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Identification of satellites due to resonant excitation and shake-off in the C *KVV* Auger line shape of polyethylene

F. L. Hutson and D. E. Ramaker
Department of Chemistry, George Washington University, Washington, D.C. 20052

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A quantitative interpretation of the C *KVV* Auger line shape of polyethylene reveals the presence of satellites arising from resonant excitation into a core excitonic state and from shake-off of a valence electron during the initial core ionization. The intensity, energy, and shape of these satellites reveal much about localization and screening processes in one-dimensional polymers.

I. INTRODUCTION

A quantitative interpretation of the C *KVV* Auger line shape of polyethylene reveals the presence of three satellite contributions. Identification of the two at high kinetic energy indicates they arise from resonant excitation into a core excitonic state; the one at lower energy arises from shake-off of a valence electron during the initial core ionization. This is the first identification of such satellites in an extended covalently bonded solid.

These satellite contributions directly reflect the localized nature of a conduction- or valence-band electron in the presence of a core hole, and thus provide direct information on the screening processes in one-dimensional (1D) polymers. Similar interpretations[1,2] of the C *KVV* Auger line shapes of graphite and diamond [the comparable two-dimensional (2D) and three-dimensional (3D) carbon systems] do not reveal such satellites. On the other hand, the Auger line shapes of several gas-phase molecules, such as cyclohexane and benzene, reveal similar satellites.[3]

II. THE *KVV* LINE SHAPE

A. Experiment

The experimental Auger line shape of polyethylene has been reported previously. Dayan and Pepper[4] recorded the data as $dN(E)/dE$ using electron excitation and rastered the beam at increasing speeds until no further damage effects were observed. Beam damage effects were clearly observed, as the line shape appeared "graphitic"-like when the beam was not rastered. Kelber *et al.*[5] recorded the data as $N(E)$ utilizing Mg $K\alpha$ x rays, which resulted in no observable damage to the sample. The apparent reduced beam damage under x-ray excitation probably arises because of the reduced beam currents involved (both total and per unit area of sample). This is evident since electron and photon damage cross sections are generally very similar,[6] and furthermore, large numbers of secondary electrons of sufficient energy to initiate damage are probably produced by the high-energy x rays in any event.

Consistent with the above, the use of Mg x rays is not expected to significantly reduce the amplitude of the resonantly excited satellites. Initially, one would not expect resonant satellites in an x-ray excited Auger spectra, since in contrast to electrons, photons must lose all of their energy in an absorption process, and the Mg $K\alpha$ photons are clearly nonresonant with the C 1*s* level at 284.6 eV.[7] However, high-energy photons produce not only photoelectrons, but also large numbers of secondary electrons with energies well above the C 1*s* level, so that they can resonantly excite the satellite. Studies in condensed benzene reveal that a resonantly excited satellite is still present with high-energy x rays, although this resonant satellite does not appear with low photon energies.[8]

Figure 1(a) compares the deconvolved spectra obtained by Dayan and Pepper[4] and Kelber *et al.*[5] Similar background subtraction and deconvolution procedures were utilized to remove the effects of secondary electrons and loss processes.[4,5] These procedures have been discussed in detail elsewhere.[1] Extensive experience with these procedures utilizing the similar C *KVV* Auger line shape of graphite reveals that an uncertainty of the order of 20% can occur near the bottom of the line shape, but that little uncertainty exists near the top of the line shape (i.e., where the resonant satellites appear). It should also be mentioned here that these deconvolution procedures remove all broadening effects in the spectra which arise from experimental resolution. Despite the different sample preparations (see below), excitation processes, and data collection procedures (one in the $d[EN(E)]/dE$ mode, the other in $N(E)$ mode with a pass energy of 50 eV), the differences in the resultant shape of the two spectra are very small. What differences are present occur primarily at lower energy where the uncertainties in the loss deconvolution process are greatest. This suggests that the uncertainty or noise level in the line shape is small.

The absolute kinetic energy of the primary peak in the two reported spectra, however, differs by over 5 eV, indicating problems exist with sample charging and energy calibration. Dayan and Pepper utilized a 700-Å film on a metalized glass disk in an attempt to reduce the charging. Nevertheless, energy shifts due to negative surface charging were observed. Dayan *et al.* indicate that these shifts overall are at most about 5 eV, and that they decreased with increasing beam raster velocity. This suggests that the spectrum in Fig. 1, obtained at the highest raster speed and with a maximum intensity at a kinetic energy ($E_{\max}$) of 261.1 eV, has at most a very small charging shift. Kelber *et al.* used a bulk slab, so that charging is expected to occur in this case; however, Kelber *et al.* also accounted for the charging shift in their analysis. They obtain a $E_{\max}$ of 251.8 eV, and claim a charging shift of 4.0±0.6 eV (the sample charges positive under x-ray excitation) giving an actual $E_{\max}$ of 255.8 eV, or 5.3 eV below that of Dayan *et al.* A systematic study of sample charging in polymers, carried out by Clark *et al.*,[9] revealed a charging shift for polyethylene under similar Mg $K\alpha$ excitation, of about 3.4 eV, in agreement with the Kelber result. On the other hand, Gaarenstroom[10] reported a polyethylene Auger spectrum with a $E_{\max}$ of 263.2 eV in closer agreement with the Dayan *et al.* result. Gaarenstroom used $K\alpha$ x rays on samples prepared as thin films solvent cast onto Al foil from xylene, and an electron flood gun to minimize charging effects. Despite several investigations, considerable uncertainty still exists in the absolute energy scale for polyethylene, a common problem with insulating samples.

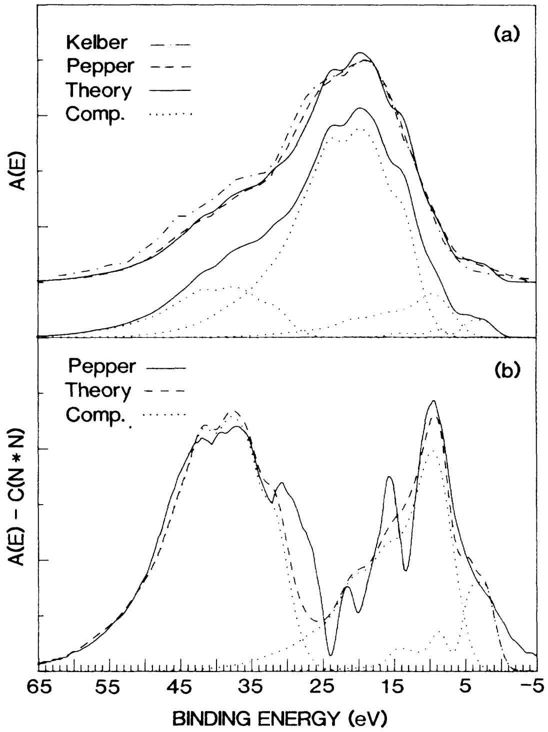

FIG. 1. (a) Comparison of the experimental line shapes (after background subtraction and loss deconvolution as described in Ref. 1) reported by Dayan and Pepper (Ref. 4) and Kelber *et al.* (Ref. 5), with the theoretical total line shape as determined in this work. The Kelber spectrum was energy aligned to that of Dayan *et al.* The components in order of increasing energy are the *ks-vvs*, *kvv*, *ke-vve*, and *ke-v*. Their relative intensities were determined by the best fit to the experimental spectra and their line shapes were determined as described in the text. (b) Comparison of the difference spectra (Dayan's experimental spectrum minus the theoretical *kvv* component) with the sum of the satellite components as indicated above.

The previous interpretations reported for the polyethylene line shape, although highly qualitative, differ sharply in their conclusions.[4,5] This arises because the interpretations depend on whether the emphasis was placed on the experimental line shape or on the energy scale. Kelber *et al.*,[5] whose polyethylene line shape was found to be essentially energy aligned with the alkane line shapes, concluded that the two-hole Auger final state was highly localized. Dayan and Pepper,[4] who emphasized the line shape over the energy scale, found that a simple self-fold of the density of states (DOS) (i.e., a completely delocalized picture) reproduced some of the features of the experimental line shape, but did not have the proper width. They further reasoned that a highly localized Auger final state would further narrow the theoretical line shape, making the agreement even worse. Thus they concluded that other processes must also be occurring, but they did not elaborate.

In this work, our theoretical approach (to be described below) strongly couples the energy scale with the spectral line shape. Thus for example, to lower the energy of the line shape requires the line shape to become narrower and sharper. We have also interpreted the polyethylene line shape in the context of our previous interpretations of the diamond and graphite line shapes,[1,2] and concurrent interpretations of the gas-phase alkane and alkene line shapes.[3] We find the polyethylene line shape and energy scale to be consistent with all of the above, provided we use the absolute energy scale of Dayan *et al.* We cannot, however, rule out the Kelber energy scale, since some unique subchain localization process, which lowers the energy of the line shape without altering its shape, could be occurring. Such a localization process would be unique to the one-dimensional polyethylene system, and would lie outside the range of our present theory; but we cannot rule it out on this basis. Nevertheless, within the current theory, and consistent with our other C KVV line-shape interpretations,[1-3] this seems unlikely. Thus in Fig. 1(a) the two-electron binding-energy scale is obtained by subtracting 280.1 eV (284.6 minus 4.5 for the analyzer work function) from the Dayan *et al.* kinetic-energy scale,[5] and the line shape of Kelber *et al.* is energy aligned with that of Dayan and Pepper. We use this energy scale throughout the remainder of this paper.

B. Theory

Polyethylene has been previously studied by electron-energy-loss spectroscopy (EELS),[11] photoemission [both x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS)],[7,12,13] uv absorption spectroscopy,[13,14] and by semiempirical and *ab initio* theoretical calculations.[15,16] The existence of the valence and core excitonic level has been clearly established;[11,13] however, the s and p components of the one-electron density of states (DOS) have not been accurately determined. We interpret the Auger line shape utilizing a bulk DOS [$N(E)$] obtained semiempirically from XPS data by a procedure similar to that described previously.[17] It is also necessary to separate the p carbon—carbon (p_{CC}) from the p carbon—hydrogen (p_{CH}) bonding DOS, since Auger contributions involving these orbitals experience different localization effects.[18] This was accomplished by identifying each of the features in the polyethylene DOS with one or more of the known one-electron molecular orbitals in cyclohexane (a comparable continuous alkane). The C—C and C—H bonding character of each molecular orbital in cyclohexane is more clearly evident.[3] The resultant semiempirical DOS, having a charge distribution of $s^1 p_{\mathrm{CC}}^{1.4} p_{\mathrm{CH}}^{1.6}$, is compared with the well-known theoretical results of McCubbin and Manne[15] in Fig. 2(a). The semiempirical results contain an effective broadening of 1—2 eV, which apparently arises from spectrometer resolution and intermolecular interactions, but the agreement otherwise is very good.

Final-state hole-hole correlation effects are included in the theoretical normal Auger line shape using the Cini expression,[19]

$$C[N(E)*N(E)]=\frac{N(E)*N(E)}{[1-\Delta U I(E)]^2+[\pi\Delta U N(E)*N(E)]^2}\ , \tag{1}$$

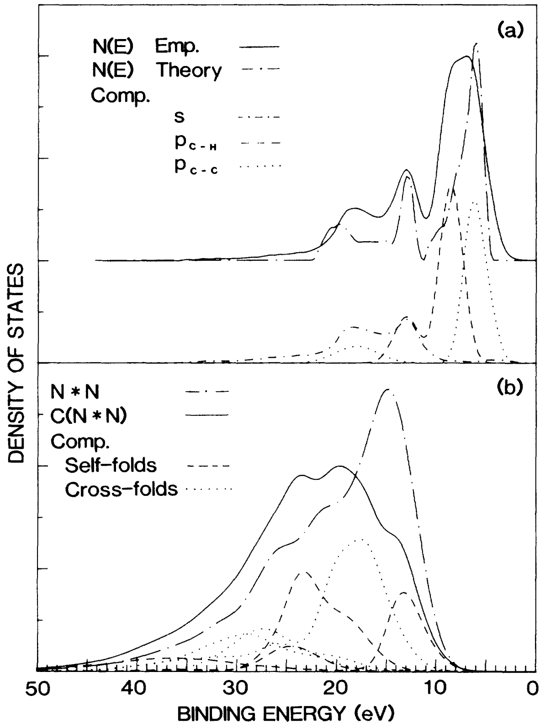

FIG. 2. (a) Comparison of the empirically determined DOS as described in the text with the theoretical DOS as reported by McCubbin and Manne (Refs. 15 and 16). The theoretical DOS were shifted upward by 2 eV to provide better agreement with the empirical DOS. The s, p_{CH}, and p_{CC} components, determined as described in the text, are also shown. (b) Comparison of the DOS self-fold ($N*N$) and the Cini distorted self-fold [$C(N*N)$] obtained by utilizing Eq. (1) and a ΔU of 1.2 eV for the $p_{\mathrm{CC}}*p_{\mathrm{CC}}$ contribution and 3 eV for all of the others. The contributions in order of increasing energy are the $s*s$, $p_{\mathrm{CH}}*p_{\mathrm{CH}}$, and $p_{\mathrm{CC}}*p_{\mathrm{CC}}$ self-folds, and the $s*p_{\mathrm{CC}}$, $s*p_{\mathrm{CH}}$, and $p_{\mathrm{CH}}*p_{\mathrm{CC}}$ cross folds.

where $N(E)*N(E)$ is the DOS self-fold, $\int N(E-E)N(\varepsilon)d\varepsilon$, $I(E)$ is the Hilbert transform,

$$I(E)=\int N(E-\varepsilon)*N(\varepsilon)/(E-\varepsilon)d\varepsilon\ , \tag{2}$$

and $C[N(E)*N(E)]$ represents the Cini distortion of $N(E)*N(E)$. In Fig. 2(b), Eq. (1) has been applied individually to the $s*s$, $s*p_{\mathrm{CC}}$, $s*p_{\mathrm{CH}}$, $p_{\mathrm{CC}}*p_{\mathrm{CC}}$, $p_{\mathrm{CC}}*p_{\mathrm{CH}}$, and $p_{\mathrm{CH}}*p_{\mathrm{CH}}$ components of $N(E)*N(E)$.[1,3] The quantity ΔU equals $U_{11}-U_{12}$, where U_{11} and U_{12} are the effective Coulomb repulsions of two holes in the same orbital, and in nearest-neighbor orbitals, respectively.[3,20] In this case the effective orbital can be pictured as a cluster orbital, consisting of four sp^3 bond orbitals surrounding a single C atom[1,20] (i.e., a methyl group orbital).

Although the ΔU's can be treated as variable parameters, we assigned them the values which provided an optimal fit in a similar interpretation of the cyclohexane Auger spectrum; namely 3 eV for all of the contributions except for the $p_{\mathrm{CC}}*p_{\mathrm{CC}}$ contribution which has a ΔU of 1.2 eV.[3] The cyclohexane gas-phase line shape exhibits more structural features and thus allows for more certainty in determining the optimal ΔU's. We assume that these ΔU's do not change on going to polyethylene, since both systems are essentially continuous alkane chains.

The resultant total line shape and six individual components are shown in Fig. 2(b). The magnitude of the hole-hole correlation effects can be seen by comparison with the DOS self-fold, as shown in Fig. 2(b). The ΔU's reflect the larger localization in the C—H bond orbitals, as expected. The ss and sp components contain elements of both C—C and C—H bond character, and thus these ΔU's are also somewhat larger than for the $p_{\mathrm{CC}}*p_{\mathrm{CC}}$ contribution.[3] The Auger line shapes for methane and ethane suggest that U_{11} for a methyl group is around 11—12 eV and U_{12} in the ethane molecule is around 8—9 eV.[3] The optimal ΔU values of 3 eV used for cyclohexane and polyethylene in the Cini expression are reasonably consistent with these U_{ij}.

Comparison of the theoretical and experimental line shapes in Fig. 1(a) reveals that the normal Auger process, *kvv* (*kvv* here refers to the normal Auger component of the total *KVV* line shape), cannot account for the total line shape; indeed upon normalizing the theoretical and experimental line shapes for best agreement near the peak region, we conclude that the *kvv* process accounts for only about 70% of the total intensity. The difference spectrum (experiment minus theory) in Fig. 1(b) shows two main contributions, the lower one centered around 36 eV, the upper one around 10 eV. The shape of the lower contribution is surprisingly similar to the theoretical *kvv* line shape, the upper one is similar to the theoretical DOS self-fold. These two line shapes are aligned in energy and compared with the corresponding difference contribution in Fig. 1(b). The three features in the lower contribution are reproduced, except the feature around 30 eV is underestimated. The three sharp features in the upper contribution are present, but much less sharp in the DOS self-fold. These comparisons indicate that the bottom contribution can be identified as an initial-state shake-Auger satellite, and the top contribution as a resonant excitation satellite.

III. THE RESONANT SATELLITE

A resonant Auger satellite arises when Auger decay occurs in the presence of a localized electron, which can be created by resonant excitation into an excitonic state upon creation of the core hole. We refer to this as the *ke-vve* satellite, i.e., resulting from the Auger process with a *k*-core hole and an excitonic electron in the initial state, and two valence holes and an excitonic electron in the final state. The existence of an excitonic state in polyethylene is well established, apparently arising from the σ^* antibonding orbitals.[11] As indicated by the electron-energy-loss spectroscopy (EELS) spectrum shown in Fig. 3(a) [it mimics the x-ray absorption spectrum (XAS)], the excitonic state has a binding energy of 1.6 eV relative to the vacuum level, or -2.9 eV relative to the Fermi level.[11]

The generally good agreement between the energies of the sharp peaks between 0 and 25 eV in the difference spectrum [Fig. 1(b)] and the DOS self-fold indicates that the excitonic electron very effectively screens the two Auger valence holes, reducing the correlation effects to zero. The poor resolution of the features in $N(E)*N(E)$, compared to that in the difference spectrum, suggests that the empirical DOS, $N(E)$, may be too broad as already suggested above. The sharper features in the resonant satellite, compared to that in the normal Auger line shape, probably reflect a smaller Franck-Condon envelope for the satellite. This is expected, since the lack of hole-hole correlation effects in the satellite means there will be less bond lengthening in the satellite final state due to the effects of the "Coulomb explosion."[21]

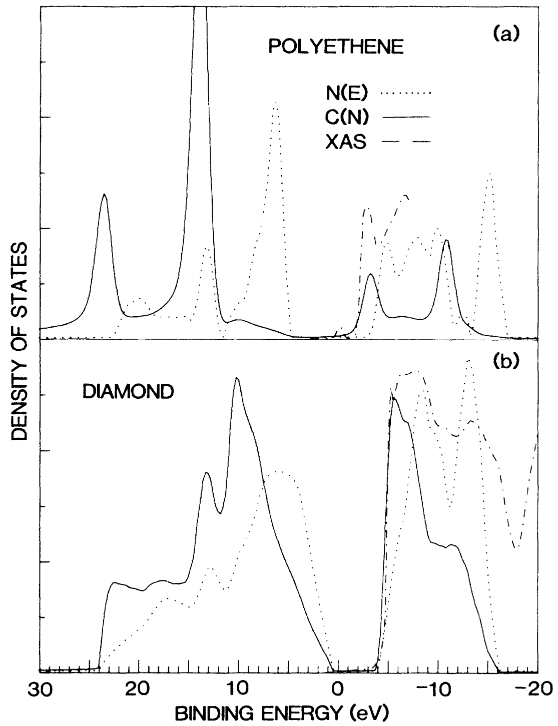

FIG. 3. (a) Comparison of the polyethylene DOS (N) with the distorted DOS [$C(N)$] obtained by utilizing Eq. (1) applied to N with a core hole polarization potential [i.e., ΔU in Eq. (1)] of 10 eV. The optimum ΔU was determined by the best fit to the EELS line shape (Ref. 11) (which mimics the XAS). The occupied and unoccupied DOS's of McCubbin and Manne (Ref. 15) are shown as reported in Refs. 16 and 12, respectively, but they were energy shifted for best agreement with the EELS and XPS (Fig. 2) data. (b) Comparison of the diamond DOS (N) with the distorted DOS [$C(N)$] obtained as above with an optimal ΔU of 5 eV. The XAS, reported in Ref. 30, and theoretical DOS, reported in Ref. 31, are shown; the DOS were energy shifted for best agreement with the XAS.

The energy of the initial state in the resonant Auger process is

$$E_c + E_e + U_{ce} \ , \tag{3}$$

where E_c and E_e are the core and excitonic electron binding energies, and U_{ce} is the polarization energy due to the core hole. The energy of the final state is

$$E_v + E_{v'} + E_e + U_{vv'} - 2U_{ve} \ , \tag{4}$$

where we have assumed pair-wise additivity, and E_v and $E_{v'}$ are the binding energies of the Auger holes and the U's are the corresponding hole-hole repulsions. The Auger energy then is the difference (initial − final) giving

$$E_{ke\text{-}vve} = E_c - E_v - E_{v'} + (-U_{vv'} - U_{ce} + 2U_{ve}) \ , \tag{5}$$

where the term in parentheses is the shift δ_s of the resonant Auger satellite relative to that given by the one-electron theory.

An estimate of U_{ce} can be obtained from Fig. 3(a), where we applied Eq. (1) (i.e., evaluated $C[N(E)]$) to the theoretical DOS to account for the presence of the core hole. In defect theory, this is called the "central-cell tight-binding approximation"[22] and U_{ce} is the polarization energy due to the increased nuclear charge on the defect or donor atom. U_{ce} was treated as a parameter and assigned the value which provided the optimal agreement between $C[N(E)]$ and the EELS spectrum, which according to the final-state rule should reflect the conduction-band DOS in the presence of a core hole.[23] As shown in Fig. 3(a), excellent agreement was obtained when U_{ce} is 10 eV.

The required shift δ_s of the DOS self-fold in Fig. 1(b) is 5 eV. Equation (5) indicates that U_{ve} must then be 7.5 eV if $U_{vv'}$ is zero. $U_{vv'}$ is probably near zero, since the *kvv* line shape, although exhibiting some correlation effects, reflects primarily delocalized valence holes. The existence of a valence excitonic state is well established.[11–14] The relative values of U_{ce} and U_{ve} are consistent with the observation that core excitons are generally more localized than valence excitons.

A high-energy shoulder near the Fermi level appears in the difference spectra which is not reproduced by the DOS self-fold. This can be identified as another resonant satellite, arising also from a resonant electron excitation, but one in which the excitonic electron participates in the Auger decay. We refer to this as the *ke-v* satellite, i.e., coming from an Auger process with a *k*-core hole and an excitonic electron in the initial state, and a single valence hole in the final state. This satellite line shape can be approximated simply by the one-electron DOS, as shown in

Fig. 1(b). The initial state of such a process is the same as in Eq. (3). The final state has a one-hole energy of E_v, giving an Auger energy of

$$E_{ke\text{-}v} = E_c - E_v - (E_e + U_{ce}) , \tag{6}$$

where the term in parentheses is the shift required in $N(E)$. In this case δ_s is equal to the exciton binding energy relative to the Fermi level. The shift in Fig. 1(b) was 3 eV, which is in excellent agreement with the exciton binding energy (≈ 3 eV) as determined by EELS.[11]

The intensities of the *ke-vve* and *ke-v* satellites are 10.7% and 2.6% respectively, relative to the total intensity. These intensities were obtained from Fig. 1, where the relative intensities of the four theoretical components were obtained by least-squares fit to the experimental line shape. The intensities of the resonant satellites depend on the electron excitation energy and the secondary cascade process, so that their absolute intensities are not very interesting. It should be pointed out, however, that by utilizing synchrotron radiation tuned to the exact resonant energy, one could obtain experimentally just the resonant contributions. This process has been called de-excitation electron spectroscopy (DES), and has been reported for both gas-phase and chemisorbed CO, where the $2\pi^*$ level is resonantly populated.[24]

Although their individual intensities are not of interest, the ratio of intensities, $I(ke\text{-}v)/I(ke\text{-}vve)$, indicates something about the character of the excitonic level. The atomic Auger matrix elements per electron are essentially the same, for the *ss*, *sp*, and *pp* contributions in *kvv* spectra.[1] Therefore, we can estimate what the ratio of intensities should be, based purely on the ratio of local electron densities, assuming a completely localized excitonic level. With an initial-state charge distribution of sp^3e, $I(ke\text{-}v)/I(ke\text{-}vve)$ should be 0.5, compared to 0.25 found experimentally. This suggests that although the excitonic level may be localized in time, it must be of a more diffuse nature spatially. The factor-of-2 reduction suggests that the core exciton spends only half of its time on the methyl group with the core hole, the other half of the time presumably on neighboring methyl groups.

IV. THE SHAKE SATELLITE

We indicated above that the satellite centered at 36 eV can be attributed to an initial-state shake-Auger process. Such a satellite arises when Auger decay occurs in the presence of a localized valence hole, which was created via the shake-off process during the initial ionization.[25] We refer to this as a *ks-vvs* satellite, i.e., arising from an Auger process with a *k*-core hole and shake hole in the initial state, and two valence holes and a shake hole in the final state. These satellites are most often seen in gas-phase spectra, when the localization of the valence hole is assured. They are rarely seen in the spectra of solids, since the valence hole normally propagates away from the core hole before the Auger decay.[26] Its presence here, and its energy, intensity, and line shape, characterizes the nature of the localized shake hole in the valence band.

The valence-band DOS for polyethylene in the presence of a core hole, obtained as described above, is shown in Fig. 3(a). It shows relatively sharp peaks indicative of localized states, for both the *s* and *p* DOS. For comparison, the valence-band DOS for diamond in the presence of a core hole is shown in Fig. 3(b), obtained exactly as for polyethylene.[2] In diamond, U_{ce} is equal to just 5 eV, compared to 10 for polyethylene, reflecting the increased screening in three-dimensional diamond. Clearly no localized valence-band states exist for diamond in the presence of a core hole, and thus no shake-Auger satellites are found in the Auger line shape.[2]

The theoretical probability for shake-off upon core ionization of a carbon atom in methane is estimated to be around 24%.[27,3] Furthermore, it has been shown that this probability is relatively independent of its molecular environment.[27,28] The experimental relative intensities of the shake-Auger satellites in ethane, ethylene, cyclohexane, and benzene are around 19—22%, compared to 17—21% in polyethylene (the latter depends on whether the Pepper or Kelber data is used). This indicates that in polyethylene, as well as in the gas-phase molecules, most of the shake holes remain localized sufficiently long enough to cause a satellite contribution.

We indicated above that the minimum subunit orbital is a methyl group orbital, and that a shake hole could not be delocalized over the whole chain or else no satellite would be visible. We can therefore consider two extreme cases for the nature of the valence shake hole; either (1) it is localized on the methyl group with the core hole, or (2) it is delocalized on some larger subcluster of the alkane chain. Now in the final state for case (1), the total repulsion energy is $3U_{11}$; it decreases to $U_{11}+2U_{12}$ when one hole moves off this methyl group. ΔU, as defined above, then is $2(U_{11}-U_{12})$ or twice what it is for the normal Auger line shape. For case (2), the total repulsion energy is $U_{11}+2U_{l,\mathrm{SC}}$ where $U_{l,\mathrm{SC}}$ is the repulsion between a hole created by the Auger process, and localized on the initial methyl group (i.e., group "1"), and the shake hole localized on some larger subcluster (SC) of the chain. When one Auger hole moves off the initial methyl group, the net repulsion reduces to $U_{12}+2U_{l,\mathrm{SC}}$, and thus ΔU is now equal to that for the normal Auger process. We conclude that for case (1) the satellite line shape should be very different from the normal line shape because of the different ΔU; in case (2) it should be the same. Case (1) is clearly appropriate for methane gas, and indeed the experimental Auger spectrum reveals different line shapes for the normal and satellite contributions.[3]

The strong similarity between the shake-Auger and normal Auger line shapes in Fig. 1(b) clearly indicates that for polyethylene case (2) is more appropriate. We conclude that in polyethylene the shake hole delocalizes onto some larger subcluster of the alkane chain. The nature of this delocalized orbital can be obtained from the size of the shift,

$$\delta_s = U_{cs} - 2U_{vs} - U_{vv'} , \tag{7}$$

of the shake-Auger satellite relative to that for the normal Auger line shape. Equation (7) is derived exactly as Eq. (5) above, except for the change in sign in front of U_{cs} and U_{vs} (here we have hole-hole repulsion instead of hole-electron attraction). The required experimental downward shift is 18 eV. A good estimate of U_{cs} can be obtained from the shift in the primary peak in the p DOS upon creation of a core hole, which is 6 eV as shown in Fig. 3(a). In the final state, the shake hole is indistinguishable from the Auger valence holes, thus $\delta_s = U_{cs} - 3U_{vv}$ and U_{vv} must be 8 eV, assuming pairwise additivity. This represents the approximate hole-hole repulsion of an ethane or propane molecule, i.e., the holes are localized on the core hole methyl group but with significant population on neighboring methyl groups.

Similar interpretations, to be published elsewhere, of the Auger line shapes of the gas-phase molecules, methane, ethane, ethylene, cyclohexane, and benzene, reveal that δ_s for the initial-state Auger satellite is relatively constant at -18 eV, in spite of the fact that the two-hole molecular hole-hole repulsion energy is increasing as the molecule gets smaller. This strongly indicates, contrary to that indicated previously,[29] that the two-hole *kvv* line shape primarily reflects molecular delocalized holes (although hole-hole correlation effects are evident), but the *ks*-*vvs* three-hole line shape reflects holes largely localized onto a few methyl groups.

V. SUMMARY

In summary, we have identified and interpreted satellites arising from resonant electron excitation and shakeoff in the Auger line shape of polyethylene. This is the first identification of such satellites in extended covalent solids. Our results provide direct experimental evidence for partial delocalization of the excitonic electron and shake hole onto nearest-neighboring methyl groups. Further, the valence two-hole final states are primarily delocalized over the entire chain, but the three-hole final states are primarily localized onto a subcluster of the chain.

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[1] J. E. Houston, J. W. Rogers, R. R. Rye, F. L. Hutson, and D. E. Ramaker, Phys. Rev. B **34**, 1215 (1986).

[2] D. E. Ramaker and F. L. Hutson (unpublished).

[3] D. E. Ramaker and F. L. Hutson, J. Vac. Sci. Technol. A **4**, 1600 (1986); and unpublished.

[4] M. Dayan and S. V. Pepper, Surf. Sci. **138**, 549 (1984).

[5] J. A. Kelber, R. R. Rye, G. C. Nelson, and J. E. Houston, Surf. Sci. **116**, 148 (1982).

[6] T. E. Madey, D. E. Ramaker, and R. S. Stockbauer, Ann. Rev. Phys. Chem. **35**, 215 (1984).

[7] J. J. Pireaux, R. Caudano, and J. Verbist, J. Electron Spectrosc. Relat. Phenom. **5**, 267 (1974).

[8] J. Nordgren, L. Selander, L. Pettersson, R. Brammer, M. Backstrom, C. Nordling, and H. Agren, Phys. Scr. **27**, 169 (1983).

[9] D. T. Clark, A. Dilks, and H. R. Thomas, J. Polym. Sci. Polym. Chem. Ed. **16**, 1461 (1978).

[10] S. W. Gaarenstroom, J. Vac. Sci. Technol. **16**, 600 (1979).

[11] J. J. Ritsko, J. Chem. Phys. **70**, 5343 (1979).

[12] K. Seki, S. Hashimoto, N. Sato, Y. Harada, K. Ishii, H. Inokuchi, and J. Kanbe, J. Chem. Phys. **66**, 3644 (1977).

[13] M. Fujihira and H. Inokuchi, Chem. Phys. Lett. **17**, 554 (1972).

[14] R. A. George, D. H. Martin, and E. G. Wilson, J. Phys. C **5**, 871 (1972).

[15] W. L. McCubbin and R. Manne, Chem. Phys. Lett. **2**, 230 (1968).

[16] J. E. Falk and R. J. Flemming, J. Phys. C **6**, 2954 (1973).

[17] J. S. Murday, B. I. Dunlap, F. L. Hutson II, and P. Oelhafen, Phys. Rev. B **24**, 4764 (1981).

[18] J. A. Kelber, D. R. Jennison, and J. E. Houston, J. Chem. Phys. **73**, 4867 (1980).

[19] M. Cini, Solid State Commun. **20**, 605 (1976); Phys. Rev. B **17**, 2788 (1978); **87**, 483 (1979).

[20] B. I. Dunlap, F. Hutson, and D. E. Ramaker, J. Vac. Sci. Techol. **18**, 556 (1981).

[21] R. J. Van Brunt, F. W. Powell, R. G. Hirsch, and W. D. Whitehead, J. Chem. Phys. **57**, 3120 (1982).

[22] E. N. Economou, *Green's Functions in Quantum Physics*, Vol. 7 of *Springer Series in Solid State Sciences* (Springer, Berlin, 1979); H. P. Hjalmarson, H. Buttner, and J. D. Dow, Phys. Rev. B **24**, 6010 (1981).

[23] D. E. Ramaker, Phys. Rev. B **25**, 7341 (1982).

[24] C. T. Chen, R. A. DiDio, W. K. Ford, E. W. Plummer, and W. Eberhardt, Phys. Rev. B **32**, 8434 (1985).

[25] E. J. McGuire, Phys. Rev. A **11**, 1880 (1975).

[26] D. E. Ramaker, F. L. Hutson, N. H. Turner, and W. N. Mei, Phys. Rev. B **33**, 2574 (1986).

[27] D. E. Ramaker and J. S. Murday, J. Vac. Sci. Technol. **16**, 510 (1979); F. L. Hutson, D. E. Ramaker, B. I. Dunlap, J. D. Ganjei, and J. S. Murday, J. Chem. Phys. **76**, 2181 (1982).

[28] H. J. Freund, E. W. Plummer, W. R. Salaneck, and R. W. Bigelow, J. Chem. Phys. **75**, 4275 (1981).

[29] J. A. Kelber and D. R. Jennison, J. Vac. Sci. Technol. **20**, 848 (1982).

[30] J. F. Morar, F. J. Himpsel, G. Hollinger, G. Hughes, and J. L. Jordan, Phys. Rev. Lett. **54**, 1960 (1985); Phys. Rev. B **33**, 1346 (1986).

[31] G. S. Painter, D. E. Ellis, and A. R. Lubinsky, Phys. Rev. B **4**, 3610 (1971).