

High-resolution electron-energy-loss spectroscopy: Relationship between loss intensity and coverage

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Depending on the primary energy a strong disproportionality has been observed between the relative loss intensity and the CO coverage on Ni(111) in high-resolution electron-energy-loss spectroscopy for dipole scattering (specular reflection). By consideration of the two-step scattering process that has been theoretically derived in the quantum-mechanical treatment of dipole scattering, it can be shown that this effect is caused by specific variations of the reflectivity as a function of coverage and primary energy. It therefore turns out that the data also prove the validity of the quantum-mechanical treatment of the dipole-scattering process experimentally in more detail.

INTRODUCTION

According to theory in dipole scattering the relative loss intensity of a characteristic mode should be proportional to the product $\mu_i \Theta_i$, with μ_i the dynamic dipole moment of an adsorbate on the adsorption site i , and Θ_i the relative coverage of this site.¹⁻⁴ It has been shown theoretically⁵⁻⁸ that disproportionalities between coverage and relative inelastic intensities may occur due to changes of the dynamic dipole moments at high coverages caused by dipole-dipole interactions or by structural phase transitions at or after exceeding a critical coverage.^{5,7} Changes of the dipole moments may also be accompanied by changes of the vibrational frequencies.⁵⁻⁷

The application of these theoretical results generally does not yield reliable quantitative predictions on the relative loss intensity as a function of coverage. Such a relation therefore needs to be established experimentally. This can be done, for instance, by comparing the relative loss intensities with flash desorption data obtained from equivalent coverages, yielding a relative measure between the two quantities. Information on absolute calibration can be obtained from known low-energy electron diffraction (LEED) superstructures.

In the present study on CO/Ni(111) this procedure has been used for coverages $\Theta > 0.40$. For smaller values we used the peak shift of the on-top stretching mode which has been found to be directly proportional to coverage⁹⁻¹¹ for $\Theta < 0.45$.¹¹

Depending on the primary energy used this calibration procedure revealed a strong disproportionality between coverage and high-resolution electron-energy-loss spectroscopy (HREELS) loss intensities in dipole scattering on CO/Ni(111). It will be shown in the present paper that this effect can be explained satisfactorily by considering the two-step scattering model derived by Mills¹ in a theoretical description of dipole scattering.

EXPERIMENTAL

The data that we report in this paper have been measured using a combination of an EELS spectrometer with

a nozzle beam source in order to do time-resolved EELS measurements on adsorption systems. Since the apparatus and our technique of taking time-resolved data have been previously described,^{11,12} only some characteristic features of the system will be mentioned here. For further details we refer the reader to these sources. During the EELS measurement the temperature of the sample can be varied between 90 and 800 K, or kept at a fixed temperature within that range for taking isothermal data with a long-term stability of $\pm 0.5^\circ$. The maximum nozzle beam flux corresponds to 0.3 L/sec (1 L = 10^{-6} mbar sec) producing a background pressure of less than 10^{-9} mbar. In the pulsed mode, the molecular pulses have a rise time of less than 10^{-2} sec, which determines our time resolution.¹³ In the case of investigating reactive systems the desorbing species can also be simultaneously analyzed as a function of time by mass spectroscopy using a mass spectrometer mounted in the specular direction to the molecular beam source.¹³ This description has been given to clarify the experimental approach. However, in order to obtain the data presented in this paper, the nozzle design is primarily used to facilitate continuous surface dosing with low background pressure simultaneously to the HREELS measurements.

RESULTS

Figure 1 shows the development of the two stretching modes versus time and frequency in response to a CO pulse which is also indicated schematically. For the interpretation and assignment of the loss peaks of this adsorption system, the reader is referred to Ref. 11. The intensities have been normalized to the no-loss peak intensity according to

$$I_{\text{rel}}(\hbar\omega) = \frac{I(\hbar\omega)B(\hbar\omega)}{I(0)B(0)}$$

with $B(0)$ and $B(\hbar\omega)$ being the full widths at half maximum of the no-loss peak and a peak at a loss energy of $\hbar\omega$, respectively. It should be noted that all intensities are measured in the specular direction with an acceptance angle specified by our spectrometer that is assumed

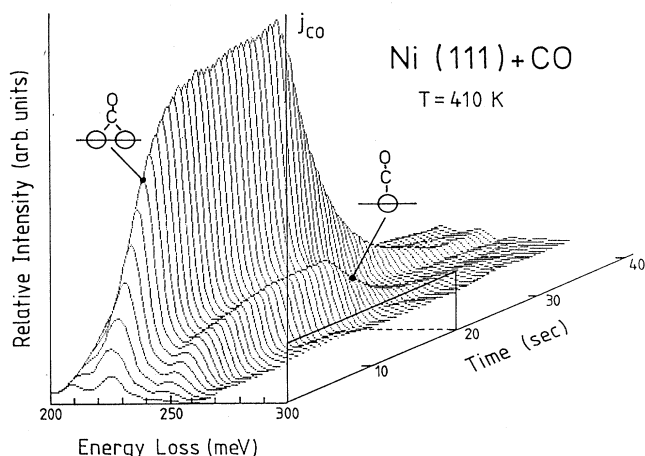


FIG. 1. Three-dimensional loss profile of the two stretching modes of CO on Ni(111). The low-energy loss corresponds to CO on bridge sites and the high-energy loss to CO on on-top sites.

to be comparable to the angular full width at half maximum (FWHM) of the no-loss peak (about 3°). The primary energy used for this experiment was 10 eV.

Figure 2 shows a comparison between the integrated relative loss intensities as shown in Fig. 1 and the shift of the frequency of the on-top position (position of the maximum of the "on-top peak"). It can be seen that the peak position is obviously a linear function of the integrated loss intensity and since it has previously been shown by other groups^{9,10} and by our own measurements¹¹ that the frequency shift is linear with coverage, Fig. 2 clearly demonstrates that the loss intensity can also be used as a relative measure of the CO coverage on Ni(111) under experimental conditions as indicated in the figure.

Searching for an optimum primary energy for Ni(111)/CO we noticed a strong dependence of the no-loss peak intensity on primary energy and coverage. This dependence is demonstrated in Fig. 3, where no-loss peak intensities are plotted versus ambient CO pressures for

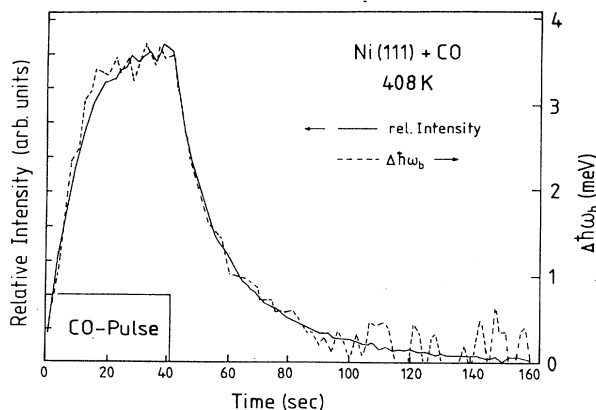


FIG. 2. Comparison of frequency shift of bridge stretching mode and integrated relative loss intensity vs time as response to the CO pulse schematically indicated.

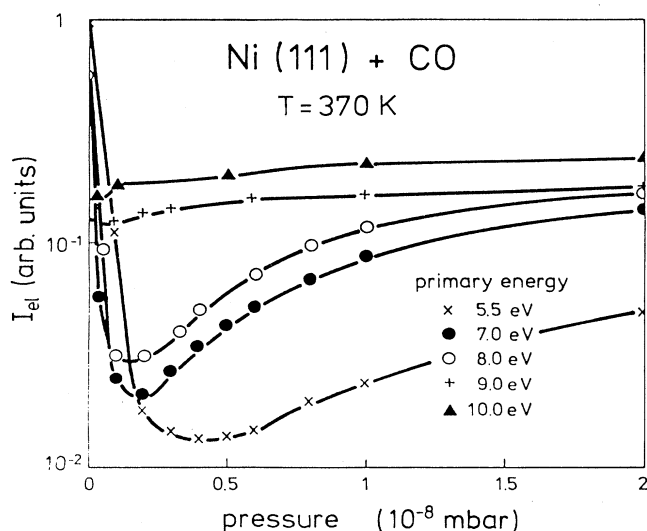


FIG. 3. Behavior of the elastically reflected current as a function of primary energy and coverage. The change of coverage results from the competition of adsorption and desorption as steady state at the given CO pressure and temperature.

several different primary energies at a sample temperature of 370 K. At that temperature there already occurs appreciable desorption, so that the corresponding coverages are given as steady-state values as determined by competition between adsorption and desorption.¹¹ The intensities are given as the measured peak height times the FWHM using a fixed sample current of 1×10^{-10} A. The angular integration is again given by the analyzer acceptance angle only. We did not observe any significant dependence of the angular FWHM on primary energy and coverage, however an investigation of the elastic background at larger scattering angles has not been carried out.

In order to rule out a maladjustment of the spectrometer due to the change of the work function during CO adsorption ($\Delta\phi_{\max} \approx 1$ eV),¹⁴ the spectrometer adjustment was controlled at each data point. As can be seen, the change of the elastic intensity is very drastic. The most interesting feature, however, is the minimum occurring in all curves shifting to smaller coverages and higher levels with increasing primary energy. This causes an intersection of any two neighboring curves. In regard to a possible interpretation of this dependence it is important to notice that the shown behavior of the no-loss intensities is essentially repeated if one increases the primary energy above 10 eV. That means with $E_p = 16$ eV there occurs again an absolute minimum like that with 5.5 eV.

In order to see whether this coverage dependence of the no-loss intensity had any effect on the relative loss intensities, we carried out measurements of the kind as shown in Fig. 1 with $E_p = 5$ eV. A comparison of such data and those taken with $E_p = 10$ eV at 383 K is shown in Fig. 4. As can be clearly seen the two curves differ drastically. The 5-eV curve exceeds the 10-eV curve at small intensities and becomes smaller in the high-intensity range with a strong structure near the intersec-

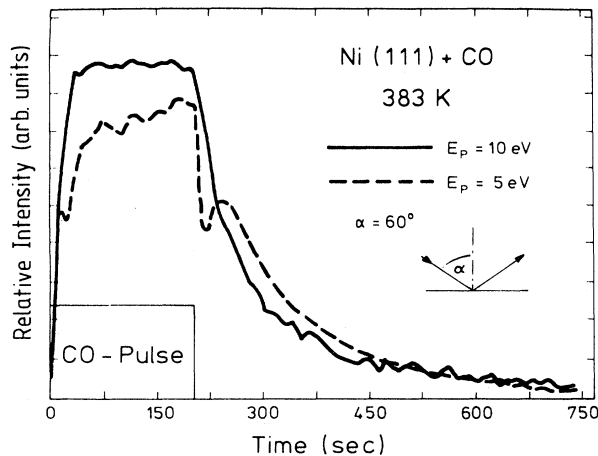


FIG. 4. Comparison of relative loss intensities of the bridge stretching mode measured with 10 and 5 eV primary energy vs time as response to the CO pulse indicated.

tion region. The intersection of the two curves occurs at about $\Theta = \frac{1}{3}$.

Following the arguments given before, it becomes obvious that the relative loss intensities of the 5 eV cannot represent the CO coverage at all in contrast to the 10-eV curve.

In the following we shall try to give an explanation for the observed difference of the two curves.

DISCUSSION

Since for both energies the excitation of the stretching modes of CO on Ni(111) is strongly dominated by dipole scattering, which we verified by off-specular measurements, the relative inelastic scattering intensity should be proportional to an expression given by Mills:¹

$$I(\hbar\omega)/I_{el} \approx \mu(\Theta)\Theta[1 + |\Delta|^2 - (4/\pi)\text{Im}(\Delta)\cos\alpha]/\sqrt{E_p}$$

with $\Delta = (R_I - R_S)/(R_I + R_S)$. (1)

R_I and R_S are the complex reflectivity coefficients before and after the inelastic event, respectively. $\mu(\Theta)$ is the dynamic dipole moment of a single adsorbate and Θ the relative coverage, E_p is the primary energy, and α is the angle of incidence. It should be noticed that Eq. (1) describes the dipole scattering as a two-step process (see Fig. 5), resulting from fully quantum-mechanical treatment of the problem. For further details we refer the reader to Ref. 1.

Except for the primary energy, the two contours shown in Fig. 4 are measured under identical conditions. It therefore should be reasonable to look for parameters in Eq. (1) which may depend on coverage and primary energy as well. These are the reflectivity coefficients R_I and R_S .

The variation of the elastically scattered intensity in the specular direction may be explained by the so-called static Debye-Waller factor. However, in this case we would only observe a monotonous energy dependence for a given coverage. On the other hand, variations of the

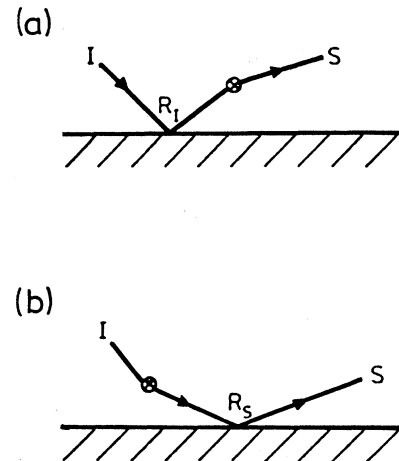


FIG. 5. Schematics of the two-step scattering process dominant in dipole scattering. The inelastic event occurs in both cases above the surface. In case (a) it occurs after the elastic reflection, in case (b) prior to the elastic reflection.

reflectivity at primary energies below 40 eV are characterized by I - V LEED measurements as LEED fine structures or electronic surface resonances.¹⁵ They appear as maxima of the reflectivitylike Rydberg series about 5–10 eV below each energy at which a new beam emerges from the surface. According to a model proposed by Thurgate *et al.*¹⁶ these variations are explained by a surface potential layer in which the wave field of the ingoing and outgoing electrons may interfere with the field of those electrons that are bound in resonance states localized perpendicular to the surface but moving parallel to it. Within this model it is easy to understand that every change of the potential layer may also change the conditions controlling the LEED fine structures. Such changes may be induced by an adsorbate. We also assume that the change of the intensities of the no-loss peak with coverage as shown in Fig. 3 may be explained by this model.

In order to explain the differences between the relative loss intensities shown as the two contours in Fig. 4 we apply Eq. (1) to the 5-eV curve in an even more simplified form. That means we neglect any possible phase difference between R_I and R_S so that the relative inelastic intensity I_{in}/I_{el} will become proportional to

$$\frac{I_{in}}{I_{el}} \propto \frac{1}{2} \left| 1 + \frac{|R_S(\theta)|^2}{|R_I(\theta)|^2} \right| \theta \mu(\theta) \quad (2)$$

with $R_I(\Theta) = R(\Theta, E_{prim})$ and $R_S(\Theta) = R(\Theta, E_{prim} - \hbar\omega)$.

Thus, if the ratio of $|R_S|^2$ and $|R_I|^2$ is known, Eq. (2) defines a correction for the inelastic intensity. Assuming that the normalized elastic intensities as defined previously are proportional to the reflectivity, we measured those values directly versus time with constant CO flux for primary energies of 5 and 4.77 eV corresponding to the frequency of the stretching modes $\hbar\omega \approx 225$ meV (see Fig. 1). The data are shown in Fig. 6. The corresponding coverages are determined separately.

In Fig. 7 a comparison of the two contours as given in

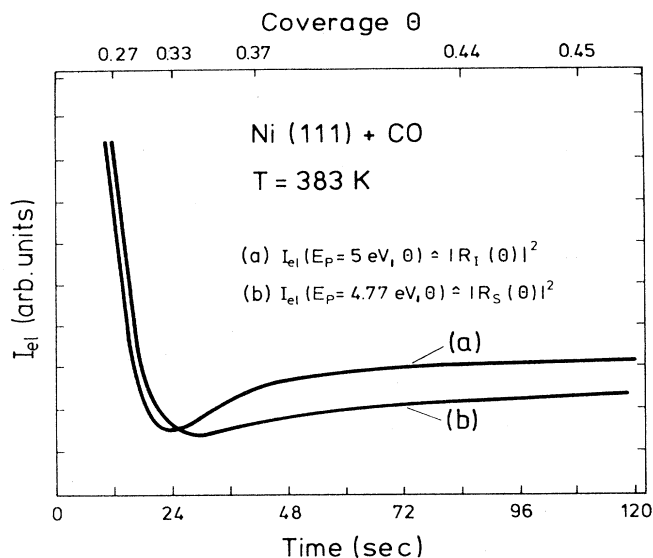


FIG. 6. Measurement of the elastically reflected intensity vs time at constant CO flux for two different primary energies.

Fig. 4 is represented with the 5-eV contour corrected according to Eq. (2) using the data of Fig. 6 as input. Only the steady-state level has been fitted to achieve the excellent agreement between the two curves.

Considering the values of $1 + |R_S|^2/|R_I|^2$, the origin of the structure in the 5-eV contour in Fig. 4 becomes understandable. The reason for this is the abrupt change of the ratio $|R_S|^2/|R_I|^2$ from values larger than 1 to values below 1 at the intersection point of the two curves in Fig. 6 occurring at $\Theta \approx 0.36$.

CONCLUSION

From the agreement between the two curves in Fig. 7 it can be concluded that the observed deviation of the uncorrected, original contour of the 5-eV measurement (Fig. 4) is not caused by a change of the dipole moment $\mu(\Theta)$ but only derives from the dependence of the elastic intensity on coverage and primary energy. This indicates that, within the limit of experimental accuracy, the dynamic dipole moment is constant for coverages below 0.4. This is very surprising in regard to the unusual strong frequency shift with coverage observed for the on-top stretching mode of CO on Ni(111). In regard to a reproducible calibration of the relative loss intensities in HREELS it can be stated that it might generally be most favorable to look for a primary energy at which the no-loss intensity has the smallest coverage dependence. This is the case for CO on Ni(111), for $E_p \approx 10$ eV.

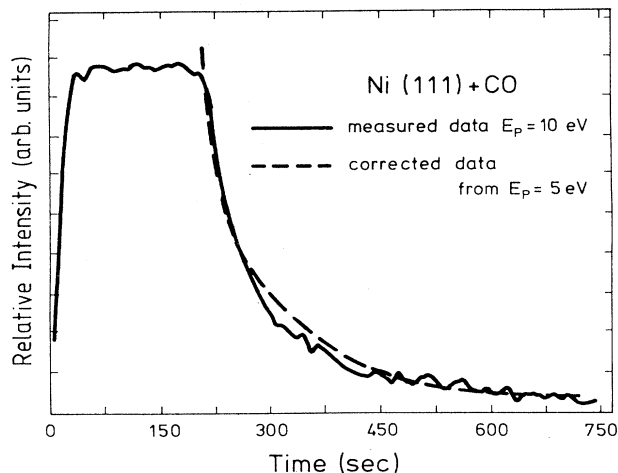


FIG. 7. Comparison of the 10-eV measurement and the corrected 5-eV measurement.

Besides these findings concerning the experimental calibration of loss intensities, the present study unambiguously demonstrates the validity and the necessity of the quantum-mechanical treatment of the dipole scattering theory showing the existence of the two-step scattering process and describing its effect on the inelastic cross section. This is in fact the only difference between the fully quantum-mechanical and semiclassical or classical treatments. In the latter cases the electron is treated as a point charge.¹⁷⁻¹⁹

It should be mentioned finally that the procedure described above may yield experimental information on the energy and coverage dependence of the phase of the reflectivity coefficient since the generally complex coefficients R_I and R_S may cause interference effects within the wave field in the vicinity of the surface. This, however, would require a much more detailed investigation than that of the present study. In this case also the behavior of the loss intensities of the metal vibration modes should be included, since it can be expected that their ($R_I - R_S$) difference should be much smaller and thus be more likely to cause constructive interference effects.

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