Orientation and substrate interaction of adsorbed CO and NO molecules probed by circular dichroism in the angular distribution of photoelectrons

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The sensitivity and utility of circular dichroism in the angular distribution of photoelectrons (CDAD) as a probe of molecular orientation is demonstrated for adsorbed CO and NO molecules. A comparison between measured CDAD spectra and calculated values for spatially oriented CO and NiCO clearly confirms the well-known perpendicular adsorption for CO on Ni(100), whereas for CO adsorbed on Fe(100) a tilted adsorption geometry was found. For NO/Ni(100) and for NO on the oxygen-preadsorbed Ni(100) surface, an average tilt angle of $\alpha = 40 \pm 10°$ was observed. In the case of the oxygen-preadsorbed Ni(100) surface, a higher fraction of NO molecules was found to be in a tilted orientation than on the clean surface.

Circular dichroism or optical activity is normally associated with chiral molecules, i.e., molecules which have neither a plane nor a center of symmetry. This dichroism is due to an interference of electric and magnetic dipole transitions and gives rise to weak asymmetries (typically less than 1%) in the absorption coefficients for left and right circularly polarized light. In the region of photoemission, circular dichroism could be characterized by the asymmetry in the photoelectron angular distributions produced by left and right circularly polarized light. Recent theoretical and experimental studies have revealed large asymmetries in the photoelectron angular distributions for left and right circularly polarized light provided the molecules are fixed in space, i.e., spatially oriented.[1−3] This circular dichroism in angular distributions (CDAD) arises in the electric dipole approximation for all spatially fixed molecules, and is of the same order of magnitude as the differential photoionization cross section itself.[1−3] Furthermore, explicit calculations for spatially oriented CO and NO molecules showed a strong dependence of these CDAD spectra on photoemission geometry, suggesting that CDAD measurements may be a useful probe of adsorbate geometry.[3] In this paper we report the experimental verification of this effect and present a quantitative comparison between measured CDAD spectra for the 4σ levels of CO and NO adsorbed on Ni(100) and Fe(100), and on O/Ni(100) and calculated spectra for spatially oriented CO and NO.

For nonchiral molecules the appearance of CDAD requires a chirality in the overall geometry of the experiment. This chirality is realized if the three axes—the photon propagation direction, the photoelectron collection direction, and the molecular axis—are not coplanar. The experimental setup providing the geometry required for measurements of CDAD spectra is described in detail

elsewhere[3] and consists of an angle-resolving ultraviolet photoemission spectroscopy (UPS) system equipped with a low-energy electron diffraction/Auger electron spectroscopy (LEED/AES) system for sample preparation. Figure 1 illustrates the experimental geometry providing the chirality required in these measurements.

Circularly polarized light was obtained from the 8.5-m normal incidence monochromator (NIM) at the Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. BESSY storage ring (Berlin). This monochromator accepts the circularly polarized synchrotron radiation emitted above and below the plane of the storage ring.[4] An upper and lower beam stop at the entrance of the monochromator can be driven up or down to select the degree and helicity of circular polarization. Typical features of this monochromator are a maximum intensity of 3×10^{11} photons/sec at $h\nu = 30$ eV (for 500-mA stored beam), and the circular polarization was set to 92% with a bandwidth of 0.5 nm. The overall energy resolution (electrons and photons) was better than 200 meV.

The substrate crystals Ni(100) and Fe(100) were cleaned by repeated cycles of argon-ion sputtering, heating in oxygen to remove carbon contamination, and flashing. The clean surfaces were then characterized by LEED. Exposure of the surfaces to CO was performed at room temperature. The clean Ni(100) surface was exposed to $3L$ CO and the Fe(100) surface to $30L$ ($1L = 10^{-6}$ Torr s). For NO/Ni(100) the substrate crystal was cooled to 140 K to achieve saturation coverage because of the weak signal of the NO 4σ orbital at photon energies around 30 eV. The base pressure during measurement was in the low 10^{-10} mbar range.

Figure 2 shows typical spectra for CO and Ni(100) and Fe(100) and NO on Ni(100). Spectra were taken for left
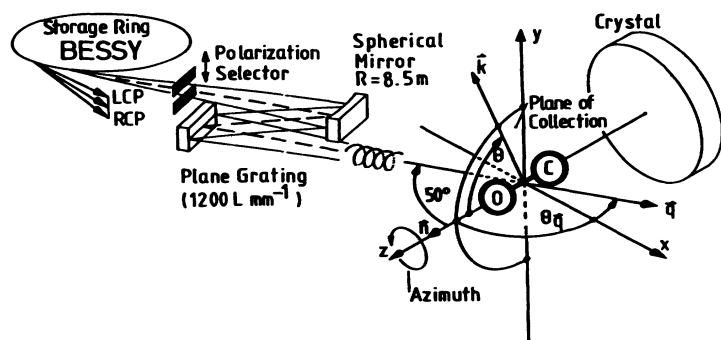
FIG. 1. Schematic drawing of the experimental setup and the 8.5-m normal incidence monochromator for circularly polarized light at the storage ring BESSY in Berlin. The experimental geometry displays the necessary chirality in the incoming light q, the direction of observation of the photoelectron k_e, and the orientation of the molecular axis n for CDAD experiments.
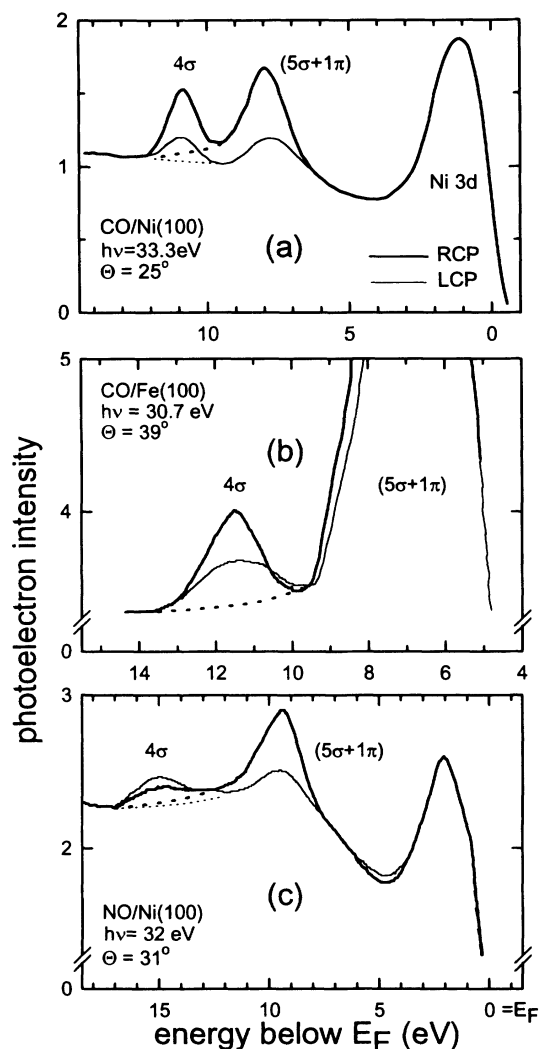

FIG. 2. (a) Typical photoelectron spectra (in arbitrary units) with right and left circularly polarized light (denoted by heavy and thin lines, respectively) for saturation coverage at room temperature. The dashed line shows the estimated background below the CO 4σ and $(5\sigma + 1\pi)$ signals. (b) Same as (a) for CO/Fe(100). The spectrum was recorded for the binding-energy range extending from 5 to 14 eV below E_F due to the weaker signal observed for this adsorbate. (c) Same as (a) for NO/Ni(100) at $T = 140$ K.

and right circularly polarized light at photon energies and emission angles where the CDAD is most significant. In Fig. 2(a) the adsorbate-induced structures at 10.9 and 8.0 eV below the Fermi energy correspond to the CO 4σ and the $(5\sigma + 1\pi)$ orbitals, respectively.[5] It is convenient to characterize the difference between the photoelectron spectra for left and right circularly polarized light by the asymmetry function A_{CDAD}

$$A_{CDAD}(\Theta) = [I^R(\Theta) - I^L(\Theta)]/[I^R(\Theta) + I^L(\Theta)] ,$$

(1)

where $I^R(\Theta)$ and $I^L(\Theta)$ denote the photoelectron intensities for right and left circularly polarized light, respectively. The asymmetry A_{CDAD} of Eq. (1) was actually determined taking the peak heights $I^R(\Theta)$ and $I^L(\Theta)$ above the smooth background that gave the same values of A_{CDAD} as the corresponding peak areas. Figures 2(b) and 2(c) are analogous spectra for the systems CO/Fe(100) and NO/Ni(100). In Fig. 2(b) we only took that part of the spectrum containing the binding-energy region of the 4σ and the $(5\sigma + 1\pi)$ orbitals since the signal count rate was low.

We will focus our discussion on the results for the CO 4σ orbital since this is the lone pair orbital located at the oxygen atom and, hence, is only weakly involved in the bonding to the surface. In the adsorbate phase, the 5σ and 1π orbitals show nearly the same binding energies and cannot be resolved.[6] The 5σ orbital is at the carbon end of the molecule and is, therefore, strongly perturbed by bonding to the metal. Figure 3 shows the measured asymmetries for photoemission from the 4σ orbital for CO adsorbed on Ni(100) and Fe(100) along with calculated CDAD spectra for a spatially oriented CO molecule. The calculated spectra assume an ionization potential of 16.5 eV, which is the measured value for CO adsorbed on Ni. Details of the calculations are given in Ref. 3. Figure 3(a) shows asymmetry curves calculated for different average molecular tilt angles of $0° < \alpha < 45°$. The maximum in the asymmetry is predicted for a perpendicularly bonded CO molecule ($\alpha = 0°$). With increasing tilt angle, the asymmetry decreases from 70% ($\alpha = 0°$) and reverses its sign at $\alpha \approx 30°$. For tilt angles $30° < \alpha < 45°$, the asymmetry stays negative and reaches the minimum at $\alpha = 45°$. The adsorption of CO on Ni(100) is known to be normal

to the surface with the carbon end pointing towards the surface.[6] In Fig. 3(b) we compare the measured CDAD asymmetries for CO adsorbed on Ni(100) for a photon energy of 30 eV with the calculated CDAD spectra for photoemission from the 4σ-like orbital of the molecular fragment NiCO. The CO tilt angle here is $0°$. A molecular fragment such as NiCO can be expected to be a slightly more realistic model for adsorbate photoemission than free CO [cf. Fig. 3(a) for $\alpha = 0°$]. The agreement between the measured and calculated CDAD spectra of Fig. 3(b) is encouraging. The differences between the calculated
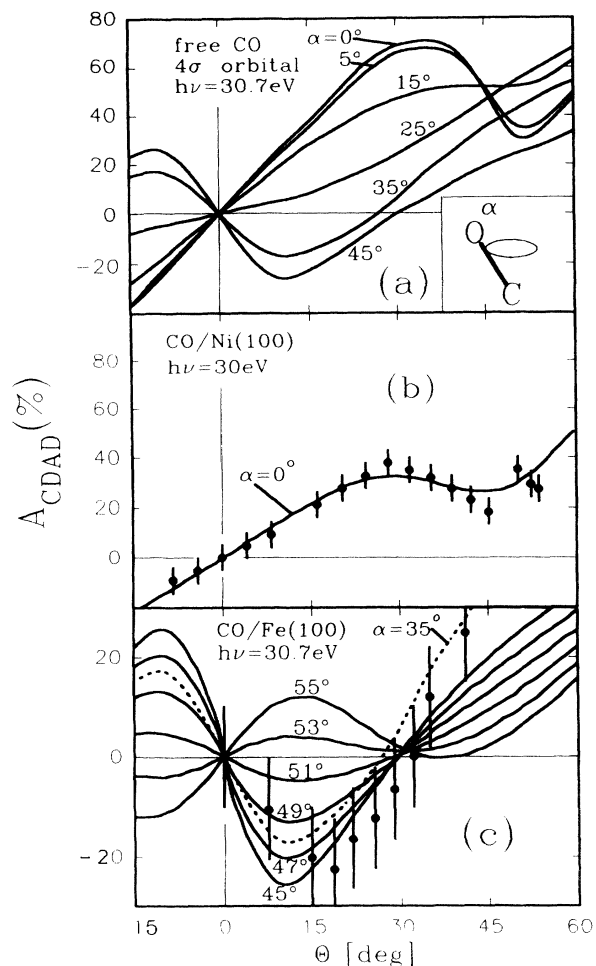

FIG. 3. Measured (solid circles) CDAD asymmetry of the CO 4σ orbital and calculated values (solid curves) for various tilt angles α of the molecular axis relative to the surface normal (see inset). The measured data are taken at room temperature and the error bars include counting statistics and reproducibility: (a) Calculated asymmetry curves for a free CO molecule fixed in space, (b) comparison of the measured asymmetry of CO adsorbed on Ni(100) with calculated values for the molecular fragment NiCO with the molecular axis along the surface normal (normal geometry), and (c) measured CDAD for CO adsorbed on Fe(100) and calculated values for spatially oriented free CO. The dashed line highlights the calculated values for $\alpha = 35°$.

CDAD spectra for CO $(\alpha = 0°)$ and NiCO are primarily due to the sensitivity of these 4σ photoemission cross sections to a well-known underlying shape resonance which occurs around this energy.[5,6] The CDAD asymmetries for the 4σ-like orbital of NiCO, however, show the same strong dependence on tilt angles seen for free CO in Fig. 3(a). Comparison between the measured and calculated asymmetries clearly confirms the well-known normal orientation for adsorbed CO on this substrate.

We now look at an adsorbate-substrate system for which CO molecules are known to be adsorbed at a tilted orientation with respect to the surface normal: CO/Fe(100). There have only been a few previous studies of the adsorption geometry in this system.[7-9] A comparison of the measured CDAD asymmetries for CO on Fe(100) and the calculated asymmetries for free CO at tilt angles between $35°$ and $55°$ is shown in Fig. 3(c). The CDAD asymmetry for a tilt angle of $35°$ is plotted as a dashed line simply to highlight these results from the others. For tilt angles between $\alpha = 35°$ and $45°$, the asymmetry changes continuously (not shown in Fig. 3). The minimum in the CDAD asymmetry occurs for a molecular tilt angle of $\alpha = 45°$. For angles $\alpha > 45°$, the asymmetry increases with the molecular tilt angle and shows positive maxima for tilt angles of $53°$ and $55°$ and $\Theta \approx 10°-15°$. For tilt angles above $45°$, the determination of the average molecular tilt angle on the basis of a comparison of measured and calculated CDAD spectra is difficult because a positive measured asymmetry may be misinterpreted as indicative of a tilt angle of $\alpha < 30°$. For such cases it might be helpful to invoke symmetry characteristics of the photoelectron intensity of σ orbitals. For the case of a molecular axis parallel to the surface, $\alpha = 90°$, the asymmetry must vanish because the photoemission geometry is coplanar.[2] Therefore, the asymmetry must be very small for tilt angles near $90°$. However, for CO on Fe(100), comparison of the measured and calculated CDAD asymmetries in Fig. 3(c) suggests an average tilt angle of the CO molecule of $\alpha \geq 45°$ with respect to the surface normal. The calculated spectra were obtained as an average over all possible azimuthal molecular orientations [indicated by the inset of Fig. 3(a)]. For this adsorbate-substrate system the molecules are actually tilted in four different directions because of the fourfold symmetry of the substrate. Some of the differences between the measured and calculated asymmetries could also be due to the presence of three distinct associatively bonded states of CO on Fe(100)—CO(α_1), CO(α_2), and CO(α_3)—which can be identified with thermal-desorption spectroscopy.[7] The photoelectron emission cross section of the different species could not be resolved because all three bonded states have nearly the same binding energy.

Moon *et al.*[8] have investigated CO adsorbed on Fe(001) using near-edge x-ray-absorption fine-structure (NEXAFS) measurements and estimated the tilt angle to be $45°\pm10°$. Later Saiki *et al.*[9] studied this system with x-ray photoelectron diffraction (XPD) which is very sensitive to bond directions due to the highly peaked forward scattering in core-level emission at energies above 500 eV. They obtained an estimate for the average tilt

angle of $55°\pm2°$ with respect to the surface normal. Our estimate for this tilt angle is in good agreement with that of Moon et al.[8] and Saiki et al.[9]

The adsorption of NO on transition-metal surfaces has been previously studied utilizing most of the techniques available in surface science.[10−19] For NO on Ni(100), temperature- and coverage-dependent adsorption sites were found and an ambivalence remains concerning the adsorption geometry. Generally, the results obtained up to now showed that NO maintains its molecular character when adsorbed at low temperatures but dissociates upon adsorption at high temperatures. No ordered overlayer structure has been reported for adsorbed NO. Vibrational spectroscopy using electron-energy-loss spectroscopy (EELS) showed several peaks in the NO stretch frequency region, indicating the existence of many different adsorption sites, e.g., on top, bridge, or hollow.[10] At saturation coverage it has been proposed from NEXAFS measurements that NO adsorbs with the molecular axis perpendicular to the surface. The geometry of low-coverage sites is rather uncertain, and perpendicular bridge-bonded[17] and tilted[18] forms have been suggested. Recent EELS results indicate that under low coverage, NO is found in perpendicularly bonded hollow sites on Ni(100).[10] Coverage-dependent x-ray photoelectron diffraction experiments[19] showed that at low coverage at least a significant fraction of NO molecules is adsorbed with the molecular axis parallel to the Ni(100) surface. We studied the system NO/Ni(100) using CDAD.

Figure 4 shows the calculated CDAD asymmetry for the 4σ orbital of free but spatially oriented NO for tilt angles $0° \leq \alpha \leq 50°$ and the measured asymmetries for NO molecules adsorbed on Ni(100) and on oxygen-preadsorbed Ni(100). Details of the calculations are discussed in Ref. 3. Generally, the behavior of the CDAD asymmetry of the NO 4σ orbital is quite similar to the CO 4σ orbital. For molecular tilt angles $0° \leq \alpha \leq 30°$, the asymmetry is positive, whereas for $30° < \alpha \leq 50°$, a negative asymmetry is seen. Again, the highest value of the CDAD asymmetry for the 4σ orbital occurs for a perpendicularly bonded NO molecule $(\alpha = 0°)$. Figures 4(b) and 4(c) show the measured asymmetries for NO adsorbed on clean and O-preadsorbed Ni(100) along with the calculated values for the NO 4σ orbital for tilt angles of 35° and 45°. We see nearly perfect agreement [cf. Fig. 4(b)] between experiment and theory for an average tilt angle $\alpha = 35°$ at lower detection angles Θ, whereas with increasing Θ, a better approximation is given by an average tilt angle $\alpha = 45°$. This difference between the measured and calculated asymmetries may be explained quantitatively as follows: The measured asymmetry is a mixture of asymmetries resulting from perpendicular and tilted bonded molecules at the surface since both adsorption sites can coexist.[10] The photoelectron intensities resulting from both types of bonded molecules must be considered calculating the asymmetry: The photoelectron emission cross section of σ orbitals is high along the molecular axis and lower elsewhere.[20] The measured asymmetry (asymmetry resulting from perpendicular and tilted molecules) is weighted by the photoelectron angular distribution cross sections due to both perpendicular and

tilted molecules on the surface. At low detection angles $(\Theta \approx 0°)$, the measured asymmetry is shifted to positive values due to the strong positive CDAD contribution (high intensity) from NO molecules that are perpendicularly bonded [cf. Fig. 4(a) for $\alpha = 0°$] and due to an only small negative CDAD contribution (low intensity) from tilted bonded molecules. At higher collection angles, the calculation predicts nearly the same asymmetry for all molecular tilt angles [cf. Fig. 4(a) for $\alpha = 50°$] and, therefore, the weighting factor for the angular distribution of the photoemission cross section is only weakly dependent on tilt angle. Hence, the agreement between the measured CDAD asymmetries and the calculated asymmetry could be viewed as quite encouraging and is within the error limits shown in Fig. 4(b).

Figure 4(c) shows the measured CDAD asymmetries for the 4σ orbital of NO adsorbed on an O-preadsorbed Ni(100) surface and the values calculated for spatially
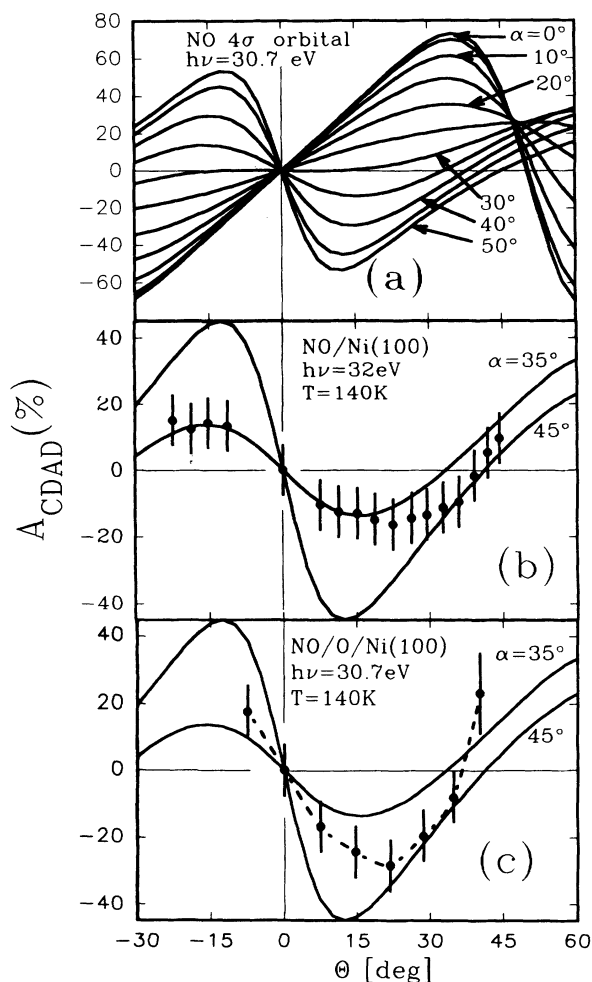

FIG. 4. Measured (solid circles) CDAD asymmetry for adsorbed NO 4σ and calculated values for spatially oriented NO: (a) Calculated asymmetries for a free NO molecule fixed in space, (b) comparison of the measured asymmetry of NO adsorbed on Ni(100) with the calculated asymmetries at $\alpha = 35°$ and 45°, and (c) same as (b) but for NO on oxygen-preadsorbed Ni(100).

oriented NO. On this substrate, the asymmetry A_{CDAD} of the 4σ orbital shows a deeper minimum compared to NO on clean Ni(100) [Fig. 4(b)]. This suggests a higher average tilt angle for NO on O/Ni(100) than on Ni(100), which agrees well with recent high-resolution electron-energy-loss spectroscopy (HREELS), NEXAFS, and angle-resolved ultraviolet photoemission spectroscopy (ARUPS) measurements of Odörfer *et al.*[10] These authors found three different binding geometries of NO on Ni(100) as a function of coverage. At low coverage, NO is bonded at fourfold hollow sites with the molecular axis parallel to the surface normal (perpendicular adsorption). With increasing NO adsorption, bridge sites with tilted and perpendicular orientation become occupied. Finally, at saturation coverage, perpendicularly bonded NO molecules occupy on-top positions. Oxygen forms a $c(2\times2)$ structure on the clear Ni(100) surface and occupies the hollow sites which were predominantly occupied by the perpendicularly bonded NO molecules. Calculations predict a large positive value for the CDAD asymmetry A_{CDAD} for perpendicularly bonded NO molecules, and the absence of a contribution from such molecules here could explain the deeper minimum for the CDAD for NO on O/Ni(100). Thus, a higher fraction of NO molecules is adsorbed in a tilted geometry on O/Ni(100).

The adsorption of NO on Ni(111) is known to occur with the molecular axis parallel to the surface normal and with the nitrogen atom pointing towards the surface. This is consistent with previously published electron-stimulated desorption ion angular distribution,[21] photoemission,[22] Auger electron spectroscopy,[23] and vibrational spectroscopy[24] results. On Ni(111), the NO molecules form a $c(4\times2)$ superstructure at 0.5-monolayer (ML) coverage. Therefore, this system should be another suitable test candidate for CDAD as a probe of molecular orientation. However, this adsorbate system is difficult to investigate by means of CDAD. On this substrate the NO-NO spacing may lead to a dipole-dipole coupling which could subsequently influence the final states. This was proposed as an explanation for NO dimerization at

the surface[25] and, in fact, was recently confirmed by vibrational spectroscopy.[24] For NO/Ni(111) we observed smaller but broader peaks around the binding energy of the 4σ orbital with a stronger dispersion than for NO/Ni(100). Because of the dipole-dipole coupling and of a generally weak photoelectron signal of the NO 4σ orbital at $h\nu=30$ eV, a definitive peak assignment was not possible. Since surface chemistry could not be excluded for this adsorbate system, a CDAD study was not carried out.

In conclusion, we have demonstrated that CDAD is an appropriate and sensitive tool for the investigation of tilt angles of molecules adsorbed on surfaces. For CO adsorbed on Ni(100), the well-known perpendicular adsorption was confirmed. For CO on Fe(100), a tilt angle of $\alpha \geq 45°$ has been determined, which again agrees with recent NEXAFS (Ref. 8) and XPD (Ref. 9) measurements. For NO on Ni(100) we found an average tilt angle of $40°\pm5°$ which again agrees well with recent EELS and EXAFS results.[10] On a clean Ni(100) surface, oxygen blocks the hollow sites preferred by perpendicularly adsorbed NO. The measured asymmetry for that system, indeed, shows a slightly deeper minimum than for the case of NO/Ni(100). This suggests a higher fraction of tilted NO molecules adsorbed on the O/Ni(100) surface than on the clean Ni(100) surface. For adsorbate systems which display strong dipole-dipole coupling, dimerization, dissociation, and chemical reaction, determination of the molecular tilt angle via CDAD is difficult since the photoelectron signal can clearly be influenced by the different reaction products.

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