

## **BREMSSTRAHLUNG ISOCHROMAT SPECTROSCOPIC STUDY OF THE SYSTEM CO/Ni(110): STRONG INTERMOLECULAR INTERACTION**

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Adsorption of CO on Ni(110) at monolayer coverage results in a  $(2 \times 1)$  p2mg overlayer structure with the CO molecular axis tilted by  $15^\circ$ – $20^\circ$  with respect to the surface normal. The low symmetry of the overlayer leads to splittings of all CO-derived levels at the center of the Brillouin zone. As a result of the high coverage and the concomitant strong lateral interaction between the CO molecules the level splittings are as large as 2 eV for both occupied and empty CO-derived levels. The same order of magnitude has been estimated from tight binding calculations for a free unsupported CO layer in p2mg structure.

### **1. Introduction**

With the development of inverse photoemission or bremsstrahlung isochromat spectroscopy (BIS) [1] as a method for probing the unoccupied electron-energy levels at surfaces now a set of questions about, e.g., bonding of

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molecules to surfaces and intermolecular interactions within the adsorbate – well studied by photoelectron spectroscopy (PES) [2] – may be addressed using BIS.

The CO adsorption system is due to the wealth of information from PES on this system particularly well suited for BIS studies. In PES the occupied CO-derived levels of the adsorbate, i.e., CO  $5\sigma$ , CO  $1\pi$ , and CO  $4\sigma$  levels are observed, and from their relative positions, level splittings, and sign and size of level dispersions information on CO–substrate binding, adsorbate symmetry, and intermolecular interaction is gained, if neutral ground state and final cation state properties are properly taken into account in the analysis [2–4].

The recent observation of a well-defined CO  $2\pi$ -derived feature in BIS spectra from chemisorption systems CO/Ni(111) [5], CO/Cu(110) [6], CO/Cu(100) [7], CO/Pd(111) [8], and CO/Pd(100) [9] proving the positive electron affinity of the system, now allows additional insight to be gained into substrate–molecule bonding not available through PES.

Since in most theoretical models for CO chemisorption [10–14] the participation of the unoccupied CO  $2\pi$  level in the chemisorptive bond is an important ingredient, BIS measurements are expected to put these theoretical models on a firm experimental basis. Studies on the variation of the CO  $2\pi$ -level position as a function of the molecule–metal bond strength, for example, should be useful for investigating the mechanism of the stabilization of the affinity level with respect to gas phase CO, and thus extract information on the CO  $2\pi$ –metal interaction. Similar to PES, two contributions have to be considered here, namely bonding interaction in the ground state and relaxation in the final anion state [7] (as opposed to cation relaxation in PES).

In PES and BIS both, initial and final state energetics are basically determined by two factors, i.e., molecule–substrate and intermolecular (direct and indirect) lateral interactions [4].

In the present BIS study of a CO overlayer on Ni(110) we concentrate on the latter aspect and report the sofar clearest evidence for lateral interactions between adsorbed molecules [15]. The system CO/Ni(110) was chosen because at 300 K the system orders in a  $(2 \times 1)$  p2mg structure with coverage  $\theta = 1$  [16]. This phase shows the sofar largest and most complete CO level-derived dispersions in PES [17]. Effects of lateral interaction on the BIS spectra should therefore be most pronounced in this system. In accord with this expectation we find a 3.5 eV wide CO  $2\pi$ -derived signal at normal incidence, which is composed of at least three components as indicated by distinct shoulders. At low CO coverage, on the contrary, the  $2\pi$  feature has a substantially smaller width of 2 eV. Since we are able to provide a detailed, satisfactory theoretical analysis of the lateral interactions and the dispersions as observed with PES [17] we transfer the analysis to the interpretation of the BIS results.

The paper is organized as follows: In section 2 we briefly describe some details of the BIS experiment. In section 3 we present our results and a

detailed discussion on the basis of band structure calculations on occupied states of a p2mg CO overlayer. Section 4 finally contains a synopsis.

## 2. Experimental details

Bremsstrahlung isochromat spectroscopy is based on the radiative transition whereby an electron incident on the sample surface is decelerated and occupies transiently an empty state above the Fermi level. The experiment was carried out in an ion-pumped UHV system with a base pressure below  $2 \times 10^{-8}$  Pa. The nickel crystal was mounted on a holder which allowed rotation about a vertical axis to place the crystal in different positions for preparation and analysis such as ion etching, LEED, and AES. The crystal could be cooled to 120 K. In order to reach this temperature with liquid nitrogen cooling a rigid mounting of the sample on the holder was inevitable. This restricts the BIS measurements to normal incidence. The BIS spectrometer has been described previously [18–20]. For normal incidence work it offers two different photon-detection geometries. Comparative studies of data collected in these two geometries allow one to identify polarization effects which in turn can be used to derive information on the symmetry of the final (anion) state involved in the radiative transition.

## 3. Results and discussion

Very recently, Behm et al. [16] reported a combined LEED and TPD study on the CO/Ni(110) system showing the existence of several phases as a function of coverage. At 130 K, a  $(2 \times 1)$  LEED pattern was observed corresponding to a coverage of  $\theta = 1$ . Using the combined information from LEED [16], metastable quenching spectroscopy [21], electron-stimulated desorption [22] and our PES study [17] a  $(2 \times 1)$  p2mg structure, with glide plane along  $(\bar{1}10)$  direction on the surface has been derived. The CO molecules are tilted from their canonical perpendicular adsorption geometry [16,17,21,22] alternating to either side of the glide plane, so as to avoid the strong intermolecular interactions in a perpendicular arrangement (intermolecular separation 2.5 Å). In the present paper we restrict the discussion to  $\bar{\Gamma}$ , since BIS spectra could only be obtained for normal incidence. Fig. 1 schematically shows the dispersion of the occupied  $1\pi$  bands in the p2mg structures as taken from ref. [17], neglecting  $5\sigma-1\pi$  hybridization. The important result is the splitting of the CO-derived levels at  $\bar{\Gamma}$  due to the presence of two molecules per unit cell induced by the alternating tilt of the CO molecules. We consider in the present context the splittings of the  $1\pi$  levels at  $\bar{\Gamma}$ . This is a consequence of the rather low  $C_{2v}$  symmetry of the adsorption system. The  $\pi$  splitting in

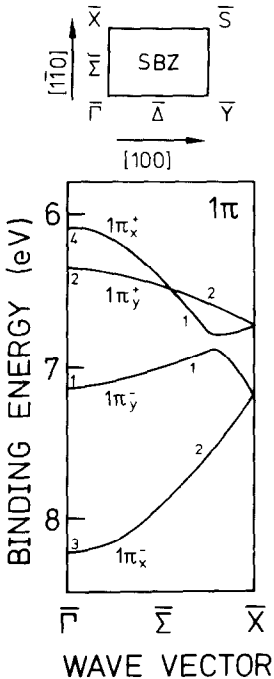


Fig. 1. Calculated  $1\pi$  dispersion along  $\Sigma$ .

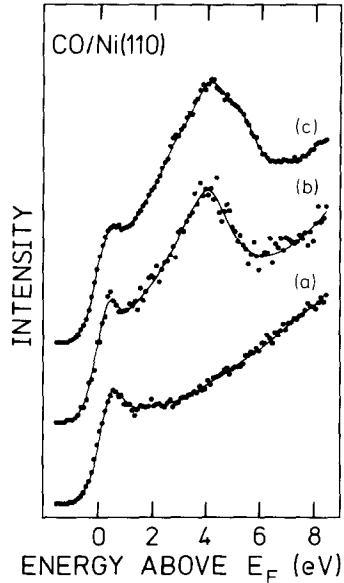


Fig. 2. BIS spectra of clean and CO-covered Ni(110) surfaces at normal incidence in mirror geometry: (a) clean surface, (b) low CO coverage, (c)  $(2 \times 1) p2mg$  CO/Ni(110) structure at high coverage ( $\theta = 1$ ).

this case is not substrate induced, as has been proposed for the case of CO overlayers on Co(0001) [4], but it would already exist in a hypothetical, free, unsupported, CO layer with a  $p2mg$  structure. Qualitatively, this can be easily understood. We can think of the molecular  $1\pi$  level as being composed of a component along the glide plane ( $x$ ) and one perpendicular to it ( $y$ ). Due to the closer packing of CO molecules along the glide plane (110) as compared to the direction perpendicular to it (100) the two components are not degenerate, i.e., the occupying electrons experience different Coulomb interactions. Furthermore, the overlap of the  $1\pi$  components along (110) is larger than along (100). Therefore, the splittings of the two  $\pi$  components are different too. The  $1\pi_y$  components are split into a  $+$  and a  $-$  component by a smaller amount than the  $1\pi_x^+$  and  $1\pi_x^-$  component as indicated in fig. 1. The center of gravity of the complete  $1\pi$  band system, as derived by simple tight binding arguments is near to the position of the  $1\pi_y^-$  band. The overall splitting of the  $1\pi$  bands as deduced from the present PES data amounts to  $\sim 2.2$  eV [17]. From our discussion of the interaction within the  $1\pi$  levels manifold it is easy to imagine

that in particular the  $1\pi_x^\pm$  splittings (components along (110)) are very sensitive to changes in the tilt angle. The overlaps decrease much more rapidly as a function of the tilt angle than according to a sine law, since the separation between oxygen atoms increases. The fact that the molecular  $1\pi$  wavefunction derives predominantly from atomic oxygen wavefunctions accentuates this effect. We have calculated the  $1\pi_x^\pm$  splitting as a function of the tilt angle and by comparison to experiments we can estimate the tilt angle of the CO molecules to be between  $15^\circ$  and  $20^\circ$ . Fig. 2 shows three BIS spectra taken at normal incidence and in mirror geometry, i.e., at  $\bar{\Gamma}$ , for the clean surface (a) and two different CO coverages (b and c) on the Ni(110) surface. The clean surface (spectrum) shows only a feature close to the Fermi energy (which is used as the reference zero). We conclude that the metal has no density of unoccupied states higher than  $\sim 1$  eV above the Fermi energy at  $\bar{\Gamma}$ , in agreement with band structure calculations of bulk Ni [22]. If we expose the surface to 1 L CO, spectrum b is obtained. A well-defined feature of about 2 eV width is observed. The maximum is situated about 4 eV above the Fermi level. The peak has a pronounced asymmetry towards the Fermi level. It is not clear what the cause of the observed asymmetry is, but since we are not certain about ordering of the adsorbate phase at low coverage (diffuse LEED) the asymmetry might be caused by simultaneously ordered and disordered parts present in the adsorbate layer. On the other hand, if we assume that the asymmetry is caused by an extra peak closer to the Fermi energy, the asymmetric line resembles the double peak CO  $2\pi$ -derived feature observed for the  $c(7\sqrt{2} \times \sqrt{2})$  structure on Cu(100) with altered peak intensity ratios.

However, we cannot use the explanation given for the CO–Cu adsorbate [7] in the case of Ni(110) since there is no density of unoccupied metal states in the region of the CO-induced feature that could hybridize. In order to resolve questions of this nature it could be important to study the BIS CO  $2\pi$ -derived peak width as a function of the long-range order in the overlayer.

Turning to spectrum c in fig. 2, which corresponds to a coverage  $\theta = 1$  and a  $(2 \times 1)$  p2mg structure characterized by a sharp LEED pattern, we find a drastic change in the spectral shape. A very broad (half width  $\sim 3.5$  eV) feature with two pronounced shoulders is observed. The peak maximum is situated at 4.1 eV and the two shoulders show up at 2.9 eV and at 5.3 eV. This suggests that it may be a superposition of several overlapping lines. In order to investigate this hypothesis more thoroughly the emission feature was first isolated by subtracting a parabolic background fitted to the experimental data in the range 6.5–8 eV. The difference was then analyzed in terms of up to four Gaussians of identical width. The width was taken from the  $2\pi$  emission of CO adsorbed to Ni(111) at low temperature which is essentially Gaussian with variance  $0.35$  (eV) $^2$ . The amplitudes and energy positions of the Gaussians were free-fit parameters. The result of this procedure was that three Gaussians were necessary to reproduce the data nearly perfectly. Experience showed that

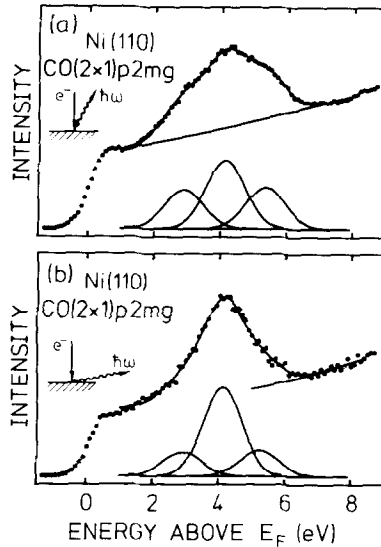


Fig. 3. BIS spectra of the  $(2 \times 1)$  p2mg CO/Ni(110) structure at normal incidence. Full lines represent the result of a line fit in terms of three Gaussians. The background assumed is indicated. (a) In mirror geometry. (b) Light collection along surface normal.

a fourth Gaussian had only negligible amplitude and led to negligible improvement in the overall fit. Moreover, the amplitudes of the first three peaks were hardly affected. Fig. 3a shows the result of the three-line fit. The width of the  $\text{CO } 2\tilde{\pi}$ -derived emission in the p2mg structure is very large. Since it is known from EELS studies [24] that there is only one bonding site present in the p2mg structure, we attribute the width and the fine structure to splittings introduced by the band structure of the CO overlayer. At first sight the overall splitting of the three components of 2.4 eV seems to be unreasonably large. However, comparison with the PES results [17] substantiates this interpretation: The  $\text{CO } 1\tilde{\pi}$ -derived splitting at  $\bar{\Gamma}$  has been measured to be 2.2 eV (see fig. 1) due to the strong lateral interaction and the low symmetry of the layer.

The value of 2.4 eV for the  $\text{CO } 2\tilde{\pi}$ -derived level is of similar magnitude. It is not expected to be exactly the same due to the different shape and the higher diffuseness of the  $\text{CO } 2\tilde{\pi}$ -derived wavefunction as compared to the  $\text{CO } 1\tilde{\pi}$ -derived wavefunction. In order to qualitatively determine the splitting that can be expected for the  $\text{CO } 2\tilde{\pi}$ -derived levels we have determined the  $\text{CO } 2\pi$  band structure of a free unsupported CO overlayer in p2mg symmetry using a tight binding method [4]. The band dispersions are very similar as in the case of the  $1\tilde{\pi}$  levels and the overall splitting at  $\bar{\Gamma}$  amounts to 2.15 eV. We have neglected in this calculation, in contrast to the one for the occupied bands, interaction of CO with the substrate and final state effects. Therefore, we only use the fact

that the calculated value is of the proper order of magnitude as additional support for our interpretation that the observed fine structure is due to lateral interactions.

Further evidence comes from fig. 3b. The adsorbate has been prepared using the same conditions as for the spectrum in fig. 3a, but the photons are collected in a different geometry (see experimental part). In this geometry,  $x$ ,  $y$ -polarized photons contribute dominantly to the spectrum while the mirror geometry is equally sensitive to  $z$  polarization. Since in either geometry the azimuthal dependence is averaged out,  $x$  and  $y$  polarization cannot be separated. Clearly, the shape of CO  $2\tilde{\pi}$ -derived emission in the BIS spectrum has changed. The decomposition, shown in fig. 3b, shows the reason for the change. The relative intensity of the central line has increased indicating different symmetries for the state giving rise to the line at 4.1 eV as compared to the states causing the lines at 2.9 and 5.3 eV. We would like to emphasize that the same peak positions were obtained in this independent least squares fit.

Such a behaviour should be expected if the various lines are caused by the sub-bands of a CO  $2\tilde{\pi}$ -level-derived band structure, since the bands have different symmetry at  $\bar{\Gamma}$ . A more in-depth analysis of the polarization behaviour would need a detailed calculation of the CO  $2\tilde{\pi}$ -derived band structure including interaction with the substrate. Also, non-normal incidence experiments are necessary to arrive at farther reaching conclusions.

#### 4. Synopsis

The present study shows BIS results on the system CO/Ni(110) at coverage  $\theta = 1$ . The adsorbate layer orders in a  $(2 \times 1)$  p2mg structure with tilted CO molecules. The symmetry of the layer induces splittings of all CO-derived levels at the center of the Brillouin zone. Due to the high coverage the very strong lateral interaction splits the occupied  $1\pi$ -derived CO levels by 2.2 eV (as observed by PES) [17] a value that can be well reproduced by tight-binding band structure calculations including molecule-substrate interaction [17]. The BIS spectra for the p2mg structure at normal incidence reveal a CO  $2\tilde{\pi}$ -derived feature centered at 4.1 eV above the Fermi level. The peak exhibits fine structure, i.e., shoulders at 2.9 and 5.3 eV above the Fermi level. If the adsorbate coverage is reduced, the width of the  $2\tilde{\pi}$ -derived feature decreases drastically and the fine structure disappears. Also, the relative intensities of the peaks constituting the broad CO  $2\tilde{\pi}$ -derived feature depend on the polarization of the collected photons.

The width of the CO  $2\tilde{\pi}$ -derived emission is consistent with a qualitative estimate for the CO  $2\tilde{\pi}$  splittings based on a tight-binding calculation.

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