

Temperature Dependence in the NEXAFS Spectra of *n*-Alkanes

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Abstract

The Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra of orthorhombic single crystals of *n*-octacosane ($n\text{-C}_{28}\text{H}_{58}$), recorded at room temperature (298 K) and at cryogenic temperatures (93 K), show distinct differences. The characteristic carbon $1s \rightarrow \sigma^*_{\text{C-H}}$ band in the NEXAFS spectrum of $n\text{-C}_{28}\text{H}_{58}$ is broader and has a lower energy onset in its room temperature spectrum than in its NEXAFS spectrum recorded at cryogenic temperatures. Density functional theory simulations show that nuclear motion and molecular disorder contribute to the observed spectral broadness and are the origin of the low-energy onset of the C-H band in the room temperature spectrum.

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Introduction

The variation of molecular spectra (NMR, IR, etc.) with temperature can be used to probe molecular dynamics. Sensitivity to molecular dynamics and motion is also expected in Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. As an example, NEXAFS spectra of gas, liquid, supercooled liquid, and solid water show sensitivity to local hydrogen bonding and changes in this bonding with temperature and phase.¹ To date, experimental studies of the temperature variation in the NEXAFS spectra of molecules are limited.

This study examines the temperature dependence in the NEXAFS spectra of *n*-alkanes. *N*-alkanes, $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ are a family of simple organic molecules consisting of methyl (CH_3) and methylene (CH_2) moieties. Despite their relative simplicity, the NEXAFS spectra of *n*-alkanes show significant complexity, with characteristic differences with phase (gas versus condensed), chain length, degree of order, and with temperature.²⁻¹⁰ Chemical analysis of these materials would be strengthened if fundamental understandings of their NEXAFS spectra (including the role of order and dynamics) were improved, and if stronger structure / spectra relationships were established.

The carbon 1s NEXAFS spectra of simple gas phase alkanes (methane, ethane, propane, etc.) are dominated by series of narrow and well resolved carbon 1s \rightarrow Rydberg transitions, with a rich array of vibronic features.^{2, 10-11} These gas phase spectra are well modeled by calculations that consider the lowest energy geometry but neglect vibronic transitions^{2, 10} as core-excited potential energy surfaces are difficult to model. When neopentane was examined in the gas and condensed phases, characteristic Rydberg transitions observed in the gas phase spectra were shifted to higher energy and were broadened in the condensed phase spectra.³ This effect was attributed to

Rydberg quenching in the solid state, and the emergence of valence (σ_{C-H}^*) character.³ In the carbon 1s NEXAFS spectra of *n*-alkane solids such as paraffin and polyethylene, two low energy transitions of nearly equal strength (the “C-H band”, at 287.6 and 288.2 eV in paraffin) dominate the spectra.^{7, 12} Schöll *et al.*⁷ examined how this C-H band changed with elevated temperature and the degree of crystallinity in polyethylene copolymers. They found that NEXAFS features were broader in the more disordered polymer as well as in molten polyethylene. The origin of these changes was not well understood, but the following observation can be made: increased disorder leads to a broader “C-H” band.

Nuclear motion is predicted to play a role in the variation of NEXAFS spectra with temperature.¹³⁻¹⁵ Pettersson and Nilsson have extensively studied the NEXAFS spectra of water (liquid, supercooled liquid and solid phases) and have shown that its oxygen 1s NEXAFS spectrum is sensitive to the local hydrogen-bonded network and its change with temperature and phase.^{1, 16} The Pendergast group¹³⁻¹⁴ have examined how ‘nuclear motion’ effects leads to spectral broadening in NEXAFS spectra of amino acids and related molecules. Their work compared DFT spectral simulations based on the lowest energy molecular geometry, to simulations that model the nuclear degrees of freedom by averaging ‘snapshots’ from molecular dynamics simulations. Their work predicted that zero-point motion and thermally excited vibrational modes contribute to the shape of NEXAFS spectra. In molecular solids such as glycine, these MD-DFT simulations predict that solid-phase vibrational modes are the origin of temperature dependent broadening.¹⁴⁻¹⁵

Gauche defects (e.g. rotation about individual C-C bonds, distorting an *n*-alkane from the lowest energy, all trans geometry) are another possible contributor to disorder in the NEXAFS spectra of *n*-alkanes, including single crystal *n*-alkanes. In the examination of the

spin-lattice relaxation time ($T_{1\rho}$) for *n*-alkanes of various lengths, Basson *et al.*¹⁷ observed a thermally populated defect below the melting point for solid *n*-alkanes of length 28 ($n\text{-C}_{28}\text{H}_{58}$) or shorter. This dynamic process was identified as a thermally populated *trans-gauche* defect motion near the end of the *n*-alkane chains¹⁷ (later classified as an end-*gauche* defects¹⁸). These defects were seen well below the characteristic pre-melting point solid / solid phase transition to the pseudohexagonal rotator phase,¹⁹ in which an increased population of *gauche* defects near chain ends was also observed.²⁰ We therefore expect that some fraction of thermally populated *gauche* defects will be present in solid *n*-alkanes, particular for shorter *n*-alkane chains.

There is little experimental temperature dependent NEXAFS spectra of organic molecules, and none that we are aware of at cryogenic temperatures. In this work, we examine the carbon 1s NEXAFS spectra of orthorhombic (o-rh) single crystals of *n*-octacosane ($n\text{-C}_{28}\text{H}_{58}$) recorded at room temperature (298 K) and cryogenic temperature (93 K). Regular diamond or parallelogram shaped *n*-octacosane crystallites with straight edges and well-defined angles were identified by optical microscopy (OM). These spectroscopic studies are accompanied by DFT simulations that model the effect of defects and vibrational modes on the NEXAFS spectra.

2. Experimental Information

2.1 Samples and Sample Preparation.

N-octacosane ($n\text{-C}_{28}\text{H}_{58}$, 99%) was purchased from Alfa Aesar and used without purification.

Isopropyl alcohol (99.9%) was ACS grade and purchased from Fisher Scientific.

Samples were prepared on 100 nm, 0.5 × 0.5 mm low stress silicon nitride (Si_3N_4) windows (Norcada Inc.). Thin single crystals of *n*-octacosane ($n\text{-C}_{28}\text{H}_{58}$) were prepared by solution casting^{5, 9} from an isopropyl alcohol solution with a mass/volume ratio of 1.0 mg/2.00 ml.

The substrate temperature during solvent evaporation was optimized in order to isolate the orthorhombic structure over its monoclinic polymorph. Thin single crystals were obtained when the samples were cast at lower solvent evaporation temperature ($\sim 8\text{ }^{\circ}\text{C}$).

The morphology of the *n*-octacosane single crystals were characterized by optical microscopy (Nikon Eclipse ME600, with a Q-Imaging CCD camera).

N-octacosane crystals were found to be rectangular or diamond in shape in optical and X-ray microscopy examination. This indicates that the (*a*,*b*) unit cell axes of the crystals are oriented in the plane of the substrate (see **Scheme 1**). Regular diamond or parallelogram shaped *n*-alkane crystallites with straight edges and well-defined angles were identified by optical microscopy (OM). *N*-alkane crystals with acute interior angles of $68^{\circ} \pm 1^{\circ}$ are orthorhombic, with those with acute interior angles of $74^{\circ} \pm 1^{\circ}$ are monoclinic.²¹⁻²³ Only orthorhombic single crystals of *n*-octacosane (*n*-C₂₈H₅₈) were examined in this work.

2.2 X-ray Spectromicroscopy Characterization.

X-ray microscope images and variable temperature NEXAFS spectra were obtained at the spectromicroscopy (SM) beamline²⁴ at the Canadian Light Source (CLS), using the cryogenic Scanning Transmission X-ray Microscope (c-STXM)²⁵ and the ambient STXM microscope (a-STXM).²⁴ STXM microscopy allows one to acquire the transmission (*I*) spectra from individual single crystals, and to measure the incident flux (*I*₀) from areas adjacent to these crystals. NEXAFS spectra were acquired at cryogenic (93 K) and ambient temperatures ($\sim 298\text{ K}$) with the c-STXM microscope.²⁵ All NEXAFS spectra were acquired using left circular X-ray polarization to eliminate potential linear dichroism from oriented crystals. Transmission spectra were converted to optical density with Beer's law, $\text{OD} = -\ln(I/I_0)$.

Data analysis were performed using aXis 2000²⁶ and spectra are presented using the Origin Lab Pro software package.²⁷ The data presentation focuses on the carbon 1s $\rightarrow \sigma^*_{\text{C-H}}$ band (287 – 288 eV), in order to highlight features that vary with nuclear motion contributions. Care was taken to exclude experimental artefacts such as radiation damage and thickness effects. In order to avoid thickness effects associated with the small fraction of higher order photons, only spectra from thinner crystals (OD < 1.5) were considered. The relatively high radiation sensitivity of *n*-alkane molecules²⁸ limits the permissible dose that can be used for NEXAFS measurements. Experimental conditions (energy point spacing, dwell time, etc.) were optimized to minimize radiation exposure, and the STXM was defocused to 150 nm diameter during image sequence data acquisition. Fresh sample areas were used for each spectrum. Radiation damage was monitored by examining the NEXAFS spectra in the carbon 1s continuum (300 eV) to test for mass loss and at the energy of the carbon 1s $\rightarrow \pi^*_{\text{C=C}}$ transition (285 eV) to test for the formation of C=C double bonds.²⁸⁻²⁹ Radiation damage was found to be minimal in the experimental conditions used.

The energy scale of the ambient temperature NEXAFS spectrum was confirmed through *in situ* calibration to the Rydberg transitions (carbon 1s $\rightarrow 3s$ ($\nu=0$) transition at 292.74 eV and carbon 1s $\rightarrow 3p$ ($\nu=0$) transition at 294.96 eV; after Ma *et al*)¹¹ in the NEXAFS spectrum of CO₂, performed in the a-STXM. These data were used to calibrate the ambient temperature NEXAFS spectrum recorded in the c-STXM. The same shift was applied to calibrate the energy scale of the cryogenic measurements.

2.3 Density Functional Theory Calculations

N-decane (*n*-C₁₀H₂₂) was used as a computational model for this study. The lowest energy geometry (all trans) of *n*-decane was determined by ω B97X-D DFT calculations at the 6-

31+G(d, p) level, performed with the program Gaussian 16.³⁰ There were no imaginary frequencies in the vibrational analysis calculation. Several variations of the *n*-decane structure were examined in order to study the effect of disorder and nuclear motion effects. The effect of gauche defects on the NEXAFS spectra are studied by rotating bond dihedrals in *n*-decane individually. The population of gauche defects at room temperature was obtained from the molecular dynamic simulation study of *n*-decane by Thomas *et al.*³¹ NEXAFS spectra were averaged according to the weights of these calculated gauche defect configurations. This method provides an estimate of the effect of gauche defects in *n*-decane, as an approximation for the effect of gauche defects in longer *n*-alkane crystals. In the solid phase, such defects could be static, but Basson *et al.* have noted that end-gauche defects can also be thermally populated at room temperature in octacosane (*n*-C₂₈H₅₈).³²⁻³³

Many forms of motion can contribute to 'nuclear motion effects' in an *n*-alkane solid, including zero-point motion and thermally populated vibrational modes. Zero-point motions should be expected to contribute at all temperatures, while the Boltzmann distribution of thermally populated vibrational modes will increase with sample temperature.

To examine the spectroscopic effect of the thermally populated modes, we have constructed a simple model based on the *n*-decane (*n*-C₁₀H₂₂) molecule, which has 90 (3N-6) vibrational modes. We have constructed geometries for the turning points of all of these vibrational modes, on the principle that the molecule's geometry will spend the most of its time at these turning points. DFT spectroscopic simulations were performed for these turning-point geometries, and were averaged according to the expected Boltzmann population of these vibrational modes at 298 K. All vibrations are considered, as weighted by their Boltzmann population. This simple approach neglects the effects of zero-point motion, as well as the

population of vibrational modes above $v = 1$, which will be significant for low-energy vibration modes.

Carbon 1s NEXAFS simulations of *n*-decane structures were obtained from DFT calculations³⁴⁻³⁵ using the deMon2k package.³⁶⁻³⁷ All NEXAFS simulations were performed using Transition Potential (TP-DFT) method with the half-core hole (HCH) approximation.³⁸ Spectral lines were simulated using 0.2 eV wide Gaussian line shapes. The molecular spectrum is generated by averaging the DFT simulation from each carbon atom. The IGLO-III basis set³⁹ was used for the core excited carbon atom, effective core potential (ECPs) for all other carbon atoms,⁴⁰ and the triple-zeta (TZVP) basis set for hydrogen atoms.⁴⁰ XAS-I augmentation orbitals were used on the core excited carbon atom.³⁸ The GEN-A4* auxiliary basis and the PBE GGA exchange-correlation functional were used.⁴¹⁻⁴²

3. Results

Figure 1 presents the variation in the C-H band of the carbon 1s NEXAFS spectra of orthorhombic *n*-octacosane (o-rh *n*-C₂₈H₅₈) with temperature, comparing the room temperature (298 K) spectrum with that recorded at cryogenic temperatures (93 K). The shape of the C-H band is significantly broader at room temperature, and the C-H band has a lower energy onset (~200 meV lower) relative to that recorded at cryogenic temperatures. A broader C-H band is expected at higher temperature, as nuclear motion will be more significant. However, the lower energy offset for the room temperature spectra is unexpected and requires further discussion. The observed spectroscopic trends (width and onset) were also observed for *n*-tetracontane (*n*-C₄₀H₈₂) powders, recorded in TEY mode on the CLS SGM beamline (11 ID-1).⁴³

Figure 2 compares the TP-DFT simulations of the carbon 1s NEXAFS spectra of *n*-decane ($n\text{-C}_{10}\text{H}_{22}$) with an all-trans minimum energy geometry, to simulations of gauche defects and thermally populated vibrational models. The shape of the TP-DFT simulation of the carbon 1s spectrum of *n*-decane ($n\text{-C}_{10}\text{H}_{22}$) (in the all trans geometry) differs from the experimental carbon 1s spectrum of *n*-octacosane ($n\text{-C}_{28}\text{H}_{58}$) on account of the length of the model. The methyl-group and the first-methylene in from the end of the chain contribute to the third band observed in Figure 2, at ~ 289.2 eV. For *n*-decane ($n\text{-C}_{10}\text{H}_{22}$), these sites correspond to 40% of the atomic sites in the *n*-alkane chain; therefore, this third band is exaggerated in this short *n*-alkane model. A full examination of the chain length and atomic site dependence in the NEXAFS spectra of *n*-alkanes is in preparation.⁴⁴

The splitting between the first two peaks in the TP-DFT simulation (~ 0.6 eV) roughly matches the observed splitting in the experimental carbon 1s spectrum of *n*-octacosane ($n\text{-C}_{28}\text{H}_{58}$) recorded at cryogenic temperatures.

When gauche defects and populated vibrational modes are considered, new contributions are observed at lower energy; these are indicated by an asterisk in Figure 2. This trend is consistent with the lower energy onset of the C-H band observed in the room temperature NEXAFS spectrum of orthorhombic *n*-octacosane (o-rh $n\text{-C}_{28}\text{H}_{58}$), relative to the spectrum recorded at cryogenic temperatures.

4. Discussion

Spectral broadening in the carbon 1s NEXAFS spectra of molecular solids is expected to have several origins. Beyond the intrinsic broadening from the core-hole lifetime (~ 80 meV), vibronic contributions, disorder, and nuclear motion are expected to contribute to the shape of the

NEXAFS transitions.^{13-14, 45} Vibronic contributions^{2, 11} should be similar for spectra recorded at ambient and at cryogenic temperatures, as the additional energy required for vibronic excitation (e.g. a C 1s($v = 0$) \rightarrow $\sigma^*_{\text{C-H}}(v = 1)$ transition) comes from the absorbed photon. Vibronic contributions will therefore appear at higher energy. Vibronic contributions therefore cannot be responsible for the low-energy onset observed in the room temperature NEXAFS spectrum of *n*-octacosane (*n*-C₂₈H₅₈).

Nuclear motion effects, via the population of vibrational modes and thermally populated molecular defects, are expected to differ with temperature. The effect of the thermal population of vibrational modes and defects on the NEXAFS spectrum of *n*-alkanes was examined using TP-DFT simulations. This distortion from the lowest energy, all trans geometry results in lower energy transitions appearing at lower energy side of the C-H band. This is a reasonable observation; as geometries are distorted from the lowest energy geometry, the HOMO-LUMO gap in a molecule is expected to decrease, and with it, the energy of the core \rightarrow LUMO transition will also decrease. This trend is observed for thermally populated gauche defects as well as vibrations.

We note that the TP-DFT simulations of thermally populated vibrations and gauche defects do not reproduce the intensity of the low energy onset observed in the room temperature NEXAFS spectrum. This is not completely unexpected, as our computational model is limited. We examined a shorter chain (10 carbon atoms long instead of 20) in order to be computationally more accessible (90 versus 252 normal modes). We have also only examined the turning points for the lowest energy thermally populated vibration ($v = 1$), and not higher quantum number vibrational states ($v > 1$), expected to be populated for low energy normal modes.

Our vibrational model is that of an isolated *n*-alkane molecule, and not a solid structure. This model does not capture changes to vibrations due to intermolecular interactions in the condensed phase, or the low-energy shifts expected from dynamic stabilization.⁴⁶ A full approach to examine the temperature dependent spectroscopy will require molecular dynamics simulations, which, with appropriate size, will be able to capture the effect of the solid-phase on nuclear motion contributions to the NEXAFS spectra, as well as thermally populated gauche defects. This requires considerable development, and will be the subject of future work.

In this work, the carbon 1s NEXAFS spectrum of a condensed *n*-alkane orthorhombic *n*-octacosane (o-rh *n*-C₂₈H₅₈) recorded at cryogenic temperatures (93 K), is compared to its NEXAFS spectrum recorded at room temperature. Characteristic differences are observed with temperature. Specifically, the distinctive “C-H band” in the NEXAFS spectrum is narrower in the spectrum recorded at cryogenic temperatures, and the onset of this band appears at higher energy. DFT simulations show that distortions from the lowest energy all trans geometry, from thermally populated vibrational modes and gauche defects, result in new features appearing at lower energy in the NEXAFS spectrum. Cryogenic temperatures restrict thermal motion in the sample, from a lower population of vibrational modes and thermally accessible defects. This results in a narrower C-H band in the spectrum recorded at cryogenic temperatures. At ambient temperatures, gauche defects will be more common, and nuclear motion effects will be enhanced.

5. Conclusions

This work reports remarkable differences in the NEXAFS spectra of an organic molecule with temperature, and attributes these spectroscopic differences to molecular vibrations and defects populated at ambient temperatures, relative to that at cryogenic temperatures. Future work will

include the acquisition of NEXAFS spectra at a broader range of temperatures and a more rigorous exploration of the temperature dependence of the observed nuclear motion effects.

Acknowledgment

SGU is supported by NSERC (Canada) and Canadian Foundation for Innovation. This Research was carried in Soft Microscopy (SM) and the SGM beamline beamline at the Canadian Light Source (CLS) which is supported by the Natural Sciences and Engineering Research Council of Canada, the National Research Council Canada, the Canadian Institutes of Health Research, the Province of Saskatchewan, Western Economic Diversification Canada, and the University of Saskatchewan. This research was enabled in part by support provided by WestGrid (www.westgrid.ca), Compute Canada Calcul Canada (www.computecanada.ca), and HPC facilities at the University of Saskatchewan. We thank L. Wilson and R. Bowles for useful discussions.

Figure 1: Carbon 1s NEXAFS spectra of orthorhombic *n*-octacosane (o-rh $n\text{-C}_{28}\text{H}_{58}$) at cryogenic (93 K) and ambient (298 K) temperatures, recorded with circular left polarization. Optical density spectra are rescaled for comparison.

Figure 2: TP-DFT simulations of the effect of thermally populated gauche defects and thermally populated vibrations ($\nu = 1$) on the NEXAFS spectra of the isolated *n*-decane ($n\text{-C}_{10}\text{H}_{22}$) molecule

Scheme 1: Schematic diagram for chain length orientation, published unit cell parameters of orthorhombic structure of *n*-octacosane ($n\text{-C}_{28}\text{H}_{58}$).^{22-23, 47}

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