Reemitted-Positron Energy-Loss Spectroscopy: A Novel Probe of Adsorbate Vibrational Levels

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Vibrational excitations of carbon monoxide on Ni(100) have been observed for the first time in the energy-loss spectrum of reemitted positrons. For Ni(100)$c(2\times 2)$CO at room temperature, energy-loss peaks are found at ~ 57 and ~ 248 meV, corresponding to Ni-C and C-O stretching vibrations, respectively. These peak positions are in good agreement with previously reported results for electron energy-loss spectroscopy. Anticipated improvements in resolution promise to make reemitted-positron energy-loss spectroscopy competitive with high-resolution electron energy-loss spectroscopy.

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When a positron is implanted into a metal it loses its initial kinetic energy in a time on the order of a few picoseconds and comes into equilibrium with the bulk sample developing into an extended Bloch-like state. After thermalization, if it was implanted with a low incident energy (<10 keV), the positron can diffuse back to the surface with a relatively high probability before annihilation. Upon its reaching the surface a variety of escape mechanisms are available to the diffusing positron. The study of these positron interactions with surfaces has been developing as a new field, and in some cases the probe-surface interaction provides unique and complementary results to other available surface techniques.[1]

If a metal has a negative positron work function (φ_+ have been measured between 0 and -2.6 eV), one escape mode for a thermalized positron is direct reemission into the vacuum. In most cases the escaping positrons are reemitted in a narrow angular cone normal to the crystal surface and also have a narrow energy spread consistent with the Boltzmann distribution with a mean value of $3k_BT/2$. This process has been compared to a similar escape mode observed for Γ-point electrons emitted from negative-electron-affinity surfaces.[2] However, a fraction of the positrons do experience some energy loss due to inelastic processes at the surface resulting in a broad energy distribution which is surface and temperature dependent.[2]

In this Letter, we describe a study that was undertaken to determine whether vibrational excitations associated with adsorbed molecules could be observed by detection of a characteristic energy loss in the reemitted-positron energy spectra. If detected, one could then compare scattering cross sections with theory as well as assessing the value of reemitted-positron energy-loss spectroscopy (REPELS) as a new surface spectroscopy. By way of example, we chose a system, CO on Ni(100), which has been well studied with electron energy-loss spectroscopy (EELS) thus making it an excellent initial system to study with REPELS.[3]

In order to measure these vibration modes of adsorbed molecules on metal surfaces we constructed a simple hemispherical electrostatic analyzer to measure the reemitted-positron energy spectrum (Fig. 1). The analyzer is mounted in an ultrahigh-vacuum system housing the positron beam[4] and operates at a base pressure of

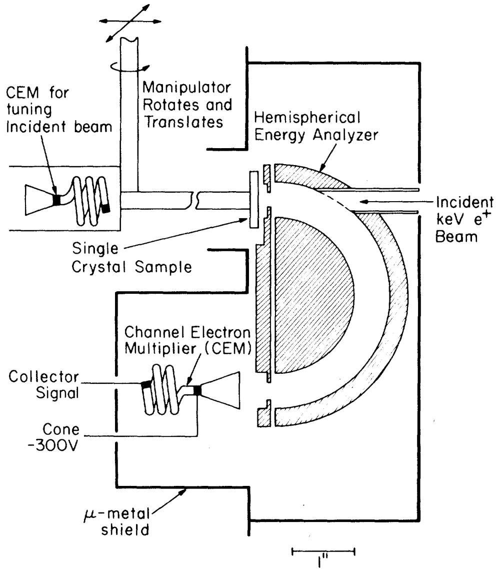

FIG. 1. Apparatus used for the measurement of reemitted-positron energy-loss spectroscopy. The analyzer and sample are contained in a Mumetal shield (heavy line) to reduce magnetic fields.

$\sim 5\times10^{-10}$ Torr. The monoenergetic ($\approx$1-eV) 3-keV positrons are focused onto the Ni(100) sample through an aperture in the outer hemisphere of the analyzer (Fig. 1). The analyzer hemispheres are constructed from oxygen-free high-conductivity Cu,[5] and the aperture is covered with a 97% transmitting grid.[5] To reduce patch effects the inside of the analyzer hemisphere and grid are coated with graphite.[6]

With our present slit arrangement and assuming an isotropic source we calculate our energy resolution $\Delta E/E \simeq 10\%$ which could be significantly improved by minor modifications.[7] In the case of reemitted positrons the resolution ($\Delta E/E$) could be as small as 7% because the positrons are reemitted in a highly forward-directed cone.[2] The analyzer is operated at a constant pass energy (0.7 eV for the data shown in Figs. 2 and 3) and repetitive energy scans are made by ramping a bias voltage between the sample and analyzer. Lower-pass-energy scans were made showing that the resolution of the analyzer was improved at the expense of counting rate. The reemitted positrons transmitted by the analyzer are counted by a channel electron multiplier (CEM) and accumulated as counts in a multichannel scaler. The hemispherical analyzer is housed in a Mumetal box to reduce stray magnetic fields below 3 mG. A second CEM is mounted opposite the sample, which when rotated into the sample position facilitates tuning the incident positron beam.

The single-crystal Ni(100) sample was etched and polished prior to insertion in the vacuum system. The sample was cleaned *in situ* by Ar^+ ion bombardment at 1 keV energy and heat treated at a temperature of 600 °C for ~20 min. After each sputtering–heat-treatment cycle surface cleanliness was monitored with Auger electron spectroscopy (AES). Contamination was kept below 0.05 monolayer as measured with AES; however, it was found that annealing at temperatures greater than 600 °C caused small amounts of sulfur to migrate and segregate on the surface in significant amounts.[8] Very sharp low-energy electron-diffraction (LEED) spots were observed after annealing. After annealing no signal of positron trapping at defects was detected,[1] by measuring the variation of the yield of reemitted positrons versus incident positron energy. CO was adsorbed on the clean Ni(100) surface at a pressure of 2×10^{-8} Torr. The characteristic $c(2\times2)$-CO structure was observed with LEED to reach a maximum in intensity at about 2 L exposure [1 L (langmuir) = 1×10^{-6} Torr sec].[3,8]

Figure 2 shows the full elastic curve,[3] as well as an expanded scale for the as-recorded data for energy-loss spectra of clean Ni(100) and Ni(100)$c(2\times2)$CO. The data shown are the result of a run 10 h long. The counting rate at the elastic peak was approximately 5×10^3 counts/sec. The width of the elastic reemitted positron peak was about 90 meV; the asymmetry of the peak on the energy gain side is attributable to the escape of nonthermal positrons. The half widths at half maximum (HWHM) on the two sides of the elastic peak were found to be 58 and 32 meV energy gain and energy loss, respectively. The first value is larger because of those positrons which are reemitted from the sample before complete thermalization. This fraction can be reduced by simply increasing the incident positron energy. The second value is fully consistent with a thermal spread if we assume a Gaussian energy distribution with an average energy of $3k_BT/2$ for the positron, where $T = 300$ K and k_B is the Boltzmann constant.

The energy-loss peak at 248 meV (first vibrational excitation of CO) appears as a shoulder on the tail of the elastic peak and is of similar width to the elastic peak. The ratio of the loss-peak to elastic-peak intensity after background subtraction was found to be ~0.4%. The ratio was not found to be sensitive to the particular method of background subtraction. For our analyzer the half angle of acceptance is $\approx 8°$ making

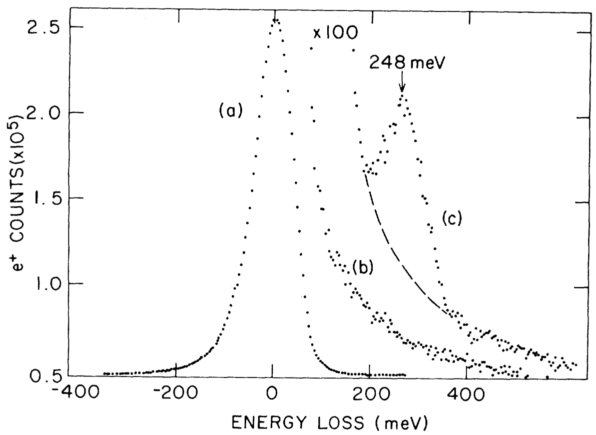

FIG. 2. Curve *a*, raw data for the elastic peak of clean Ni(100). Curves *b* and *c* show an expanded scale (× 100) of the reemitted-positron energy-loss spectra for clean Ni(100) and Ni(100)$c(2\times2)$CO at 298 K. The C-O vibrational energy-loss peak is indicated by an arrow at 248 meV.

possible nearly full collection of the loss-peak intensity with adequate resolution.

In the dipole scattering theory the relative loss intensity is given by[9]

$$\frac{I_v}{I_o} = \frac{4\pi m e^2}{h_2 E_0} \mid \mu_v \mid^2 \frac{n_s}{\cos\alpha} f(E_0, \alpha),$$

where m is the electron mass and E_0 is the primary energy, which in this case is φ_+, as measured from the total reemitted positron energy spectrum.[1] μ_v is the dipole matrix element between vibrational states o and v, n_s is the number of molecules per unit surface area, and α is the angle of incidence. $f(E_0, \alpha)$ is a geometrical factor.[9] Applying these relations strictly to our REPELS experiment taking $\varphi_+ = 1.6$ eV,[10] $\mu_v = (4.09 \pm 0.08) \times 10^{-2} e a_0$,[9] $n_s = 8.06 \times 10^{18}$ molecules/m^2,[5] we calculate I_v/I_o to be $\sim 1 \times 10^{-2}$.

The major difference in the relative loss intensity between REPELS and EELS is that the reemitted positrons traverse the CO molecule once, whereas in an EELS experiment electrons have two chances to interact, approaching and departing from the surface. Therefore after modifying the relative loss intensity (I_v/I_o) by $\frac{1}{4}$ for positrons (i.e., the scattering cross section is the square of the scattering amplitude for coherent scattering), we find that the results agree to less than a factor of 2. No significant difference between positrons and electrons is expected in the intensity ratio for dipole scattering.

Figure 3 shows the ratio of peak normalized positron counts for Ni(100)c(2×2)CO to clean Ni(100). This figure indicates the presence of a 57-meV loss peak in addition to the 248-meV peak already discussed. The 57-meV loss feature is attributed to the Ni-C stretching mode as previously described by Andersson.[3] Although the presence of this peak is conclusive, its relative intensity to the 248-meV peak is highly dependent on the coincidence of the two spectra at zero energy loss before the division of the two normalized spectra. The scatter in the data at energy loss greater than 400 meV is due to the low statistics of the data in this region; therefore we were not able to resolve the overtone peak at 496 meV.

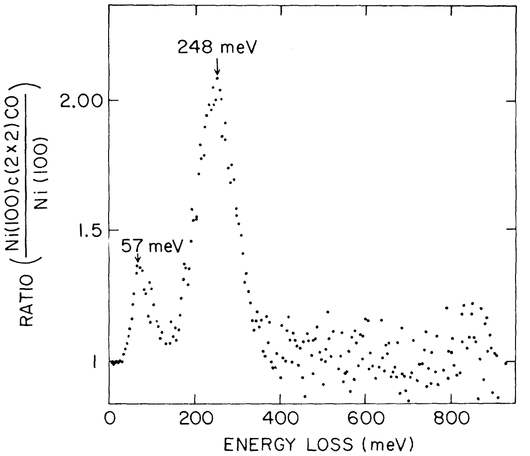

FIG. 3. Ratio of the normalized peak counts in the Ni(100)c(2×2)CO to clean Ni(100) positron-loss spectra. The Ni-C stretch is indicated at 57 meV and the C-O stretch at 248 meV.

In conclusion our data have demonstrated the existence of vibrational energy-loss features in the reemitted-positron energy spectrum. REPELS has fundamental differences from EELS in that the sample itself provides the source of positrons. It is interesting to note that EELS cannot look in the forward scattering direction for specular reflection. For short-range energy-loss processes (impact theory)[11] REPELS allows the exclusion of the exchange interaction in cross-section calculations. It should be noted that positrons that are polarized do not lose their polarization upon thermalization[12] which should be useful for systems in which the impact theory dominates. In molecules with unpaired spins and exhibiting impact energy loss such as nitric oxide (NO) the scattering cross section will have a polarization dependence. Of course this will require a positron polarization analyzer.

The narrowing of the thermal distribution has already been verified in a magnetically guided positron beam apparatus at high temperatures [unpublished data for Ni(100)] and at low temperatures (~40 K) for Cu(111)+S. As shown by Kubica and Stewart[13] positrons thermalize in metals to nearly liquid He temperatures. Thus, by lowering the sample temperature to ≈10 K and increasing the implant energy we hope to improve our energy resolution to ≈ 2 meV. This lower temperature should also make the reemitted beam almost completely normal to the sample, enabling the analyzer to be operated at very low pass energies with little blowup of the reemitted beam due to deceleration. It is worth noting that Schultz and Lynn[14] found that the inelastic fraction, those positrons in the energy-loss side of the peak, decreased with decreasing sample temperature for Cu(111). If this holds true in general, the lower-temperature experiments should also have a lower background than the present results.

Angle-resolved studies (i.e., nonspecular EELS) can easily be performed by simply rotating the sample with respect to the analyzer. Finally REPELS has been shown to be a new surface spectroscopy which will also provide complementary results to EELS.

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