Spectroscopic evidence for carbon–carbon bonding in “carbidic” layers on metals

F.L. Hutson *
Chemistry Department, George Washington University, Washington, DC 20052, USA

D.E. Ramaker
Chemistry Division, Naval Research Laboratory, Washington, DC 20375, USA

and

B.E. Koel **
Department of Chemistry and Biochemistry, and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder, CO 80309, USA

Received 31 May 1990; accepted for publication 4 December 1990

We examine previously reported ultraviolet photoelectron, C K electron energy loss, and C KVV Auger spectroscopic data from “carbidic” layers formed at temperatures between 500 and 650 K on Ni(100) and Ni(111). The “carbidic” layers studied were made from either CO or C2H4 exposure to the metal surface. These data indicate that significant amounts of carbon–carbon bonding exists on the surface in addition to the carbon-metal bonding with the substrate, revealing the presence of chemisorbed species, such as C2, and maybe even C3, etc. Quantitative interpretations of the Auger data indicate that 20 to 30% of the total electron density has carbon–carbon bonding character. Observed changes in the spectra obtained from different surfaces or at different coverages are accounted for by variations in the fraction of carbon–carbon bonding character.

1. Introduction

The interaction of ethylene and acetylene with single-crystal metal surfaces has been studied for many years. From techniques such as high-resolution electron energy loss spectroscopy (HREELS) [1–9], temperature programmed desorption (TPD) [6–14], and ultraviolet and X-ray photoelectron spectroscopy (UPS and XPS) [13–16], it has been possible in several cases to identify the mode of adsorption of these C2 hydrocarbons and determine the paths for dehydrogenation at higher temperatures. Recently, emphasis has been placed on the carbonaceous layers which result at still higher temperatures, since these layers are thought to be present under the conditions existing in various hydrocarbon conversion reactions and also in Fischer–Tropsch synthesis. The latter process converts carbon monoxide and hydrogen into a mixture of hydrocarbons [6–26]. The recent interest in the production of synthetic diamond has also motivated such studies [27]. In addition to those basic techniques mentioned above, recent work has utilized electron energy loss spectroscopy (EELS) [15,17,18], surface extended en-
nergy loss fine structure (SEELFS) [19,28], secondary ion mass spectroscopy (SIMS) [6,10,11,20], X-ray absorption near edge structure (XANES) [21], and Auger electron spectroscopy (AES) [17,18,22–25,29].

At least two, and possibly three, distinct carbonaceous states have been observed on transition metal surfaces [17,18,22–25]. A carbidic carbon which is very active in the methanation and Fischer–Tropsch synthesis exists at temperatures ranging from 450–600 K. A graphitic carbon, which poisons the catalytic metal surface above 650 K, has also definitely been identified [22–25]. Evidence for an intermediate state on some metals between 570 and 670 K has been given, but little is known about it, and no structure has been proposed [17,18]. These states will be referred to and identified in the figures of this paper as the C, G, and I phases, respectively.

HREELS has been very powerful for elucidating the structure of hydrocarbons on surfaces [1–9]. However, it has not been used very often for studying carbonaceous layers at higher temperature. This may be due to the weaker intensities and broader loss peaks associated with the C–M and C–C stretching and bending vibrations compared with the C–H stretching modes. It may also arise from the expectation that all C–C and C–H bonds are broken at higher temperatures, thus motivating fewer EELS investigations. SIMS has been very helpful in indicating the degree of mobility of the carbon atoms at different temperatures [19] and the presence or absence of hydrogen atoms. However, the nature of SIMS is such that one is never certain if the various fragments (e.g., \( C_x \)) analyzed actually existed on the surface or were formed in the “plasma” above the surface [6,10,11,20]. A recent SEELFS study [19] has been helpful in determining the structure of isolated C on Ni(100), but again it is not useful for identifying the different states.

AES, EELS, and UPS have been the most helpful in identifying the three different phases or states of the carbonaceous overlayer. In particular, AES has been most helpful in identifying the “carbidic” and “graphitic” forms of carbon [22–25], and indicating a distinct intermediate (with unknown form) around 570–670 K on Ni and Cu [17,18]. EELS has also suggested the presence of an intermediate form in this temperature range [17,18].

In this work we carefully examine and interpret previously reported UPS [14,15], EELS [17], and AES [23,24,29] data from carbonaceous layers on Ni(100), and Ni(111) heated to temperatures above 500 K. The layers were made from either CO or \( C_2H_4 \) exposure to the metal surface. Little differences are noted in the data for CO versus \( C_2H_4 \), or expected in this temperature region, provided similar carbon coverages are obtained. All spectra indicate significant amounts of C–C bonds (i.e., chemisorbed \( C_x \) species with \( x = 2, 3 \), etc.) exist below 670 K. In fact, only 40–65% of the “carbidic” Auger spectra, which are semi-quantitatively interpreted, actually arise exclusively from carbidic bonding (i.e., carbon–metal bonding). The intermediate carbonaceous state, in the temperature range 570–670 K, is shown to arise from a relative decrease in the C–C bonding character. This decrease is due to partial C–C bond cleavage, which apparently occurs on Ni(100) and Cu(100) at temperatures below that for the formation of graphite. The differences seen in the published Auger spectra following CO decomposition on various metals at 650 K are attributed to differing amounts of \( C_x \) present on the surface, as this obviously varies with carbon coverage, temperature, and surface treatment.

We believe this work to be the first to identify direct electron spectroscopic evidence for the existence of \( C_x \) in carbonaceous layers on metals. It is, however, consistent with the work of Lauderback and DeGass [10], who utilized isotopic \( ^{13}C_2H_4 \) and \( ^{12}C_2H_4 \) mixtures and temperature programmed negative ion SIMS. This data suggests that close C–C distances for the two carbon atoms of the parent ethylene molecule are preserved up to 600 K on Ru(001), followed by an enhanced carbon mobility above 600 K. In contrast, White and co-workers [6,11] utilizing several techniques concluded that coadsorbed K and \( C_2H_4 \) on Pt(111), and coadsorbed CO and \( C_2H_4 \) on Ru(001) proceeded sequentially from CCH or \( C_xH \) to \( C_x \) to graphite, without complete C–C bond cleavage. This different behavior on Pt and Ru will be discussed in section 6.
The ability to distinguish C–C versus C–M bonding character in adsorbates from electron spectra arises because these two bonds are primarily responsible for features at very different binding energies, as we will see below. This arises because electrons in the C–C bond have much larger binding energies than those in the C–M bond. In gas-phase hydrocarbons, electrons in the C–C and C–H bonds have such similar energies that delocalized molecular orbitals are formed, which are characterized by the global symmetry of the molecule. However, at the metal surface, the electrons localized near the C–C and C–M bonds have such different binding energies that some MOs are localized primarily on the C, adsorbate and others on the C–M adsorbate–substrate bonds. Thus, electron spectroscopic line shapes should have spectral regions which reflect the C–C bonds (and C–H bonds if present) and regions which reflect the C–M bonds. This makes it possible to determine the extent of each.

We acknowledge that it is difficult to distinguish C–H and C–C bonding from many types of electron spectroscopic data. For example, the C core levels have similar binding energies in these two cases [16,30], and so do the valence levels. HREELS, SIMS and TPD data indicate the near lack of hydrogenated carbon species present on the surface after flashing to high temperatures (500–800 K) [6,10–12,20]. However, since all of the electron spectroscopic data are obtained at room temperature or lower after flashing to the indicated higher temperatures [14,15,17,23,24], the highly active carbon could rehydrogenate from the H, in the background before the data taking is completed. Therefore, unless HREELS or SIMS data were obtained simultaneously with the electron spectroscopic data, one cannot rule out some C–H bonding at the surface in the case of the published spectra. However, rehydrogenation is not of major importance under most experimental ultrahigh vacuum conditions. Therefore the C–C bonding character observed arises primarily from C–C bonds, but we cannot rule out the existence of some C–H bonds.

Sections 2, 3, and 4 summarize our interpretation of previously reported UPS, EELS, and AES data, respectively. Section 5 gives a theoretical background on the interpretation of Auger spectra. A brief summary and conclusions are given in section 6.

2. Interpretation of UPS data

Fig. 1 compares estimates of the C valence band density of states (DOS) for a carbonaceous layer on different metals. Rosei et al [15] obtained UPS ($h\nu = 35$ eV) data for carbidic overlayers ($\theta_C = 0.3$ ML) obtained by heating a Ni(111) surface at about 500 K in CO. Koel et al. [14] obtained UPS ($h\nu = 40.8$ eV) data for carbidic overlayers ($\theta_C = 0.45$ ML) obtained by saturation exposure to C$_2$H$_4$ of a Ni(100) surface at 100 K
and a subsequent warm-up to 580 K. The difference between the UPS spectra for the clean and carburized Ni surface, as given in fig. 1, represent an estimate of the DOS on the C atoms. Since the data are expected to vary with carbon coverage, care is taken to indicate the C coverage throughout, but these estimates are often crude.

The UPS difference spectra are compared with LCAO-MO calculated DOS in fig. 1. Feibelman's [31] results were obtained for a \((1 \times 1)\) overlayer of C atoms on an 11-layer Ru(0001) film, with only one third of the threefold sites filled with carbon atoms. In this theoretical model, the carbon atoms are relatively isolated since the nearest C–C distance is greater than 5.0 au compared with a C–C distance of 2.68 au in graphite [31]. The results of Bullett and Dawson [32] were obtained for 0.5 ML of carbon atoms in a \((2 \times 2)\) mesh on a 4-layer slab of Ni atoms modelling a Ni(100) surface. Here the carbon atoms occupy fourfold hollow sites which are enlarged by rotation and translation of the four Ni atoms around each adsorption site. The carbon atoms themselves define a \(c(2 \times 2)\) surface mesh, but the true mesh is \(p(2 \times 2)\), due to the Ni displacements (this is called a \((2 \times 2)\) C \(p4g\) carbidic phase on Ni) [32]. We assume in both cases that the theoretical DOS is indeed representative of only C–M bonding.

The calculated results indicate that the narrow feature near the Fermi level in both the empirical and calculated “DOS” is due predominantly to a nonbonding \(p_z\) orbital. The broad feature between 2 and 8 eV arises primarily from the bonding \(p_{xy}\) orbitals, and the feature from 10 to 15 eV arises mainly from the \(s\) orbitals [31]. Feibelman suggests that the DOS for his results can be qualitatively understood as arising from C atoms tetrahedrally \(sp^3\) bonded with its three neighboring substrate atoms, leaving a nonbonding, dangling \(p_z\) band partially filled. He further attributes the activity of the carbidic carbon to the partially filled \(p_z\) band, and the inactivity of the graphitic layer which forms at higher coverages to the \(\pi\) bonding between the \(p_z\) orbitals [31].

Qualitative agreement between the four curves in fig. 1 is found, but significant differences are noted. First, all four curves exhibit the \(p_z\) feature near the Fermi level, but they are significantly different in size. This is to be expected for the two experimental curves, considering that the metal DOS is very large near the Fermi level, so that the difference spectra are very sensitive to the subtraction procedure. Furthermore, the UPS difference curves actually go negative right at the Fermi level because of shifts in the metal 3d DOS [14,15]. The slight shoulder around 1 eV in the Koel data may reflect the \(p_z\) feature, with the dominant peak at 1.5 eV actually arising from the \(p_{xy}\) contribution. This interpretation would make the intensity of \(p_z\) features comparable in the two experimental curves.

The agreement between the Rosei data and Feibelman’s results for the \(p_{xy}\) feature is remarkable, both containing roughly the same structure. The Koel data reveals two large \(p_{xy}\) peaks roughly similar to the Feibelman data, but shifted by about 2 eV toward the Fermi level. This is particularly true if we identify the feature around 1.5 eV in the Koel data with the \(p_{xy}\) contribution as indicated above. In contrast, the \(p_{xy}\) peaks in Bullet’s results are shifted about 1 eV away from the Fermi level, compared with Feibelman’s results.

The reason for the shift of the \(p_{xy}\) feature in the Koel data relative to Rosei’s data and Feibelman’s results is not clear. Calculations by Joyner et al. [26] indicate that the \(p_{xy}\) feature moves slightly toward the Fermi level as the carbon–metal bond energy decreases, and we expect the Ru–C bond to be stronger than the Ni–C bond. However, Rosei’s data for the Ni(111) surface, and Feibelman’s calculations for a Ru(0001) surface have the \(p_{xy}\) features aligned very nicely. Perhaps the nature of the bonding of C on the different Ni surfaces (110) versus (111)) are responsible for the differences in the Rosei and Koel data. In any event, the Auger data for C/Ni(100), to be discussed below, indicate that indeed the \(p_{xy}\) feature has a binding energy intermediate between Koel’s data and the other three results in fig. 1.

The “s” feature is sharp at about 11 eV in Feibelman’s DOS, at 11–15 eV in Bullet and Dawson’s DOS, very broad and centered at 15 eV in the Rosei data, and centered about 12 eV in the Koel data. Utilizing a more sophisticated full-potential linearized augmented-plane-wave (FLA-
PW) method, McConville et al. [33] place the C 2s feature at 11–13 eV for the Ni(100)-(2 × 2) C P 4g carbidic phase. The slow tailing off of the empirical “s” feature in the Rosei data may be an artifact of the subtraction procedure. Perhaps the maximum at 13 eV in the Rosei data more correctly determines the position of the s DOS, which gives better agreement with the other two curves. Thus the C 2s feature apparently falls around 12–13 eV for C/Ni.

Most significant in fig. 1 is the peak at 8.5 eV in the Koel data. We believe this arises from C–C bonding. For ethylene chemisorbed on Ni(100), the σ C–C orbital has been previously [14] identified at 8.4 eV, and a peak still remains at this binding energy at 580 K when all hydrogen has desorbed. This feature is completely absent in the theoretical results in fig. 1, as expected in the absence of C–C bonding. It is also essentially absent in the Rosei data; this could be due to the lower carbidic carbon coverage (θ C < 0.3 ML as estimated by Rosei), the different Ni surfaces ((111) versus (100)) or perhaps because of different surface conditions or treatment.

3. Interpretation of K edge EELS data

We report elsewhere [34] on an extensive investigation of the C K edge EELS data. That investigation included comparison with DOS calculations, and calculations which explicitly included excitonic effects. It also made comparison with gas-phase XANES results. This work is much too extensive to be included here, but the results clearly indicate the formation of C 2 on the surface [34]. For completeness, we briefly summarize the results of that investigation.

Fig. 2 compares the d N(E)/d E 2 K edge EELS curves for four different carbonaceous layers on metals [15,17]. Curve a is for a graphitic carbon layer on Ni(110) (since a graphitic layer does not easily form on Ni(100) in UHV, we show the results for Ni(110) here), curve b for a so-called "carbidic" layer on Ni(100), curve c for an "intermediate" layer on Ni(100) at 620 K, and curve d for a 0.3 ML "carbidic" layer on Ni(111). Curves a–c were reported by Caputi et al. [17], who prepared the carbon layers by exposure of the metal surfaces to CO at a pressure of 1 × 10⁻⁵ Torr for 30 min at 520 K, with subsequent heating to form the various carbon layers. Although Caputi et al. do not estimate the C coverage, the coverage is believed to be similar to that seen by Rosei et al. [15] (curve d with θ C = 0.3 ML), since similar exposures were performed by Rosei et al. (i.e., CO exposures around 10⁻² Torr × s at 520 K). The K binding energy is about 283–284 eV for graphite [35], and 282.9 eV for a carbidic layer on Ni(100) [14].

The peaks at 285 and 292 eV are known to arise from 1s-π and 1s-σ excitations respectively in graphite [15]. XANES data for a surprisingly wide range of organic molecules also reveal peaks at 285 and 292 eV, which are similarly attributed to the C–C π and σ antibonding orbitals [35]. How-
ever, XANES data for bulk carbides, such as TiC, do not show peaks at these energies, since the metal–carbon antibonding bands appear at different energies [36] (above we indicated that the bonding orbital energies for C–C and C–M bonds also were different). Furthermore, for organic molecules on metal surfaces, the intramolecular π and σ contributions dominate the XANES spectra, while the intermolecular C–M contributions are very weak, if visible at all [35].

The C K EELS data for the "carbidic" phases (figs. 2b and 2d), which reveal large peaks at 285 and 292 eV, thus also indicate the presence of C–C bonding on the surface, most likely in the form C$_2$. The EELS data for the "intermediate" phase at 620 K reveal a dramatic reversal in the intensities of the π and σ peaks compared with the "carbidic" phases, figs. 2b and 2d. We have shown elsewhere [34] that this arises because some of the C$_2$ species tip up normal to the surface at this temperature. However, most of the remaining C$_2$ species dissociate to form a true "carbidic" carbon, which has only C–M bonds present and contributes very little intensity to the XANES spectrum.

4. Interpretation of Auger data – empirical

4.1. The "bulk" carbide line shapes

The transition metal carbides, MC$_x$, have been studied often with AES. Shulga and Gutsev have presented $dN(E)/dE$ Auger spectra for a series of carbides in the first three rows of the transition metal series [37]. These spectra show a small high energy feature around 275 eV, the principal peak around 272, a doublet around 263, and a small feature at 253 eV. Pehrsson and Ramaker [38] reported a detailed interpretation of the TiC and NbC line shapes, and Gruzalski et al. [39] interpreted the TaC line shape. They identify the 253, 263, 272, and 275 eV features as arising predominantly from the ss, sp, pp, and pp components, respectively, of the DOS self-fold. Both the principal and high energy features arise from the pp component (this is sometimes separated into the σσ and σπ components), the doublet at 263 arises because the sp component splits into $^1P$ and $^3P$ multiplets due to the spin interaction. The pp component is apparently unaffected by localization effects (i.e., the line shape is not significantly distorted from the one-electron self-fold); but, the sp and ss components do exhibit some localization effects [38,39]. Pehrsson and Ramaker [38] have also correlated these effects with the heat of formation ($\Delta H_f$) of the metal carbide; the highly stable carbides are more ionic, the unstable carbides more metallic. Thus the ratio of the two pp peaks (i.e., the ratio of the high energy shoulder over the principal peak; $I(275)/I(272)$) decreases but the two features narrow and become more distinct with increasing $\Delta H_f$. The $^1P–^3P$ separation of the doublet 2p peak at 263 eV increases with $\Delta H_f$. The shift to higher binding energy (i.e., the localization effects) of the ss and sp contributions increase with $\Delta H_f$. Finally the shift of the C 1s binding energy relative to graphite increases with $\Delta H_f$ [38].

Ni$_3$C is a thermally unstable carbide [26,40]. It is generally produced by the carburization of Ni films in CO around 550–650 K resulting in a "thin" film of Ni$_3$C rather than a true bulk carbide. Ni$_3$C has been studied previously by X-ray diffraction, LEED, TEM, AES, and XPS [40–42].

The AES line shape of Ni$_3$C was first presented by Coad and Riviere [41]; somewhat higher resolution line shapes have been presented by Chang [43] and Salmeron et al. [44]. C KVV Auger line shapes, $N(E)$, for Ni$_3$C are presented in fig. 3 (curves b and c). They were obtained from the data of Chang [43], and Salmeron et al. [44], respectively. The two spectra have been placed on a two-hole binding energy scale by aligning the principal peak with that in the Koel data [24], curve f. No attempt was made to deconvolute out experimental broadening in these two curves (b and c), so that these two spectra are believed to be at much lower resolution than all of the others in fig. 3. The two spectra are similar except for an apparent greater broadening of the Salmeron et al. spectrum. This may be due to the lower resolution of their spectrometer.

The two "bulk" spectra in fig. 3 are consistent with that expected for a relatively unstable carbide
as indicated above. The shoulder at 15 eV is large but not resolved. The $^3P - ^3P$ separation is not visible, and the C 1s binding energy is within 1 eV of that for graphite (i.e., about 282.9 eV for carbides [14] versus 283–284 for graphite [35]). To be totally consistent within the above trends, no localization effects should be visible in any of the ss, sp or pp features. Thus a self-fold of the one-electron DOS with the appropriate atomic matrix elements and screening factors should closely reproduce the Auger spectra for Ni$_3$C.

4.2. The surface carbidic line shapes

Fig. 3 also compares several Auger line shapes that have been referred to in the literature as "carbidic". The top line shape (curve f) is that reported by Koel [24] upon heating ethylene chemisorbed on Ni(100) to a temperature of 600 K. The second line shape (curve e) is that observed by Houston et al. [22,23] upon exposure of a Ni(100) surface to 24 Torr CO for 1000 s at 600 K. The third line shape (curve d) also reported by Houston et al. [23] is that from a Ni(111) surface after electron beam cracking of CO. Catalytic or electron beam cracking of CO can produce "carbidic" carbon on either Ni surface [22]. The coverages for the latter two have been roughly estimated to be about 0.1–0.2 ML, while that for the Koel data is $\theta_c = 0.45$ ML. The bottom curve, curve a, is from the data of Caputi et al. [17]. All of the line shapes were obtained from the raw Auger data after integration, subtraction of a linear background, and deconvolution of inelastic loss contributions. For the Caputi data, the loss contributions were subtracted by the Shirley method [45] so that instrumental broadening was not subtracted in this case, like it was for the Koel and Houston data. The Caputi and Koel data were placed on a two-hole binding energy scale referenced to $E_v$ (vacuum level) by using a C 1s binding energy of 282.9 eV and a work function of 5.4 eV [14]. The Houston data were energy aligned with the Koel data.

Several observations can be made from fig.3. The carbide and surface carbidic line shapes all have the familiar ss, sp and pp features, but otherwise they are quite different. The so-called ss and sp features in the carbidic adlayer line shapes are much sharper and larger than in the bulk carbide line shapes. The high energy shoulder is also much more distinct in the carbidic adlayer line shapes.

Within the surface carbidic line shapes, surprising agreement exists between the data of Koel [24] and Houston et al. [23] for the Ni(100) surface. Six similar features are seen at the same relative energies in both spectra, only the relative intensities are somewhat different. This is true in spite of the fact that the Koel data were generated by the decomposition of C$_2$H$_4$, and the Houston data by the decomposition of CO. On the other hand, the Houston data for Ni(100) and Ni(111), both generated by the CO carburization of Ni, are very different. Indeed the data for the Ni(111) surface appear closer to the bulk carbide data.
Houston et al. [23] have suggested that the differences between the carbidic line shapes on Ni(100) and (111) are due to the different sp" hybridizations on a two- or three-fold bonding site. Hybridization effects are clearly evident in the line shapes exhibited by gas phase methane, ethylene, and acetylene [46]. However, we have shown previously that for larger molecules, such as benzene and cyclohexane, the DOS self-folds are surprisingly similar; only after the hole–hole localization effects are included do the line shapes significantly vary [46]. Thus for the carbidic adlayers at the metal surface, where the hole–hole repulsions are drastically reduced due to metallic screening, hybridization effects are not expected to play a significant role.

In this work we will show, via a quantitative interpretation (presented in section 5), that differing amounts of C–C and C–M bonding character can account for the observed differences between the surface carbidic line shapes as well as between the surface carbidic and bulk carbide line shapes. That indeed both C–C and C–M bonding character actually exists in the Auger line shapes is indicated just by examining the differences between the surface carbidic line shapes reported by Caputi et al. [17] at 500 and 620 K (i.e., the C and I curves in fig. 4). One might suspect that the line shape for I is simply some linear combination of the line shapes for C and that for graphite (i.e., I = aC + bG); the latter formed predominantly at still higher temperatures. However, after attempting a least-squares fit of aC + bG – I, Caputi et al. [17] indicated that this was not the case. We have verified this conclusion by making our own least-squares fit (result not shown). The 4 peaks in the dN(E)/dE spectra for C and I fall at different energies so that such a least squares fit is unsuccessful. Caputi et al. concluded that a unique new species is present on the surface at 620 K. We believe that only differing relative amounts of C–C and C–M bonding are present at 500 and 620 K.

To be consistent with the UPS and core EELS data, and the discussion above, the AES spectra for C and I should reflect the presence of both C–C and C–M bonding, the I line shape reflecting the presence of relatively more C–M bonding than in the C line shape. If we assume this is true, then an appropriate difference of the two spectra should reflect pure C–M bonding. We show various difference spectra (I – xC) in fig. 4, where “x” is a weighting factor between the two curves when the peak-to-peak height is normalized equally. The difference curves and the full spectrum have similar structural features, but the difference curves are shifted to lower binding energy by about 2 eV. Fig. 5 compares N(E) data for the “carbidic” 500 K spectrum and for the difference curves. The I – xC difference curves were generated by taking the differences between the N(E) curves for the C and I phases (i.e., I – xC, when C and I are normalized to equal areas). The “x” factors in figs. 4 and 5 do not necessarily correspond; however, curves similar to those in fig. 5 could be obtained by simply integrating those in fig. 4.

Fig. 4. Comparison of Auger data for CO/Ni(100) at 520 K and 620 K as reported by Caputi et al. [17]. These represent the carbidic (C) and intermediate (I) phases, respectively. Also shown are difference curves, I – xC, with the weighting factor, x, indicated for equal peak-to-peak heights in I and C.
difference curves in fig. 5 have been normalized to equalize peak heights.

A comparison of the $1-xC$ curves with a self-fold of Feibelman’s theoretical DOS, which reflects only C–M bonding, is shown in fig. 5. The exact method for generating this self-fold will be described in section 5. Features in the DOS self-fold, although shifted by around 1–3 eV with those in the difference curves, have similar intensities, particularly for the case when $x=0.8$. The features in the difference curves seem to shift with “$x$”, so we are not particularly concerned with these remaining 1–3 eV energy shifts. Therefore we conclude that the difference curves apparently reflect more C–M bonding character. On the other hand, features in the full 520 K spectrum (top curve) are all shifted by around 7 eV from comparable features in the DOS self-fold, and do not have the same relative intensities. We believe the full 500 K spectrum, and indeed all of the spectra in fig. 3, contain additional contributions due to the C–C bonding character.

5. Interpretation of Auger spectra – theoretical

We have quantitatively interpreted the carbidic line shapes based on the ideas indicated above. The results are shown in figs. 6, 7, and 8, and the relative intensities of the components are given in table 1. The theoretical line shape is generated by a least-squares fit of three components to the experimental line shape. We use the word “theoretical” here to differentiate the calculated line shape from the experimental line shape. However, some may prefer that we use “computational” or “empirical” line shape, since we have utilized a least-squares fit and an approximate DOS for the three components. The three components consist of (1) the C–M DOS self-fold, (2) the cross-fold of the C–C and C–M DOS, and (3) the C–C DOS self-fold; that is

$$N(E) = A\rho_{C-M} \ast \rho_{C-M} + B\rho_{C-C} \ast \rho_{C-C} + C\rho_{C-C} \ast \rho_{C-C},$$  

(1)

where $\rho \ast \rho$ indicates

$$\rho \ast \rho(E) = (1 - P_{so}) \int \rho(E - \epsilon) \rho(\epsilon) \, d\epsilon$$

$$+ P_{so} \int \rho(14 + E - \epsilon) \rho(\epsilon) \, d\epsilon,$$  

(2)

The coefficients $A$, $B$, and $C$ are determined by a least-squares fit. As indicated in section 4.1 above, no correlation effects are expected in the relatively unstable Ni$_2$C, so that these self-folds, modulated by the appropriate atomic Auger matrix elements,

$$\rho \ast \rho = P_{kss} \rho_s \ast \rho_s + 2P_{ksp} \rho_s \ast \rho_p + P_{kpp} \rho_p \ast \rho_p,$$  

(3)

are sufficient. Here $P_{kss} : P_{ksp} : P_{kpp}$ was taken to be $0.8 : 0.5 : 1.0$ consistent with that used previously [47,48].

The second term on the right in eq. (2) above is to account for the initial state shake-Auger (i.e., the kv–vvv) contribution, which accompanies the normal kvv Auger contribution. Upon creation of
the initial core hole, there is some probability that
a valence electron will leave with the core electron
as a result of the dynamic screening process [49].
When the Auger decay occurs in the presence of
this valence hole, this leaves 3 holes localized on a
single carbon atom and results in a shift of the
satellite relative to the main contribution. This
kv−vvv contribution has been seen for several of
the gas-phase hydrocarbons [49], and for molecular
and fragmented ethylene chemisorbed on
Ni(100) at various temperatures [29].

For π-bonded ethylene chemisorbed on Ni at
100 K, the satellite shift relative to the main
feature was found to be about 14 eV [29]; in the
gas phase the shift was approximately 18 eV [41].
This difference reflects screening by the substrate
electrons. A shift of 14 eV also gave the best fits
for the surface carbidic line shapes.

The probability for shakeoff (Ps,) has been
estimated to be about 0.2 for a free C atom
[48,49]. We have found this value to be best also
for the hydrocarbons [47] and for π-bonded ethyl-
enes on Ni [29]. However, as the bond with the
metal substrate becomes more intimate, one might
expect that the probability for escape of this
shake-hole before Auger decay might increase.
This would decrease the relative intensity, Ps, of
the shake-off Auger contribution. In this work we
have tested the quality of the least-squares fits
with Ps, in eq. (2) set at 0.1, 0.15, and 0.2.
Inclusion of the kv−vvv contribution clearly im-
proves the agreement of theory with experiment,
indicating that some kv−vvv contributions are pre-
sent in the carbidic line shapes, but the difference
between the quality of the fits is not sufficiently
dramatic to determine the exact magnitude of Ps,.
However, it lies somewhere between 0.15 and 0.2.
We report the results for Ps, = 0.15 in figs. 6−8,
and for 0.1, 0.15, and 0.2 in table 1. The effect of
varying the shakeoff contribution is most dramatic
on the C−C* C−C component, since its intensity
is largest where the shakeoff contribution is also
large. Generally, the variation in the component
intensity with the change in percent shakeoff gives
an indication of the uncertainty in the results in
theoretical results of Feibelman

[31] given in fig. 1. To be more consistent with the
empirical results, as reported in fig. 1, we have
shifted the “s” peak from 11 to 13 eV. We find,
however, that the entire C−M self-fold, ρC−M* ρC−M,
must be shifted by 2 eV to lower binding
energy to provide an optimal fit to experiment, eq.
(1). This is consistent with the observed shift of
the large px,y features seen in the Koel UPS data
compared with the Feibelman result. Thus effec-
tively the px,y and p DOS of Feibelman are shifted
by 1 eV to lower binding energy and the “s” feature by 1 eV to higher binding energy.

The calculations of Feibelman [31] suggest a
ground state electronic configuration per C atom
of s2 px,75 px,91, or a charge transfer of 0.66 elec-
trons from the metal to the carbon. In contrast,
the calculations of Joyner et al. [26] suggest little
charge transfer. However, with the non-self-cons-
stistent cluster method and problems with the
Wigner–Seitz radii used by Joyner et al., charge
transfer is difficult to determine [26]. Finally, Bul-
let and Dawson [32] obtain a C charge configuration
of s1.7p8.0, or a charge transfer of 1.7 elec-
trons. This latter result seems unreasonably high,
so below, we will use the results of Feibelman to
normalize the s and p DOS. In the presence of a
core hole, we expect an additional electron trans-
fer to make the electronic configuration s2 px,75 px,91.
Since the final state rule [50] indicates that the
Auger line shape should reflect the electronic
charge configuration appropriate to the core hole
state, we have normalized the calculated s and p
DOS to reflect this electronic configuration.

The DOS representing the C−C bonding is
more difficult to obtain. We will use the fact, as
mentioned in section 1 above, that C−C bonds are
indistinguishable from C−H bonds in an Auger
line shape, and nearly so in UPS data. Evidence
for this comes from several sources. Reported
calculations on the CKV line shape in neopen-
tane [51], a molecule containing four methyl groups
surrounding a central carbon atom, indicate that
the DOS self-fold for the methyl carbons is virtu-
ally identical to that for the central carbon. Our
previous work on the CKVV Auger line shape for
the H-terminated diamond surface indicated simi-
lar results [52]. Demuth [30] has shown that C−H
bonds in CH species on metals produces a UPS
peak around 7–8 eV similar to the 8.4 eV C–C bonding feature seen by Koel (see fig. 1 and section 2). By comparison, CO/Ni(100) has its valence band or p DOS centered around 9 eV, and the s band around 29 eV [53]. We would expect the valence band for C$_2$/Ni to similarly have an energy around 9 eV, but would expect the s band to be more similar to that for CH$_4$.

Most orbital structure within a valence band DOS is essentially lost in the self-folding procedure, which is required to approximate the Auger line shape [47]. Therefore, the similarities in the DOS and the self-folding procedure allow us to approximate the C–C DOS self-fold by self-folding the C–H DOS for methane.

Methane has a simple UPS spectrum with s and p peaks at 18 and 9 eV, respectively [47]. The p peak reproduces the relatively narrow 8.4 eV band in fig. 1. The s feature is beyond the reported range of the UPS data in fig. 1, but we believe evidence does exist for a C–H s* s component in the Auger line shapes in figs. 6–8.

Figs. 6–8 show the results of the least-squares fit of eq. (2) to the experimental Auger data. These figures give direct evidence that the amount of C–C and C–M bonding in the carbonaceous layer is reflected in the Auger line shape. The C–M DOS self-fold gives peaks at 32, 22, 13 eV (these are the ss, sp and pp features) compared with 45, 36, and 27 eV for the C–C self-fold. This places the pp feature of the C–C self-fold at about the energy of the sp feature of the C–M self-fold. In fact, the principal peak in the experimental spectra appears to arise mostly from the pp feature of the C–C*C–M cross-fold. The larger so-called ss and sp features in the experimental surface carbide line shapes compared with the "bulk" carbidic apparently result from the ss and sp components of the C–M*C–C cross-fold and sp and pp components of the C–M self-fold. The
distinct high energy feature in the surface carbidic line shapes appears to result from the pp peak in the C–M self-fold. The fact that each of the three components in eq. (2) accounts primarily for a different feature in the experimental spectra, decreases the linear dependence in the least-squares fit, and allows for a more quantitative determination of the relative amounts of C–M and C–C bonding character in each case.

The agreement between the experimental spectra and the theoretical fits is generally very good, particularly in the important region between 15 and 38 eV. The larger differences beyond 40 eV probably occur because of uncertainties in removing the large extrinsic loss and background contributions in this region [54]. Furthermore, as a general rule, the “ss” features in the Auger line shape are broadened due to the vibrational manifold [55], which is not adequately included in our empirical DOS self-folds. The very large differences seen between 5 and 15 eV are believed to arise because the nonbonding p, orbitals become involved in the C–C bonds. This causes the p, orbitals to become part of the C–C DOS. Therefore for self-consistency, a fraction of the p, *p, p, s, and p, *p, contributions in the C–M DOS self-fold should have been eliminated. Since the larger p, *p, and p, *p, contributions fall in the 5–15 eV region, we made no attempt to eliminate them, but in anticipation of this effect, performed the least squares fit utilizing only the 15–40 eV region. The resultant large overestimate of the Auger intensity between 5 and 15 eV provides evidence that the p, orbitals are indeed involved in the C–C bonding.

The relative intensities of the three components for each of the fits is given in table 1. Also shown are the component relative intensities expected for various C–C/C–M ratios. Comparison of these indicates that the C–C/C–M ratio is around 0.3 for C₂H₄/Ni(100), 0.5 for CO/Ni(100), and 0.35 for CO/Ni(111) (or the fraction of C–C bonding character is 0.23, 0.33, and 0.26, respectively, of the total carbon electron density). This sequence is consistent with the relative heights of the shoulder at 15 eV, but inconsistent with the sharpness and apparent intensity of the peaks at 30 and 40 eV. This suggests that the 15 eV shoulder is the best qualitative indicator of the extent of C–C/C–M bonding. The 30 and 40 eV peaks have contributions from all three components, and figs. 6–8 suggests their sharpness and intensity can change dramatically and non-uniformly with changes in the C–C/C–M ratio.

One might be surprised that for the three line shapes studied, the smallest C–C/C–M ratio is obtained from Koe1s C₂H₄/Ni(100) data. First, we might have anticipated that the extent of C–C bonding would increase with total carbon coverage, yet the estimated coverage is larger for Koe1s data (roughly 0.1–0.2 ML estimated by Houston for his Ni(100) and Ni(111) surfaces versus 0.45 ML estimated by Koe1 for his Ni(100) surface). Second, we might have guessed that a carboaceous layer produced from C₂H₄ might contain some nascent C, bonding on the surface, compared with one produced from CO. Assuming our results are correct, several explanations are possible. First the estimates of the C coverages are very rough and may be incorrect. After flashing to 500 K, the source of C (CO or C₂H₄) is probably not significant, since all C–H and C–O bonds have

### Table 1

<table>
<thead>
<tr>
<th>System</th>
<th>x</th>
<th>Percentage shake-off</th>
<th>C–M*</th>
<th>C–M*</th>
<th>C–C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₄/Ni(100)</td>
<td>10</td>
<td>63</td>
<td>31</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>600 K</td>
<td>15</td>
<td>60</td>
<td>37</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>60</td>
<td>31</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>CO/Ni(100)</td>
<td>10</td>
<td>42</td>
<td>45</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>500 K</td>
<td>15</td>
<td>43</td>
<td>47</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>47</td>
<td>42</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>CO/Ni(111)</td>
<td>10</td>
<td>55</td>
<td>33</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>500 K</td>
<td>15</td>
<td>53</td>
<td>37</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>68</td>
<td>30</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Theory
C–C/C–M = x

\[ N = \frac{100}{(x^2 + 2x + 1)} \]

\[ N' = \frac{100}{x^2 + 2x + 1} \]

\[ N'' = \frac{100}{x^2 + 2x + 1} \]

\[ N''' = \frac{100}{x^2 + 2x + 1} \]

Note: N = 100/(x² + 2x + 1).
been broken above 580 K. And perhaps the experimental conditions are the most critical. We note that Koel’s data were taken after flashing to 600 K while Houston flashed to only 500 K. The Caputi et al. [17] “intermediate” phase data were taken at 620 K, only 20 K higher than that for Koel’s data. It is probable that Koel’s data were taken after some of the C–C bonds formed at lower temperatures have already been broken. In any event, a more careful and extensive study of the variation of this ratio on experimental conditions should be performed.

We have not attempted to quantitatively interpret the low-resolution curves a–c in fig. 3. The shoulders at 15 eV in these broadened spectra are much less visible, but it is clearly present, particularly in curve c. We expect that the C–C/C–M ratio is not dramatically different from that for curve d, since they all are similar to this curve. For the “bulk” carbidies (actually thick carbidic layers grown on Ni) one might anticipate significant amounts of C–C character on the surface. However, the carbidic layers underneath should consist primarily of C–M bonding and also contribute to the Auger spectra. Therefore, the spectra for the “bulk” carbidies are also expected to exhibit significant amounts of both C–C and C–M bonding.

6. Summary and conclusions

A detailed interpretation of UPS, CK EELS, and CKV Auger data has provided direct spectroscopic evidence for significant amounts of C–C bonding on the surface in carbonaceous layers under conditions typically referred to as forming “carbidic” carbon. The C–C bonding apparently arises mostly from C, and maybe even C, or higher carbon polymer fragments chemisorbed on the surface. Our interpretation of the core EELS and AES data on Ni(100) then suggests that the C, fragments primarily breakup in the temperature range 570–670 K, i.e., below the temperature for formation of graphite; however, some apparently tip up to form vertical C,.

The breakup of the C–C bonds on Ni(100) at 570–670 K is consistent with trends seen in the data for ethylene fragmentation on other transition metals. On Ru(001), negative ion SIMS studies [10] utilizing 50/50 isotopic 13C2H4 and 12C2H4 mixtures show that the bonds (or at least the close association) between the two carbon atoms of the parent molecule remain up to 600 K. However, above 600 K, essentially complete carbon mobility exists, as suggested by the 13C–13C, 13C–12C, and 12C–12C ion ratios (completely statistical at 1:2:1) coming off the surface. (Note, direct polymerization of the ethylene fragments into longer chains, for example, and then random fragmentation in the SIMS process would give ion ratios of 2:1:2.) This strongly suggests the breakup of the C–C bonds above 600 K. In agreement with this data, Henderson et al. [6] found that ethylene on Ru decomposes initially to CCH3 (ethyldiene) which then decomposes via C–C bond cleavage. However, coadsorption of CO and ethylene on Ru(001) causes the CCH3 to decompose at higher temperatures to C2H (acetylene), which then polymerizes ultimately to graphite without C–C bond cleavage. Henderson et al. [6] conclude that the stabilization of CCH3 by the CO on Ru mainly results from inhibition of C–C bond cleavage.

Generally, ethylene decomposes via two routes on transition metals. The first route initially involves acetylenic species (CCH, C2H3, and others), which typically occurs on the first row transition metal series, such as Ni(111), Fe(111), etc. [6,9]. Although vinyl is the first decomposition fragment on Ni(100), we include Ni(100) in this group. The second route initially involves CCH3 (ethyldiene), which typically occurs on Pt(111), Rh(111), Pd (111) etc. [6,9]. The stabilization of ethyldiene apparently also results from inhibition of C–C bond cleavage on these latter metals. Thus Zhou et al. [11] conclude that on Ni the C–C bonds tend to break more easily than the C–H bonds, while on Rh(111) and Pt(111), etc. the reverse is true. Consistently, they find on Pt(111), that C, units polymerize directly to graphite. Our finding that on Ni and Cu(100) the C–C bonds break around 600 K before graphitization is also consistent with this picture.

Recent calculations utilizing effective medium theory (EMT) [56] are also relevant here. In the EMT approach, the atom positions are determined by the electron density, each atom seeking its own
unique optimum density. Utilizing this EMT approach and assuming that the metal and carbon charge densities add, Jacobsen and Norskov [57] predicted a continuous evolution from carbidic carbon to graphite. However, very recently Darling et al. [58], performed EMT calculations but calculated the electron density quantum mechanically. These quantum mechanical calculations revealed that the C atoms repel or reduce the electron density at the metal surface, so that the C atoms move into the surface to increase their electron density. In graphite, the C–C bonds attract the electrons from the other carbons and still repel the Ni d electrons, but now the graphite moves away from the surface to increase the total charge density. Thus at intermediate coverage, the C–C interaction drives atoms closer to Ni, but in a graphite layer, the C–C interaction drives them away from the surface. They conclude then that the carbidic to graphite evolution is clearly discontinuous, so that a nucleation step is involved.

These calculations also suggest that a horizontal C$_2$ species on a Ni(111) surface is not stable at high temperature, but that a vertical (i.e., perpendicular) C$_2$ species is stable on the Ni surface [58]. However, this vertical C$_2$ is too close to the surface to serve as a nucleation site for graphite formation by itself. Only a C$_3$ species moves sufficiently far from the surface to serve as a nucleation site. Darling et al. [58] then postulate that a vertical C$_2$ species may either “tip over” to form a C$_3$ species, which moves away from the surface and forms a graphite nucleation site, or a graphitic layer forms on top of a carbidic layer (i.e., the outer C of the vertical C$_2$ may become part of the graphite layer, and the inner C may ultimately undergo dissolution into the bulk). In either case, the vertical C$_2$ is a precursor to a nucleation site.

Our spectroscopic results are consistent with these theoretical results. First, our core EELS investigations indeed indicate that at 620 K some vertical C$_2$ is formed along with considerable C$_1$. However, the EELS data also suggest that vertical C$_2$ is formed only at higher coverages. At higher coverages, we envisage that some of the C$_2$ are forced to flip up to make room for the neighboring horizontal C$_2$'s to dissociate. If these vertical C$_3$'s then serve as the precursor for the nucleation of graphite, it would explain the lack of graphite formation from C$_2$H$_4$/Ni(100) (i.e., low coverages). Further exposure to C$_2$H$_2$ at higher temperatures (i.e., producing C coverages greater than 0.75 ML) does lead to graphite formation on Ni(100) [59].

The partial breaking-up of many of the C–C bonds on Ni in the 570–670 K range would suggest that the reactivity of the carbon layers would increase in this temperature range. This is of significant interest for Fischer–Tropsch synthesis, and for controlling the amounts of CH$_4$ and C$_2$H$_6$ produced in the process [22]. Obviously more work is required here to fully understand the mechanism for graphite formation on metals. We have shown in this work that electron spectroscopy can provide significant information for these studies.

References


