Interpretation of the carbon Auger line shapes for the adsorption and decomposition of ethylene on Ni(100)

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The CKVV Auger line shapes of ethylene chemisorbed on Ni(100) at 100, 250, 300 and 600 K are reported and consistently interpreted. These line shapes are representative of π-bonded ethylene (C\textsubscript{2}H\textsubscript{4}) at 100 K, a-bonded vinyl (CH\textsubscript{2}CH\textsubscript{3}) at 250 K, a mixture of ethynyl (C\textsubscript{2}H\textsubscript{2}) and methylidyne (CH\textsubscript{2}) at 300 K, and carbidic carbon (C\textsubscript{r}) at 600 K on the surface. The Auger line shape of graphitic carbon adlayers on Ni is also interpreted. The line shapes are found to consist of adsorbate-adsorbate, adsorbate-substrate, and substrate-substrate components, which are denoted by the final location of the two holes created by the Auger process. The adsorbate-adsorbate component, for the C\textsubscript{2} chemisorbed species, reflects primarily the valence density of states of ethylene and shows negligible hole-hole correlation effects due to electron transfer from the metal. This is in contrast to the graphitic adlayer where the adsorbate-adsorbate component has the same line shape as bulk graphite and exhibits significant correlation effects. The adsorbate-substrate and substrate-substrate components seen in all of the line shapes directly reflect the adsorbate-substrate π or σ bonding character, and the extent of screening via charge transfer from the metal to the core excited adsorbate.

1. Introduction

The formation and study of carbon and hydrocarbon species on single-crystal transition metal surfaces is important to a mechanistic understanding of catalytic methanation and Fischer–Tropsch synthesis [1]. This has motivated many studies of the adsorption and decomposition of ethylene and acetylene on metal surfaces, by many different techniques, including high-resolution electron energy loss spectroscopy (HREELS) [2–10], temperature programmed desorption (TPD) [7–13], ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) [14–17], electron energy loss spectroscopy (EELS) [18,19], surface extended energy loss fine structure (SSIMS) [7,11,12,21], near-edge X-ray absorption fine structure (NEXAFS) [22], and Auger electron spectroscopy (AES) [18,19,23–27]. Similar techniques have been used to study the catalytic methanation reaction, 3H\textsubscript{2} + CO \rightarrow CH\textsubscript{4} + H\textsubscript{2}O [23,24, and references therein].

Of these many techniques, AES has been particularly useful for determining the total carbon coverage [14,15,23], and also for characterizing the chemical nature of the surface carbon (carbidic or
graphitic) [23,24] which is formed at higher temperatures from the decomposition of hydrocarbons or from catalytic methanation on the surface. AES has, however, the potential to provide much more, namely, chemical structure and bonding information on some of the adsorbed intermediates formed in hydrocarbon decomposition or in methanation. The CKVW Auger line shape, for example, should reflect the type of C–metal bonding (e.g., $\pi$ or $\sigma$ bonding) of small hydrocarbons to the surface, as well as indicate something about the nature of various $C_nH_m$ species. Despite all of the other techniques utilized, it remains difficult to unambiguously determine the chemical nature, the mode of bonding, and the geometry of the adsorbed hydrocarbon molecules, so that additional supporting information from AES would be extremely useful.

AES has not realized its full potential because of the complexity in quantitatively interpreting the various Auger line shapes; not because of the lack of AES data. Auger line shapes have been reported for several chemisorbed systems. Salmeron et al. [27] reported AES data for chemisorbed atoms (O, S, N, and C) on Cu, Ni, and Fe, and noted the presence of features due to interatomic transitions involving deexcitation of the initial adsorbate core hole from electrons in the substrate valence band. Netzer [28] reviewed the literature on AES of chemisorbed molecules as of 1981, summarizing the data for CO, NO, NH$_3$, $C_2H_4$, $C_2N_2$, and $C_6H_6$ chemisorbed on metal surfaces. He noted the presence of intermolecular features in the spectra and a decrease in the hole–hole repulsion energies of the intramolecular features. More recently Kamath et al. [29] reported C, N, and O KVV Auger derivative (d$N(E)/dE$) “fingerprints” for O$_2$, H$_2$O, CH$_3$OH, HCHO, CO, N$_2$, NH$_3$, CH$_3$NH$_2$, and (CH$_3$)$_2$NH chemisorbed on Ni, Cu, Pd, or Ag. Houston et al. [24] reported the “carbidic” and “graphitic” Auger line shapes for the surface carbon species arising from the reaction of CO with Ni(100) and Ni(111) at different temperatures.

Netzer [28] indicated in his early review the need for a level of interpretation beyond the “fingerprinting” technique to understand the changes introduced by the presence of the substrate and the surface chemical bond. Recently, we reported detailed and quantitative interpretations of the CKVW Auger line shapes of graphitic [30], diamond [31], polyethylene [32], and of the gas-phase molecules, methane, ethane, ethylene, benzene, and cyclohexane [33]. These interpretations revealed the presence of satellites arising from resonant excitation, initial-state shake, and final-state shake processes. The principal line shape also revealed the presence of hole–hole correlation effects. These complexities make it understandable why the line shapes for chemisorbed species were not previously interpreted in detail. However, we are now in a position to provide near quantitative interpretations of these line shapes.

In this work, we report the CKVW line shapes for chemisorbed ethylene ($C_2H_4(aq)$) on Ni(100) at 100 K and the various products on Ni(100) formed by ethylene decomposition at 250, 300, and 600 K. The experimental lineshapes at 100 and 600 K [25] and brief reports of the interpretations [34] of all of these lineshapes have been given previously. Here we present detailed interpretations of the lineshapes for the chemisorbed hydrocarbons formed at 100, 250, and 300 K and of that for a graphite adlayer on Ni. An interpretation of the carbidic carbon line shape (i.e., the surface carbon formed by ethylene decomposition at 600 K) will be published elsewhere [35]. The most significant results of this work can be summarized briefly as follows:

1. Although the adsorbate versus comparable gas-phase Auger line shapes exhibit some similar features, the line shapes are largely shifted in energy and are the sum of very different principal and satellite components due to screening via charge transfer from the metal.
2. The $\sigma$ and $\pi$ bonds, which bond the adsorbate to the substrate, are reflected directly in the Auger line shape of the adsorbate.

2. Experimental and data manipulation techniques

The instrument, sample cleaning and experimental techniques are described in detail elsewhere [36]. Briefly, a PHI model 548 photoelectron spectrometer with an Al X-ray source was used, with
the 0.2 μm Al window removed to allow available Bremsstrahlung radiation to escape. This procedure gives a significant increase in X-ray flux at the sample, and with careful outgassing causes no detectable accumulation of impurities at the sample as measured by thermal desorption and/or electron spectroscopy. The cylindrical mirror analyzer (CMA) was operated in the angle integrated mode, with an integrated average electron collection angle of 50° with respect to the surface normal. The Auger spectra were obtained in 30 minutes with the CMA operating in the retarding mode (E_{pass} = 100 eV, ΔE = 1.6 eV).

The raw data also has intensity due to Ni(100) features, as determined by taking a spectrum from a clean Ni(100) surface. Peaks at 273 and 207 eV kinetic energy were observed, and are due to excitation of Ni(3d) and Ni(3p) levels by O Kα radiation (278 eV) arising from impurities on the X-ray anode surface. These "ghost" photoelectron peaks are similar to those discussed previously due to O Kα radiation [37]. Background subtraction, along with subtraction of the clean Ni(100) spectrum is thus required. Scaling of the clean Ni(100) spectrum in the subtraction procedure was used to eliminate the peak due to clean Ni at 207 eV kinetic energy. Although the Ni(3d) ghost peak at 273 eV overlaps the Auger transitions, this peak intensity scales with the Ni(3p) ghost peak and thus both are removed together. Also, other spectra taken with the Al window in place on the X-ray source (although at poorer signal-to-noise) show no signs of the C Kα ghost lines and give results identical to those reported here within experimental error. We emphasize the discussion of this point as a warning, since we would not have known that there was a distortion to the C KVV line shape if we would not have obtained the spectra over a window wide enough to catch the 207 eV ghost peak.

The line shapes given in fig. 1 result after a background has been subtracted and an inelastic and elastic backscattered spectrum has been deconvoluted from the raw data. The large secondary emission background has been removed by using the model function of Sickafus [38], \( N(E) = A(E - E_0)^{-m} \), where \( E \) is the electron kinetic energy, \( N(E) \) is the secondary emission intensity, \( A \) is a constant, and \( m \) and \( E_0 \) are determined from the data. We fixed \( m = 1.3 \) [38], and treated \( A \) and \( E_0 \) as parameters to fit the data.

A backscattered electron spectrum with the incident beam energy \( (E_p) \) equal to the primary Auger kinetic energy, and taken under the same experimental conditions as the Auger spectra, was used to model the analyzer broadening and energy losses [39]. The iterative van Cittert deconvolution procedure was used along with a correction suggested by Wertheim to reduce the effects of noise buildup [40].

Details of this normal Auger data treatment have been given several times before [40]. This deconvolution procedure is necessary to remove the large secondary electron and extrinsic-loss contributions which appear as distortions in any line shape taken from a condensed phase or solid. This data treatment is not necessary for line shapes taken from gases [33,41]. The similarity in spectral
line shape between the extrinsic and intrinsic (i.e., the k-vv process) loss contributions means that all of the k-vv intrinsic satellite contribution (discussed below) is unavoidably removed from an experimental KV line shape for a condensed phase.

3. The gas phase versus chemisorbed ethylene line shapes

3.1. The gas-phase ethylene line shape

We have interpreted the gas-phase ethylene line shape previously [33]. The experimental KV line shape [41], our theoretical result, and the various components are shown in fig. 2a and summarized in table 1. We refer to the satellite components as the ke-ve, kv-vv, and k-vv components, arising from resonant excitation, initial-state shake, and final-state shake, respectively. The notation here indicates the particles in the initial and final state before and after the hyphen, respectively. The “k” refers to the initial 1s core hole, the “e” to the resonantly-excited bound electron, and the “v” to a valence hole created either by the shakeoff process or by the Auger decay. We use kvv to indicate the principal or normal Auger contribution to differentiate it from the total KV experimental line shape. We use kv rather than k-vv to be consistent with that used historically.

The principal kv line shape is obtained by applying the expression [33],

\[ N(E) = B \sum_{\mu \nu} \left[ R_{\mu \nu} R_{\nu \mu} \rho_{\mu \nu} A(E + \delta_{\mu \nu}, \Delta U_{\mu \nu}, \rho_{\mu \nu}) \right] \]

(1)

Here \( A \) is the Cini expression [42],

\[
A(E + \delta_{\mu \nu}, \Delta U_{\mu \nu}, \rho_{\mu}, \rho_{\nu}) = \frac{\rho_{\mu} \cdot \rho_{\nu}}{\left[ 1 - \Delta U_{\mu \nu} I(E) \right]^2 + \left[ \Delta U_{\mu \nu} \rho_{\mu} \cdot \rho_{\nu} \right]^2},
\]

(2)

applied to the self-fold of the one-electron density of states (DOS = \( \rho_{\nu} \)),

\[
\rho_{\mu} \cdot \rho_{\nu} = \int \rho_{\mu}(E - \epsilon) \rho_{\nu}(\epsilon) d\epsilon.
\]

(3)

The sum is over the components \( l \) and \( l' \) (i.e. the \( \sigma_0 \cdot \sigma_0, \sigma_0 \cdot \sigma_1, \sigma_0 \cdot \sigma_1, \sigma_0 \cdot \pi \), and \( \sigma_0 \cdot \pi \) components). The atomic Auger matrix elements, \( P_{k_{\mu \nu}} \) are obtained from experimental and theoretical results for neon. The relative magnitudes utilized in this work are \( P_{k_{ss}} = 0.8 \), \( P_{k_{sp}} = 0.5 \), and \( P_{k_{pp}} = 1.0 \) as reported previously [43]. \( I(E) \) is the Hilbert transform of the DOS and the \( R \) are core hole screening factors as defined below.

In eqs. (1) and (2), \( \Delta U \) is the effective final state hole–hole correlation parameter equal to the

Notes to table 1:

1) This column indicates the basic source of the component line shapes, such as a fold (\( \rho \cdot \rho \)) of the indicated density of states (the DOS of either gas phase ethylene, bulk Ni, Ni, C, or bulk graphite), the experimental Auger line shapes (the NiL, W or bulk graphite C KV), or the theoretical Bethe line shape as described in ref. [33].
2) The effective hole–hole correlation parameter in eq. (2).
3) The effective delocalized hole–hole repulsion parameter in eq. (2).
4) Relative intensity normalized to 100.
5) Signifies values of 2 eV for the \( \sigma \) orbitals, 1 eV for the \( \sigma \pi \), and 0 for the \( \pi \pi \).
6) Signifies values of 9 eV for the \( \sigma \) and 11 eV for the \( \sigma \pi \) and \( \pi \pi \) orbitals. The 9 eV is indicated in parentheses above.
7) Signifies values indicated in f above plus 5 eV, providing a value of 14 eV for the \( \sigma \pi \) orbitals.
8) Although the experimental NiL, W Auger line shape was utilized, the effective \( \Delta U \) has been shown to be around 2.5 eV, see ref. [62].
9) Although the experimental C KV bulk graphite Auger line shape was utilized, the effective \( \Delta U \) has been shown (ref. [33]) to be the same as for gas-phase ethylene, which are indicated in e above.
10) As indicated in h above, the effective \( \Delta U \) in the experimental NiL, W line shape is 2.5 eV; however, fig. 4 suggests that it should be much smaller. In the text, we attribute this indicated decrease to reverse (i.e., graphite to Ni) electron screening in the Auger final state.
difference between the one-center and two-center repulsion integrals (i.e., $U_{11} - U_{12}$), and $\delta$ is the effective hole–hole repulsion for holes delocalized completely over the entire molecule [33]. $\Delta U_{\pi'}$, $\delta_{\pi'}$, and the normalization constant $B$ are obtained empirically from the best fit of eq. (1) to the experimental line shape. The subscripts $l$ and $l'$ on the $\Delta U$ and $\delta$ parameters are to make explicit that these parameter vary with the nature of the orbital combination. We allow just three

Table 1
Summary of components comprising the theoretical Auger line shapes

<table>
<thead>
<tr>
<th>Component</th>
<th>Basic character</th>
<th>$\Delta U$</th>
<th>$\delta$</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(eV)</td>
<td>(eV)</td>
<td></td>
</tr>
<tr>
<td>$C_2H_4$, gas</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VV</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{eth}}$</td>
<td>$\Delta U$ (e)</td>
<td>$\delta$ (e)</td>
<td>52</td>
</tr>
<tr>
<td>kvv</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{eth}}$</td>
<td>0</td>
<td>0</td>
<td>45</td>
</tr>
<tr>
<td>kv-vvv</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{eth}}$</td>
<td>$\Delta U$ (e)</td>
<td>$\delta + 5(14)$ (e)</td>
<td>11</td>
</tr>
<tr>
<td>V$\pi'$$\pi'$$\pi'$$\pi'$</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{Ni}}$</td>
<td>0</td>
<td>0</td>
<td>27</td>
</tr>
<tr>
<td>kv</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{Ni}}$</td>
<td>0</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>kv-vvv</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{Ni}}$</td>
<td>0</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>$C_2H_4$/Ni at 100 K: $\pi$-bonded ethylene ($C_2H_{4\pi}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VV</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{eth}}$</td>
<td>2.5 (b)</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>kv</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{eth}}$</td>
<td>2.5 (b)</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>C$_2$H$<em>4$/Ni at 250 K: $\sigma$-bonded vinyl (CHCH$</em>{2\sigma}$)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VV</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{eth}}$</td>
<td>0</td>
<td>0</td>
<td>22</td>
</tr>
<tr>
<td>kv</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{eth}}$</td>
<td>0</td>
<td>14</td>
<td>6</td>
</tr>
<tr>
<td>V$\sigma$$\sigma$$\sigma$$\sigma$</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{carb}}$</td>
<td>0</td>
<td>0</td>
<td>39</td>
</tr>
<tr>
<td>kv</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{carb}}$</td>
<td>0</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>kv-vvv</td>
<td>$\rho_{\text{eth}} \ast \rho_{\text{carb}}$</td>
<td>0</td>
<td>14</td>
<td>10</td>
</tr>
<tr>
<td>$C_2$H$<em>4$/Ni at 300 K: ethynyl ($C_2H</em>{\pi\pi}$) + methylidyne ($CH_{\pi\pi}$)</td>
<td></td>
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<td></td>
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<tr>
<td>Experimental lineshapes of</td>
<td></td>
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<tr>
<td>$C_2H_4$/Ni at 250 K: $\sigma$-bonded vinyl (CHCH$_{2\sigma}$)</td>
<td></td>
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<tr>
<td>$C_2H_4$/Ni at 600 K: &quot;carbidic&quot; carbon ($C_{\pi\pi}$)</td>
<td></td>
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<tr>
<td>$CO, H_2$/Ni(111) at 650 K: graphitic adlayer</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>VV</td>
<td>bulk CKVV</td>
<td>$\Delta U$ (j)</td>
<td>0</td>
<td>85</td>
</tr>
<tr>
<td>kv</td>
<td>bulk CKVV</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>V$\pi'$$\pi'$$\pi'$$\pi'$</td>
<td>$\rho_{\text{graph}} \ast \rho_{\text{Ni}}$</td>
<td>0</td>
<td>0</td>
<td>11</td>
</tr>
<tr>
<td>kv</td>
<td>$\rho_{\text{graph}} \ast \rho_{\text{Ni}}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$C_2$H$_4$/Ni at 100 K: ethylene on Ni(100)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

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different $\Delta U$s and $\delta$s, namely for the $\sigma\sigma$, $\sigma\pi$, and $\pi\pi$ contributions.

We have shown previously [44] that in covalent systems, intermediate levels of localization can occur. The holes may localize from a molecular orbital to a “cluster” orbital, or further to a bond orbital. A simple examination of the MOs for the alkenes suggests strongly that the appropriate local orbital is the planar arrangement of three $sp^2$ bond orbitals about a single carbon atom for the $\sigma$ bonds, and a single $p$ orbital for the $\pi$ bonds [33]. In light of the above, the $\Delta U$s can be interpreted in this work as the difference between the hole repulsion when two holes are localized on the same local (cluster or atomic) orbital verses when they are localized on different neighboring local orbitals.

The DOS for ethylene was obtained empirically from X-ray emission (XES) [45] and XPS [46] data in a procedure described previously [33]. Briefly the XES spectra reflect the $\sigma_p$ and $\pi$ DOS, the XPS spectra reflect primarily the $\sigma_s$ DOS (actually $\sigma_s + (1/14)(\sigma_p + \pi)$) [47]. The DOS components were weighted to provide an electronic configuration of $\sigma_s{\pi_r}^{1.8}\pi^{1.2}$.

The factors $R_f$ in eq. (1) are to make our theory consistent with the previously derived final state rule for Auger line shapes [48]. The final state rule indicates that (1) the shape of the individual II contributions should reflect the DOS in the final state, and (2) the intensity of each II contribution should reflect the electron configuration of the initial state [48]. For the kvv line shape, the final state is without the core hole. We assume that the DOS in the final state and ground state are similar, so the spectral shape should reflect the ground state DOS. However, the initial state in the kvv process has a core hole, therefore the relative intensities should reflect the electron configuration of the initial-core-hole (CHS) state. The $R_f$ factors are defined,

$$R_f = \int p_{CHS}(\epsilon) \, d\epsilon / \int p_f(\epsilon) \, d\epsilon,$$

(4)

to include this effect. In systems where a single $l$ component dominates the core screening, such as in the chemisorbed species, these $R_f$ factors can significantly alter the total line shape. In ethylene, all $l$ components change similarly, so that the $R_f$ factors can be ignored [33].

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 or bound state upon creation of the core hole [49]. The excited electron can either be a spectator to the Auger decay or participate in it, producing the ke-vve or ke-v contributions, respectively.

The resonant line shapes can be obtained from the one-electron DOS. The spectator case has a two-hole final state so that a self-fold of the DOS

Fig. 2. (a) Comparison of the C KVV experimental and theoretical Auger line shapes for ethylene gas as reported previously [33]. The various contributions (kvv, kv vvv, kv v v, ke v, ke ev-v) were obtained as described in the text and in ref. [33] and are summarized in table 1. (b) Comparison of the experimental and theoretical Auger line shapes for ethylene chemisorbed on Ni(100) at 100 K ($\pi$-bonded ethylene) as obtained in this work. The three component (VV, V$\pi^*$, $\pi^*$-$\pi^*$) line shapes were obtained as described in the text and summarized in table 1. The relative intensities were obtained by a least-squares fit to the experimental data.
is appropriate. Correlation effects can again be introduced by utilizing the Cini expression. However, the spectator electron can screen the two holes and reduce the hole-hole repulsion. In this work we assume correlation effects are negligible in the ke-vv satellite so that its line shape is given simply by the DOS self-fold [33]. The ke-v satellite has just one final state hole, so its line shape is given accurately by the one-electron DOS. Like for the kv line shape, energy shifts to higher binding energy are again required [33]. \( \delta_{ke-vv} \) is approximately equal to \( U_v - U_{ke} \) and \( \delta_{ke-v} \) to \( E_v + U_{ke} \). Here \( U_{ke} \) and \( U_v \) are equal to the core(or valence)-hole, excited-electron attraction energy, and \( E_v \) is the excited-electron binding energy in the absence of the core hole. \( E_v + U_{ke} \) is the excited-electron binding energy in the presence of the core hole.

Initial-state shake, kv-vvv, satellites arise when Auger decay occurs in the presence of a localized valence hole, which was created via the shake-off process during the initial ionization [50]. We have determined previously that the line shape for the kv-vv satellite in alkenes can be approximated by a self-fold of the DOS, but with twice the \( \Delta U \) and \( \delta \) parameters [33].

Final-state shake, k-vvv, satellites arise when Auger decay occurs simultaneously with shakeoff of a valence hole [50]. The energy required for the shakeoff process decreases the kinetic energy of the Auger electron, so that the k-vvv satellite appears as a rather structureless contribution over a wide range of energies near the bottom of the total line shape. We have utilized [33] a function due to Bethe to approximate this line shape. In general, one can expect approximately the same amount of final-state as initial-state shake, so that these two satellite contributions should have comparable intensity [33].

Table 1 summarizes the results found previously for gas-phase ethylene [33]. Note that the kvv principal component accounts for only about half of the total KVV line shape. The kv-vve and k-vvv shakeoff satellites have almost equal intensity, which is about equal to the probability for shakeoff. The \( \delta s \) for the kvv contribution are relatively large, around 10 eV. \( \delta_{ke-vv} \) is reduced to 3 eV due to the screening of the \( \pi^* \) electron as indicated above. \( \delta_{ke-v} \), which as indicated above should be equal to the binding energy of the \( \pi^* \) orbital in the presence of a core hole, is 7 eV, consistent with that indicated by core-hole absorption spectra [33].

3.2. The chemisorbed ethylene line shape

The molecular chemisorption of ethylene on Ni(100) at low temperatures has been studied extensively [15,51,52]. Vibrational spectroscopy, in particular HREELS, has been very useful in determining the structure of chemisorbed hydrocarbons on metal single-crystal surfaces [53,54]. At low temperatures (near 100 K) ethylene adsorbs on different metals and different crystal faces either as a \( \pi \)-bonded complex or a di-\( \sigma \)-bonded complex [53,54]. HREELS results for \( \text{C}_2\text{H}_4 \) on Ni(100) [8,51] show that ethylene is \( \pi \)-bonded to the Ni(100) surface with the C=C bond nearly parallel to the surface. Thus, the Auger line shape for ethylene chemisorbed on Ni(100) at 100 K (see fig. 2b) corresponds to that for \( \pi \)-bonded molecular ethylene.

Some theoretical work has been done for this system. Multiple scattering X\( \alpha \) calculations [55] for ethylene chemisorbed on Ni(100), modeled by a 10-atom Ni cluster, reveals that charge donation occurs from the \( \text{C}_2\text{H}_4 \) \( \pi \) orbital to a Ni \( \sigma_{pd} \) orbital, and corresponding backdonation of charge into the \( \text{C}_2\text{H}_4 \) \( \pi^* \) orbital. The Ni levels near the Fermi energy are virtually unaffected; the valence \( \sigma \) orbitals appear to uniformly shift to higher binding energy by about 1.5 eV and the \( \pi \) orbital remains nearly unshifted [55].

We will model the chemisorbed ethylene one-electron DOS by using the DOS obtained previously [33] for gas-phase ethylene. We will include the Auger contributions arising because of the partial electron occupation of the \( \pi^* \) orbital in the chemisorbed state by including separate VV, V\( \pi^* \), and \( \pi^*\pi^* \) contributions, where V indicates collectively the normally occupied valence orbitals.

The VV contribution should be directly relatable to that utilized for gas-phase ethylene. However, a major difference arises because, in the final state, charge transfer from the substrate into the \( \pi^* \) orbital occurs to screen the two or three holes
left by the Auger or shakeoff-Auger process. This charge transfer into the \( \pi^* \) orbital is known to occur for CO and NO chemisorbed on metals [56], and it has been indicated earlier for other unsaturated [57] and even saturated [58] molecules. This charge transfer has the affect of decreasing the \( \Delta U \) and \( \delta \) parameters; the transferred charge playing the role of the resonantly excited electron in the gas phase as reflected in the resonant satellite. Indeed, the line shape for the principal kv\* contribution to the VV component should be similar to the ke-ve line shape for ethylene, i.e., a DOS self-fold with \( \Delta U = 0 \) (see table 1).

Resonant satellites do not appear in the VV contribution because now the Auger spectrum was obtained using nonresonant X-rays. However the \( V^* \pi^* \) contribution should be similar to the ke-\( \nu \) contribution for ethylene gas since both should reflect the one-electron ethylene DOS. We must fold the ethylene DOS, \( \rho_{\text{eth}} \), with the \( \pi^* \) DOS. In the LCAO-MO approximation, the \( \pi^* \) orbital mixes with much of the Ni(3d) valence band [59], indeed the hole left by the Auger decay involving the \( \pi^* \) orbital probably ends up in the Ni. Therefore we fold \( \pi \) with the Ni(3d) DOS as obtained from band calculations [60], and shown in fig. 3a.

Finally, as mentioned above, Salmeron et al. [27] and Netzer [28] have noted the presence of "inter"-atomic or \(-\)molecular features near the top of most Auger line shapes of chemisorbed species. These are again probably facilitated through an intra-atomic \( \pi^* \pi^* \) Auger process, but which ultimately appears inter-atomic in character because both holes end up on the substrate. Thus we model the \( \pi^* \pi^* \) line shape by utilizing the Ni\( L_3VV \) Auger line shape [61]. This line shape reflects a self-fold of the d-DOS, but with significant correlation effects consistent with the Cini expression [62]. The Ni\( L_3VV \) line shape is shown in fig. 3b on a two-hole binding energy scale relative to the vacuum level. This was obtained from the experimental kinetic energy scale utilizing an \( L_3 \) binding energy of 855 eV and a work function of 5 eV [62]. This line shape was utilized unshifted for the \( \pi \pi^* \) component in fig. 2b.

Each of the three components (i.e., the VV, \( V\pi^* \), \( \pi^* \pi^* \) components) will also have a kv-\( \nu \nu \nu \) satellite contribution. The kv-\( \nu \nu \nu \) satellite contribution to VV should be similar to the kv contribution in ethylene gas (i.e., the kv-\( \nu \nu \nu \) line shape in the chemisorbed molecule should be similar to the kv line shape in the gas). The kv-\( \nu \nu \nu \) line shapes for the \( V\pi^* \) and \( \pi^* \pi^* \) components were assumed to be the same as the principal kv contributions. A constant energy shift (i.e., 14 eV) to higher binding energy to account for the larger repulsion of the 3 final state holes in the kv-\( \nu \nu \nu \) process was included for all three components. The kv-\( \nu \nu \nu \) satellite was fixed at 25% of the kv contribution for all three components. The energy shift and the 25% relative intensity of the kv-\( \nu \nu \nu \) satellite was determined to give optimal agreement with experiment. A final-state shake kv-\( \nu \nu \nu \) satellite contribution does not exist in the chemisorbed ethylene line shape because it has been subtracted out in the background and deconvolution processes as mentioned above.

Table 1 summarizes the intensities of the individual components comprising the theoretical Auger line shape for \( \pi \) bonded ethylene chemisorbed on Ni(100) at 100 K. The total theoretical
line shape was generated by a linear least squares fit of the three (i.e., the \( VV, V\pi^*, \pi^*\pi^* \)) components to experiment. Fig. 2b shows each component and compares the total theoretical line shape with the experimental one. The agreement between theory and experiment is good; all features present in the experimental line shape appear also in the theory with nearly the same energy and relative intensity, except for the feature around 26 eV which is a little too large in the theory. This is comparable to the peak at around 40 eV in ethylene gas (see fig. 2a) where the theory is similarly too large. In the gas phase, this over-estimate was attributed to the absence of multiplet effects in the theory. This is probably also the problem for chemisorbed ethylene, since the screening charge in many solids is known to drastically reduce the absolute values of \( U \), but not the separation between the multiplets [63].

The relative intensities of the three components can be understood within the final state rule, as defined above. The electronic configuration per carbon atom in the ground state of the chemisorbed ethylene, assuming charge neutrality, is nominally \( \sigma^3\pi^1-x\pi^*x \), where the \( x \) indicates the \( \pi \) bonding and \( \pi^* \) backbonding charge transfer involved in the interaction with the metal substrate. Upon creation of the core hole, we assume the valence electronic configuration, again assuming charge neutrality, becomes \( \sigma^3\pi^1\pi^*y \) or \( V^4\pi^*y \), where \( y \) is the net charge transfer in the presence of the initial core hole. The relative intensities of the components, \( VV : V\pi^* : \pi^*\pi^* \) should then be \( 16 : 8y : y^2 \), or upon including the \( P_{kl} \) matrix elements \( 13 : 7y : y^2 \). Best agreement with the results obtained from the fit to the experimental lineshapes as reported in table 1 is obtained when \( y = 1.3 \), which gives relative intensities of \( 55 : 38 : 7 \) (total normalized to 100) compared to \( 56 : 34 : 10 \) in table 1. The 1.3 total electron transfer is consistent with the 1.3 core hole screening electrons found in benzene as determined from ab initio theoretical calculations [30].

4. The line shapes for the ethylene decomposition products

The line shapes obtained after warming the chemisorbed ethylene monolayer to 250 and 300 K, shown in fig. 4, are different from those at 100 K, suggesting either decomposition of the ethylene or a bonding mode change on the surface. HREELS [8,51] and other data [13–15] indicate that by 180 K, \( \text{C}_2\text{H}_4 \) dehydrogenates to vinyl (CHCH\(_2\)) chemisorbed on the surface of Ni(100). This is stable on the surface to 280 K [13]. The bonding of chemisorbed vinyl can be considered as \( \eta^2-\text{C} \) vinyl species with retention of the C–C \( \pi \) bond and bound to Ni through both carbon atoms. Two \( \sigma \) adsorbate–substrate (C–M) bonds are now involved instead of a single \( \pi \) C–M bond as for chemisorbed ethylene at 100 K. We anticipate that the strong \( \sigma \) adsorbate–substrate bonds
will significantly contribute to the Auger line shape so that it is still composed of three components (as previously discussed), only now we label them the VV, Vσ, and σσ components. The VV component is exactly as that found above, but the σσ component should be different from the π∗π∗ component.

We approximate the C−M σ bonding DOS by utilizing the DOS for transition metal carbides, in this case that for carbidic carbon chemisorbed on Ni. The approximate carbidic DOS can be obtained from two different sources. Rosei et al. [16] obtained UPS data for carbidic overlayers obtained by heating a Ni(111) surface at 200–250 °C in CO. The difference between the UPS (hv = 35 eV) spectra for the clean and carburized (0.3 ML carbon) Ni surface is given in fig. 3c. This difference spectrum is compared with the LCAO-MO calculated DOS obtained by Feibelman [64] for a (1 × 1) overlayer of C atoms on an 11-layer Ru(0001) film. The calculated results indicate that the narrow feature near the Fermi level in both the measured and calculated “DOS” is due predominantly to a non-bonding p₂ orbital. The broad feature between 2 and 8 eV arises primarily from the bonding pₓᵧ orbitals, and the feature around 11 eV arises mainly from the s orbitals. Reasonable agreement between the measured and theoretical DOS is found except for the “s” feature. It is sharp and around 11 eV in the calculated DOS, very broad and centered at 15 eV in the measured DOS of Rosei et al. The slow tailing off of the empirical “s” feature may be an artifact of the subtraction procedure, but more likely it is due to the presence of chemisorbed C₂ species which may also reside on the surface [35]. The C₂(a) species are expected to have the “s” feature at significantly higher binding energy, thus explaining the tailing off of the “s” feature in the Rozei data. Comparison of self-folds with the experimental carbidic Auger line shape [35] suggests that the s DOS should peak around 13 eV. For the work to be described below, we will utilize the theoretical DOS, but with the s feature shifted to 13 eV binding energy.

The self-folds of the theoretical and measured carbidic carbon DOS are indicated in fig. 3d. The self-fold of the theoretical DOS was Gaussian-broadened by 2 eV. Comparison of the σ and π∗ C−M bonding DOS and the π∗π∗ and σσ kvv components, as we have approximated them, indicates very significant differences exist between these two chemisorption bonds. Although the dominant feature in both components falls at 14–16 eV, the σσ component has significant contributions down to 40 eV, whereas the π∗π∗ contribution extends down to only 20 eV. The large differences in the DOS means that the cross-folds (i.e., the Vσ and Vπ*) will also be different. We believe that these differences in the component line shapes, and differences in the relative intensities of each component, are the reasons for the differences in the total Auger line shapes at 100 and 250 K.

We wish to emphasize the basic differences between the σ and π adsorbate–substrate bonds as we believe they are reflected in the Auger line shapes. The weak π chemisorption bond does not significantly alter the Ni DOS, as suggested by MS-Xα calculations [55], thus it only provides a means for the charge transfer so that the final state Auger holes may end up on the substrate Ni atom nearest the ethylene. Our utilization of the Ni DOS and L₂,3VV line shape above reflects this assumption. On the other hand, the stronger σ C−M bonds do alter the Ni DOS, and we assume a carbidic C−M bond character. Our utilization of the carbidic carbon DOS and self-folds reflects this assumption.

Our previous studies [65] of metal carbide C KVV Auger line shapes [66,67] have indicated that the hole–hole correlation effects decrease as the heat of formation of the metal carbides decreases. Since Ni₂C is thermally unstable (i.e., it decomposes into its elements above 575 K [66]), the Ni₁₂C Auger line shape should have little or no correlation effects [65–71], and this is consistent with our findings [35]. Therefore we approximate the three components to the 250 K Auger line shape by simple folds of the appropriate DOS. The kv-vvv contributions to the components are approximated also by simple folds, however consistent with the 100 K spectrum, the kv-vvv contributions were shifted to 14 eV higher binding energy to account for the hole–hole repulsion of the 3-hole final state. The relative intensity of the
kv-vvv to kvv components was varied, but best agreement with experiment was found at 25%, consistent with that found for the 100 K spectrum.

The optimal fit of the 3 components, VV, Vσ, and σσ, is shown in fig. 4a, the relative intensities and description of each component is given in table 1 for π-bonded vinyl (CHCH₂(a)). The σσ component was shifted 2 eV toward the Fermi level to provide better agreement with experiment. A similar shift was required to give optimal agreement for the carbide line shapes [35]. This shift simply suggests that the carbide DOS utilized to approximate the σσ component must be shifted by 1 eV to better approximate the C–M DOS in chemisorbed systems. Reasonably good agreement is found in fig. 4a; however, not as good as found for the 100 K spectrum shown in fig. 2b. This may result from the deconvolution process, which is the most uncertain near the bottom of the spectrum, where most of the disagreement lies. More likely, it could result from a change in the C(1s) binding energies which is not accounted for in the theory. K edge NEXAFS data [22] suggest that the C(1s) binding energy for the carbon atom bonded to the surface is up to 2.5 eV less than the outer carbon atom. This could introduce the 2 eV shift required for the uu Auger component discussed above. It could also broaden the VV and Vσ components which if included in the theory might improve the agreement with experiment. Alternatively, it may result from an even more basic breakdown in our approximation as described below.

Comparison of the VV : Vσ : σσ relative intensities for CHCH₂(a) to that found for VV : Vπ* : π*π* for C₃H₄(a) reveals a significantly greater substrate–substrate contribution in the 250 K spectrum for CHCH₂(a). This is to be expected for the intimately π-bonded adsorbate at 250 K, because even in the ground state some C–M charge transfer occurs. Quantitatively, the relative VV : Vσ : σσ component intensities (28 : 49 : 23) for CHCH₂(a) suggest an electron configuration per carbon atom in the core hole state of around (C=C,H)²(C–M)².5. The notation here indicates that each C atom has 3 electrons shared in C=C and C–H bond orbitals and 2.5 electrons in the C–M bond orbitals. Since the agreement between the theoretical and experimental line shapes in fig. 4a is not very good, a considerable uncertainty exists in the relative component intensities, and thus in the electronic configuration above. Nevertheless, this electronic configuration is plausible if one makes the reasonable assumption that 1 electron is shared in each of the C–C, 2 C–H, and C–M bonds in the ground state, and that 1.5 additional electrons transfer from the substrate into the C–M bond orbitals in the presence of a C core hole. The magnitude of this charge transfer is slightly greater than the 1.3 electrons found for π-bonded ethylene above, and is consistent with the more intimate σ chemisorption bond for CHCH₂(a). However, we cannot be sure that this difference is significant because of uncertainties in the component intensities here.

The Auger spectrum at 300 K (figs. 1 and 4b) is different again from that found at 250 K. HREELS [51] and SIMS [13] data indicate decomposition of vinyl to ethynyl (C₂H₂(a)) and/or methylidyne (CH₂(a)), and perhaps also to rehybridized η₂-C₃ acetylene (C₂H₂(a)) species, in this temperature region [8,14]. Further heating to 600 K gives yet a different spectrum, which we show elsewhere [35] is due to carbide surface carbon. In addition C₂, C₃, etc. species also are present on the surface at 600 K [35]. Both the ethynyl and rehybridized acetylene species presumably retain some C=C double-bond character, but with an increased amount of C–M bonding compared with the vinyl species at 250 K. The 600 K spectrum is dominated by the C–M bonding contributions. Therefore the 300 K spectrum should be approximated by a sum of the 250 and 600 K spectra. We test this in fig. 4b which shows an excellent fit. Table 1 shows that the relative intensities are 35 and 65% for the 600 and 250 K spectra, respectively, but because of the number of different species involved at 300 K, it is difficult to arrive at any firm conclusions.

5. The graphite line shape

Fig. 5 compares the experimental and theoretical C Auger line shapes for graphite chemisorbed on the surface of Ni(111) [24]. The chemisorbed
Fig. 5. Comparison of the experimental and theoretical Auger line shapes for a graphitic adlayer on Ni(111). The component (VV, Vπ*, and π*π*) line shapes were obtained as described in the text and summarized in table 1. The relative intensities were obtained by a least-squares fit to the experimental line shape.

The relative component intensities, VV : Vπ* : π*π* = 85 : 11 : 4 can again be used to calculate the charge transfer from the Ni substrate in the presence of a carbon core hole. We can use the expression derived above for ethylene, namely 13 : 7y : y^2. Unfortunately, the relative component intensities above do not provide a consistent value for the charge transfer, y, as they did for ethylene. The ratio Vπ* : VV gives y = 0.24, while the π*π* : VV ratio gives y = 0.78. However, the relative intensity of the π*π* component is very uncertain because around 10 eV, where the π*π* component dominates, the theoretical and experimental line shapes are in poor agreement. Therefore, we accept the 0.24 electron transfer. This is considerably less than for chemisorbed ethylene. We attribute this decreased charge transfer in graphite to the greater substrate–adsorbate bond distance known for a fully developed two-dimensional monolayer of graphite on Ni [35]. The decreased substrate screening also accounts for the lack of a significant change in the VV component line shape from the bulk line shape. We have shown previously that the bulk line shape contains significant correlation effects, with ΔU of the order of 2 eV in the σσ components [30]. Apparently on the surface of Ni, no significant change in ΔU occurs.

6. Discussion and summary

Comparison of the results summarized in table 1 and figs. 2–5 reveals some interesting points. First, note that the optimum kv-vvv shakeoff intensity, 20% of the total intensity, is the same for the gas-phase ethylene and the chemisorbed species, and is equal to that for a free carbon atom [34]. This shakeoff intensity is a direct measure of the probability for the shakeoff “hole” to remain near the atom with the initial core hole and “witness” the Auger decay. Escape before the Auger decay results in a normal kvv contribution. For the adsorbates, we would have anticipated that the shakeoff “hole” might escape through the adsorbate–substrate bond (i.e., electron transfer from the substrate), but apparently this is not occurring. In bulk graphite, no kv-vvv satellite appears at all,
because the shakeoff hole does not remain on the atom with the initial core hole, but propagates throughout the graphite [30]. This is apparently still true in the graphitic adlayer.

The second point concerns the correlation effects as indicated by the $\Delta U$ parameter. In the $\pi$-bonded ethylene case, $\Delta U$ is zero for the $k\nu\nu$ contribution to the $V\nu$ and $V\pi^*$ components, but not for the $\pi^*\pi^*$ component, since in the experimental $L_{23}VV$ Auger line shape utilized for $\pi^*\pi^*$, $\Delta U$ is known to be around 2.5 eV [62]. This may appear inconsistent at first. However, $\Delta U$ is very dependent on the spatial arrangement of the two final state holes. The Ni $4sp$ valence electrons cannot effectively screen two holes in the relatively local $d$ orbitals on a single Ni atom ($U_{11}$), holes on two different Ni atoms ($U_{12}$) are easily screened. Hence the effective $\Delta U (= U_{11} - U_{12})$ in bulk Ni, or in this case for the $\pi^*\pi^*$ component, is significant. In chemisorbed ethylene, the two holes on a single C$_{sp^2}$ cluster orbital are apparently easily screened by the $\pi$ and $\pi^*$ electrons in the adsorbate, hence $\Delta U$ is negligible in the $VV$ component. Likewise, $\Delta U$ is expected to be small in the $V\pi^*$ component. For the chemisorbed species, $\Delta U$ is found to be negligible for all three components. Here $\Delta U$ is zero for the $\sigma\sigma$ component, because two holes in the more delocalized C–M $\sigma$ bonds are easily screened by the Ni metallic electrons [65]. $\Delta U$ is zero for the $VV$ and $V\sigma$ components just as for chemisorbed ethylene.

The correlation effects in the graphitic overlayer are also very interesting. The $VV$ component is the same as for bulk graphite, where large correlation effects are present. We suggested previously [30] that this probably arises because of a decrease of $U_{12}$ by screening, leaving $\Delta U$ relatively large. The small charge transfer from the Ni substrate does not change this in the overlayer. However, the poor agreement around 10 eV between the theoretical and experimental line shapes for the graphitic overlayer suggests that our approximation of the $\pi^*\pi^*$ component by the $L_{23}VV$ Ni lineshape is not a very good one, although it was fine for chemisorbed ethylene. Fig. 5 suggests that better agreement would have been obtained if we had utilized a simple fold of the Ni one-electron DOS, which would have peaked much closer to the Fermi level. This suggest a most interesting "reverse" (graphite to Ni) screening process; i.e., when both holes end up on the Ni substrate, the graphitic overlayer apparently causes $\Delta U$ to be less than for pure Ni. Although the diffuse Ni $s$ valence electrons cannot effectively screen two localized $d$ holes, the electrons in the graphitic $\pi$ and $\pi^*$ orbitals, which are intimately bonded with the surface Ni $d$ orbitals, apparently can effectively screen these two $d$ holes.

We have also indicated previously that the $\delta$ for the $k\nu\nu$ contribution reflects the repulsion of two holes delocalized about the entire molecule, but that the $\delta$ for the $k\nu-v\nu$ contribution reflects the repulsion of holes localized on a $CH_n$-like cluster orbital. This is consistent with the data in table 1. Upon chemisorption, the $\delta$ for the $k\nu\nu$ contribution for ethylene reduces from 9 eV to 0. The electron transferred from the metal obviously screens very effectively the two holes delocalized over the molecule. However, the $\delta$ for the $k\nu-v\nu$ contribution decreases from 18 eV to just 14 eV. As one might expect, the transferred electron cannot effectively screen the two holes localized on a single $CH_n$-like cluster orbital.

Finally, we should point out a significant difference in character between the gas phase and chemisorbed hydrocarbon Auger line shapes. In the gas phase, the C–C and C–H bonds are all similar in nature, so that delocalized molecular orbitals are formed, which are characterized by the global symmetry of the molecule. However, the Auger line shape reflects only the self-fold of the DOS, which obscures all but the gross features of these DOS. Thus, the comparable alkanes and alkenes have very similar DOS self-folds (e.g., those for ethane versus ethylene, cyclohexane versus benzene, and graphite versus diamond are surprisingly similar). The experimental line shapes do reflect significant differences however. We have shown that this arises because of the different correlation effects in the $\sigma\sigma$ versus the $\pi\pi$ contributions (i.e., $\Delta U$ is around 2 eV in the $\sigma\sigma$ contributions and 0 in the $\pi\pi$ contributions). On the surface, all hole–hole correlation effects are effectively removed because of the charge transfer from the metal, so that the experimental line shapes now reflect primarily the DOS self-fold. But, now
the bonds are not all similar, since the C–H and C–C bonds are very different in character from the C–M (metal substrate) bonds. In this case some molecular orbitals (MOs) are localized primarily on the molecular adsorbate, and some on the C–M adsorbate–substrate bond. Thus the experimental line shape clearly has regions at higher two-hole binding energy which reflect the intramolecular MOs and those at lower binding energy which reflect the C–M MOs. Furthermore, we have shown that the intramolecular component can be approximated by the DOS self-fold for the gas-phase molecules at least for the case of the weakly chemisorbed, π-bonded ethylene. In the case of adsorbed vinyl, the experimental line shape does not agree with the theoretical lineshape as well as we might have hoped. This may result from a breakdown in this approximation, although other problems were also mentioned in section 4 above.

In summary, we have consistently interpreted four different CKVV Auger line shapes, namely those for the adsorbed hydrocarbon species formed from ethylene on Ni(100) at 100, 250, and 300 K, and for a graphite adlayer on Ni(111). We have shown that the intra-adsorbate (VV) components reflect the DOS of the gas-phase molecule, or the bulk solid in the case of graphite, so that the chemisorption bond can be treated independently from the intra-adsorbate contributions. For ethylene, intra-adsorbate correlation effects are reduced to zero because of charge transfer from the substrate, so that the various contributions to the line shape are significantly different for the gas phase. This in fact makes the Auger line shape for adsorbates more directly reflect the molecular DOS than that for gas-phase molecules. In graphite, no significant reduction of the correlation effects is seen for the chemisorbed layer on the surface so that the VV component of the chemisorbed line shape and the bulk line shape are the same.

Significant adsorbate–substrate Auger components (VV* and π*π* or Vσ and σσ) are evident. These directly reflect the σ or π chemisorption bond character. The extent of charge transfer from the metal to the adsorbate, in the presence of a core hole, is seen directly from the intensities of these components, as well as from the changes in the VV component line shapes.

We suggest that Auger spectroscopy can be used to find valuable information about chemisorbed systems, and that it can effectively complement other spectroscopies in the study of adsorbed hydrocarbons important to catalytic reactions and Fischer–Tropsch synthesis.

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[49] This process is also referred to as autoionization or resonant photoemission: see for example E. Bertel, R. Stockbauer and T.E. Madey, Surf. Sci. 141 (1984) 355.