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Correlation in the Auger spectrum of polyethylene

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The Auger spectrum of polyethylene has been obtained on an energy scale calibrated relative to the threshold of the valence band and independent of problems associated with energy calibration and charging. The spectrum has a broad, featureless shape which has been previously interpreted in terms of a perturbed self-fold of the density of states. The calibrated C(*KVV*) spectrum reported here, however, is shifted by at least 10 eV relative to a perturbed self-fold of the density of states. This spectral shift requires a hole-hole correlation energy of at least 10 eV if one assumes that the threshold region reflects normal Auger transitions and >10 eV if the threshold region involves shakeup processes. Similar results are observed for the class of saturated linear alkanes. This behavior is shown to be inconsistent with recently calculated spectra for polyethylene in which small values of U_{eff} (1.2 eV for the C—C subband and 3 eV for the remaining contributions) were used to distort the self-fold of the density of states, and, moreover, inconsistent with any existing theoretical representation of Auger spectra.

I. INTRODUCTION

The Auger-electron spectrum (AES) of polyethylene has recently been interpreted by Hutson and Ramaker[1,2] in terms of the Cini-Sawatzky theory,[3–5] which leads to a distortion of the self-fold of the density of states (DOS) due to final-state hole-hole correlation effects. They find reasonable agreement with the AES spectral shape for correlation energies of 1.2 eV for the C—C subband and 3.0 eV for the remainder of the contributions, and interpret the difference between the experimental and calculated spectra in terms of satellite contributions. However, the reported experimental spectra,[6–8] which agree in terms of the spectral shape, disagree as to the energy scale, a common problem with insulating solids. Hutson and Ramaker[1,2] point out that if the spectrum of polyethylene is highly localized (i.e., large correlation effects) as reported by Kelber *et al.*,[7] then polyethylene would lie outside their theory, although they considered this unlikely. The present paper will show that the Auger spectrum of polyethylene is, in fact, highly localized, with the necessary conclusion that the theoretical approach of Hutson and Ramaker[1,2] is not valid. Moreover, it would appear that a spectrum such as polyethylene whose shape can be approximated by a perturbed self-fold of the density of states and at the same time experimentally characterized by a large correlation energy is inconsistent with any present theoretical representation of Auger spectra.

The kinetic energy E_{kinetic} of a core-valence-valence (*KVV* for a core hole in the *K* shell) Auger transition is given approximately by

$$E_{\text{kinetic}}=I_c-I_{v'}-I_{v''}-U_{\text{eff}}(v',v'',s)\ , \qquad (1)$$

where the *I*'s refer to the binding energies of the core and valence electrons involved in the transition and $U_{\text{eff}}(v',v'',s)$ is the spin-dependent interaction of the two final-state holes, a Coulomb repulsion term. For completely uncorrelated final-state holes, the spectral shape is determined by all possible combinations of $I_{v'}+I_{v''}$ for molecules, or by the equivalent self-fold of the density of states in the case of solids. In the case of molecules the spectrum would be shifted by a U_{eff} determined by the finite size of the system. Within the framework of the Cini and Sawatzky theories,[3–5] the effect of correlation is to distort the self-fold of the density of states by shifting spectral intensity to lower energy *without changing the minimum and maximum energies;* for sufficiently large correlation effects, sharp atomiclike states can be split off from the band. Just this behavior is needed to explain, for example, the sharp atomiclike spectrum obtained for metallic copper.[9]

The calculations of Hutson and Ramaker,[1,2] which are based on a Cini-Sawatzky approach, require a correlation energy of less than 3 eV (1.2 eV for the C-C components which contribute to the threshold region and 3 eV for the remainder) to describe the spectral shape of polyethylene. In contrast, both Kelber *et al.*[7] and Dayan and Pepper[8] suggested that while the Auger line shape of polyethylene was approximately given by the self-fold of the density of states, the energy appeared inconsistent with an uncorrelated (or weakly correlated) final state. However, the spread in reported spectral energies, usually ascribed to charging, made an accurate experimental determination of U_{eff} difficult on the basis of previous data.

The important question, of course, is the value of U_{eff} in Eq. (1). Rogers, Rye, and Houston[10] have shown that U_{eff} *can be obtained independent of charging and calibration* provided all the experimental quantities in Eq. (1) are simultaneously obtained in an x-ray-excited Auger spectrum (XAES). In terms of U_{eff}, Eq. (1) becomes

$$(E_{\text{kinetic}}-I_c+I_{v'}+I_{v''})=-U_{\text{eff}}\ , \qquad (2)$$

where the binding energies I_x are given by the difference between the photon energy $h\nu$ (accurately known) and the kinetic energy,

$$I_x = h\nu - (E_{\text{kinetic}})_x \tag{3}$$

Provided all terms on the left-hand side of Eq. (2) are measured in either kinetic energy or binding energy in the same experiment, all linear uncertainties due to calibration or charging cancel.[10] One should note that the kinetic-energy scale of the Physical Electronics double-pass cylindrical mirror analyzer used here is approximately referenced to the sample vacuum level while the binding-energy scale, when calibrated against Au, is referenced to the Fermi level.[11] For the present data all experimental spectra were obtained in the binding-energy mode. This approach has been applied to polyethylene with the result that U_{eff} is comparable in magnitude to the 14 eV observed for methane.[12]

II. EXPERIMENT

X-ray-excited spectra were obtained using a Physical Electronics double-pass cylindrical mirror analyzer (CMA) and a Vacuum Generators dual x-ray source (Mg and Al). Spectra were recorded in the retarding mode with a pass energy of 100 eV using Mg $K\alpha$ x rays (1253.6 eV). Through computer control of the spectrometer, signal-averaged x-ray-photoemission spectroscopy (XPS), XAES, and x-ray-excited valence-band spectra were obtained in the spectrometer's binding-energy mode by multiplexing between the three spectra. Since in the determination of U_{eff} all questions of spectrometer calibration cancel, no special attention was paid to calibration, although the spectrometer binding-energy scale was calibrated against the Au 4f peaks. The sample consisted of a 0.76-mm-thick sample of high-density polyethylene. XPS scans showed no obvious indications of contamination.

III. RESULTS AND INTERPRETATION

Figure 1 contains the valence-band region obtained in Mg $K\alpha$ binding-energy mode referenced to the Fermi level. The vertical arrow marks the valence threshold at an apparent (uncorrected) binding energy of 4.3 eV. The equivalent apparent C 1s binding energy (I_c) occurs at 289.5 eV. Figure 2 contains the "raw" experimental AES spectrum of polyethylene obtained in the Mg $K\alpha$ binding-energy $(E_{\text{binding}})_{\text{AES}}$ mode referenced to the Fermi level.

If the threshold of the polyethylene valence band, Fig. 1, is a measure of highest occupied molecular orbital (HOMO), the left-hand side of Eq. (2) becomes

$$[(E_{\text{kinetic}})_{\text{AES}} - I_c + 2I_{\text{HOMO}}] \ . \tag{4}$$

Since all the quantities in this expression have been experimentally determined, the sum is independent of reference and/or charging and has been used to establish the energy scale for Fig. 3. If Eq. (1) is combined with Eq. (4), one can show that the latter is equivalent to

$$(I_{\text{HOMO}} - I_{v'}) + (I_{\text{HOMO}} - I_{v''}) - U_{\text{eff}}(v',v'',s) \ . \tag{5}$$

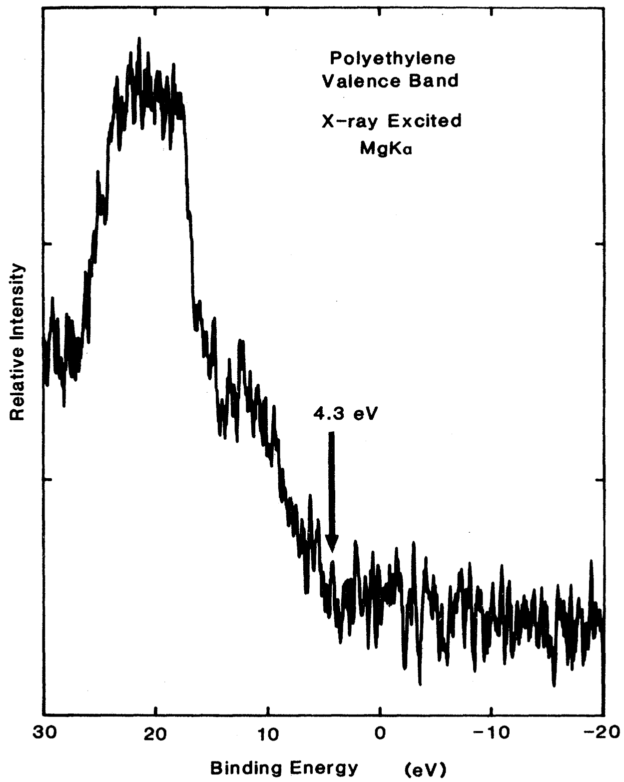

FIG. 1. Polyethylene valence band excited by Mg $K\alpha$ x rays.

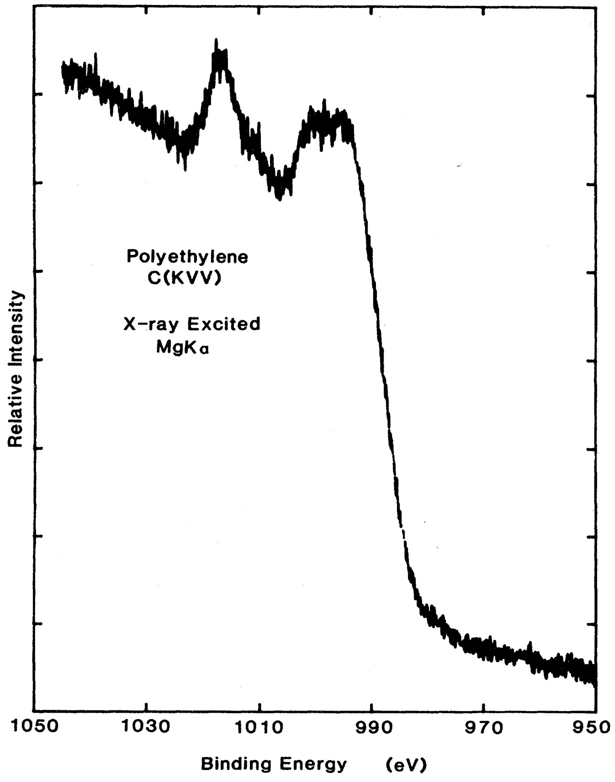

FIG. 2. Polyethylene C(KVV) Auger spectrum. Taken in binding-energy mode with Mg $K\alpha$ x rays. The feature at 1017 eV is an O $K\alpha$ ghost.

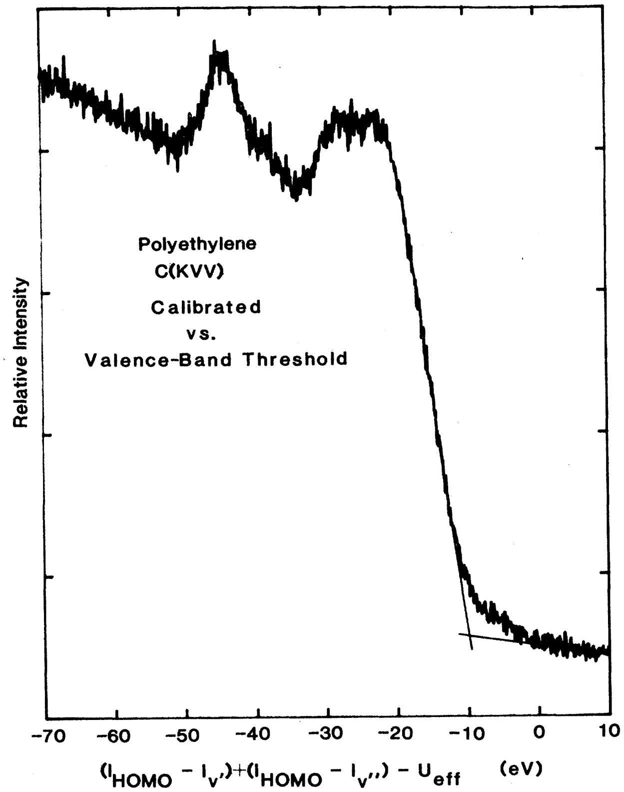

FIG. 3. Polyethylene C(*KVV*) spectrum on a two-hole binding-energy scale relative to the valence-band threshold. This energy scale is compensated for errors due to calibration and charging (see text).

Thus, the use of Eq. (4) places the experimental spectrum on a two-hole binding-energy scale relative to the HOMO, which is free of linear inaccuracies from calibration and/or charging. If one can identify the Auger transition involving the HOMO, usually the threshold in the case of a solid or the first major peak in the case of a molecule, the energy of this transition on a two-hole binding-energy scale relative to the HOMO has a unique value of $U_{\mathrm{eff}}(\mathrm{HOMO,HOMO},s)$.

It is clear from the spectrum in Fig. 3, even without background correction or deconvolution to remove electron-energy-loss effects,[13] that U_{eff} for transitions involving the HOMO is at least 10 eV. The AES threshold is approximately given by the intersection of the two lines at ≈ 10 eV in Fig. 3. The energy of the threshold would yield ≈ 10 eV for U_{eff}, but if there are shakeup processes contributing to the threshold region, the normal Auger transitions would lie deeper in energy and U_{eff} would be larger. The spectrum in Fig. 3 obviously has a large contribution from an O$K\alpha$ ghost peak at -44 eV.[11,14] As a result, instead of correcting the spectrum in Fig. 3 for background and electron-energy losses, our previously published[7] loss-corrected polyethylene spectrum will be calibrated against the energy scale in Fig. 3 by shifting the previous spectrum until the best agreement is reached over the entire region between the threshold and the peak maximum. The resulting background- and loss-corrected spectrum is given by the solid curve in Fig. 4 on a corrected energy scale relative to the threshold of the valence band.

IV. DISCUSSION

Figure 4 also contains theoretical spectra from Fig. 2 of Hutson and Ramaker.[1] The dashed curve is their self-fold of an experimentally determined density of states shifted down by 6.2 eV to agree with the energy scale in Fig. 4. The threshold of their DOS is at ≈ 3.1 eV, reflecting the insulating character of polyethylene. In order to compare the theoretical and experimental Auger spectra on a common two-hole binding-energy scale relative to the HOMO, the calculated self-fold was shifted down by 6.2 eV, or twice the DOS threshold energy. Clearly, a simple self-fold which should give the experimental Auger spectrum for a zero value of U_{eff} cannot represent the experimental spectrum in either shape or energy position. The dotted curve is the calculated spectrum (again shifted down by 6.2 eV) resulting from application of the Cini expression[3,4] to the components of the polyethylene band. Hutson and Ramaker[1] used U values of 1.2 eV for the C—C subband and 3 eV for the remain-

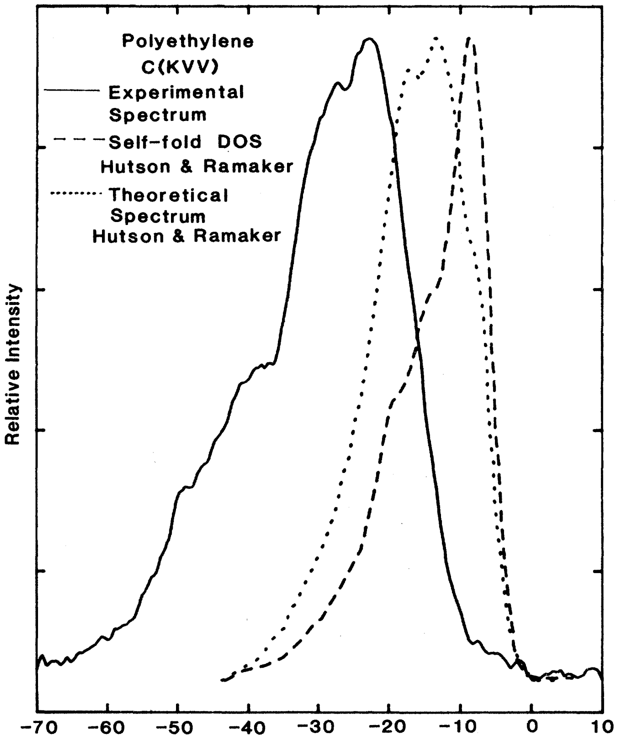

FIG. 4. Loss-corrected polyethylene C(*KVV*) spectra from Ref. 7 on a two-hole binding-energy scale relative to the valence-band threshold. Solid curve, experiment shifted to align with the spectrum in Fig. 3; dashed curve, self-fold of the DOS from Ref. 1; dotted curve, theoretical spectrum from Ref. 1.

ing contributions to obtain the dotted-line spectrum. These values are only slightly larger than those previously found to give a reasonable representation of both the shape and energy of the graphite spectrum.[15] In the case of polyethylene, however, the same theoretical approach gives a reasonable representation of the spectral shape, but there is a major energy shift of the theoretical spectrum relative to experiment. Since there are large differences in the energies reported for the polyethylene Auger spectra,[6-8] Hutson and Ramaker[1] compared their theoretical spectrum to the experimental spectrum of Dayan and Pepper,[8] but concluded that if the apparent value of U_{eff}, Eq. (2), was as large as suggested by Kelber *et al.*,[7] then unique localization processes occur in polyethylene and their theoretical approach would not be applicable. It is clear from the experimental spectrum in Fig. 4 that when the energy scale is carefully calibrated the Auger spectrum of polyethylene is characterized by a large value of U_{eff}. Moreover, the calculated spectrum, when placed on the same calibrated energy scale, is shifted up in energy by ≈ 10 eV with respect to the experimental spectrum. One must therefore conclude that the theoretical approach of Hutson and Ramaker[1,2] is not applicable to polyethylene.

Similar behavior was observed previously for the class of linear alkanes[16] with the experimental spectra characterized by a common value of U_{eff} independent of size, while the calculated spectra systematically shifted up in energy with increasing size, reflecting a calculated U_{eff} which decreased with increasing chain length. The polyethylene spectrum from Fig. 4 is given in Fig. 5, directly compared to the spectra of methane and *n*-hexane[16] on a common two-hole binding-energy scale relative to the HOMO. The Auger kinetic energies for the molecules are referenced to the vacuum level as are the core and valence binding energies from Ref. 17 used with Eq. (4) to place the gas-phase spectra on the energy scale in Fig. 5. Clearly, the degree of hole-hole correlation reflected by the U_{eff} term in Eqs. (1) or (4) is experimentally found to be comparable for methane, hexane, and polyethylene, while calculations based on delocalized molecular orbitals in the case of the gas-phase molecules[16] or delocalized band orbitals in the case of polyethylene predict U_{eff} to decrease with increasing molecular size.

The normal alkane series is the classical example of localized bonding and localized chemical effects, and, as such, it is perhaps not surprising to find that the two-hole Auger final state is localized as well. In contrast, the classical example of delocalized chemical bonding occurs in the aromatic ring systems . Figure 6 contains the spectra of benzene[18,19] and graphite[15] again compared to methane on a two-hole binding-energy scale equivalent to that in Fig. 4. For benzene the Auger spectrum is from Ref. 18 with core and valence binding energies from Ref. 17, while the graphite spectrum is from Ref. 15. The arrow in the benzene spectrum marks the location of the Auger transition involving the HOMO. Detailed analysis of the methane, benzene, and graphite spectra show what is graphically illustrated in Fig. 6, a shift to lower U_{eff} with increasing size: U_{eff} of 14 eV for methane,[12] 7 eV for benzene,[18] and near zero for graphite.[15] These values are consistent with the two final-state holes resulting from the Auger process being delocalized to the extent possible given the size of the system.[20,18]

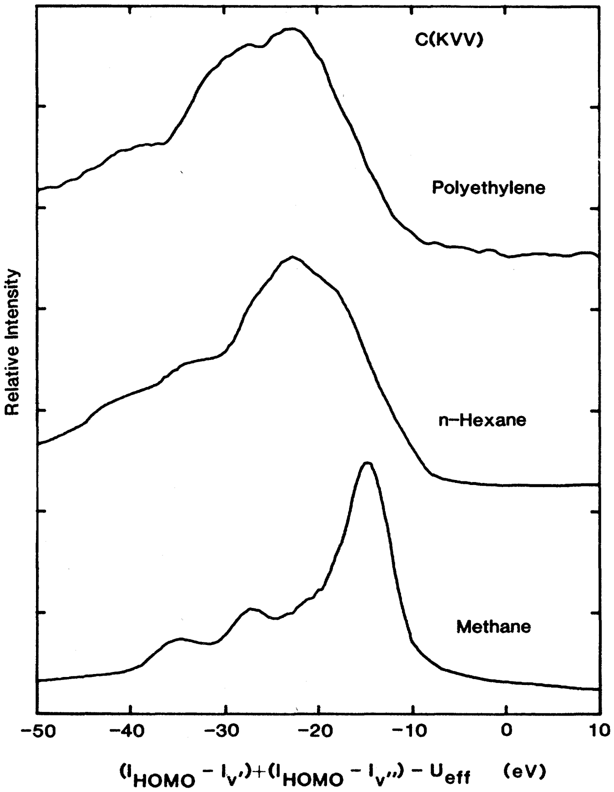

FIG. 5. C(*KVV*) spectra for polyethylene, *n*-hexane, and methane plotted on a common two-hole binding-energy scale relative to the HOMO.

Thus, there appear to be two broad classes of Auger spectra: those that involve delocalized final-state holes and those for which the final-state holes are localized. The delocalized final-state case appears to present no major theoretical problems. In this case U_{eff} can be given by a simple Coulombic repulsion integral based on one-electron wave functions. Such calculated values of U_{eff} will be zero for an extended system and have a value determined by the size of the system for a finite-size molecule.[18,20] In this case the spectrum is given by a self-fold of the DOS in the case of solids or all possible combinations of final states in the case of finite-size molecules. In each case the self-fold is simply shifted by the value of U_{eff}.

For localized Auger final states the problem becomes more complicated. The effects of hole-hole interactions resulting from Auger final-state localization have been modeled for simple systems by Cini[3,4] and Sawatzky.[5] Basically the localization of the two final-state holes causes a distortion of the simple self-fold description. The band does not shift, but the hole-hole interaction

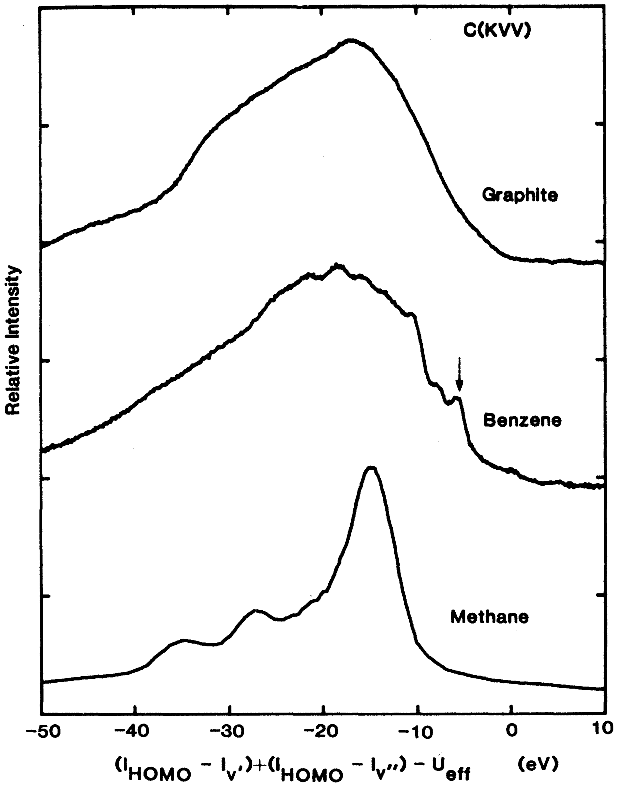

FIG. 6. C(KVV) spectra for graphite, benzene, and methane plotted on a common two-hole binding-energy scale relative to the HOMO.

causes a shift of spectral intensity towards the low-energy end of the line shape (see the difference between the dotted and dashed curves in Fig. 4). For large values of U_{eff} this distortion can be sufficiently large as to produce atomiclike behavior, as is seen in the case of the Cu(L_3VV) spectrum.[9]

Within the framework of the Cini-Sawatzky theory as used by Hutson and Ramaker,[1,2] there is an apparent contradiction with the present results: the *shape* of the spectrum appears basically bandlike and can be approximated by a self-fold of the DOS distorted by only small values of U_{eff}. The experimental results, however, require a large value of U_{eff}, at least 10 eV and probably larger given the expectation of shakeup contributions to the threshold region. Hutson and Ramaker state that such a large value of U_{eff} would be outside their Cini-Sawatzky–type approach. Further, it would appear that no current theoretical approach is consistent with this bandlike shape and large value of U_{eff} that exists for the normal alkanes.

V. SUMMARY

There exist major differences in the literature over the experimental energy for the Auger spectrum of polyethylene, differences which relax the constraints on theoretical representations of the spectrum. The main questions with polyethylene result from the problems associated with obtaining an accurate energy scale. In the present work it has been shown that if one obtains the Auger kinetic energy, the core binding energy, and the threshold of the valence band in the same experiment, an Auger spectrum can be obtained relative to the threshold of the valence band on an energy scale *independent of calibration and charging.* From considerations of spectra on this energy scale, one can draw the following conclusions.

(1) The Auger spectrum of polyethylene has an apparent bandlike shape, but is shifted by at least 10 eV from that expected for an uncorrelated (or weakly correlated) bandlike spectrum. This shift reflects a high degree of final-state hole-hole correlation.

(2) The linear alkanes, in general, show the same degree of final-state hole-hole correlation as polyethylene.

(3) Previously published theoretical spectra for polyethylene are shifted by 10 eV relative to the present experimental spectrum.

(4) A bandlike spectrum with a large value of U_{eff} is apparently inconsistent with existing theoretical representations of Auger spectra.

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