AUGER LINESHAPE DETERMINATION OF THE HYBRIDIZATION OF ETHYLENE ADSORBED ON Ni(100)

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The C(KVV) X-ray excited Auger (XAES) spectrum for ethylene adsorbed on Ni(100) has been obtained and deconvoluted to provide the *undistorted* lineshape. Direct comparison of this lineshape with the C(KVV) spectrum of gas-phase ethylene determines unambiguously that little rehybridization occurs upon adsorption of ethylene on Ni(100) at 100 K.

1. Introduction

Determination of the nature of chemical bonding and the structure of adsorbed hydrocarbons on metal surfaces is central to understanding hydrocarbon conversion reactions over metal catalysts. In particular, surface science research has been aimed at elucidating the origin of the structure sensitivity of catalytic reactions by characterizing the properties of adsorbed hydrocarbon molecules on single-crystal metal surfaces. Despite continued improvements in techniques such as XPS, ARUPS, ESDIAD, and HREELS, it remains difficult to unambiguously determine the chemical nature, mode of bonding, and geometry of adsorbed molecules. Additional supporting information from a complementary technique would be extremely useful.

Over the past few years, high-resolution Auger electron spectroscopy (AES) has been used to establish that the carbon (KVV) Auger lineshape is a sensitive probe of carbon hybridization in gas-phase hydrocarbons. The C(KVV) spectra of the three gas-phase molecules CH_4, C_2H_4, and C_2H_2, in which the carbon hybridization is sp^3, sp^2, and sp, respectively, are dramatically different [1–3]. In contrast to the above, the C(KVV) spectra of gas-phase CH_4, CH_3OH, and $(CH_3)_2O$, in which the carbon hybridization in sp^3 in all cases, are quite similar [1,2]. The C(KVV) spectrum of CH_3CN, which contains both sp^3 and sp hybridized carbon atoms, has been shown to be approximated by a combination of CH_4 and C_2H_2 spectra [4]. Also, the C(KVV) spectra of small alkanes and cycloalkanes are consistent with the previous observations of local hybridization sensitivity of AES [5,6]. Thus, Auger lineshape analysis can be used as a "fingerprinting" probe of *local* valence electronic structure. This unique sensitivity is due to the direct coupling in the Auger transition of the localized core hole and the valence electrons immediately surrounding the atom containing the core hole.

In spite of the tremendous promise of this technique, high-resolution Auger spectra of only a relatively few adsorbed molecules have been obtained (reviewed in refs. [7,8]). Much of this previous work has focused on obtaining O(KVV) or N(KVV) spectra for distinguishing associative and dissociative adsorption states of small molecules, e.g. CO, N_2, NO, N_2O, NO_2, and NH_3. Netzer and Matthew have measured the electron excited AES (EAES) C(KVV) spectra for C_2H_4, C_2H_2, and C_6H_6 adsorbed on Pt(111) [9], and also for C_6H_6 and C_5H_5N on Ir(111) [10]. Canning and Chesters obtained EAES C(KVV) spectra of C_2H_2 adsorbed on Pt(111) and Cu(111) [11], and also C_2H_4 adsorption and decomposition on Pt(111) and Fe(110) [12].

While the work on Pt(111) and Cu(111) [11] showed the sensitivity of AES to the nature of adsorbate–metal bonding, no other studies of adsorbed hydrocarbons have been reported since. Two possible reasons for this are the electron-beam damage which

often occurs in EAES (varying enormously with the adsorbate and metal surface), and the relatively poor X-ray excited AES (XAES) sensitivity, due to the small C(1s) photoionization cross section and the small X-ray flux from typical X-ray line sources.

In the present paper, we extend high-resolution AES studies of adsorbed hydrocarbons to ethylene adsorbed on Ni(100) at 100 K. The significant aspects of this work are the use of X-ray excitation to avoid the rapid beam damage caused by electron bombardment and the accurate removal of extrinsic contributions to the spectra from background and energy loss processes. The temperature dependence of the Auger spectra for this system will be published elsewhere [13]. Both of these papers demonstrate dramatically the utility of the AES lineshape as a fingerprint probe to determine the hybridization of chemisorbed hydrocarbon molecules.

The Auger electron kinetic energy KE can be written as

$$KE = I_c - I_k - I_j - U_{eff}(j,k,s), \qquad (1)$$

where I_c is the core level binding energy, I_j and I_k are the valence level binding energies, and U_{eff} is a spin-s-dependent final state interaction term which includes [14] the Coulomb interaction between holes in levels j and k and a static relaxation term. Rearrangement of eq. (1) to give

$$KE - I_c = -I_j - I_k - U_{eff} \qquad (2)$$

places the Auger spectrum on a two-hole binding energy scale and allows for an experimental evaluation of U_{eff}. Using this binding energy scale, U_{eff} is empirically determined as the energy shift needed to align the measured Auger transition energies with energies calculated for the various two-hole final states using the measured valence level binding energies. These final states are derived using possible combinations of the valence levels. Consistent with our previous observations of CO adsorbed on Ni(100) [15], the C(KVV) spectrum of adsorbed ethylene is shifted to higher kinetic energy than the gas phase, due to near elimination of Coulombic repulsion between the two final-state holes, and shows a new high-energy peak due to transitions involving metal–adsorbate bonding valence orbitals.

2. Experimental

A description of the experimental technique has been given in detail previously [15,16]. Briefly, the Ni(100) crystal was cleaned by heating in 1×10^{-5} Torr of O_2 for 100 s at 1200 K, followed by reduction in 1×10^{-5} Torr of H_2 for 5 min at 1200 K. Cleanliness was judged by AES. Ethylene (CP, minimum purity 99.5%, Union Carbide Corp., Linde Div.) was passed through a dry ice/acetone trap and dosed to the crystal by a stainless steel multichannel array doser. The crystal temperature for exposure and analysis was 100 K, and saturation ethylene exposures of 40 L ($1 L \equiv 10^{-6}$ Torr s) were used. A condensed multilayer of C_2H_4 cannot be formed under these conditions.

The XAES spectra were taken with a cylindrical mirror analyzer (CMA) operated at 100 eV pass energy (resolution $\Delta E = 1.6$ eV) with angle-integrated detection averaging 50° (range 10° to 70°) from the surface normal. Spectra were obtained in about 30 min by pulse counting and signal averaging using a multichannel analyzer. The excitation source was an Al Kα X-ray source operated at 600 W with the 0.2 μm Al window removed to allow all available Bremsstrahlung radiation to escape.

Distortions of the true Auger lineshape occur in the measured XAES spectrum of adsorbed molecules and these must be removed following data collection to allow direct comparison with gas-phase spectra or theory. The following procedure was used: (1) removal of large secondary-electron background using a functional form of the background suggested by Sickafus [17]; (2) subtraction of a scaled, clean Ni(100) spectrum to remove "ghost" photoelectron peaks in the C(KVV) region due to C Kα radiation from the X-ray source (similar in origin to the O Kα artifacts reported previously [18]); (3) deconvolution of the background-subtracted spectrum with a total instrumental and loss broadening function, as measured by an electron backscatter spectrum at an incident energy $E_p = 290$ eV KE (near the Auger electron energy), using an iterative technique suggested by van Cittert [19] and developed by Madden and Houston [20]; and (4) correction for the $(KE)^{-1}$ dependence of the CMA sensitivity. Comments on the deconvolution procedure and the instrumental and loss broadening function are discussed elsewhere [13,21].

3. Results and discussion

In fig. 1 we reproduce results of Rye et al. [1,2] comparing the electron-excited C(KVV) spectra of gas-phase CH_4, C_2H_4, and C_2H_2 [1]. The carbon Auger spectra for these three molecules have been placed on a common two-hole binding energy scale referenced to the vacuum level by subtracting in each case the C(1s) binding energy from the experimental Auger kinetic energy. The C(KVV) lineshape shows dramatic differences consistent with the large changes in the local electronic structure about the carbon atoms as the hybridization varies from one molecule to another. The methane lineshape shows a single large peak with three smaller peaks at lower kinetic energy, the ethylene
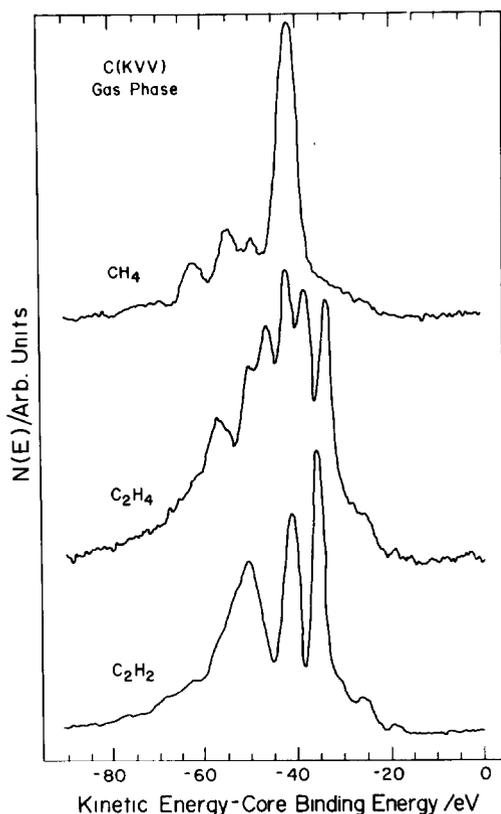

structure has six peaks of similar intensity, while the acetylene lineshape contains three major peaks. These spectra are unique for the hybridization of the carbon atoms in free molecules. Since no extrinsic electron energy loss processes distort these low-pressure gas spectra, they can serve directly as fingerprints to identify the hybridization of carbon atoms in adsorbed hydrocarbon molecules.

Another spectrum that provides a useful fingerprint for interpreting adsorbed-hydrocarbon spectra is that of gas-phase C_2H_6 [5]. While the large central peak is broader than for $CH_{4(g)}$, the spectrum is clearly distinguishable from that for $C_2H_{4(g)}$. The ethane lineshape shows a much narrower central feature than for ethylene, and the large peak in the ethylene spectrum with the highest kinetic energy (lowest two-hole binding energy) is absent in the ethane spectrum.

Theoretical calculations of the gas-phase C_2H_4 KVV spectra have been made [22,23] and the high-kinetic-energy peak in the $C_2H_{4(g)}$ spectrum has been assigned to $(\pi_{CC})^{-2}$, $(\pi_{CC})^{-1}(\pi'_{CH_2})^{-1}$, and $(\pi'_{CH_2})^{-2}$ final states [23]. While the other peaks are due to accidental superpositions of many final states with σ and/or π holes, this peak is distinct for involving only the highest lying π orbitals. Thus, while all of the peaks in the lineshape contribute to the observed carbon hybridization sensitivity, this high-kinetic-energy peak should be extremely sensitive to the chemical environment.

The *undistorted* C(KVV) lineshape we have obtained for a saturation coverage of adsorbed ethylene on Ni(100) at 100 K is shown in fig. 2. The lineshape was obtained from the directly recorded X-ray excited C(KVV) spectrum after correcting for the secondary-electron background and the effect of extrinsic loss processes and instrumental broadening by loss deconvolution. The directly recorded spectrum and details of the deconvolution are presented elsewhere [13]. The adsorbed ethylene lineshape is also placed on a two-hole binding energy scale referenced to the vacuum level, with careful consideration of energy level references. The C(1s) binding energy (BE) of 283.8 eV for this surface was determined in previous studies [16], referenced to E_F = 0.0 eV BE and Ni($2p_{3/2}$) = 852.2 eV BE. The vacuum level for a saturation coverage of adsorbed ethylene was determined using the sample work function $\phi_{sat, C_2H_4/Ni(100)}$ = 4.40 eV [16].

Fig. 2 also shows a direct comparison of the deconvoluted adsorbed-C_2H_4 lineshape that we have obtained

Fig. 1. Gas-phase electron-excited C(KVV) spectra of CH_4, C_2H_4 and C_2H_2, showing the sensitivity of C(KVV) lineshapes to carbon hybridization [1,2]. The spectra are placed on a two-hole binding energy scale (described in the text) that is referenced to E_{vac} for purposes of direct comparison to adsorbate spectra.
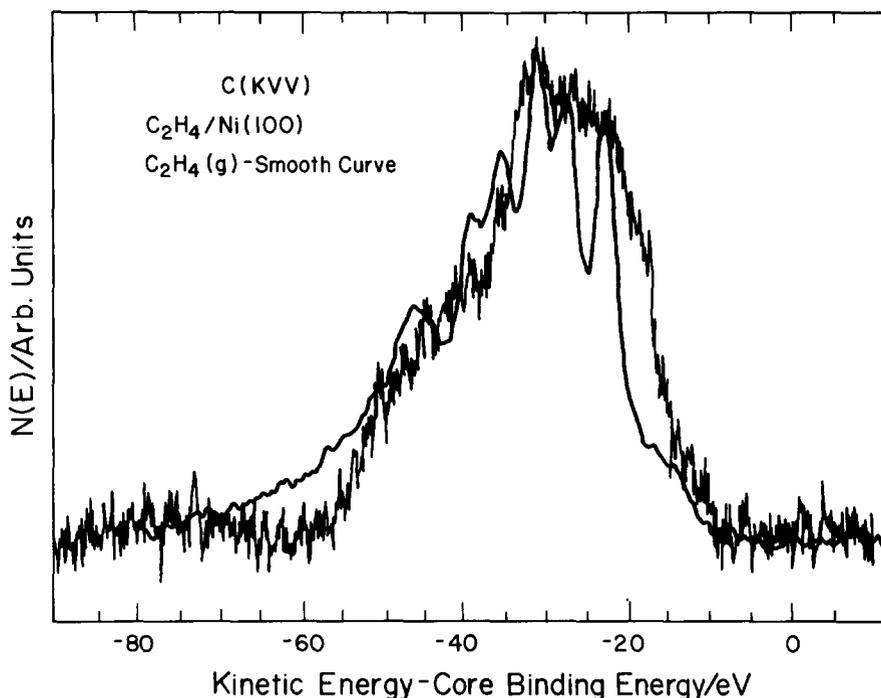
Fig. 2. X-ray excited C(KVV) lineshape for C_2H_4 adsorbed on Ni(100) at 100 K after correction for the secondary-electron background and the effects of extrinsic loss processes and instrumental broadening by loss deconvolution. The smooth curve is the $C_2H_{4(g)}$ lineshape from fig. 1 which has been arbitrarily shifted in energy to produce the best fit. The excellent correspondence between the two curves indicates that little rehybridization occurs upon adsorption of C_2H_4.

with the $C_2H_{4(g)}$ spectrum (smooth curve) from fig. 1 obtained by Rye et al. [1,2]. The gas-phase spectrum has been shifted arbitrarily to $\approx$ 12 eV higher kinetic energy to best fit the adsorbed-C_2H_4 lineshape. It is immediately clear that the π-bonded ethylene fingerprint of sp^2 hybridized carbon atoms seen in the gas phase is still present in the adsorbed state, clearly indicating that little rehybridization of ethylene occurs upon adsorption. All of the major features of the gas-phase spectrum are carried over to the adsorbate lineshape, i.e. the relative intensity and relative energy spacing of all six major peaks in the gas-phase spectrum are remarkably well reproduced in the adsorbate lineshape, including the peak assigned to the π^{-2}-like final states. With the exception of a new peak in the lowest two-hole binding energy region (about -18 eV) which will be discussed next, many of the small differences can be explained by the solid-state broadening due to phonon effects that occurs for adsorbed C_2H_4, similar to that seen for condensed molecular solids [1,2],

and possibly by a small inaccuracy in the loss deconvolution of the adsorbed C_2H_4 spectrum. It appears that the low-kinetic-energy wing of the adsorbate lineshape may be just slightly too low in intensity due to excessive removal of extrinsic loss contributions which are the largest in this area of the spectrum. However, this region has been shown [23] to be dominated by correlation effects so that the observed differences in the lineshapes may reflect subtle differences in the local electronic structure or the "many-body" effects that accompany the Auger transitions.

In this fingerprint approach, it is important to note that angular effects in Auger emission intensity for chemisorbed ethylene may complicate the direct comparison of the chemisorbed lineshape to gas-phase spectra. Large angular effects have been observed in XPS by Egelhoff [24], and in AES by Umbach [25]. However, the use of the CMA, which gives angle-integrated detection over a wide range of angles for our experimental geometry, apparently averages out these effects. This

is indicated by the quality of the fit of the spectra shown in fig. 2.

We should also note that two general features of our adsorbate spectrum are consistent with all previous Auger studies of chemisorbed species, namely the large shift of the spectrum to higher kinetic energies and the appearance of a new high-kinetic-energy peak when compared to gas-phase spectra. The observation that the gas-phase spectrum must be shifted to higher kinetic energy by ≈ 12 eV in order to line up with the adsorbate spectrum has to do with the value of U_{eff} for transitions in the two spectra. In the gas phase, U_{eff} for two valence level holes in typical small molecules is about 15 eV [7]. In an adsorbed molecule, the lifetime of the initial core-hole state allows virtually complete screening of this hole by charge transfer from the metal [26]. The decay of this fully screened core-hole state has been proposed to occur by two major mechanisms: (1) Auger-like de-excitation forming a two-hole, one-electron final state, where the screening electron is a spectator to a normal Auger transition and effectively "cancels" one hole in the final state [15], and (2) auto-ionization-like de-excitation forming a single-hole final state, where the screening electron is ejected in the Auger process [27]. In either case, U_{eff} is predicted to be about zero for Auger spectra of adsorbates and accounts for the large shift in kinetic energy for the spectra. The new peak which appears at a higher kinetic energy than any Auger final state predicted from shifted gas-phase molecular orbitals can be attributed to Auger decay involving new nickel–ethylene π-bonding orbitals formed upon adsorption. This peak is similar in origin to the high-kinetic-energy peak observed for adsorbed CO [15] due to transitions involving the 2π-bonding orbital, and a similar interpretation has been applied to other metal–ligand systems [28].

Our results demonstrate unambiguously that ethylene adsorbs molecularly on Ni(100) at 100 K with little rehybridization of the carbon atoms to form a π-bonded surface species. The Auger lineshape for chemisorbed C_2H_4 shown in fig. 2 is also similar to the EAES spectrum obtained by Canning and Chesters [11] for C_2H_4 adsorbed on Cu(111). Copper and silver surfaces have been shown by a variety of techniques to form only weakly bonded π-complexes. A detailed comparison of the two lineshapes is difficult since the spectra in ref. [11] were obtained at lower resolution and sensitivity, and since no loss deconvolu-

tion was performed in their study.

Importantly, our results are in agreement with, and give general supporting evidence for, a recent vibrational study of this system using HREELS [29]. Zaera and Hall [29] have also concluded that ethylene adsorbs molecularly on Ni(100) at temperatures below 150 K, with very little rehybridization in a π-bonded state. They observe a very weak C–C stretch peak at 1570–1580 cm^{-1}, shifted less than 50 cm^{-1} from the gas phase value of 1623 cm^{-1}. Stuve and Madix [30] have defined a $\pi\sigma$ parameter calculated from vibrational spectra as an indication of the extent of C_2H_4 rehybridization upon adsorption. This parameter ranges from zero for gas-phase ethylene (sp^2) to unity for $C_2H_4Br_2$(sp^3). Using their formula the data of Zaera and Hall give a $\pi\sigma$ value of 0.09, consistent with our interpretation.

Our conclusion is also consistent with previous theoretical calculations [31] and UPS studies on Ni(100). The HeI and HeII photoemission spectra of C_2H_4 adsorbed on Ni(100) at 100 K show a peak at 4.7 eV BE assigned to a shifted C_2H_4 π-level [16], in agreement with the previous results of Horn et al. [32], who made angle-resolved HeI photoemission studies.

One question that still remains regards the geometrical configuration of the adsorbed ethylene, for example a twist about the C–C bond axis. It is difficult to reach a definite conclusion based on the ARUPS or HREELS data. Perhaps theoretical calculations and comparisons to the Auger lineshape presented herein would provide the sensitivity required to determine this information.

Finally, these results further emphasize the structural sensitivity of adsorption and reactivity of unsaturated hydrocarbons on nickel surfaces. It now seems clear the C_2H_4 adsorption on Ni(100) leads to a π-bonded C_2H_4, while on Ni(111) a di-σ-bonded C_2H_4 is formed. The different reactivities of these two forms of adsorbed C_2H_4 may explain results that indicate that ethylene and acetylene adsorption at 300 K produces different surface species on Ni(100) [16,32] and the same surface species on Ni(111) [33,34].

4. Conclusions

We have obtained the *undistorted* C(KVV) lineshape of adsorbed C_2H_4 on Ni(100) using XAES and loss

deconvolution. This lineshape is directly compared to gas-phase Auger spectra of several hydrocarbons in order to determine the extent of C_2H_4 rehybridization that occurs upon adsorption. The excellent correspondence between the adsorbate lineshape and the gas-phase C_2H_4 spectrum establishes that C_2H_4 undergoes little rehybridization upon adsorption and forms a π-bonded surface species on Ni(100). This result is in agreement with other work on Ni(100) using UPS and HREELS, and is in contrast to the di-σ-bonded form of C_2H_4 which is formed on Ni(111).

The Auger spectrum of adsorbed C_2H_4 is also consistent with previous spectra of other chemisorbed species which show little hole—hole repulsion energy in the Auger final states and which show a high-kinetic-energy peak not seen in the gas phase due to transitions involving new orbitals involved in forming the chemisorption bond.

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