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Abstract. In photoemission the observed changes in band intensities as a function of light polarization, electron emission direction, and photon energy can be used to deduce information, for example, about geometry, two-dimensional band structures, intermolecular interactions and chemical reactivity of molecular adsorbates. To characterize the ion states of molecular adsorbates in the so-called inner valence electron region we discuss results from autoionization spectroscopy as a method that yields complementary information to photoemission in this spectral region. We use results on CO,  $N_2$ , and  $CO_2$  adsorbates to discuss the various aspects of photoemission of molecular adsorbates.

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The study of adsorption of molecules on surfaces with photoelectron spectroscopy started in the early seventies with the landmark paper by Eastman and Cashion [1] on the system CO/Ni. In many of the early studies, unpolarized light and angle integrating electron spectroscopy were applied. Today, electron storage rings provide intense synchrotron radiation with a high degree of polarization, and angle resolved electron spectroscopic techniques (ARUPS) are implemented in many cases. Still much of present research [2, 3] on molecular adsorption is being done on CO adsorbates or co-adsorbates. It may sound surprising therefore, that even in the case of CO adsorbates not all ion states of the CO molecule known from the gas phase have been identified in the adsorbate. The complete inner valence regime connected with the ionization of the CO  $3\sigma$  electron appears to be a "white spot" on the "spectroscopic map" of adsorbed CO. This demonstrates that a unified view of the ionization of adsorbates is still missing. Nevertheless, many of the fundamental aspects of photoemission of molecular adsorbate systems can be illustrated using experimental results on CO adsorbates. In an attempt to order the various aspects of angle resolved photoemission on molecular chemisorption systems we have divided the present review into three parts: the first covers the molecular aspects and the second deals with

intermolecular interaction in connection with the formation of two dimensionally ordered overlayers. A subdivision in this manner is natural because molecular chemisorption is determined essentially by these two types of interactions. The third part shows how a spectroscopy of the inner valence regime can be attempted.

Figure 1 illustrates on the basis of one-electron level diagrams how the molecule-substrate, and the intermolecular interactions affect the electronic states of the adsorbate. It shows on the right-hand side a oneelectron level diagram for a single isolated CO molecule correlated with a level diagram of a CO molecule interacting with a single metal atom or a small metal cluster. The electronic states of the system can be classified according to the point group of the CO-metal cluster. On the left-hand side the band structure of an isolated CO overlayer is shown and compared in the middle with the full band structure of the CO adsorbate on a fcc (111) single crystal metal surface. In this case the point group of the local CO-metal site is not sufficient to characterize the electronic states of the system. The full global space group of the periodic arrangement has to be considered. Clearly, the relative magnitudes of molecule-substrate and intermolecular interaction potential determine whether local or global symmetry dominates. Since ARUPS, as will be shown



Fig. 1. Schematic one-electron diagrams for diatomic molecules (CO) interacting with a transition metal surface. The level scheme for a molecule-metal cluster (right) is correlated with the band scheme of a free unsupported molecular layer (extreme left) and the band scheme of the quasi-twodimensional adsorbate (middle). The band structure of the metal projected onto the surface is schematically shown as the hatched area

below, allows us to study symmetry properties of the electronic states of adsorbate systems, it may be possible to disentangle via ARUPS in favourable cases which of and how these two types of interactions are active in the adsorbate. We note at this point that all of our examples refer to adsorbate systems on transition metal single crystal surfaces, because the majority of data is available for these systems. There are very few examples of ARUPS studies of molecular adsorbates on semiconductor surfaces.

## 1. Molecular Aspects

Let us start with the "molecular aspect" of the COmolecule-substrate interaction, i.e. the right-hand side of Fig. 1. What happens electronically can easily be explained in terms of the so-called Blyholder model [4]: The carbon lone pair is donated into empty d or slevels of the metal atom, establishing a  $\sigma$  metalmolecule interaction; synergetically, metal d electrons are donated into empty molecular orbitals  $(2\pi^*)$  of CO forming a  $\pi$  metal-molecule interaction. From the view point of the molecule we can look at this process as a  $\sigma$ -donation- $\pi$ -back-donation process. This means that the distribution of electrons among the subsystems, i.e. CO molecule and metal atom, in the metal-CO cluster is considerably different to the non-interacting subsystems. For example, the electron configuration of the metal atom in the cluster may be different from the isolated metal atom, or the electron distribution within the CO molecule bonded towards the metal atom may look more like the electron distribution of an "excited" CO molecule rather than the ground state CO molecule [5]. Nevertheless, as a consequence of the relatively weak molecule-substrate interaction only certain electronic levels of the subsystems are strongly influenced, so that it appears to be justified to classify the electronic levels of the interacting adsorbate system according to the nomenclature used for the isolated



Fig. 2. Set of normal emission CO adsorbate spectra [6–11] (s.u.: shake-up satellite)

subsystems. Naturally, the distortions of the molecular as well as the metal levels are reflected by changes in the ionization energies of those levels, their ionization probabilities, and the line shapes of the ionization bands. Figure 2 shows a set of angle resolved, normal emission valence electron spectra of CO adsorbates on different single crystal surfaces [6-11]. The binding energy  $(E_{\rm B} = hv - E_{\rm Kin})$ , refers to the vacuum level. (Often the binding energy is referenced to the Fermilevel  $(E_{\rm F})$  of the system. The binding energy with respect to the vacuum level and the binding energy with respect to the Fermi level are connected via the workfunction  $\Phi$  of the adsorbate system.) The region where we expect emission from the three outer valence levels of CO, i.e. the  $5\sigma$ ,  $1\pi$ , and  $4\sigma$  levels (see Fig. 1) is shown, and most of the following discussion will concentrate on these levels. From the bottom to the top the heat of adsorption increases from 19 kJ/mol to 142 kJ/mol [12–16]. This is accompanied by clearly recognizable changes in the photoelectron spectra as compared to the gas and solid phase spectra which are shown for comparison. There are several interesting differences in binding energies, line intensities and line shapes between gas, condensed and adsorbate phases, which we shall comment on in the following. In order to do so we have to cover many different aspects such as symmetry considerations, relaxation energies, line widths, shakeup satellites and so on. We shall use Fig. 2 as a basis for discussing the various aspects as they occur in going from the gas phase via weakly chemisorbed to strongly chemisorbed adsorbates.

In CO/Ag(111) at T=20 K CO is physisorbed as documented by the small  $E_{ad} = 19 \text{ kJ/mol}$ . This explains why a spectrum similar to condensed CO is observed for this adsorbate. The splitting in the  $4\sigma$  and  $5\sigma$  emissions are connected with the formation of a two-dimensional overlayer as will be discussed in the second part of this review. In comparison with the gas phase, however, rather dramatic changes are observed upon condensation and physisorption, namely a shift of about 1 eV towards lower binding energies and a considerable increase in line width which destroys the vibrational structure observed in the gas phase. Theories have been developed that allow one to understand these observations on the basis of hole hopping and relaxation together with adsorbatesurface vibrations within the condensed quasi-two- or three-dimensional molecular solids [17-20]. The shift of the band to lower binding energy is a consequence of the electronic relaxation in the final ion state, which is considerably more pronounced when the molecule is bound to a readily polarizable medium, because metal electrons screen the positive charge introduced by the ionization process more effectively than do the electrons on the isolated molecule. The more pronounced screening stabilizes the final hole state relative to the initial state, which lowers the binding energy as observed. Measured temperature dependences of line widths in molecular solids and model systems support the developed theoretical ideas [20,21]. It is likely that other processes, for example Auger decay or other radiationless decay mechanisms, contribute through life time effects to these line widths as well.

If the heat of adsorption increases to about 47 kJ/mol [14] (weakly chemisorbed), like, for example, in the case of a CO adsorbate on a Cu (111) surface, the features in the spectrum shift and the intensities of the lines are altered considerably with respect to the physisorbate. The line widths, on the other hand, are quite comparable in both systems. Three lines are still found, but their assignment is, as we shall see below, quite different from the one for the condensed molecular solid.

Before we discuss how angle resolved photoelectron spectroscopy establishes this assignment let us first turn to the spectra of the strongly chemisorbed adsorbate systems, i.e. CO/Ni(111) and CO/Pd(111), which are only two examples out of a wealth of experimental data [22-38]. In the case of strong chemisorption the spectra show two bands, whose binding energies are almost independent of the particular system under consideration, but are shifted by more than 2 eV to lower values with respect to the gas phase. ARUPS has been instrumental in showing that these two CO-induced bands are really caused by three CO ion states, and that the CO molecules are oriented with their axes parallel to the surface normal [22]. Figure 3b shows an angular distribution pattern for the  $4\sigma$  ion state intensity of a CO/Pd (111) adsorbate as recorded with an elliptic mirror analyser employing polarized synchrotron light [28]. The polarization plane is placed along the  $0^{\circ}/180^{\circ}$ -azimuth, i.e. the horizontal line in the angular coordinate diagram shown in Fig. 3a. With respect to the Pd (111) surface this corresponds to a mirror plane of the system. Figure 3c shows a quasi-three-dimensional plot of the emission intensity distribution (shaded areas on the half-sphere) as a function of azimuthal ( $\phi$ ) and polar ( $\theta$ ) angles in direct relation to the geometric structure of the molecular adsorbate. The angular distribution pattern clearly shows how the symmetry of the adsorbate wavefunction with respect to this mirror plane determines the angular distribution of the emitted electron current. The reason for this remarkable behaviour has been discussed long ago by several groups [22, 23, 39] on the basis of symmetry considerations for the photoemission matrix element [40, 41]:

$$I \propto |\langle \Psi_{\rm f} | p | \Psi_{\rm i} \rangle|^2$$

(1)

С



Fig. 3A–C. CO  $4\sigma$  emission from CO/Pd (111) as recorded with an elliptical mirror analyser [28]. (A) Polar diagram, the direction of the light polarization vector is indicated by an arrow. (B) Intensity distribution pattern. Light regions correspond to high emission current. (C) Quasi-three-dimensional representation of the relation between geometric structure of the adsorbate and the measured  $4\sigma$  emission intensity as a function of  $\phi$  and  $\theta$ . The emission intensity is given by the shaded areas

ີ e=340

and we shall briefly repeat the arguments: Firstly it has to be remembered that  $\Psi_f$  is the final state after electron excitation consisting of the ion state  ${}^{N-1}\Psi_{e,E}$ and the emitted electron  $\Phi_e(n)$ , and  $\Psi_i$  represents the neutral ground state of the system. Since p is a one electron operator, the matrix element can be rewritten as [42]:

$$I \propto \left| \sum_{k,e} \langle \Phi_{e}(n) | p_{n} | \Phi_{k}(n) \rangle \langle^{N-1} \Psi_{e,E} | a_{k} \Psi_{i} \rangle \right|^{2}, \qquad (2)$$

where  $a_k$  and  $\Phi_k(n)$  are the annihilation operator and the one-electron wavefunction of the electron that is being emitted, respectively. These  $\Phi_k(n)$  are called initial states in the following. The first matrix element determines the angular distribution pattern, the second matrix element defines the absolute value and contains the internal degrees of freedom of the system, e.g. the line widths. The sum takes all possible ion states  $^{N-1}\Psi_{e,E}$  into account and explains the existence of satellite structure [42].

Since we are interested in ARUPS, much of the discussion will concentrate on the first matrix element. Secondly, in order to evaluate whether this matrix element is finite, and thus leads us to expect a finite photoelectron current into a specific direction in space, symmetry arguments can be used. In principle the space group of the adsorbate under consideration has to be chosen, and then we have to classify the wavefunctions according to its irreducible representations. Often, it is sufficient to consider one specific symmetry operation belonging to the point group, instead of all possible symmetry operations, in order to predict the angular variations of electron emission. In the present case we refer to one of the mirror planes of the Pd (111) surface. If we classify the wavefunctions of the electron  $\Phi_e$  and  $\Phi_k$ , as well as the momentum operator p as "even" or "odd" with respect to this mirror plane, we are in a position to differentiate between "even" and "odd" initial states by choosing certain light polarizations and detecting the angular distribution pattern as long as spin-orbit interaction is not important [43].

For the above given situation the light polarization direction is within the mirror plane. This corresponds to even symmetry of the momentum operator. Therefore, initial states with even symmetry will emit into the direction of the mirror plane because the final states have to be even in order for the matrix element not to vanish. In principle, one would expect a finite emission probability along the whole mirror plane. In the present case, however, one has to take into account the cylindrical symmetry of a CO molecule, bonded linearly to the metal surface. Even initial states of a cylindrical molecule cannot emit into a direction given by the plane perpendicular to the mirror plane which



Fig. 4. ARUP spectra of CO/Pd(111) in "forbidden" and "allowed" geometry (see text). The CO-induced features are marked. Pd emissions show strong symmetry related intensity variations as well [11]. The light polarization was placed along a Pd(210) mirror plane

contains the light polarization vector. This latter property can easily be understood if we remember that any plane in a cylindrical system containing the cylindrical axis is a symmetry plane. Combining this property with the fact that the momentum operator is odd with respect to this second plane, means that there cannot be any emission of even states into this direction. Therefore, in order to fulfil both conditions simultaneously, we do not expect an intense CO  $4\sigma$ emission along the surface normal for light polarized in the surface plane.  $4\sigma$  emission along the surface normal can only be achieved by using a light polarization perpendicular to the surface plane, because in this case the momentum operator is even with respect to any plane perpendicular to the surface plane. If we combine the considerations so far we verify the above angular distribution pattern.

As a consequence of the outlined behaviour of even initial states, we expect a complementary behaviour of odd initial states. This is exactly what is observed experimentally and is shown as a set of electron distribution curves, which is the usual way to look at ARUP spectra, in Fig. 4. In this figure the complementary behaviour of  $\sigma$ - and  $\pi$ -emissions, which was first observed by Plummer and coworkers [22] is obvious: If we record a spectrum perpendicular (so-called "forbidden" geometry) to the incidence plane we do not observe emission in the region of the  $4\sigma$  level but only in the region of the  $5\sigma/1\pi$  levels. Note, that the  $1\pi$  ion state of CO has two degenerate components, one of which always transforms according to the even representation. Thus, we expect to see the one odd component of the  $1\pi$  ion state. A spectrum recorded with the analyser placed within the incidence plane, the socalled "allowed" geometry, shows all states with even symmetry. From Fig. 4 it is clear that the band at 8 eV below the Fermi energy (Fig. 2) contains two states, i.e. the  $1\pi$  and the  $5\sigma$  ion states. Their energies are, in contrast to the gas phase, nearly (within a few tenths of an eV) degenerate in the adsorbate. This is a situation predicted by the simple one-electron level scheme in Fig. 1. It is due to the donation of the  $5\sigma$  carbon lone pair into empty metal levels, thus stabilizing the CO  $5\sigma$ level with respect to the  $1\pi$  level which is not as intimately involved in the molecule-metal interaction for linear metal-molecule bonding.

The logic so far has been that we have assumed a geometry of the adsorbate site, thus knowing the symmetry of the system, i.e. CO perpendicular to the surface plane, and have verified this via an analysis of the angular photoemission spectra. Usually, the arguments are turned around, namely, the observed angular behaviour is used to deduce an adsorbate site symmetry.

The adsorbate induced features exhibit, in addition to the described angular dependences [44], characteristic photon energy dependences, which, when recorded in an angle dependent fashion, can be used to get further information about adsorbate site geometry [22]. Figure 5 shows a plot of the intensity of the  $4\sigma$  ion state as a function of photon energy. The data have



Fig. 5. Intensity variations of the  $4\sigma$  intensity in CO/Co (0001) as a function of photon energy. Filled circles refer to normal emission, open circles and crosses to off-normal emission as indicated [25]



Fig. 6. Intensity variations in normal emission of the CO  $4\sigma$  intensity in (a) CO/Pd (111), and (b) CO+Na/Pd (111) as a function of photon energy between 25 eV and 110 eV [47]

been recorded for the system CO/Co (0001) [25] for three different electron emission angles. The observed resonance feature is caused by the so called shape resonance, which is well known from CO gas phase studies [45]. It can be traced back to a molecular final state of  $\sigma$  symmetry in the ionization continuum, quasi-bound by a centrifugal barrier in the molecular potential. Its symmetry confines the electron emission direction to the molecular axis, and its localization directs the  $4\sigma$  emission out of the oxygen end of the molecule. This means that for the case of a molecule oriented along the surface normal, carbon end bound to the surface, the resonance should peak along the surface normal. Experimentally, we find in Fig. 5 the expected behaviour, i.e. a pronounced attenuation of the resonance intensity for off normal emission, which corroborates the assumed adsorbate orientation. Another interesting property of this resonance is its coherent forward emission character [46]. Coherent forward emission leads to an oscillatory behaviour of the photoionization cross-section. The periodicity is determined by the distance of the interfering emission sources, which in the present case are the carbon and oxygen atoms participating in the ion state wavefunction under consideration (4 $\sigma$ ). Examples are shown in Fig. 6 for the system CO/Pd(111) and CO + Na/Pd(111) [47]. At a photon energy of 35 eV the resonance corresponding to the one shown in Fig. 5 is found. As predicted by theoretical calculations [46], at about 95 eV a second feature with larger width and smaller amplitude is observed. Potentially, the energy separation can be used to estimate the CO bond length in adsorbates as proposed by Gustafsson [46]. Very similar results, as those discussed so far for the  $4\sigma$ ion state are found for the  $5\sigma$  ion state. A comparison of the resonance positions in different CO systems shows [47–49], that it is not so much dependent on the specific system, as was originally expected, and this absence of changes is somewhat surprising on the basis of current theoretical models.

If we apply the geometry sensitive experiments, just presented, to investigate the geometric structure of physisorbed molecules, for example CO/Ag(111) [8], Fig. 2, we find that the orientation of the molecular axis is not, like in the chemisorbates, perpendicular to the surface but rather parallel. The reason is that, due to the electronic structure of the substrate, not enough energy can be gained via the above mentioned  $\sigma$ -donor- $\pi$ -acceptor interaction, for which a vertical orientation is a necessary prerequisite. As we shall see below, intermolecular interactions are important for understanding the electronic structure of physisorbates.

At this point we can return to the assignment and analysis of the spectra of the weakly chemisorbed system. The assignment of the spectrum of the CO/Cu (111) system, given in Fig. 2, indicates that the arguments presented so far are not complete and sufficient to explain all experimental findings. It has been shown theoretically that for weakly chemisorbed systems so-called shake-up excitations accompanying the "normal" electron emission have to be considered [50-54]. These shake-up excitations are manifestations of the fact that the ionization process is a rather complicated many-electron process [42, 55]. They can be assigned to electron excitations in addition to electron emission. Their intensity is determined by the second matrix element in equation (2) whose magnitude is governed by the projection of the wavefunction of the shake-up state  ${}^{N-1}\Psi_{e,E}$  onto the "frozen" ion state  $a_k\Psi_i$ . Shake-up intensities are rather low for chemisorbed, and for physisorbed systems but reach the maximum for intermediate metal-molecule coupling, i.e. weak chemisorption [51-56]. Again, ARUPS can be employed to support the assignment as given in Fig. 2 for the CO/Cu(111) system. If the most intense CO features were due to  $1\pi$  emission, as might be suspected by comparing the spectra of the CO/Cu(111)system with CO/Ag(111), a resonance behaviour for this particular peak would not be allowed. Mariani et al. [57] showed that both bands at higher binding energy are due to states of  $\sigma$  symmetry by investigating the shape resonance discussed above. The  $4\sigma$  ion state as well as the accompanying shake-up transition exhibited parallel resonance behaviour as expected according to the assignment in Fig. 2. A spectrum rather similar to the one of the CO/Cu system, but with

even slightly more intense satellite structure, has been found for the system CO/Au [58]. In the latter system the adsorption energy is between the one for CO/Ag and CO/Cu which leads us to expect more intense satellites, and corroborates the ideas presented.

In our discussion so far we have only considered the molecule induced peaks at binding energies higher than the metal states, i.e. those states that correspond to "molecular" ion states. However, as is obvious from Fig. 1, there are also levels of the adsorbate system within the region of the metal projected density of states, due to the coupling of unoccupied molecular states to occupied metal states. There have been several attempts to identify these states [59-61]. The most done recent one was on the system  $CO(2 \times 1)p2mg/Ni(110)$ , whose structure will be discussed in detail in connection with intermolecular interactions [24]. The symmetry and high CO density of this system allows measurement of the adsorbate induced peaks in the *d*-band region of the Ni substrate [61]. Figure 7 shows a selected set of spectra that demonstrate the intensity, symmetry and energy position of the CO induced, d-like states for this system. The spectra of the clean surface are given as dashed curves for comparison. The usually dominant CO molecular ionizations [24] are not shown in this figure. The various peak intensities are strongly polarization dependent, and this, together with the measured dispersion discussed in the section on intermolecular interactions, supports an assignment of these features to CO- $2\pi$ -Ni-3d states.

To summarize the results so far, the ARUP spectra are found to reflect the bonding with the surface. It is possible to differentiate between physisorbed, weakly chemisorbed, and strongly chemisorbed CO adsorbates. However, the differences in the shape of the spectra for various chemisorbed systems are not very pronounced which limits the applicability of photoemission with respect to fingerprinting. On the other hand, ARUPS is sensitive to the local site symmetry via the angular emission pattern, as well as the angular dependence of resonance features in the ionization cross-section. For special cases the back-bonding states in the region of the metal substrate states can be identified.

In order to appreciate in more detail how these aspects of photoemission have been used to study molecule surface interactions under the influence of variations of the substrate and co-adsorbed species we briefly discuss two out of many examples [62], i.e.  $N_2$  and  $CO_2$  adsorption.

Firstly, we consider  $N_2$  adsorption. The dissociation of  $N_2$  on Fe(111) has been the model system to investigate the mechanism of ammonia synthesis [63]. It is known that  $N_2$  dissociation is the rate limiting



Fig. 7. ARUP spectra in normal emission for different light polarization directions of  $CO(2 \times 1)$  p2mg/Ni(110) (full lines) in comparison with the clean Ni (110) surface (broken lines) in the region of the metal emissions [61]

step, and that there exist molecular precursor states for dissociation where  $N_2$  has been presumed to be side-on bonded to the iron surface [64]. Via ARUPS a strongly inclined  $N_2$  species was identified [65] in addition to a vertically bound N<sub>2</sub> species which only existed at lower temperature. Figure 8 shows a set of angle resolved spectra at low temperature (vertically bound  $N_2$ ) and higher (T = 110 K) temperature (N<sub>2</sub> bound inclined). Figure 8A reveals the  $\sigma$  shape resonance in normal emission for z-polarized light at T < 77 K. Figure 8B shows a  $\sigma$  resonance, but only in off-normal emission for s-polarized light (compare Fig.  $8B_1$  and Fig.  $8B_2$ ) at T = 110 K, supporting the proposed inclined geometry in the second case. A more detailed discussion including the theoretical aspects of the two N<sub>2</sub> bonding modes is given in [64]. Another interesting feature can be demonstrated on the basis of the present results. Both, the  $3\sigma_g$  as well as the  $2\sigma_u$  state exhibit the shape resonance behaviour, while in the gas phase the  $\sigma_{e}$ resonance is symmetry forbidden. The reason is very simple: The inversion symmetry of the homonuclear N<sub>2</sub> molecule is broken upon adsorption which makes the final resonance state accessible to both  $\sigma$  states. This was demonstrated earlier by Horn et al. [66] for the system  $N_2/Ni(110)$ . In contrast to the case  $N_2/Fe(111)$  where  $N_2$  dissociates at low temperature (T>140 K), N<sub>2</sub>-metal coupling is usually rather weak [32, 66–69]. This leads to the existence of rather intense shake up structure as noted for several  $N_2$ -transitionmetal systems [32, 66-69]. The experimental findings



Fig. 8A, B. ARUP spectra of  $N_2/Fe(111)$  for grazing light incidence (z-polarization) and normal emission (A), and s-polarization (near normal incidence) and two electron emission angles [b1: normal emission; b2: off-normal (60°) emission]. For each measurement geometry typical spectra at different photon energies are plotted [65]



Fig. 9. ARUP normal-emission spectra of  $CO_2/Ni(110)$  as a function of temperature (spectra b-f) in comparison with the clean Ni(110) surface (spectrum a) and a O-adsorbate (spectrum g) and a CO adsorbate (spectrum h) [88]

are corroborated by several theoretical calculations [50, 54, 70, 71].

The adsorption of  $CO_2$  on transition metals is another interesting example of activating an otherwise rather inert molecule by adsorption on a metal surface.  $CO_2$  adsorption has been treated recently on several substrate surfaces [72-74] where the molecule was found to dissociate around 200 K into adsorbed CO and oxygen. A series of normal emission spectra of the system CO<sub>2</sub>/Ni (110) [72] in Fig. 9 indicates the usefulness of ARUPS to identify reaction intermediates in favourable cases. At low temperature CO<sub>2</sub> adsorption leads to mixed chemisorbed/physisorbed layers [spectrum b)], and the physisorbed species desorbs selectively by elevating the temperature [spectra b)-e]. Around 200 K a spectrum of the pure chemisorbed species is found which shows three features marked with arrows. One additional feature around 5 eV (see arrow) is forbidden in normal emission indicating  $C_{2y}$ symmetry of the adsorption site. Comparison with results of cluster calculations [75] shows that this is a bent anionic  $CO_2^-$  species. Whether the  $CO_2^-$  species is carbon or oxygen bound to the surface cannot be decided on the basis of these results. Above 200 K (spectrum f)) this species dissociates into CO and O, both adsorbed on the surface, as is clear from a comparison with the spectra of pure CO and O adsorbates [spectra g)-h)]. It was concluded from this study that  $CO_2^-$  is an intrinsic precursor for  $CO_2$ dissociation. Note that  $CO_2^-$  is isoelectronic, and isostructural to  $NO_2$ , which is known to dissociate rapidly upon adsorption also at low temperature [76].  $CO_2$  is known to react on Ag(110) surfaces with coadsorbed oxygen to form a carbonate  $CO_3$  species. ARUPS has been employed [77, 78] to study the  $CO_3$ orientation. It is found that  $CO_3$  assumes an orientation with  $C_s$  symmetry and that the plane along the (110) direction is a mirror plane for the adsorbate.

# 2. Intermolecular Interactions in Ordered Overlayers

Intermolecular interactions are always present in real adsorbate systems. Intermolecular interactions determine, among other things, the chemical reactivity between adsorbed species, and also the ordering of the adsorbed overlayers. The present section is dedicated to this latter aspect, because ordering leads to a two dimensionally periodic arrangement of adsorbed particles. As mentioned in the introduction and illustrated in Fig. 1 we can assign a certain space group to this arrangement, and then classify the electronic band states of the system according to the space group. Experimentally, band dispersions were first observed by Horn et al. [79, 23] for CO overlayers, and based on tight-binding calculations [79, 29] on free unsupported two-dimensional CO arrangements.

As an introduction to the quasi-twodimensional band structure of molecular overlayers we discuss the band dispersions and the symmetry properties of a hexagonal overlayer [25] of CO molecules on a fcc(111) surface as shown in Fig. 1. If the intermolecular interaction potential is large enough to demand consideration of the two-dimensional crystal periodicity, the overlap of adsorbate wavefunctions is sufficient to produce two-dimensional Bloch states  $\Psi_k$ , and to make a band description of the electronic structure more appropriate. Then the wavefunction at a lattice site  $R_1$  is related to the wavefunction at site  $R_2$ by:

$$\Psi_{k}(R_{1}) = \exp[ik(R_{1} - R_{2})]\Psi_{k}(R_{2}), \qquad (3)$$

where  $\exp[ik(R_1 - R_2)]$  gives the phase difference between the two sites for a state specified by the twodimensional wave vector k. Before we consider the changes in the band structure introduced by the substrate we will briefly discuss the qualitative behaviour of the band dispersion of a hypothetical support free molecular layer [79] as shown on the left of Fig. 1. We can illustrate the qualitative features of the dispersion by plotting schematically the real parts of a tight-binding wavefunction in real space for values



Fig. 10. (a) Schematic representation of the real and reciprocal space structures of a hexagonal  $(|\sqrt{3} \times |\sqrt{3})$ R30° CO overlayer. (b) Schematic representation of a two-dimensional  $\sigma$ -wavefunction and two two-dimensional  $\pi$ -wavefunctions at two points of high symmetry in the Surface Brillouin Zone [25]

of k corresponding to high symmetry points in reciprocal space. Figure 10A shows the real- and reciprocal-space unit cells for the hexagonal structure. The real and reciprocal lattices have two mirror planes, on along the  $\Gamma - M - \Gamma$  line (in reciprocal space), and the other one along the line  $\Gamma - K - M - K$ . The wavefunctions along these lines will be even (a') or odd (a"). Figure 10B illustrates the phases of a  $\sigma$  and the two  $\pi$  states at  $\Gamma$  and M. At  $\Gamma$  (k=0) all of the wavefunctions at the different lattice sites are in phase. This results in a strongly bonding configuration for the  $\sigma$ state (top row), but an antibonding configuration for both  $\pi$  states because the individual  $\pi$  functions change sign about the molecular axis. The  $\pi$  functions have been chosen so that one is even and one is odd with respect to the mirror plane. Because at  $\Gamma$  the wave functions transform according to  $C_{6v}$ , the two  $\pi$ components are degenerate. Therefore, at  $\Gamma$  we have a strongly bonding  $\sigma$  band and a degenerate antibonding  $\pi$  band. Along the mirror plane k increases from 0 at  $\Gamma$  to  $\pi/(a\cos 30^\circ)$  at the zone boundary M. The second column shows the wavefunctions at M where the arrow indicates the direction of k. All rows of atoms



parallel to k have the same phase but each row has a phase change of  $\pi$ . The result for the  $\sigma$  states is that each atom is surrounded by four atoms of opposite phase (antibonding) and two bonding atoms. The  $\sigma$ bands therefore disperse upward from  $\Gamma$  to M. In contrast, the even  $\pi$  state is strongly bonding since each lobe of the molecular  $\pi$  orbitals sees only bonding nearest neighbours. The even  $\pi$  band disperses downward from  $\Gamma$  to M with the largest difference in the  $\pi$ band energy. The odd  $\pi$  state at M is just slightly more bonding than the  $\pi$  state at  $\Gamma$  since the overlap of the lobes in a line perpendicular to k is antibonding but the overlap between the lines of atoms is bonding. This means that at M the two  $\pi$  derived bands are no longer degenerate as a consequence of the lower symmetry of the M point. Thus we have explained the qualitative features of the dispersions in the  $\Gamma$  to M direction shown in Fig. 1. Analogously the dispersions in the other directions of high symmetry in the Surface Brillouin Zone can be explained, and we refer to the literature for a more detailed discussion [25].

Such dispersions can be determined via ARUPS as shown in Fig. 11, where spectra of a  $(2|\sqrt{3} \times 2|/3)R30^{\circ}$  CO/Co (0001) overlayer for different values of the wave vector k are plotted. The wave vector is varied by varying the photon energy and the emission angle within the direction of the considered surface azimuth as noted in the figure. The connection between k and the varied quantities is given by:

$$k = (2m_{\rm e}h^{-2}E_{\rm kin})^{1/2}\sin\theta, \qquad (4)$$

where k is the wave vector parallel to the surface, which is the conserved quantity. Figure 12 shows a comparison of calculated dispersions for the  $4\sigma$ -derived band with measured  $4\sigma$  dispersions of CO/Co (0001) adsorbates in the  $\Gamma - M$  direction in two hexagonal

Fig. 11. ARUP spectra of a  $(2|/3 \times 2|/3)$ R30°CO overlayer on Co (0001) for different values of the two-dimensional wave vector  $k_{\parallel}$  as indicated in the figure. The positions of the CO-induced features are marked with arrows [25]

 $(\sqrt{3} \times \sqrt{3})$ R30° and  $(2\sqrt{3} \times 2\sqrt{3})$ R30° layers (partially based on Fig. 11).

We have artificially set the lengths of the two Brillouin zones equal for a more convenient comparison. Due to the smaller CO-CO distance in the  $(2\sqrt{3} \times 2\sqrt{3})R30^{\circ}$  layer, the overlap of the  $4\sigma$  CO wavefunctions increase, and concomitantly, the band



Fig. 12. Measured (circles) and calculated (full lines)  $k_{||}$  dispersions of the  $4\sigma$  level in two hexagonal CO overlayers on Co (0001). Filled circles refer to the  $(1/3 \times 1/3)$ R30° structure, open circles to the  $(21/3 \times 21/3)$ R30° structure [25]

width increases. Figure 12 illustrates that the increase in band width can be quantitatively reproduced by simple tight binding calculations in the case of  $4\sigma$ derived bands. In the present case the comparison can be made directly because the number of nearest neighbours is the same in both systems. If, on the other hand, we want to compare dispersions in hexagonal and cubic systems, the observed band widths have to be corrected for the different number of nearest neighbours. Such a correction is straightforward on the basis of simple tight binding considerations. The result of such a comparison for several different adsorbate systems is shown in Fig. 13 [9, 23–26, 28, 29, 31, 32, 37, 80-83]. The data points follow an exponential dependence on the nearest neighbour distance with a decay length of 1.25 Å if we disregard the CO-K coadsorbate for the moment. This strongly supports the conclusion that the  $4\sigma$  dispersion is caused by direct CO-CO overlap. Intuitively, this is reasonable, because the  $4\sigma$  CO level is not strongly involved in the metal substrate bonding. At the same time we expect a completely different behaviour for the  $5\sigma$  level, because in this case the interaction with the substrate as indicated in the middle of Fig. 1 should have a marked influence on measured dispersion. There is no such linear dependence of the observed band width as a function of CO–CO distances as for the  $4\sigma$  level [32]. A similar plot as for the  $4\sigma$  level exhibits no particular functional dependence, which may be an expression of the participation of indirect substrate-mediated interactions in the intermolecular interaction. Care has to be exercised not to jump to this conclusion prematurely, because, due to the stabilization of the  $5\sigma$  level into the region of the  $1\pi$  level (see Fig. 1) we expect strong  $5\sigma/1\pi$  hybridization effects which have to be taken into account in the prediction of band dispersions [25].

There are only very few cases, where the complete band structure in the  $5\sigma/1\pi$  region has been determined. One such example, which shall be considered in the following, is the system  $CO(2 \times 1)p2mg/Ni(110)$ [24]. In this system the coverage is  $\theta = 1$ , and the lateral stress is particularly demanding. Figure 14 shows a model of this structure. The interesting structural feature is the glide plane along the densely packed rows ([110] azimuth) of the Ni (110) surface. The unit cell of this overlayer contains two CO molecules, which leads to peculiar consequences for the ARUP spectra. Figure 15 shows the measured dispersions and a calculated tight binding band structure for comparison. A doubling of the number of bands is found. Therefore we observe eight, instead of 3 (if  $1\pi$  is degenerate) or 4, features for the  $\Gamma$  point in the Surface Brillouin Zone. The eight features are classified in Fig. 15 according to the wavefunction character of the



Fig. 13. Plot of the  $4\sigma$  bandwidths of various CO overlayers as a function of the CO-CO separation [9, 23–26, 28, 29, 31, 32, 37, 80–83]. The CO-CO separation has been estimated on the basis of published structure models used to explain the observed LEED patterns



Fig. 14. Structure model of the  $CO(2 \times 1)p2mg/Ni(110)$  adsorbate [24]



Fig. 15. Comparison of measured (circles) and calculated (full lines) quasi-two-dimensional band structure of the  $CO(2 \times 1)p2mg/Ni(110)$  system [24]





Fig. 16. Schematic representation of a CO- $\sigma$ , and the two CO- $\pi$  wavefunctions at  $\Gamma$  of a p2mg structure [24]

parental molecular ion state  $(4\sigma, 5\sigma, 1\pi)$ , and even and odd behaviour with respect to operation of the glide plane ( $4\sigma^+$ ,  $4\sigma^-$ , etc.). Due to the twofold symmetry of the adsorbate, the two components of the  $1\pi$  level  $[1\pi_x]$ pointing along the (110) azimuth;  $1\pi_v$ , pointing along the (100) azimuth] are not degenerate. All bands degenerate pairwise at the X-point which is required by symmetry of the p2mg nonsymmorphic space group [84]. The important point is that the p2mg system allows a detailed assignment and comparison with calculations in the region of the  $5\sigma/1\pi$  band system. Figure 16 shows schematic representations of the  $1\pi$ and  $5\sigma$  wavefunctions at  $\Gamma$ . The two  $1\pi_x$  orbitals in the unit cell interact strongly due to the short distance along the (110) azimuth and split by more than 2 eV. The  $1\pi_{v}$  orbitals interact much less strongly, and split only by 0.7 eV. The  $5\sigma$  orbitals split by more than 1 eV. Without the theoretical calculation one is tempted to determine the  $5\sigma$  band width by taking the splitting between the  $5\sigma^+$  and the  $1\pi_x^-$  bands which is only 0.6 eV. The observed band dispersion is caused by hybridization of the crossing  $1\pi_x^-$  and the  $5\sigma^+$  bands, which along  $\Sigma$  belong to the same irreducible representation in the p2mg space group. The values used to correlate  $5\sigma$  band widths versus CO–CO distance as mentioned above have been determined without detailed knowledge of  $5\sigma/1\pi$  hybridization. Therefore we reach the conclusion that several such detailed theoretical analysis for various systems have to be carried out, before an exponential decay for the  $5\sigma$  band widths can be excluded.

There is yet another interesting aspect of the p2mg band structure: The splitting between the two  $1\pi_x$  derived bands at  $\Gamma$  is a strong function of the CO tilt angle with respect to the surface normal. Band structure calculations [24] as a function of the tilt angle

showed that the optimum theoretical fit of the measured band structure can be obtained for a tilt angle of  $17\pm2^{\circ}$ . This value is in excellent agreement with results of other structure sensitive methods [85, 86]. It shows that similar to the gas phase, where photoelectron spectroscopy has been extensively used to determine, e.g. ring conformations [87], adsorbate photoemission can be used in favourable cases to extract structural information.

The examples for dispersions in quasi-twodimensional systems have been chosen so far from the many examples of strongly chemisorbed systems. One question is what happens to the dispersions when weakly chemisorbed or physisorbed systems are considered. The latter case is easy:

Figure 17 shows the dispersions measured via ARUPS for the system CO/Ag(111) [8]. We know from the previous section that in this system the CO molecules are oriented with their axis parallel to the surface. It is known from LEED studies that CO molecules physisorbed on graphite form herring bone structures [88] as shown in the inset in Fig. 17. Such structures again belong to nonsymmorphic space groups with two molecules in the unit cell. This is the reason why the molecular ionization bands appear split in two components, i.e. a bonding and an antibonding combination at  $\Gamma$ . From symmetry considerations it is clear that these two bands are degenerate at the zone boundary. The splitting is larger for the  $\sigma$  levels than for the  $\pi$  level, which is not unreasonable on the basis of intermolecular overlap considerations. A particularly interesting observation has been made for this system if the temperature is increased. These physisorbed overlayers are known to undergo orderdisorder transitions [88]. The CO molecules are then no longer locked into a herringbone structure but rotate



Fig. 17.  $k_{\parallel}$  dispersion of the  $5\sigma$  levels for the system CO/Ag(111) [8]. The inset shows the assumed herring bone structure



Fig. 18.  $k_{||}$  dispersion of the CO induced features (filled circles) for the system  $CO(\sqrt{7} \times \sqrt{7})/Cu(111)$  [9] including the  $4\sigma$  satellite (see text). The dispersion calculated via the analysis of the spectral function according to Eq. (5) is shown as open circles [9]

freely on their site. This destroys the nonsymmorphic structure and concomitantly the splitting of the  $\sigma$  levels disappears. CO/Ag(111) is a system where ARUPS can be used to study phase transitions in quasi-two-dimensional systems [8].

In the case of weakly chemisorbed systems the situation is slightly more complicated: The reason for this complication is the shake-up structure identified in the previous section [9]. Figure 18 shows the dispersions for the system  $(\sqrt{7} \times \sqrt{7})CO/Cu$  (111), for which Fig. 2 showed an electron distribution curve [9]. In this case the CO molecules are oriented perpendicular to the surface as in the case of the strongly chemisorbed systems. While the integrated  $5\sigma/1\pi$  dispersion is compatible with other CO overlayer systems, the  $4\sigma$ dispersion is considerably smaller than expected for the given intermolecular separation. The observed value is represented in Fig. 13 by the dashed circle. The shake-up, which is, as noted above, associated with the  $4\sigma$  ionization, shows almost no dispersion, but a slight variation in relative intensity with respect to the  $4\sigma$ ionization. There are sum rules [89] relating intensity and ionization energy of the peaks in the observed spectral function  $A(\omega, k)$ , which is a function of frequency  $\omega$  and momentum k, with the quasi-particle energy  $\varepsilon_k^{\text{HF}}$ . These sum-rules are of the type:

$$\varepsilon_k^{\rm HF} = \int_{-\infty}^{+\infty} \omega A(\omega, k) d\omega \,. \tag{5}$$

We can apply this sum rule to the observed data and regain a dispersion shown as the open circles in Fig. 18. This renormalized  $4\sigma$  band widths can now be favourably compared with the values measured for the strongly chemisorbed systems. This shows that it is the ionization process that introduces the deviations in the observed band widths and not a different intermolecular interaction potential in this case.

A way to investigate the substrate-mediated intermolecular interactions may be the analysis of the dispersion of the above mentioned molecule-induced changes in the region of the metal substrate ionizations (see solid lines in the region of the projected band structure in Fig. 1). Such an analysis has been carried out for the  $CO(2 \times 1)p2mg/Ni(110)$  system [61]. Before the dispersions are analysed we have to ensure that the bands are really localized at the surface of the solid, i.e. the CO- $2\pi$ -Ni-3d features should not exhibit a dispersion as a function of photon energy in the normal emission, which is the criterion usually applied for a surface state. Once this has been done, we can determine the dispersion via off-normal emission, and vary the photon energy such that we choose an appropriate cross section of the feature under consideration. The result of such a very tedious analysis has been obtained by Kuhlenbeck et al. [61] and is shown in Fig. 19 for two directions of the Surface Brillouin Zone. There are two important qualitative features of the dispersion curves. First there are no band gaps at zone boundary X, which as Hund pointed out in 1936 [90] is a consequence of the glide plane in the  $\Sigma$  direction. Secondly, the lower, wellresolved band can be fitted very well with a tight binding type curve (full line). A detailed discussion, for which we refer to the original literature [61], reveals a rather clear picture of the nature of the CO- $2\pi$ -Ni-3d interaction. For the case of Ni(110) this interaction



Fig. 19.  $k_{\parallel}$  dispersions of the Ni-3*d*-CO-2 $\pi$ -back-bonding states in the region of the metal emissions in the system CO(2×1)p2mg/Ni(110) [61]. The full lines are the results of qualitative tight-binding estimations

creates new surface resonances positioned from 1 to 2.7 eV below the Fermi energy with the appropriate symmetry and intensity. This picture seems to be quite incompatible with the Newns-Anderson model [91] of CO chemisorption, where the CO- $2\pi$  orbital is resonantly broadened by interaction with the metal. The tails of this broadened band would extend below the Fermi energy and therefore create a degree of  $2\pi$ occupancy. In contrast to the inadequacies of the Newns-Anderson model [91], it is quite easy to understand the data using the Blyholder model [4] used to explain Fig. 1. In this model we have a  $2\pi$  level the width of which is not very important, far above the Fermi energy as the molecule approaches the surface. This level (or the symmetry adapted combination of levels) mixes into the metal levels because there is a finite overlap between them. Since the overlap is a matter of symmetry it determines which of the metal bands will couple with the CO- $2\pi$ . The question which of the  $2\pi$ -induced bands are actually observed is then determined by the strength of the CO- $2\pi$ -metal coupling, and will depend upon the nature of the metal, the crystal face, and the structure of the CO layer.

Summarizing this section so far we have shown that ARUPS allows the observation of level specific dispersions. For those levels not strongly involved in the molecule-substrate interaction we can describe the measured dispersions by through-space intermolecular interactions that depend exponentially on the intermolecular separation with a decay length of 1.25 Å independent of whether they are strongly or weakly chemisorbed. Chemisorbed systems cannot be compared with physisorbed systems because the adsorption geometry changes from perpendicular to parallel orientation. The observed dispersions reflect the global symmetry of the adsorbed layer, and can, in favourable cases, be used to obtain structural information of the adsorbed molecules. In certain systems the dispersion of metal-molecule-backbonding states can be observed.

Quasi-two-dimensional level dispersions have so far mainly been investigated for pure CO overlayers. Very recently, several groups have started to study other systems. For example, the dispersions in  $N_2$ overlayers on Ni (100) [68] and on Ni (110) [92] have been determined. Some studies [32, 80, 82, 93] on coadsorbate systems have been published very recently. In the following we briefly review what is known about band dispersions in ordered co-adsorbates.

The first molecular co-adsorbate system that has been studied with ARUPS with respect to level dispersions were ordered K/CO overlayers [32, 82, 93]. The band width found for the  $4\sigma$  level is included in Fig. 13 as the filled triangle. Unfortunately, the structure model for the co-adsorbate is not unique [94]. The CO–CO distance used in the present case is based on the assumption that a  $(|\sqrt{3} \times |\sqrt{3})R30^{\circ}$  CO overlayer is co-adsorbed with a  $(|\sqrt{3} \times |\sqrt{3})R30^{\circ}$  K overlayer, which leads to the observed  $(3 \times 3)$  overlayer structure [94]. There are other structures possible, which would give shorter CO–CO distances, but the result would always lead to a relatively large band width as compared with pure CO overlayers. Obviously, the co-adsorption of K causes the  $4\sigma$  wave function to change considerably, in the sense that the CO–CO interaction is mediated via the co-adsorbed potassium.

Very recently, an ordered CO/O co-adsorbate on Pd(111) has been studied using ARUPS [80]. Early angle integrated photoemission results [95] were basically reproduced. The co-adsorption of oxygen shifts the positions of the  $4\sigma$  and  $5\sigma/1\pi$  bands to higher binding energies. This has been taken as evidence for a strong oxygen-CO interaction. The ARUPS study shows that the  $4\sigma$  dispersion, as represented in Fig. 13 by the half-filled square is in line with those of pure CO adsorbates. Therefore, if there is any distortion of the wavefunction it is smaller than in the case of K/CO adsorbates. Further comparison with other pure CO adsorbates on Pd(111) revealed that the observed chemical shift of the CO peaks can be explained exclusively via CO-CO interaction. Therefore, the reason for the high tendency of the CO + O/Pd(111) to form  $CO_2$  well below room temperature [95] must be due to CO-CO and O-O repulsive interactions rather than strong attractive CO-O interactions within the adsorbate.

## 3. Inner-Valence Ion States of Molecular Adsorbates

Photoemission has failed so far to allow detailed spectroscopic investigations of the inner valence ionization region of adsorbed molecules, where by "inner" we mean any valence ionization below the  $4\sigma$  ionization. From the point of view of the gas phase the inner valence region appears particularly interesting because here the simple one electron picture of photoemission is known to break down [42]. In other words, instead of observing only one inner valence ion state, for example, the  $3\sigma$  ion state in CO, a whole series of ion states, due to shake-up satellites is found experimentally [96]. These shake-up satellites partly borrow their intensity from the outer valence ionizations [97]. Therefore, the intensity of these lines is rather low. Only very few attempts have been published to spectroscopically investigate the inner valence region of adsorbed CO [98, 99]. Several groups have recently chosen a different approach [100–106]: Electron spectroscopy via autoionization of highly excited states of the adsorbate. These highly excited states are popu-



Fig. 20. Schematic total energy level diagram for ground and excited states of the neutral *N*-electron system (left panel), the single hole state N-1-electron system, and the double hole state N-2-electron system. Wiggly arrows indicate photon excitation, straight arrows radiationless decay chanels. The energy scale is broken in order to separate valence- and core-excited states

lated through core-to-bound excitations with synchrotron radiation, and decay radiationlessly into valence ion states of the adsorbate. Figure 20 illustrates the connection between autoionization and photoemission:

In the left panel ground and excited states of the neutral system are indicated. If we excite the system with a photon hv (wiggly line) into a state, high enough in energy, this state may decay radiationlessly via autoionization into the lower ion states of the system (middle panel of Fig. 20). The emitted electron carries a kinetic energy

$$^{\text{Auto}}E_{kin} = E(M_n) - E(M_0^+) \tag{5}$$

which is via:

$$hv = E(M_n) - E(M_0) \tag{6}$$

and

$$IP = E(M_0^+) - E(M_0) \tag{7}$$

equal to the kinetic energy of an electron that is emitted as a consequence of a photoemission event with the same photon energy, and leading to the same final ion state:

$$^{\text{PES}}E_{\text{kin}} = hv - IP. \tag{8}$$

This allows us to put photoemission and autoionization spectra on a common binding energy scale relative to  $E_F$ . Of course, for photon energies unequal to hv, autoionization does not occur, while photoemission is still possible. In other words, at particular photon energies we expect to find the superposition of the photoelectron and the autoionization spectrum in an electron spectrum of an adsorbate. This is shown in Fig. 21 where electron spectra of a  $CO(2 \times 1)p2mg/$ Ni(110) adsorbate are plotted for different photon energies. The spectra were recorded at near normal incidence with s-polarization parallel to (100), and near normal emission employing light from the exit slit of a high energy-TG-monochromator at the BESSY storage ring.

The lowest spectrum shows for comparison the spectrum of a clean Ni(110) surface taken with hv = 288 eV. Except for the *d*- and *s*-bands (and valence shake-ups) of clean Ni(110) there are no intense features found below 10 eV binding energy. Upon CO adsorption the photoelectron spectrum taken with 278 eV photon energy shows very low intense  $5\sigma/1\pi$ and  $4\sigma$ -features at ~8 eV and 11 eV, as expected, but hardly any structure below 15 eV binding energy. If the photon energy is increased to 288.0 eV, an energy for which the clean Ni (110) spectrum is shown below, we are in resonance with the lowest energy  $C1s \rightarrow 2\pi$ excitation, which decays into the valence ion states and leads to the observed intense adsorbate spectrum with six features as indicated. The intensity of these features is drastically attenuated if we change from nearnormal to near-grazing light incidence. This attenuation documents the dipole selection rules for the initial  $C1s \rightarrow 2\pi$  excitation: The CO molecules are tilted only slightly from normal orientation ( $\sim 20^\circ$ ) so that a  $C1s \rightarrow 2\pi$ -excitation exhibits its highest oszillator strength for near (20°)-normal light incidence, because the polarization vector should be oriented perpendi-



Fig. 21. Normal emission electron spectra [114] for various photon energies as indicated. Those spectra taken in resonance with a core-to-bound excitation are marked

cular to the C-O-bond axis. Thus, it is clear that the observed intensity (spectrum C) is proportional to the population of the resonance state, as expected for autoionization. Upon increasing the photon energy to 304 eV (spectrum D) we reach the region of the  $C_{1s} \rightarrow \sigma$ -shape resonance excitation, which is a coreto-continuum excitation [107]. Therefore, the dominant decay mechanism in the latter case is Auger decay, i.e. a radiationless transition from a core-hole state (middle panel of Fig. 20) to a two-valence-hole state, as indicated in the right panel of Fig. 20. In this case, the Auger KVV-transitions appear as low intense features at higher binding energy, because they stay fixed in kinetic energy while the photoemission peaks shift. This is documented by the spectrum taken with hv = 320 eV. With this photon energy one is well above the core-ionization threshold. The Auger peaks are shifted with respect to the previous spectrum by the difference in photon energy. At this point, a note concerning the difference between Auger decay and autoionization decay in connection with adsorbate



Fig. 22. Comparison of the gas-phase photoelectron spectrum of CO in the valence region [96] and the CO autoionization spectrum after  $C1s \rightarrow 2\pi$  excitation [100, 101, 111]. The spectra are plotted on a common binding energy scale

studies appears necessary. It has been argued [103, 105, 105]106] that for chemisorbed molecules the difference between autoionization and Auger decay vanishes because the screening electron (see discussion below) has been transferred from the metal to the molecule before the radiationless decay takes place. Then, the wavefunction of the molecule looks similar to a coreto-bound excited system as in the case of autoionization. Of course, since the amount of charge transfer is a matter of the molecule-substrate coupling strength, this argument only holds for very strong coupling. Detailed studies on this aspect will certainly be persued in the future, and we shall not dwell on this subject here. Returning to Fig. 21 we finally reach the  $O1s \rightarrow 2\pi$ resonance, and we observe resonance enhanced features at the same binding energy position as in the case of the C1s $\rightarrow$ 2 $\pi$  induced spectrum, because Eqs. (5)–(8) hold.

To interpret the autoionization spectra of the adsorbate, we may consider the corresponding spectra in the gas phase [101, 108–111]. Figure 22 shows a comparison of the valence photoemission spectrum of CO with the autoionization spectrum. The message is here that the shake-up peaks occurring with very low intensity in the inner valence region of the photoelectron spectrum of CO exhibit rather large intensities in the autoionization spectrum. The reason is the different matrix element governing a photon induced dipole transition

$$I \propto |\langle \psi_{\rm f} | p | \psi_{\rm i} \rangle|^2 \tag{9}$$

in photoemission with respect to a radiationless transition

$$I \propto |\langle \psi_{\rm f} | 1/r_{ij} | \psi_{\rm i} \rangle|^2 \tag{10}$$

in autoionization. It has been shown numerically that this accounts for the experimental observations [112]. It therefore seems obvious to try a corresponding interpretation in the adsorbate case. The bands situated at binding energies above the photoemission features at 8 eV and 11 eV correspond to shake-up states which are very weak in photoemission and have so far not all been observed in photoemission spectra of adsorbed molecules. However, theoretical calculations have predicted the existence of such states [54]. Figure 23 shows an autoionization spectrum in comparison with a calculated photoemission spectrum of a Ni<sub>2</sub>-CO cluster. The character of the states, as given by the calculation, is indicated. In the photoelectron spectra the  $5\sigma/1\pi$  and  $4\sigma$  ionization are most intense. These states are partially screened [50–56], and they correspond to configurations  $M^{-1}5\sigma^{-1}(1\pi^{-1})2\pi$  and  $M^{-1}4\sigma^{-1}2\pi$  of the adsorbate where M denotes a metal level. In order to deduce from this calculation how the relative intensities of the various change when going from photoionization to autoionization we resort to the qualitative discussion of autoionization matrix elements outlined in [112]. In general, the intensity of an autoionization decay is given by (10). A more detailed analysis [112] shows that the calculation can, under certain approximations, be reduced to matrix elements of the type:

$$\langle \Phi_{lm}, \Phi_{v}|1/r_{ij}|\Phi_{v}\Phi_{1s}\rangle,$$

where the  $\Phi_1$  are one-electron levels and the index v stands for valence. The autoionization intensity for the screened  $5\sigma/1\pi$  and  $4\sigma$  states is small because it is governed by matrix elements of the type

$$\begin{split} &\langle \Phi_M \Phi_{lm} | 1/r_{ij} | \Phi_{1s} \Phi_{4\sigma} \rangle, \\ &\langle \Phi_M \Phi_{lm} | 1/r_{ij} | \Phi_{1s} \Phi_{5\sigma} \rangle \\ &\text{or} \\ &\langle \Phi_M \Phi_{lm} | 1/r_{ij} | \Phi_{1s} \Phi_{1\pi} \rangle, \end{split}$$

where  $\Phi_{lm}$  is the continuum orbital of the outgoing electron characterized by the angular quantum numbers l and m. This has to be compared with matrix elements of type  $\langle \Phi_{lm} \Phi_{4\sigma} | 1/r_{ij} | \Phi_{1s} \Phi_{2\pi} \rangle$  etc. for the free molecule. In the latter case all active orbitals are localized on the molecule, i.e. in the same region of space, leading to large coulomb matrix elements, while in the former case, the metal orbital involved is spatially removed from the molecule reducing the coulomb matrix element considerably. A different situation is expected for the unscreened state, i.e. configurations of type  $5\sigma^{-1}$ ,  $4\sigma^{-1}$  or  $1\pi^{-1}$ . Their



Fig. 23. Assignment [114] of the CO  $(2 \times 1)p2mg/Ni$  (110) autoionization spectrum after  $C1s \rightarrow 2\pi$  excitation on the basis of a Ni<sub>2</sub>-CO cluster calculation [54]

intensity should be large, as are the spectator decay lines in the free molecule. These unscreened states, which are the intense states in photoemission in the gas phase, correspond to shake-up satellites with rather low intensity in the case of photoelectron spectra of adsorbates, and are situated at higher binding energy than the screened states. The calculation presented places the lines involving the  $5\sigma^{-1}$  unscreened states at slightly lower binding energies as compared with the  $M^{-1}4\sigma^{-1}2\pi$  screened ion state. However, the shakeup states involving the  $4\sigma^{-1}$  configuration are situated several eV below those involving the  $5\sigma^{-1}$  shake-ups. We expect the  $5\sigma^{-1}$  shake up states to exhibit larger intensities as compared with the  $4\sigma^{-1}$  shake-up states for the  $C1s \rightarrow 2\pi$  decay because of the preferential localization of the  $5\sigma^{-1}$  configuration on the carbon atom. We identify peak (1) in Fig. 21 as a  $5\sigma^{-1}$  shakeup state, because its intensity is attenuated in the  $O1s \rightarrow 2\pi$  decay spectrum. The calculation places the  $4\sigma^{-1}$  shake-up states into the flank of the most intense peak. The most intense peak appears to be a superposition of states mainly due to  $5\sigma^{-1}1\pi^{-1}2\pi$ , and  $1\pi^{-2}2\pi$ configurations which is consistent with its large intensity in both the  $C1s \rightarrow 2\pi$  and  $O1s \rightarrow 2\pi$  decay spectra. In the region below the most intense peak, the situation becomes rather complicated, because many configurations start to mix and an assignment has to await more detailed explicite calculations of the autoionization intensities. However, there is reason to believe, that we can also achieve more detailed experimental information. As Umbach and Hussain [113] demonstrated, electron emission via radiationsless decay can



Fig. 24. Angle resolved  $C1s \rightarrow 2\pi$ -autoionization spectra of the system CO (2 × 1)p2mg/Ni (110) as reported in [114] for the [110] and [100] Ni (110) surface azimuths. The light polarization was along the [100] azimuth. The chosen polar angles are indicated in the figure

lead to strong angular dependences of the emission intensities. These angular dependences can be connected with the symmetries of the final states, and can help to assign the spectra.

Figure 24 shows a set of spectra for the  $CO(2 \times 1)p2mg/Ni(110)$  system, and it is obvious that there are angle dependent effects even as a function of the surface azimuth. Without a detailed discussion of these spectra, which will be published elsewhere [114], we realize for example, a strong intensity increase of the  $5\sigma^{-1}$  shake-up state, assigned above, for off-normal emission. This has to be expected for a matrix element of type

$$\langle \Phi_{lm} \Phi_{5\sigma} | 1/r_{ij} | \Phi_{1s} \Phi_{2\pi} \rangle$$

because in order for the integrand to become totally symmetric, which is a prerequisite for it not to vanish,  $\Phi_{im}$ , the continuum orbital of the outgoing electron, has to have  $\pi$ -symmetry. A continuum orbital with  $\pi$ -symmetry shows increasing intensity for off-normal emission. As is obvious from Fig. 24, there are several peaks, exhibiting pronounced angular variations and these can be used to confirm and disentangle the assignment of the autoionization spectra in more detail in the future.

This last section served mainly to show that via a study of autoionization spectra we may be in a position to fill the "white spot" on the "spectroscopic map" of adsorbed CO.

### 4. Conclusion

We have shown that for molecular adsorbates photoelectron spectroscopy provides a useful method to study the electronic structure of these systems. Via angle resolved measurements molecule - substrate and intermolecular interactions can be disentangled. For adsorbates like carbon monoxide the wealth of available spectroscopic information allows us to form a detailed picture of the electronic interactions in these systems. However, even for such well-studied systems there remain a number of unanswered questions. We have chosen as an example for such an unanswered question the spectroscopy of the inner valence ion states of adsorbed CO, where we only start to learn by applying new electron spectroscopic techniques. Therefore, even though for some people it may sound like a lack of ideas, if someone resorts to the study of CO adsorbates, there is still a lot to be learned from the study of carbon monoxide adsorbates. However, the present review is not meant to leave the reader with the impression that no systems other than CO studied using photoelectron spectroscopy. Two examples out of the many available studies serve to show that photoemission applying angle resolved techniques keeps its firm position in the hierarchy of methods applied in surface science even if the problems are chemically more involved than in the case of a carbon monoxide adsorbate system.

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