

Identification of C—H resonances in the *K*-shell excitation spectra of gas-phase, chemisorbed, and polymeric hydrocarbons

J. Stöhr and D. A. Outka

IBM Almaden Research Center, San Jose, California 95120-6099

K. Baberschke and D. Arvanitis

*Institut für Atom und Festkörperphysik, Freie Universität Berlin,
D-1000 Berlin 33, West Germany*

J. A. Horsley

Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015

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We demonstrate the existence and angular dependence of C—H resonances in the carbon *K*-shell excitation spectra of hydrocarbons. Near-edge x-ray-absorption fine-structure spectra of oriented polyethylene chains exhibit pronounced resonances which are associated with C—C and C—H bonds as determined from their angular dependence and from $X\alpha$ multiple-scattering calculations. The presence of C—H resonances is also found in *K*-shell excitation spectra of free ethylene and ethylene chemisorbed on various metal surfaces.

The near-edge x-ray-absorption fine-structure (NEXAFS) technique has been extensively used for the structural investigation of chemisorbed molecules.¹ The structural information is contained in the existence, the intensity, and the energy position of so-called σ^* and π^* scattering resonances close to the *K*-shell excitation threshold. For the carbon *K* edge, the observed resonances were previously associated with excitations to antibonding π^* and σ^* orbitals arising from the intramolecular bonding between carbon and its C, N, O, or F neighbors.² It has been assumed that NEXAFS, like the (surface) extended x-ray-absorption fine-structure [(S)EXAFS] techniques³ is not sensitive to the bond to hydrogen neighbors. Here we present unambiguous proof for the existence of C—H scattering resonances in C *K*-shell NEXAFS spectra. We find that such resonances exist for gas-phase and chemisorbed molecules and in polymers and that they may have a large intensity. For oriented molecules the C—H resonances exhibit a pronounced angular dependence which allows the determination of the orientation of the C—H bond.

In particular, we find that NEXAFS spectra of highly oriented polyethylene chains, $(\text{CH}_2)_n$, exhibit a pronounced C—H resonance, which is largest for orientation of the electric field vector **E** perpendicular to the chain direction, i.e., in the plane of the C—H bonds. $X\alpha$ multiple-scattering calculations for propane support this assignment and the observed angular dependence. Inspection of the NEXAFS spectra of free ethylene (C_2H_4) and C_2H_4 chemisorbed on various metal surfaces clearly reveals a similar resonance. The existence and angular dependence of C—H resonances for hydrocarbons opens the door for NEXAFS studies of hydrogenation and dehydrogenation reactions and of the orientation of C—H bonds.

The spectra were recorded on beam line I-1 at the Stan-

ford Synchrotron Radiation Laboratory with use of the grasshopper monochromator, except for the spectra of C_2H_4 on Cu(100) and Ag(100), which were measured at the storage ring BESSY in Berlin using the SX-700 monochromator. The NEXAFS spectra were obtained by partial-Auger-yield detection with a retarding voltage of -50 V for bulk polyethylene and -200 V for chemisorbed ethylene.¹ The angle of x-ray incidence was varied from 20° incidence (**E** near surface normal) to normal incidence (**E** in surface plane). The oriented polyethylene was a high-density material (Dow Chemical LP 51.1), drawn with a draw ratio of 30 at a drawing temperature of 380 K and a drawing pressure of 1 kbar. The orientation of the C-C chains was parallel to the surface of the sample, along the drawing direction, and the sample was mounted such that, at normal incidence, **E** was along the chain direction. Spectra of chemisorbed ethylene on various metal surfaces were recorded at monolayer or submonolayer coverage and temperatures 90 K for Pt(111),⁴ 60 K for Cu(100),⁵ 90 K for Ag(110), and 60 K for Ag(100).⁶

The NEXAFS spectra of oriented polyethylene are shown in Fig. 1 at two angles of **E**-vector orientation along the hydrocarbon-chain direction and nearly perpendicular to it. Two principle peaks are observed in the spectra: a resonance at 288 eV which is most pronounced for **E** perpendicular to the chain direction and a resonance at 293 eV with the opposite polarization dependence. Similar peaks have been observed in the gas-phase spectra of saturated linear hydrocarbons⁷ and for free, condensed, and chemisorbed cyclic hydrocarbons⁸ and were attributed to transitions to C—H and C—C antibonding orbitals. Our data are also in good agreement with those obtained for polyethylene in the region 282–292 eV with electron-energy-loss spectroscopy,⁹ but offer additional information through the polarization dependence of the spectra.

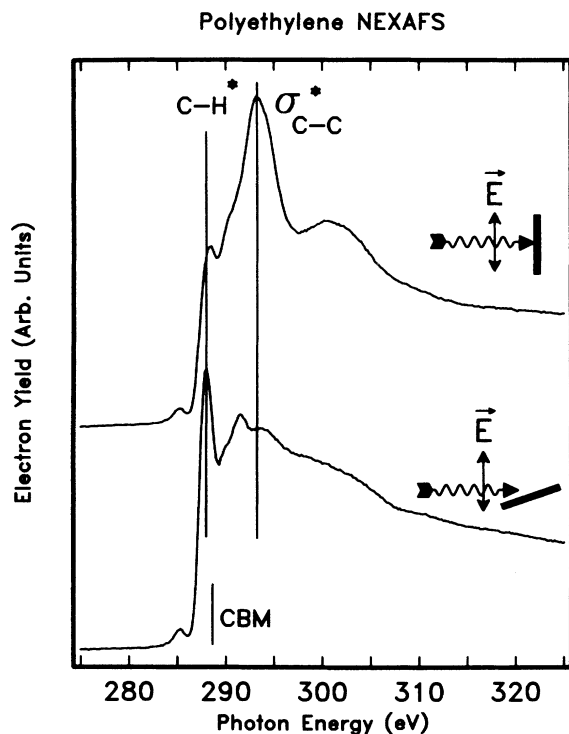


FIG. 1. Carbon *K*-shell NEXAFS spectra of highly oriented polyethylene for **E** parallel and nearly perpendicular (70°) to the chain direction. The polymer chains are oriented parallel to the sample surface. The vertical line at 288.5 eV marks the C 1s excitation energy to the conduction-band minimum (CBM) in polyethylene (Ref. 13).

Since the NEXAFS intensities depend on the projection of the **E** vector on the direction of a specific bond, the polarization dependence of the spectra in Fig. 1 allows a one-to-one assignment of the resonances with bonds in the oriented chains. The labeling of the peaks in Fig. 1 follows from the fact that the C—C σ bond (note that there is no π bonding in the saturated polyethylene chain) has its largest component along the chain direction, and the C—H₂ bonds lie in a plane perpendicular to the chain.

In order to verify this assignment we have carried out *X α* multiple-scattering calculations for the central C atom in the propane molecule. The central C atom in propane has an identical nearest-neighbor geometry as C in polyethylene, as is illustrated in Fig. 2(a). The propane geometry was taken from the microwave spectroscopy data of Lide.¹⁰ The method of calculation was that used in earlier calculations of NEXAFS spectra of various hydrocarbons.^{4,8,11} Partial waves up to $l=6$ on the outer sphere, $l=2$ for the carbon atoms, and $l=0$ for the hydrogen atoms, were included in the calculations. The bound and continuum cross sections were obtained in separate calculations. The cross sections were convoluted with a Gaussian of 1 eV width to account for the instrumental resolution.

The results of the calculations are shown in Fig. 2. For **E** along the chain direction, i.e., along the *z* axis in Fig. 2(a), a large σ shape resonance due to the C—C bond is

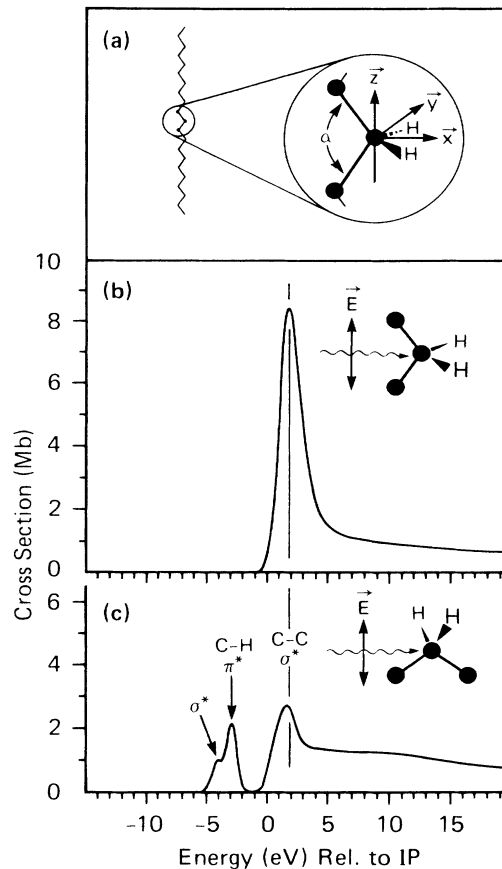


FIG. 2. NEXAFS spectra calculated with the *X α* scattered wave method for the central carbon atom in propane. (a) Schematic of a polyethylene chain and an enlarged view of the geometry of a carbon atom in the chain which is identical to that of the central carbon atom in propane. The *z* axis is the macroscopic chain direction and the C—H bonds are intercepted by the *x* axis in the *x*-*y* plane. Calculated spectra for **E** parallel (b) and perpendicular (c) to the chain direction. The C—H π^* and σ^* bonds lie along the *y* and *x* axes, respectively. Energies are relative to the ionization potential (IP).

obtained about 2 eV above the ionization potential. The same resonance also remains when **E** is perpendicular to the chain direction, however, with a much reduced intensity as shown in Fig. 2(c). In the calculation of the intensities we have assumed cylindrical symmetry about the chain direction. For **E** in the *x*-*y* plane, i.e., perpendicular to the chain direction, the intensity is reduced relative to **E** along the chain direction because the C—C bond has a smaller projection [$\alpha=112^\circ$ in Fig. 2 (a)] and because of azimuthal averaging. In addition, we find two other resonances, labeled C—H π^* and σ^* , which fall below the ionization potential. The symmetry labeling is relative to the C—C bonds such that the C—H π^* and σ^* orbitals lie along the *y* and *x* axes in Fig. 2(a), respectively. The so-called C—H π^* and σ^* states are found to be of mixed Rydberg and valence character. A strong mixing of Rydberg and C—H antibonding orbitals occurs when the Rydberg orbital has the same nodal pattern as the

valence orbital.¹² For excitations from the localized C 1s state the valence character of the final state dominates.

The results of the calculations agree nicely with the polarization dependence of the polyethylene NEXAFS spectra and support the experimental assignment of the two dominant resonances. Our peak assignment also explains the electron-beam-induced intensity decrease of the 288-eV resonance previously observed by Ritsko⁹ in the *K*-shell electron-energy-loss spectra of polyethylene. The intensity loss is caused by C—H bond breaking. The resulting formation of unsaturated C=C bonds is seen in Ritsko's spectra as an increase of a peak at 285 eV, which is due to the C=C π^* resonance. Our spectra in Fig. 1 also exhibit a weak peak at 285 eV, arising from some unsaturated bonds in the bulk or on the surface. Therefore the C—H π^* and σ^* components predicted by the calculation are both contained in the peak at 288 eV. The calculation does not reproduce the absorption step underlying the resonances in the spectra in Fig. 1. The step is a solid-state effect and originates from transitions to states above the conduction-band minimum (CBM).¹³ Also, the calculation does not show the resonance near 302 eV, which is observed at normal x-ray incidence and exhibits the same polarization dependence as the prominent σ^* C—C peak at 293 eV. The origin of the 302-eV peak is presently not understood, but it may arise from interaction of the individual C—C bonds in the chain.

The fact that the C—H resonances may have a significant intensity in NEXAFS spectra of hydrocarbons raises the question of whether such resonances can also be observed for chemisorbed molecules.¹⁴ This would be of considerable importance in the light of the possibility of monitoring changes in the C—H bonds during chemical reactions and transformations on surfaces. In Fig. 3 we show results for the ethylene molecule which contains C—H₂ groups like polyethylene. The *K*-shell excitation spectrum of gas phase C₂H₄ (Ref. 15) has three resonances below the ionization potential: a C=C π^* resonance at 285 eV and two weaker resonances at 288 and 289.5 eV. The latter two resonances have been associated with pure Rydberg transitions in the past.^{15,16} NEXAFS spectra of ethylene chemisorbed on various metal surfaces indicate that this assignment is not entirely correct. Pure Rydberg transitions are expected to disappear upon chemisorption because of the large spatial extent of the Rydberg orbitals,¹⁷ as observed in the NEXAFS spectra of chemisorbed N₂ and CO.¹⁸ Therefore, the resonance observed around 289 eV for C₂H₄ on Ag(100) and Ag(110) in Fig. 3 must be associated with a valence-orbital final state which is concentrated on the molecule. This leads us to associate the two resonances at 288 and 289.5 eV in C₂H₄ gas with C—H antibonding orbitals. Upon chemisorption, the resonances broaden into a peak around 289 eV as clearly observed for C₂H₄ on Ag(100) and Ag(110). The C—H resonance is less evident for Pt(111) and Cu(100) substrates because it overlaps, with a higher energy structure, the C—C σ^* resonance. This latter resonance changes its energy position from about 300 eV for C₂H₄ gas^{2,15} and C₂H₄ on Ag(100) to about 293 eV for C₂H₄ on Pt(111) due to an increasing C—C bond length.^{4-6,19}

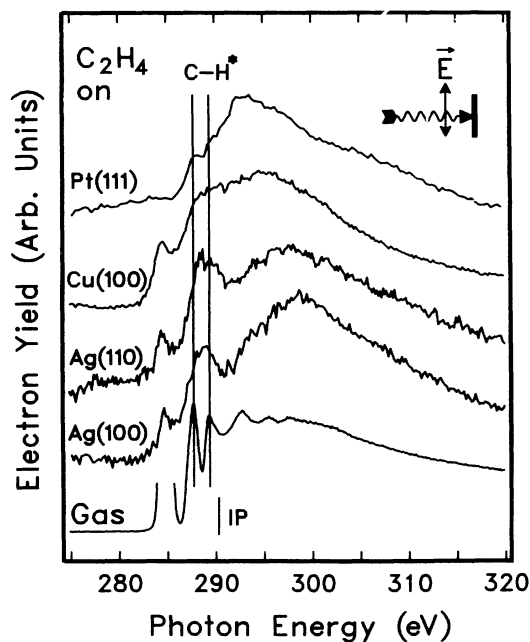


FIG. 3. NEXAFS spectra of C₂H₄ on various metal surfaces (Refs. 4–6) recorded at normal x-ray incidence and *K*-shell excitation spectrum in the gas phase (Ref. 15). The resonances associated with transitions to antibonding orbitals of the C—H bonds in ethylene are marked by vertical lines. The vertical line at 290.6 eV is the C 1s ionization potential relative to the vacuum level in C₂H₄ gas.

Since the spectra in Fig. 3 were taken at normal x-ray incidence the small intensity of the C—C π^* resonance at 285 eV and the pronounced C—C σ^* resonance clearly show that in all cases C₂H₄ lies down on the surface.⁴⁻⁶ For the C—C σ bond parallel to the surface the C—H₂ plane is also expected to be parallel to the surface for an unperturbed molecular geometry. This would lead to a much reduced C—H resonance intensity at grazing x-ray incidence. Although quantitative determinations of the angular dependence of the C—H resonance intensities for chemisorbed molecules are difficult at present we find a sizable C—H resonance intensity for C₂H₄ on Ag(100) and Ag(110) at grazing incidence (not shown). This suggests that the C—H₂ plane is tilted up from the surface as found in Zeise's salt.²⁰

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