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Inelastic Photoemission due to Scattering by Surface Adsorbate Vibrations

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By measuring the very low energy photoemission spectra of the CO/Cu(001) surface with a high resolution, we have found the energy loss components due to inelastic scattering of electrons near the Fermi level by the CO vibrational modes. The main energy loss structure appears as a step at 254 meV below the Fermi edge for ¹²C¹⁶O. An isotope shift of the step to 240 meV was observed when ¹³C¹⁸O was adsorbed. This observation confirms that this step arises from the energy loss of photoelectrons near the Fermi level through the excitation of the C-O stretching mode.

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In the conventional photoelectron spectroscopy of metal surfaces, it has been assumed that the photoexcited electron in the skin depth region emerges from the surface with initial kinetic energy imparted by the exciting photon. Then the spectrum has a shape determined by the convolution of the electron density of states (DOS) with the Fermi-Dirac distribution function. This interpretation of the photoelectron spectrum has been generally assumed, and this assumption has not caused any noticeable contradiction. However, when one considers the process of photoemission in detail, one realizes that the photoelectron must interact with elementary excitations localized in the surface region through which the emerging electron passes before exiting to the vacuum space.

From the above considerations, we have come to believe that the true photoelectron spectrum from a metallic surface should contain inelastic components that result from the interaction of photoelectrons that lose or gain energy as they pass through the surface region. We expect that the interaction cross section should be greater for electrons of lower energy. The exciting photon energy used in the usual photoemission experiments is on the order of ~ 10 eV, with the emerging electrons having a kinetic energy of several eV. Since we expect lower energy electrons to have a larger inelastic interaction cross section, we focused on very slow electrons that barely clear the work function. To obtain such electrons, we used a tunable laser as the exciting photon source and tuned the photon energy several hundred meV above the work function. By careful setup and measurement, we have succeeded in finding the spectrum of inelastically scattered photoelectrons whose existence is expected by the above consideration.

To illustrate the expected spectrum, we begin with a simple model. Let us consider the photoemission process from a metal surface covered by an adsorbate, e.g., the Cu(100) surface with adsorbed CO molecules as in the present experiment. The photoelectrons are excited by a photon with energy $h\nu$ (h is the Planck constant, and ν is the incident photon frequency) that is slightly higher than

the work function of the surface [see Fig. 1(a)]. For simplicity, we assume that the electron DOS is flat and that no inelastic scattering occurs within the bulk of the metal. Then the photoelectron spectrum is represented by the well-known Fermi-Dirac distribution curve [Fig. 1(b)]. However, a fraction of the emitted photoelectrons can lose energy through excitation of a vibrational mode of the CO molecule having the energy of $h\nu_{\text{vib}}$, where ν_{vib} is the molecular vibration frequency. This inelastic process will produce a spectral component whose shape is a replica of the Fermi-Dirac distribution, which is down-shifted in energy by $h\nu_{\text{vib}}$ and has amplitude determined by the inelastic scattering cross section. When this inelastic component is superposed to the elastic component (i.e., the

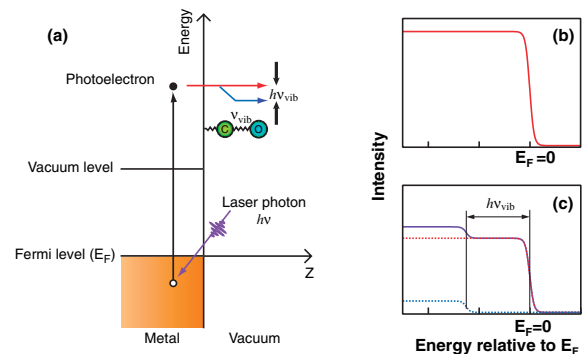


FIG. 1 (color). (a) Schematic energy diagram of the interaction between the molecular vibration and the photoelectron. If there is no interaction between the molecular vibration and the photoelectron emitted from the surface, the spectral line shape is expected to be the well-known Fermi-Dirac distribution curve as shown in (b). When the photoelectron loses its kinetic energy by $h\nu_{\text{vib}}$ through excitation of the molecular vibration, the photoelectron spectrum will show a step at $h\nu_{\text{vib}}$ below E_F as shown in (c). This spectrum consists of two parts: one (red dotted line) describes the photoelectron that is emitted without exciting molecular vibrations; the other (blue dotted line) represents the energy distribution of photoelectrons that has excited the molecular vibration.

usual Fermi-Dirac distribution curve), a step appears at $h\nu_{\text{vib}}$ below the Fermi edge (E_F) in the spectrum [Fig. 1(c)].

Although conceptually simple, the measurement requires careful experimental planning. In a typical electron energy loss spectroscopy (EELS) measurement of CO adsorbed on metallic surfaces, the ratio between the inelastically and elastically scattered components is on the order of 10^{-3} [1,2]. Thus, we expect the height of the step to have this relative level. Since the height of the step is expected to be proportional to the inelastic scattering cross section, we need to maximize the cross section. For this purpose, we want to generate photoelectrons with a very small kinetic energy, so that they will pass through the molecular layer slowly and spend long enough interaction time to produce a large cross section. Thus, we used a tunable laser source and tuned the incident photon energy ($h\nu \sim 5$ eV) [3,4] only several hundred meV above the work function. Then the photoelectron has a kinetic energy comparable to the vibrational energy of the CO molecule. There is an additional advantage in using low energy incident photons, because the photoionization cross section of *s* and *p* atomic orbitals (which make up the electronic states near E_F of Cu) tends to increase with decreasing excitation energy [5].

Previously, various spectral structures have been observed in the core-level photoelectron spectra [6]. For example, an asymmetric line shape due to electron-hole pair excitation and energy loss satellites due to plasmon excitation have been reported. These structures arise from the strong Coulomb potential due to the core hole. In addition, high-resolution core-level photoelectron spectroscopy enables one to measure the internal molecular vibrations of surface adsorbed molecules in the core-ionized state [7,8]. On the other hand, what we have observed in this study is the vibrational energy loss of very low energy photoelectrons excited from the valence band near E_F . For the itinerant valence electron system as in our case, the electron correlation effect is weak. Thus, the vibrational energy determined by the very low energy photoelectron spectroscopy should be identical with that measured by a conventional vibrational spectroscopic technique such as EELS.

We have chosen the CO/Cu(001) system for the first test of our prediction, because the bonding configuration of the CO molecule and the electronic and vibrational levels have been well characterized for this system [1,9–16]. The CO molecules adsorb vertically on the top site of the Cu(001) surface with the C atom attached to the Cu atom [9]. The relation between the CO coverage and the work function of the surface is known [17]. The minimum work function occurs at the coverage of half a monolayer of CO. At this coverage, an ordered $c(2 \times 2)$ structure is formed. There are four vibrational modes: C-O stretching, C-Cu stretching, frustrated rotation (FR), and frustrated trans-

lation (FT). These vibrational energies have been measured by EELS [1,2], infrared reflection absorption spectroscopy (IRAS) [13,14], scanning tunneling microscope inelastic electron tunneling spectroscopy (STM-IETS) [15], and helium atom scattering [16]. Their energies only weakly depend on CO coverage.

The Cu(001) surface was cleaned with repeated cycles of 600 eV Ar ion sputtering and annealing at 500 °C. The CO molecules were dosed on the surface after sample cooling. Our apparatus consists of a Ti:sapphire laser system (2 ps pulse width, 82 MHz) and a hemispherical electron energy analyzer placed in an ultrahigh vacuum chamber. *P*-polarized ultraviolet light generated by frequency tripling the output of the Ti:sapphire laser impinged onto the surface along the direction 54° from the surface normal. We used two photon energies, 4.621 or 5.041 eV, to match the work function shift caused by CO adsorption. The spot size and the continuous wave equivalent power of the laser light at the sample surface were approximately 100 μm in diameter and 30 μW (photon flux of 4×10^{13} photons/sec), respectively. The photoelectrons were measured in the normal emission geometry using a hemispherical electron energy analyzer with energy resolution of 4 meV. To minimize the distortion of the spectrum caused by stray electric and magnetic fields, a bias voltage of -7.0 V was applied to the sample with the analyzer entrance hole grounded. Judging from the laser power dependence of the spectra, we have confirmed that the nonlinear effect and space charge effect did not distort the spectral line shape. The spectral line shape and work function did not change during the measurements, which indicates that damage of the sample surface and desorption of CO molecules by laser irradiation were negligible. All measurements were performed under the ambient pressure of $\sim 2 \times 10^{-11}$ mbar and temperature at 95 K.

Figure 2 shows the photoelectron spectra of the clean Cu(001) and CO/Cu(001) surfaces. These spectra were generated by laser light of $h\nu = 5.041$ and 4.826 eV, respectively. The work function decreases by 0.215 eV ($=5.041 - 4.826$ eV) when the surface is covered by CO. We adjusted the incident photon energy to place the Fermi edge at the same point in the spectrum for the clean and CO covered surfaces as shown in Fig. 2(a). By comparing the work function change with a calibration curve [17], we estimated the CO coverage to be 0.5 monolayer. This estimation is consistent with the low energy electron diffraction result, which showed sharp spots for the $c(2 \times 2)$ surface.

One can see a step at 254 meV below E_F in the CO/Cu(001) spectrum [Fig. 2(b)]. The step does not appear in the clean Cu(001) spectrum. The energy of 254 meV agrees with the vibrational energy of the C-O stretching mode measured by other vibrational spectroscopic techniques [1,12–16]. This agreement indicates that this step arises from the excitation of the C-O stretch-

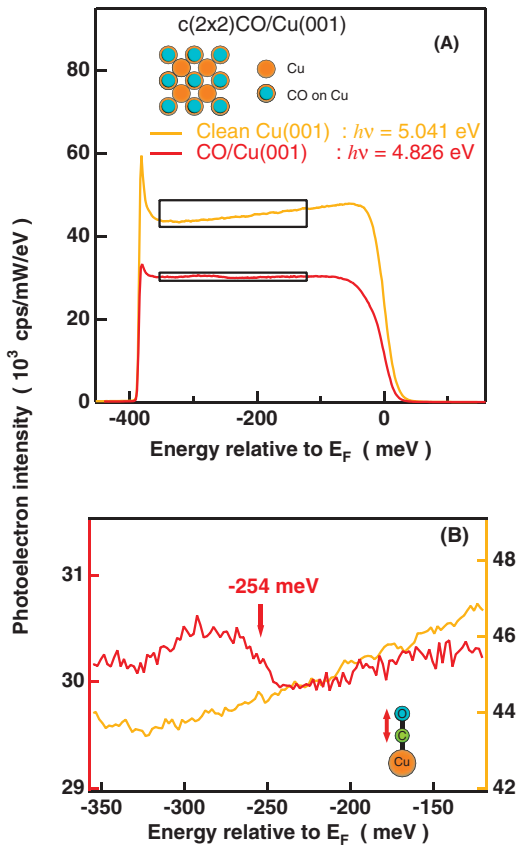


FIG. 2 (color). (a) Photoelectron spectra of the clean and CO adsorbed Cu(001) surfaces. The inset shows the top view of the $c(2 \times 2)$ structure of CO on the Cu(001). (b) Enlarged view of the rectangular areas in (A) to highlight the spectral line shape. Note the presence of a step at 254 meV below E_F for the CO/Cu(001) spectrum, while there is no step in the clean Cu(001) spectrum. This step arises from the C-O stretching vibration of CO on the Cu(001) surface. The corresponding motion of this mode is illustrated in the inset.

ing mode by the photoelectron. Incidentally, a spike structure that appears at the lower cutoff energy arises from the energy loss of photoelectrons by interaction with the image charge, which was already reported in our previous papers [3,4].

Measuring the isotope shift is the most direct way to confirm the vibrational origin of the observed step. The spectra of the $^{12}\text{C}^{16}\text{O}/\text{Cu}(001)$ and $^{13}\text{C}^{18}\text{O}/\text{Cu}(001)$ (Fig. 3) show the step at -254 and -240 meV, respectively. This energy difference is in close agreement with the isotope shift of the C-O stretching mode determined by IRAS and STM-IETS measurements [13,15]. Thus, we have concluded that this step arises from the excitation of the C-O stretching mode by the photoelectron.

As mentioned before, there are three vibrational modes in addition to the C-O stretching mode: C-Cu stretching, FR mode, and FT mode. The corresponding energies determined by other vibrational techniques are 42, 36, and 4 meV, respectively. To examine these low energy vibra-

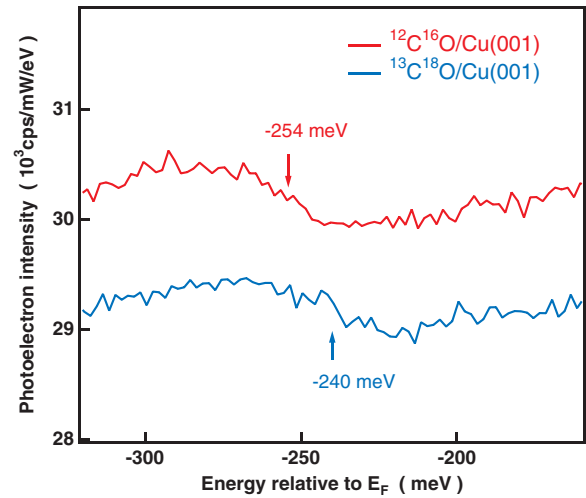


FIG. 3 (color). Isotope shift of the C-O stretching mode observed by using the photoelectron spectroscopy.

tional modes, we need to analyze the spectral line shape near E_F in detail. The spectrum for the clean Cu(001) agrees with a single Fermi-Dirac distribution curve (Fig. 4) [18]. From a simple observation alone, one can see that the spectrum of the CO/Cu(001) is not described by a single Fermi-Dirac distribution curve. To interpret the spectrum of the CO/Cu(001) surface near E_F , we decomposed the experimental spectrum into a sum of two indi-

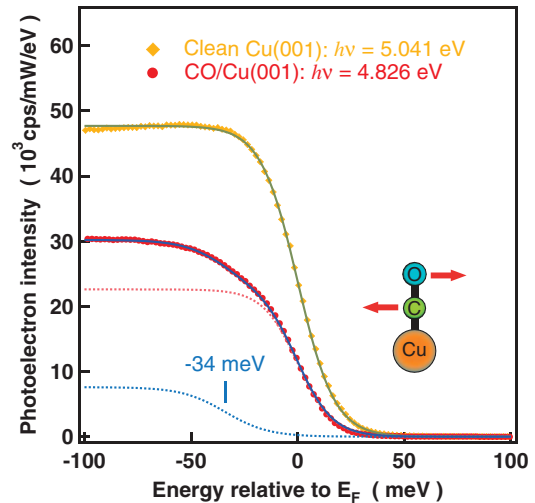


FIG. 4 (color). Photoelectron spectra near E_F for the clean and the CO adsorbed Cu(001) surfaces. The solid curves are the best-fit calculated results. The single Fermi-Dirac distribution function fully reproduces the experimental data for the clean Cu(001) but does not describe the experimental data for the CO/Cu(001). The sum of $f_{\text{FD0}}(E)$ and $f_{\text{FD1}}(E)$ (see text) that are represented by the dotted curves reproduces the experimental data for the CO/Cu(001). The vertical bar shows the energy position of the half maximum point of $f_{\text{FD1}}(E)$. The 34 meV loss is due to the vibrational excitation of the FR mode. The corresponding motion of this mode is illustrated in the inset.

vidual Fermi-Dirac distributions $f_{\text{FD0}}(E)$ and $f_{\text{FD1}}(E)$. $f_{\text{FD0}}(E)$ represents the energy distribution of photoelectrons that excited no molecular vibration (elastic component) and is identical to the function used in the fitting procedure for the clean Cu(001) surface except for the intensity. $f_{\text{FD1}}(E)$ represents the energy distribution of the photoelectrons that excited a molecular vibration. We found that the half maximum point of $f_{\text{FD1}}(E)$ is located at 34 ± 2 meV below E_F . Hence, $f_{\text{FD1}}(E)$ describes the photoelectrons that lost energy by 34 meV. Based on comparisons with previous studies, we assign this 34 meV loss to the excitation of the FR mode. Because of the thermal broadening of the spectrum near E_F , the isotope shift (1 meV) for the FR mode could not be observed.

By a curve fitting procedure, we have evaluated the step height of each inelastic component relative to that of the elastic one. The relative height corresponding to the C-O stretching mode and the FR mode is approximately 0.04 and 0.4, respectively. These values are significantly larger than the relative loss intensity measured by EELS [1], which means that the inelastic scattering cross section of the *slow photoelectron* is significantly larger than that of the electron used in the ordinary EELS experiment. The FR mode is observed in our experiment, while it is forbidden in the EELS experiment with the specular geometry.

In the present stage, we do not have a definitive explanation as to why the cross section is so large. However, we can make a reasonable guess at the cause of this unusually large cross section. First, the electron's path in photoemission is different from that in EELS. In the case of dipole scattering in EELS, the electron feels the Coulomb force above the surface and turns around, presumably without actually touching the surface. In contrast in our photoemission experiment, the very slow electron passes through the layer of vibrating adsorbates. Thus, intuitively, one would think that the electron-vibration interaction is much stronger than in the case of EELS. We think that two factors work together to produce the observed large cross section: a slow electron with long interaction time and the fact that the electron penetrates through the vibrating molecular layer. That the electron penetrates through the molecular layer may also explain the different selection rule; i.e., the electron is not scattered by a distant dipole but by direct overlap of the electron wave functions.

Identification of the remaining two vibrational modes is difficult. The vibrational energy of the FT mode is very low (4 meV), and, hence, the inelastic component corresponding to this mode is buried under the thermal broadening of the spectrum near E_F . The oscillator strength of the C-Cu stretching mode is weaker than that of the C-O stretching mode by a factor of ~ 40 [14]. We expect the step size corresponding to this mode to be smaller than that of the C-O stretching mode by a similar factor. Thus, its observation is difficult under the current experimental conditions. A photoelectron spectroscopy system with a very high reso-

lution [19] may be useful in detecting these vibrational modes.

To conclude, we have measured the low energy photoelectron spectra of the CO/Cu(001) surface excited by laser light. We succeeded in finding the energy loss of photoelectrons by scattering from the vibrational modes of the adsorbed molecule. The energy loss structure appears as a step in the spectrum. Finally, we point out that, in some high-resolution photoelectron experiments, this energy loss process should be taken into account in the interpretation of the details of spectral line shape around E_F .

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