested that the observed changes in intensity are due to intermolecular interactions rather than the conformation of a polymer chain [8]. Zou et al. have compared the NEXAFS spectra of *n*-tetracontane and *n*-nonadecane. They observed a substantial blue shift for the lower density material which could not be explained by Rydberg matrix effects as described by Weiss et al. [7]. Comparison to calculations of Schöll et al. [8] has also not been satisfactory. Following Ref. [8], Zou et al. suggested 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 understanding and assignment of observed NEXAFS spectral features and their difference in gaseous and condensed phase alkanes have also not been unanimous. The primary point of disagreement has been the assignment of the pre-edge features which has been reported variously as a progression of C1s → Rydberg transition [9–13] for gaseous alkanes and $C1s \rightarrow \sigma^*_{C-H}$ valence transitions in condensed phase [14,15]. With these features in focus and the need for exceptionally well-defined materials, we report here the NEXAFS spectra and dichroic signature of various well-formed *n*-alkanes crystallites. We have investigated $C_{27}H_{56}$ (*n*-heptacosane), $C_{29}H_{60}$ (*n*-nonacosane), $C_{30}H_{62}$ (*n*-triacontane), $C_{31}H_{64}$ (*n*-hentriacontane), $C_{32}H_{66}$ (*n*-dotriacontane), $C_{33}H_{68}$ (*n*-tritriacontane), $C_{34}H_{70}$ (*n*-tetratriacontane), $C_{40}H_{82}$

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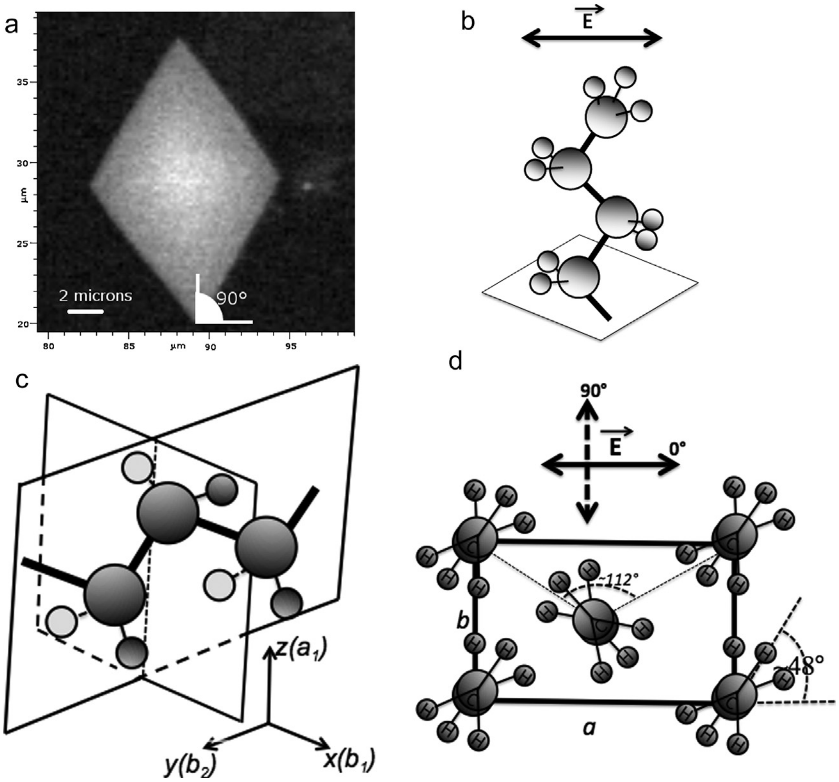

Fig. 1. (a) STXM optical density image of a *n*-tetracontane ($C_{40}H_{82}$) crystallite taken at 288 eV. (b) Schematic representation of an alkane chain with respect to the substrate plane and the electric field vector. (c) Symmetry planes containing the C—C backbone unit and C-H units. (d) Orthorhombic unit cell of *n*-tetracontane as viewed from (1 1 0) direction.

(*n*-tetracontane), $C_{50}H_{102}$ (*n*-pentacontane) and $C_{60}H_{122}$ (*n*-hexacontane) crystals to cover a broad range of *n*-alkanes with different backbone lengths.

2. Experimental

2.1. Material and sample preparation

Chemicals purchased from Sigma–Aldrich GmbH (Germany) and used without any purification. Thin and well-formed crystals of all the long chain alkanes were cast from a Toluene solution with a mass/volume ratio of 0.1 mg/ml. The solution was drop cast on 100 nm thin silicon nitride (Si_3N_4) membranes and dried at −8 °C for $C_{27}H_{56}$, $C_{29}H_{60}$, $C_{30}H_{62}$, $C_{31}H_{64}$, $C_{32}H_{66}$, $C_{33}H_{68}$, $C_{34}H_{70}$, at room temperature for $C_{40}H_{82}$ and in toluene environment for $C_{50}H_{102}$ and $C_{60}H_{122}$.

2.2. STXM and NEXAFS

Well formed crystals were investigated with scanning transmission X-ray microscope (STXM) at advanced light source (ALS) Beamline 5.3.2 with a spatial resolution of ~20 nm and energy resolution greater than 2000 [16]. Beamline 5.3.2 delivers X-rays linearly polarized in the horizontal plane. The samples were mounted perpendicular to the optical axis thus allowing a sample geometry with the polarization direction in the plane of the membrane. The NEXAFS spectra from crystallites of different thickness were compared to exclude the possibility of any thickness related effect. Dichroic spectra from the same crystallite were obtained by rotating it in the plane of the Si_3N_4 membrane. 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 [17]. The energy scale calibration was done using characteristic vibronic peaks of gaseous CO_2 [18]. The spectra were carefully normalized to the incident intensity.

3. Results and discussion

Fig. 1a shows the STXM optical density image of a *n*-tetracontane crystallite taken at 288 eV. Acute angle of ~68° was measured for the crystallite. This angle is in accordance with {1 1 0} terminated orthorhombic unit cells [6]. Fig. 2 shows the NEXAFS spectra of a single *n*-tetracontane crystal rotated in steps from 0° to 90°. Absence of strong spectral changes upon rotating the crystallites by 90°, such as shown in conventional dichroic NEXAFS spectra of *n*-hexatriacontane (HTC) [19], *n*-pentacontane (PC) [20] and *n*-hexacontane [21] upon changing of polarization from parallel to the backbone to perpendicular to the backbone, suggests that the Carbon backbone in our samples is perpendicular to the substrate surface. A representation of the orientation of the molecules with respect to the substrate and the electric field vector is given in Fig. 1b. The assignment of the spectral features in Fig. 2 is according to Stohr [14]. The dominant features include two prominent C1s → $\sigma^*_{C\text{–}H}$/Rydberg peaks at ~287.5 and ~288.1 eV, and two broad C1s → $\sigma^*_{C\text{–}C(C')}$ features at ~289.5 and ~291.3 eV. Systematic changes in the lower energy region can be clearly observed where the peaks at 287.5 and 288.1 eV show intensity changes relative to each other. The signal maxima and minima for the 287.5 eV and the 288.1 eV features were observed with the *a*- and *b*-axis aligned with the horizontal or vertical. Minor changes can also be seen in the features above the ionization edge. The ratio between at 291.3 and 289.5 ($I_{291.3}/I_{289.5}$, not shown) decrease as the angle is changes from 0° to 90°. The NEXAFS signal resonance intensities depend on the angle α between the electric field vector of incident X-rays (E)