Temporary Negative-Ion Formation in Chemisorbed Species: The Energy and Angular Dependence of Vibrational Losses for Electron Scattering Studies of HCOO/Ni(110)

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We have studied both the energy and angular dependence of vibrational losses for the formate species chemisorbed on Ni(110), using high-resolution electron-energy-loss spectroscopy. Temporary negative-ion formation, at an incident electron energy of ~14 eV, leads to a dramatic enhancement in the intensity of the symmetric O-C-O stretch. Electron emission shows a strong angular dependence which peaks at high emission angles away from the surface normal. This effect is compared to previous photoemission studies of adsorbed CO, where the scattering in the σ-shape resonance is directed along the C—O bond.

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Although it has long been recognized that the resonant capture of an incident electron into a quasibound state of gaseous molecules, giving rise to a temporary negative ion, may result in a strong enhancement of the intensities of vibrational excitations,[1] it is only comparatively recent that similar resonant scattering behavior has been observed for molecules adsorbed on surfaces.[2-6] The first conclusive evidence for such an effect arose from inelastic electron scattering studies of weakly bound systems, such as O_2 and N_2 *physisorbed* on silver surfaces.[2,3] For more strongly bound adsorption systems, Kesmodel has recently reported an enhancement in the intensity of the symmetric C-H stretching mode for benzene *chemisorbed* on Pd(100), which was attributed to a resonance centered at an incident electron beam energy of $E_i \sim 2.7$ eV.[6] Essentially all of these studies have been concerned with probing the energy dependence of the resonance and the mode selectivity.[6,7] An extension of these observations has recently been reported for *physisorbed* O_2 on graphite by Palmer *et al.*,[4] in which a negative-ion resonance was observed at $E_i \sim 9$ eV. Palmer *et al.* also investigated the angular distribution of the inelastically scattered electrons which revealed a peak at $15° \pm 5°$ relative to the surface normal, independent of the incident electron angle. From this study, information regarding the orientation of the O_2 molecules at the graphite surface was obtained.[4]

In this Letter, we demonstrate strong resonant enhancement of the symmetric O-C-O stretching mode, ν_s(COO), centered at $E_i \sim 14$ eV, for the surface formate species, HCOO, *chemisorbed* on Ni(110). We relate this to the so-called σ resonance in near-edge x-ray-absorption spectroscopy (NEXAFS) at ~15 eV for HCOO on Cu(110) and Cu(100), involving transitions from the O-1s and C-1s core levels to a quasibound state, which is localized in the C—O bonds of the adsorbed species.[8,9] In addition, we find that there exists a strong angular dependence in the inelastically scattered electron distribution which is peaked at high emission angles away from the surface normal and along the ⟨110⟩ azimuth, corresponding to an enhanced emission in directions correlated with the C—O bonds of the formate species. This represents the first energy *and* angular study of resonant scattering from a chemisorbed system.

Experiments were carried out in an ultrahigh vacuum chamber (base pressure $< 2\times10^{-10}$ Torr) equipped with high-resolution electron-energy-loss spectroscopy (HREELS), low-energy electron diffraction (LEED), and mass spectrometry. The HREEL spectrometer (VSW Scientific Instruments Ltd.) consists of a fixed hemispherical monochromator and a rotatable hemispherical analyzer. The spectrometer can operate with an incident electron beam energy of $E_i = 1$-250 eV, while maintaining a resolution (FWHM) of 6-9 meV. The Ni(110) crystal was cut to a precision of 0.5°, polished, and then cleaned *in situ* by standard Ar^+-bombardment and annealing (~1000 K) procedures. Surface cleanliness was monitored by the appearance of a sharp $p(1\times1)$ LEED pattern and the absence of any loss peaks in the tail of the elastic HREELS peak. The sample was exposed to formic acid, HCOOH (after several freeze-pump-thaw cycles to remove residual dissolved gases), at a substrate temperature of ~340 K until saturation coverage was obtained (~3 L) (1 L$=10^{-6}$ Torr s). At this stage, a sharp $c(2\times2)$ LEED pattern was obtained but prolonged exposure to the electron beam caused degradation of the pattern.[10] Deprotonation of the formic acid occurs at the surface, leading to an adsorbed formate ion, $HCOO^-$.[11] We see no evidence of significant coadsorbed CO molecules as reported by Madix *et al.*[12] The formate is bonded symmetrically to the Ni atoms via the two oxygen atoms, sitting upright at the surface and oriented with the plane of the formate lying along the close-packed ⟨110⟩ rows.[13,14]

A typical energy-loss spectrum for HCOO/Ni(110) at an incident beam energy of $E_i = 14$ eV and $\theta_i = 60°$ is shown in Fig. 1 (the electron scattering plane here and for all the other data presented in this Letter lies along

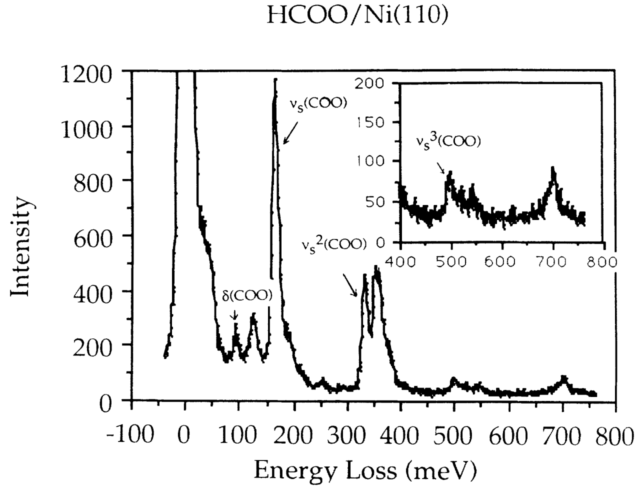

FIG. 1. Off-specular HREELS spectrum for HCOO/Ni(110) recorded with $E_i = 14$ eV, angle of incidence $\theta_i = 60°$, and scattered angle $\theta_s = 50°$ (relative to the surface normal) and with the electron scattering plane aligned along the ⟨110⟩ azimuth. The relevant vibrational transitions, both fundamental and overtone, are labeled. Inset: The second overtone and some combination bands which are observed as a consequence of the resonant phenomenon.

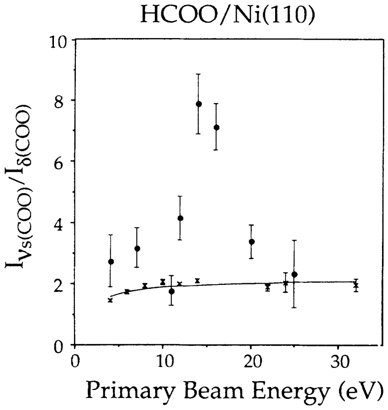

FIG. 2. The relative intensities of the symmetric COO stretching mode and the deformation OCO mode, $I_{\nu_s(\mathrm{COO})}/I_{\delta(\mathrm{COO})}$, as a function of primary beam energy. Both specular and off-specular intensities are shown, along with the calculated dipole-scattered intensity ratio (Ref. 16). All measurements were made with a fixed angle of incidence $\theta_i = 60°$ and off-specular data were collected with a scattered angle of $\theta_s = 50°$. Note that all angles are given relative to the surface normal and the electron scattering plane was aligned along the ⟨110⟩ azimuth.

the ⟨110⟩ azimuth). In order to observe the enhancement fully, the electrons have been collected 10° off specular ($\theta_s = 50°$) where the dipole-scattered losses are very weak (the angular resolution of the spectrometer is ~2° FWHM). A full spectral assignment covering both specular and off-specular measurements, employing a wide range of primary beam energies (up to 100 eV), has been carried out and will be reported elsewhere.[13] However, for the purposes of this Letter, Table I summarizes the relevant band assignments and compares the frequencies measured here with those taken for bulk sodium formate.[15] By far, the most striking feature of Fig. 1 is the dominant band at 167 meV, which is assigned to ν_s(COO). Unfortunately at this frequency there is an accidental degeneracy of the in-plane C-H deformation, δ(C-H), and ν_s(COO). Spectra recorded with use of deuterated formic acid (DCOOD) have enabled us to unambiguously assign the dominant band in Fig. 1 to ν_s(COO) since the δ(C-D) mode shifts down in frequency to 115 meV (see Table I).[13] Also shown in Fig. 1 (inset) are the corresponding first and second overtone losses (i.e., $\nu = 0 \rightarrow 2$ and $0 \rightarrow 3$ vibrational transitions) associated with this mode. Spectra recorded at lower ($E_i < 6$ eV) and higher ($E_i > 25$ eV) incident electron beam energies, employing the same scattering geometry ($\theta_i = 60°$, $\theta_s = 50°$), do not show this dramatic enhancement in intensity at 167 meV or a strong overtone intensity.

TABLE I. Assignment of the major spectral features for HCOO/Ni(110) for HREEL spectra recorded with a primary beam energy of $E_i = 14$ eV. These are compared to the frequency values obtained from vibrational studies of bulk sodium formate (Ref. 15). The frequency values in parentheses refer to DCOO. A full spectral analysis is reported elsewhere (Ref. 13).

Assignment	$Na(HCO_2)$	HCOO/Ni(110)
ν(Ni-O)	⋯	53 (49)
δ(OCO)	97 (95)	96 (91)
π(C-H)	134 (115)	⋯
ν_s(COO)	169 (166)	167 (162)
δ(C-H)	173 (129)	⋯ (115)
ν_a(COO)	198 (198)	193 (189)
ν(C-H)	353 (265)	358 (268)
$2\nu_s$(COO)	⋯	334 (329)
$3\nu_s$(COO)	⋯	495 (491)

The energy dependence of the intensity ratio $I_{\nu_s(\mathrm{COO})}/I_{\delta(\mathrm{COO})}$, is plotted in Fig. 2. From the geometry and orientation of the HCOO species at the surface, both of these vibrational modes are expected to be surface-dipole active.[13] To confirm this, $I_{\nu_s(\mathrm{COO})}/I_{\delta(\mathrm{COO})}$ obtained from data taken in specular geometry ($\theta_i = 60°$, $\theta_s = 60°$) is plotted in Fig. 2 along with the calculated ratio from dipole-scattering theory.[16] For close to specular detection, the long-range dipole-scattering interaction is the dominant excitation process. For dipole scattering, an increase of E_i leads to a decrease in the intensity of both bands.[16] Moreover as expected, Fig. 2 shows that for specular scattering the higher-frequency mode decays less dramatically than the lower-frequency mode. Thus we believe that the dramatic increase in the intensity of

ν_s(COO) compared to δ(COO) (and all the other dipole-active modes), observed in off-specular scattering geometry, which is particularly obvious at $E_i \sim 14$ eV, is due to a resonant enhancement. On a cautionary note, short-range, impact scattering can dominate off-specular measurements, particularly with increasing E_i.[17] We prefer to explain the data in terms of a resonant process since off-specular spectra recorded with $25 < E_i < 100$ eV show no noticeable enhancement in the intensity of the band due to ν_s(COO).[13] Further confirmation of the resonant enhancement is the observation of the first and second overtones of ν_s(COO). It is well recognized that one of the signatures of a resonant scattering event is the enhancement in the intensity of overtones and combination bands.[1-7,16,18] We observe the overtones only in the 8-20-eV incident electron energy range where the resonant process is occurring.

Figure 3 shows the angular behavior of the intensity of ν_s(COO), again relative to the dipole-scattered mode δ(COO), as a function of electron scattering angle θ_s, for a fixed angle of incidence $\theta_i = 40°$, along the $\langle 110 \rangle$ azimuth and with a primary electron beam energy $E_i = 14$ eV. Again, as expected from dipole-scattering theory,[16] there is a dramatic decay in the intensity of both bands as θ_s is increased (or decreased) away from specular. However, at high θ_s, there is a very strong increase in $I_{\nu_s(\mathrm{COO})}$ compared with $I_{\delta(\mathrm{COO})}$. Measurements along the perpendicular azimuth ($\langle 100 \rangle$) show no evidence for the resonant enhancement and we therefore conclude that the resonant scattering enhancement for ν_s(COO) is accentuated for high emission angles and along the $\langle 110 \rangle$ azimuth. We have also observed that, for any given electron scattering angle, the enhancement is favored by electrons having a high incidence angle relative to the surface normal. This feature would appear to be a consequence of time-reversal symmetry.

At this point, it is appropriate to address the problem of what is the physical basis of this enhancement. It is well documented, from angle-resolved photoemission studies that a σ-shape resonance exists at around 30 eV for CO adsorbed on transition metals.[19] Moreover, the scattering is dominantly directed along the C—O bond, yielding information concerning the orientation of the CO molecules at the surface.[20] NEXAFS studies of molecules containing carbon-oxygen bonds, namely, CO, methoxy (CH_3O), and HCOO, adsorbed on Cu(100) have shown that the energy of the so-called σ-shape resonance is critically dependent on the C—O bond length.[21] For formate adsorption, the equivalent resonance drops to ~ 15 eV.[8,9,21] It would appear that we are observing a *similar* resonance, involving the same type of final state, for HCOO/Ni(110) using electron scattering. In the NEXAFS results for HCOO on Cu(100) and Cu(110), the resonance occurs at 15 eV relative to the Fermi level corresponding to the creation of a C-1*s* or O-1*s* core hole as the quasibound state is filled. In the HREELS experiment, there is no core hole and its stabilizing effect is lost. We expect, therefore, that the state is at a higher energy. The observed resonance is centered at $E_i = 14$ eV, i.e., at ~ 19 eV relative to the Fermi level when an allowance is made for a work function of ~ 5 eV. This suggests an energy stabilization of ~ 4 eV due to the presence of a core hole. We are confident, therefore, that the final states involved in both the NEXAFS and HREELS processes are equivalent.

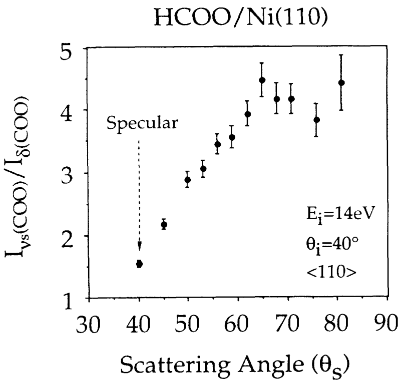

FIG. 3. The relative intensities of the symmetric COO stretching mode and the deformation OCO mode, $I_{\nu_s(\mathrm{COO})}/I_{\delta(\mathrm{COO})}$, as a function of electron scattering angle relative to the surface normal (θ_s), and with a fixed angle of incidence $\theta_i = 40°$. All data were collected with a primary beam energy $E_i = 14$ eV and with the electron scattering plane aligned along the $\langle 110 \rangle$ aximuth.

Rigorously one should not refer to the σ resonance in the case of the adsorbed HCOO species for which the appropriate point group is C_{2v} and not $C_{\infty v}$. For the CO molecule, the quasibound state derives from an antibonding interaction of C- and O-based 2*p* orbitals directed along the C—O bond. An expansion in terms of spherical harmonics, centered on the C-O axis (*z* axis) between the C and O nuclei, would be dominated by the f_{z^3} term. For the HCOO species, there are of course, two C—O bonds and hence two significant final states of a_1 and b_1 symmetry, corresponding to in-phase and out-of-phase combinations of the f_{z^3} terms, based on the C—O bonds, respectively. The two states have been identified in recent NEXAFS studies for HCOO/Cu(110) at the C-1*s* edge though, not at the O-1*s* edge.[22] The existence of two states effectively prevents the use of polarization measurements in NEXAFS for the determination of the O—C—O bond angle.[23] Although, the width of the resonance observed in our HREELS experiment prevents a resolution of the two resonance states, the difficulty in extracting bond-angle information from the angular dependence shown in Fig. 3 remains, although a strong relationship must obviously exist and our observation of enhanced scattering at high emission angles along the

⟨110⟩ azimuth is compatible with the structure and orientation of the adsorbed formate species.[24] More detailed information can only be obtained by comparison of the experimental data with good calculations of the molecular wave functions for an adsorbed formate species with an additional electron.

In conclusion, using inelastic electron scattering, we have observed a strong resonant enhancement of certain vibrational features for formate chemisorbed on Ni(110) at a primary beam energy of $E_i \sim 14$ eV. This is manifested as a dramatic enhancement in the intensity of ν_s(COO). We show that this involves the electron being temporarily capture in the same quasibound state, localized in the C—O bonds of the formate species, which also gives rise to the so-called σ-shape resonances observed in NEXAFS studies for HCOO on Cu(110) and Cu(100), and photoemission studies of adsorbed CO. Moreover we have observed the first angular enhancment of the scattered electrons for a *chemisorbed* system which indicates that the electrons are dominantly scattered at high emission angles relative to the surface normal and along the ⟨110⟩ azimuth, correlated with, but not identical to the direction of the C—O bonds.

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