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Autoionization spectroscopy of CO on metal oxide surfaces

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Abstract

Angular resolved autoionization spectra of CO after C1s $\rightarrow 2\pi^*$ excitation on different epitaxially grown metal oxide surfaces are presented. The spectra of the adsorbates on the oxide substrates differ with variation of the substrate. The spectra are compared with those obtained both for gas phase CO and for CO adsorbed on different metals, and differences in the bonding mechanisms are discussed. Qualitative calculations of the angular dependence are presented together with the measured spectra. Valence CI calculations of the states reached by the decay are also given.

Keywords: Autoionization spectroscopy; C1s $\rightarrow 2\pi^*$ excitation; CO; Metal oxide surface; Valence-CI calculation

1. Introduction

Adsorbates on metal substrates have been subject to a number of studies using electron spectroscopic techniques. However, adsorbate systems with insulating substrates, e.g. oxides, have not been as thoroughly studied. This is partially because of the existing experimental difficulties connected with sample charging and poor thermal conductivity. Epitaxially grown oxide films on metal single crystals allow the methods of electron spectroscopy to be applied to these systems without charging effects and also allow the systems to be cooled for adsorption studies [1,2].

A technique which has recently proved to be most useful in studies of the electronic structure of adsorbates is autoionization spectroscopy (also

known as deexcitation electron spectroscopy, DES, or resonant Auger spectroscopy) [3]. In this method the photon energy is tuned to match a core-to-bound excitation, which in the case of a free CO molecule corresponds to excitation of either a C1s or an O1s electron into the initially empty $2\pi^*$ orbital. The decay of this highly excited state by electron emission results in two types of final state. There are single hole states, where the electron excited to the $2\pi^*$ orbital takes part in the decay, which are referred to as participator decay states. These states are the same as those reached directly by photoemission. The other type of state is that in which the excited electron remains in the $2\pi^*$ orbital, which is denoted the spectator decay state. The latter type of decay hence results in final states with two holes in the valence region and the spectator electron in the previously unoccupied orbital, i.e. 2 hole-1 particle states (2h-1p).

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Autoionization spectroscopy after core-tobound excitation has proved to be a valuable complement for the investigation of the inner and outer valence spheres of molecules. In the photoemission spectrum, the inner valence region is dominated by many particle effects, exhibiting a multitude of weak satellites. However, the relaxation of coreto-bound excited states results in a spectrum strongly dominated by the 2h-1p states, which in the case of a free molecule corresponds to the weak shake-up states observed by photoemission [4]. This difference is attributable to the fact that the matrix elements which govern the processes are different. The photoemission is described by a dipole matrix element, whereas the matrix element for the decay process in the autoionization is of coulombic type [5,6].

In the case of an adsorbed molecule, the presence of the substrate may have a strong influence on both the photoemission spectrum and the deexcitation spectrum, owing to the possibility of charge transfer screening. It has been found that, by comparing the autoionization spectrum with the normal Auger spectrum recorded with a photon energy clearly above the ionization limit, valuable information can be obtained regarding the adsorbate-substrate interaction strength [7–9].

The autoionization and Auger spectra for physisorbates are essentially identical to those observed in the gas phase, and show only rigid shifts due to image screening by the substrate and polarization of the surrounding adsorbates. However, it has been found that an electron may be transferred either to or from the adsorbate on the time scale of the core hole lifetime, i.e. typically 10^{-15} s. If this process takes place, the resulting core hole decay spectrum consists of a gas phase-like autoionization and an Auger spectrum, with a relative intensity depending on the charge transfer rate [7]. Because the charge transfer process takes place in order to reach the energetically lowest core hole state, the direction of the charge transfer, i.e. to or from the adsorbate, may be predicted by a comparison of the energy for the lowest neutral core hole state, as measured by X-ray absorption spectroscopy (XAS), and the energy for the lowest core ionized state [the binding energy obtained by X-ray photoelectron spectroscopy (XPS)] [7,8].

If a chemical bond is formed, i.e. in the case of chemisorption, charge transfer occurs at the timescale of the photoemission process, which is in the order of 10^{-17} s. The very efficient neutralization and relaxation processes yield a core excited state prior to the decay which is independent of the excitation energy. Thus the autoionization and Auger spectra become nearly identical, which has been observed experimentally for CO adsorbed on a number of metal surfaces [9–14].

Nevertheless, the core hole decay spectra for chemisorbed CO show a strong dependence on the choice of substrate [13], and although the same information can be obtained from the Auger spectrum, the autoionization technique has the advantage of yielding a spectrum with much higher intensity owing to the high cross section for the core-to-bound excitation. It was found that the shape and relative intensity of certain features at the low binding (or high kinetic) energy side of the C1s decay spectrum varied strongly depending on the strength of the chemisorption bond [13]. This was not too surprising, because these peaks have been identified as due to a decay involving the $2\pi^*$ -Me hybrid orbital formed upon chemisorption [10-12].

In order to assign all the features appearing in the autoionization spectrum, theoretical calculations have been performed in the case of CO/ Ni(110) [14]. Furthermore, if the molecules are ordered on the surface, an identification of the different peaks is possible by studying their angular dependence, a technique which was first utilized in the Auger spectrum for CO/Ni(100) [15,16].

In the present work, autoionization spectra of CO on epitaxially grown metal oxide surfaces are discussed. We will present C1s autoionization and Auger spectra for different coverages of CO very weakly bound on an $Al_2O_3(111)$ surface and compare them with the gas phase autoionization. Then the C1s autoionization spectra for CO adsorbed on three different transition metal oxide surfaces [Cr₂O₃(111), NiO(100) and NiO(111)] are presented and discussed. A comparison between the autoionization and the UP spectra of CO on NiO(111), NiO(100) and Ni(110) will be given. An assignment of the peaks appearing in the different spectra is given based on the angular

dependence and previous results. Finally, results of valence CI calculations are presented.

2. Experimental procedure

The experiments were performed in a magnetically shielded (double μ -metal shield) vacuum system containing facilities for low energy electron diffraction (LEED), Auger electron spectroscopy (AES), residual gas analysis with a quadrupole mass spectrometer, and an angle resolved hemispherical photoelectron detector (VSW HA 50). The measurements were carried out at the BESSY I storage ring on the high energy toroidal grating monochromators 1 and 2 (HE-TGM 1, HE-TGM 2). The base pressure in the system was below 4×10^{-10} mbar.

Before each C1s autoionization spectrum, a C1s NEXAFS spectrum was recorded up to the maximum of the π resonance in order to obtain the correct monochromator setting. No absolute photon energy calabration was made. All the binding energy scales in the figures are relative at the Fermi level of the metallic substrate.

The crystals were spot welded to two tungsten rods mounted on a sample manipulator. The sample could be cooled with liquid nitrogen to 80-85K. Heating was achieved via electron bombardment from a filament on the reverse side of the crystal. For the experiments with Al₂O₃, liquid helium cooling was installed to allow the crystal to be cooled to ≈ 30 K.

The oxide films were prepared by oxidation of Ni(100), Ni(111), Cr(110) and NiAl(110) single crystals in an oxygen atmosphere [17,18]. The surface of the crystal was cleaned by argon or neon ion bombardment, followed by annealing. The CO adsorption was performed by cooling the sample to T = 80-85 K with a background pressure of 1×10^{-8} mbar CO. In the case of Al₂O₃ the crystal was cooled to 35 K and then heated until a suitable coverage was reached. The background pressure was $\approx 2 \times 10^{-8}$ mbar of CO. This was used to gain a stable coverage (saturation coverage). Because the multilayer desorbs at a slightly lower temperature than the monolayer–multilayer transition by

monitoring the intensity of the NEXAFS π resonance as a function of temperature. The fit routine used to fit the spectra of all angles simultaneously is described elsewhere [19].

3. Results and discussion

3.1. CO/Al₂O₃(111)

The thin alumina film formed on NiAl(110) has been found to be atomically flat and well ordered [18]. The oxide surface is believed to be oxygen terminated and thus to interact only weakly with an adsorbate; e.g. the CO monolayer desorbs at 55 K [18]. Fig. 1 shows the C1s autoionization spectra for different coverages of CO on $Al_2O_3(111)$ recorded at normal emission. The spectrum at the bottom of the figure is the well known gas phase autoionization spectrum of CO [20] with the assignment published by Freund and Liegener [21]. It is shifted with respect to the energy axis in



Fig. 1. Autoionization spectra of CO in the gas phase [20] with the assignments of [21] and autoionization of different coverages of CO on an $Al_2O_3(111)$ surface.

Coverage	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	
Multilayer	1.57	1.47	1.76	1.91	2.07	
Intermediate coverage	1.45	1.58	2.11	2.03	2.31	
Mono- or submonolayer	(3.59)	1.72	2.24	2.72	2.95	
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FWHM of the peaks in the autoionization spectrum of CO/Al₂O₃(111). The values are the results of a fit

order to fit the Al_2O_3 spectra above. The spectrum above is that of a multilayer of CO condensed onto the Al₂O₃ surface. The two spectra are very similar. They reveal five peaks in the energy region up to 25 eV. The three peaks at low binding energy are due to the decay into the participator or single hole states $(5\sigma^{-1}, 1\pi^{-1}, 4\sigma^{-1})$ in the gas phase spectrum, and the following two peaks are formed by 2h1p satellite states (spectator decay) with the dominating configurations $4\sigma^{-1}5\sigma^{-1}2\pi^*$, $5\sigma^{-2}2\pi^*$ and $5\sigma^{-1}1\pi^{-1}2\pi^*$ [21]. The differences between the gas phase and the multilayer spectrum are small and it can be stated that the assignment of the peaks is the same in both cases. On decreasing the coverage of CO on the Al_2O_3 surface the spectra change slightly.

The spectrum at the top of Fig. 1 is that of a mono- or submonolayer of CO. The spectrum below corresponds to a slightly higher coverage, approximately a double layer. In all spectra the overall shape is the same. They exhibit five peaks at the same binding energies. But the FWHM increases with decreasing coverage, as shown in Table 1. This could be due to an increasing number of states gaining intensity in the autoionization process or to lifetime effects [22]. Moreover, the peak at the lowest binding energy, the $5\sigma^{-1}$ state, exhibits significant variations. The relative intensity decreases with decreasing coverage or broadens very strongly, which causes it almost to vanish in the monolayer spectrum. A continuous shift towards higher binding energies cannot be excluded.

CO normally chemisorbs on a metal with the carbon end down, which is the preferential location of the 5σ orbital. This leads to a shift towards higher binding energies, as observed by photoemission, and the 5σ orbital becomes almost degenerate with the 1π orbital. Although the nature of the bonding is different [23], a similar effect has been

observed for CO bonded on NiO(100), where the molecules are oriented perpendicularly to the surface with the carbon end down [24]. Unfortunately, the orientation of the CO molecule on the Al₂O₃ surface is not known, and the molecules might very well be randomly oriented [25]. However, the decrease of the $5\sigma^{-1}$ signal may be taken as a hint of a contribution of the 5σ orbital to the bonding mechanism.

As a next step, normal emission Auger spectra were recorded for the different situations in order to see whether these spectra also show a strong resemblance to the case of free CO. In the multilayer situation a spectrum like the CO gas phase Auger spectrum [20] can be observed, as expected. However, if the coverage is lowered to approximately one monolayer, the sharp structures vanish and only a large, extremely broad feature is visible, as shown in Fig. 2. The difference spectrum was obtained by subtraction of a spectrum recorded at a photon energy below the π resonance, thereby removing structures due to direct photoemission. It is difficult to give a detailed interpretation of this behaviour, but a few conclusions can be drawn. The CO molecule is not chemisorbed as it is on a metal, because this would lead to an Auger spectrum that is very similar to the autoionization spectrum.

The similarity of the autoionization spectrum to that of free CO instead indicates an extremely weak (if any) interaction between the $2\pi^*$ orbital and the oxide. That the Auger spectrum does not resemble the gas phase spectrum is probably caused by the electrostatic interaction with the oxide substrate upon the creation of the doubly ionized final states. As seen in Fig. 1, a broadening appears also in the case of autoionization, where the final states are singly ionized. This effect might very well be strongly enhanced in the Auger spectrum.

Another effect to take into account is the possibility of tunnelling effects, as observed for

Table 1



Fig. 2. Auger spectrum of CO on AlM_2O_3 . The Auger spectrum is the spectrum at the top of the figure. The spectrum below it is a shifted one which has been taken at an energy below the resonance. The third spectrum is the difference spectrum. The subresonance spectrum has been shifted to fit to the Auger spectrum and was normalized to the O2s peak marked in the figure.

physisorbates. If the neutral, core excited C $1s^{-1}2\pi^{1}$ state (the "XAS state") had a lower total energy than the C $1s^{-1}$ core ionized state (the "XPS state"), the situation would be the same as for $N_2/$ graphite [7]. Thus, if a tunnelling process occurred during the lifetime of the C1s hole, this would give rise to autoionization features in the Auger spectrum. We can easily see in Fig. 2 that this is not the case; no sharp autoionization peaks are present. There are two possible reasons for this: either tunnelling from the oxide is not present, or reduced, or the energy relationship between the XAS and XPS states is reversed. The latter effect would instead result in the presence of the broad Auger features in the autoionization spectrum. Upon close inspection of Fig. 1, we find that this possibility cannot be

ruled out; a broad Auger hump could be present underneath the sharp autoionization features.

A plausible explanation for the reversal of the XAS-XPS relationship could be the proximity of the negatively charged oxygen terminated oxide, which would lower the total energy for creation of a positively charged molecule. However, it is quite obvious that carefully calibrated XAS and XPS data are necessary to solve this problem fully.

Summarizing, it can be said that the states populated in the case of the autoionization of CO on the Al_2O_3 surface are the same as in the case of the CO gas phase autoionization. The effect of the substrate is mainly the broadening, which seems to be even more pronounced in the Auger spectrum. This behaviour is corroboration that CO bonds mainly via electrostatic interaction rather than by formation of a "normal" chemical bond, as for CO adsorbed on metals.

3.2. CO on transition metal oxide surfaces

Fig. 3 shows the C1s autoionization spectra for CO adsorbed on three different transition metal oxide surfaces, namely $Cr_2O_3(111)$, NiO(100) and NiO(111), recorded at normal emission. The CO adsorption properties have previously been found to differ significantly between these oxide surfaces: it has been proposed that the hexagonal $Cr_2O_3(111)$ surface consists of both oxygen- and chromium-terminated patches. However, at a temperature of 80 K (which is the case here), CO bonds only to the Cr atoms. ARUPS and NEXAFS show that the molecular axis is, in this case, oriented parallell to the surface [26]. On the NiO(100) surface, which consists of Ni and O atoms in a NaCl structure, CO adsorbs at 80 K on only the Ni atoms in a perpendicular fashion, as deduced from ARUPS and NEXAFS results [24]. The NiO(111) surface, however, is unstable and reconstructs by forming (100) facets. The CO molecules adsorbs on the (100) facets with the axis perpendicular to the (100) surface, i.e. the molecular axis is



Fig. 3. Autoionization spectra of CO on different transition metal oxide surfaces (Cr₂O₃(111), NiO(100) and NiO(111)) after resonant C1s $\rightarrow 2\pi^*$ excitation.

thus tilted 45° with respect to the (111) surface [27,28].

The spectra shown in Fig. 3 all reveal two broad features in the low binding energy region (up to 18 eV) and two intense features at higher binding energies. The spectra look very similar apart from some differences in the relative intensities. Because all the spectra are taken at normal emission and the orientation of the CO on the surface is different in all three cases, these differences may be caused by the angular dependence of the autoionization peaks and also by different decay mechanisms.

Compared with the spectra of CO on Al_2O_3 there are some obvious differences. The FWHM of the peaks in the transition metal case is comparable with that for peaks in the CO monolayer spectrum on Al_2O_3 , but in the low binding energy region only two peaks are observed, whereas three peaks were observed for CO/Al₂O₃. In the higher binding energy region two peaks again appear, but those of the transition metal oxides are shifted about 1 eV to higher binding energies with respect to those in the autoionization of CO on the Al₂O₃ surface.

In the following paragraphs we discuss the spectra taken on the various substrates in more detail. We will deal first with the low binding energy region. In the gas phase spectra and, presumably, also in the case of CO on Al₂O₃, the low binding energy region is dominated by single hole states. This is in contrast to the autoionization spectra of CO on metals, where charge transfer states, i.e. states due to a decay involving the 2π -Me hybrid orbital, dominate this region, as shown by Porwol et al. for the case of CO on Ni(110) [14]. Significant differences are observed when comparing the C1s autoionization spectrum of CO on Ni(100) and Ni(110) with that of CO on NiO(100) and Ni(111). In the low binding energy region, two peaks are observed for CO on the oxide surfaces, whereas this region is dominated by one peak for CO on Ni metal. The same is observed in the binding energy region 18-27 eV, where there are two strong peaks for CO/NiO but only one strong feature for CO/Ni.

As mentioned previously, the autoionization spectra for CO on metal surfaces change strongly depending on the adsorbate-substrate interaction, but it is argued that charge transfer states dominate the low binding energy region in all the spectra [13]. In the case of CO on a Ag(110) surface, where the molecules are very weakly bonded (desorption temperature ≈ 50 K), the spectrum looks very similar to the spectra of CO on the transition metal oxides [13]. Now the question arises whether the COtransition metal oxide bonding is comparable with an extremely weak CO-transition metal bonding.

The core hole decay spectra for CO/Ag(110) have been found to exhibit the typical behaviour for chemisorbed CO, that is, the Auger spectrum is nearly identical to the autoionization spectrum [29]. In order to check whether this applies also for CO on a transition metal oxide, an attempt was made to measure the C1s Auger spectrum for CO/NiO(100), using nonmonochromatized Al $K\alpha$ X-rays. Owing to intensity problems, the obtained spectrum was of poor quality, but it appeared to be similar to the Auger spectrum for CO/Al₂O₃. This would indicate a bonding which also in this case is strongly dominated by electrostatic forces rather than π -backdonation as in the case of CO on metals.

To elucidate further the possible single hole character of the low binding energy peaks in the autoionization spectrum, a comparison was made with UPS results. As shown in the literature, the same states are reached in the autoionization process and in photoemission for the free molecule [4]. For that reason the comparison between the autoionization and the photoelectron spectrum provides an interesting possibility for deciding about the nature of the structures in the spectrum. Fig. 4 shows the UP and the autoionization spectrum of CO on NiO(111) and in addition an assignment of the peaks in the UP spectrum [28]. The UP spectrum was recorded in the so-called "allowed" geometry to ensure that both σ and π states are visible and with a photon energy of 35 eV.

It can be stated that the low energy peaks in the autoionization spectrum are at about the same location as the structures in the UP spectrum, indicating that the same states are populated in both types of spectra. This is a strong hint of a major single hole character of the structures in the autoionization spectrum and it explains the number of



Fig. 4. UP (1) and autoionization (2) spectra of CO on a NiO(111) surface. The structures in the low binding energy region of the UP spectra are due to substrate emission. The adsorbate-induced features are marked in grey.

peaks in the low energy region. The $5\sigma^{-1}$ state is shifted towards the $1\pi^{-1}$ state owing to the electrostatic interaction between the CO and the surface, which has been experimentally demonstrated and discussed for the case of CO on NiO(100) in [24]. Thus we assign the first peak as being due to $5\sigma^{-1}$ and $1\pi^{-1}$ states and the second peak as being due to the $4\sigma^{-1}$ state. In the case of CO on Cr₂O₃, because of the change in adsorbate orientation a different assignment has been suggested [26], but the important point is that the autoionization peaks line up with the peaks in the UP spectrum.

Comparing the autoionization spectra of CO on the transition metal oxides with those for CO on the Al₂O₃ surface, it can be seen that the peak at a binding energy of 14 eV in the case of the transition metal oxide spectra is considerably more intense than the $4\sigma^{-1}$ state in the Al₂O₃ spectra.

We now turn to the high binding energy region. We assume that the assignment of those peaks is identical in all cases, including the gas phase, for simplicity. Then the observed shifts are reasonable considering the change in the $5\sigma^{-1}$ binding energy. With the $5\sigma^{-1}$ state shifted to higher binding energies, it is clear that a $4\sigma^{-1}5\sigma^{-1}2\pi^*$ or a $5\sigma^{-2}2\pi^*$ or even a $5\sigma^{-1}1\pi^{-1}2\pi^*$ state, which are the leading states for the peaks in the gas phase as calculated [21], should also be shifted to higher binding energies.

At this point we can summarize that the basic assignments of the autoionization peaks in the $Cls \rightarrow 2\pi^*$ spectra for CO on the oxide surfaces appear to be similar to the gas phase assignment. However, the substrates induce some differences in the spectra, compared with free CO, which leads to some uncertainty. The assignments need therefore to be further established, which can be achieved by use of the angular dependent intensity variations.

3.3. Discussion of the angular dependence

The angular dependence of the autoionization spectra has proved to be a valuable tool in assigning the spectra [14-16], owing to the fact that the orbitals taking part in the decay fix the angular distribution of the outgoing electrons, which can be understood by simple symmetry considerations of the matrix element ruling the decay process [14]. Anisotropies due to correlation between the excited state and the emitted electron are too small to influence the spectra perceptibly, and diffraction effects can also be excluded, because only the relative intensities of the peaks in the autoionization spectra are considered [15,16].

In the following we present the analysis done here for the case of CO on the NiO(100) surface. CO is adsorbed on NiO(100) perpendicular to the surface, as NEXAFS investigations [24] and ab initio calculations [23] have shown. To perform an analysis of the angular dependence it is necessary to fit the spectra, and Fig. 5 shows an example of such a fitted spectrum. The peaks we will deal with are those marked with the numbers 1-4, and they will be compared with calculated angular dependences of the gas phase spectrum referred to as pure configurations. In the calculations we thus consider only pure configurations (no configuration interaction is taken into account), and furthermore the so-called one centre approximation was used for the calculation of the matrix elements [6]. The wave functions employed were single zeta CO ab initio wave functions and the program was that described in [14]. The measurement of the angular dependences of gas phase autoionization has been possible to some extent by using polarized light and has been performed by Hemmers and coworkers [30,31]. The results of these measurements are in good agreement with the angular dependences calculated here. Fig. 6 shows the intensities



Fig. 5. (a) C1s autoionization spectrum of CO/NiO(111) for different polar angles showing the relative intensity variations. (b) C1s autoionization spectrum of CO/NiO(111) with the fitted curves. The peaks marked with numbers are those referred to in the text.

of the peaks (measured as areas of the fitted peaks) as a function of the polar angle. The first thing to be seen is that the dependence is very weak for all four peaks.

Fig. 6(a) shows the angular dependence of the first peak located at 11 eV binding energy. The intensity of this peak rises with the polar angle. At 0° polar angle it is $\approx 50\%$ of the highest intensity. If the low energy region of the spectrum is due to single hole final states the assignment should be $5\sigma^{-1}$ and $1\pi^{-1}$. Fig. 7(a) and (b) shows the angular dependences to be expected for those states. The dependences of the states assigned as $1\pi^{-1}$ are shown in Fig. 7(b). They differ for the two components $1\pi_x^{-1}$ and $1\pi_y^{-1}$ of this final state owing to the reduced symmetry of, e.g., the $1s \rightarrow 2\pi_x$ excited intermediate state. For the two configurations we obtain two continuum orbitals (channels) having mixed σ and δ symmetry and purely δ symmetry,



Fig. 6. Experimental angular dependences of the four main peaks in the autoionization of CO on NiO(100).

respectively. The contribution properly describing the dependence for higher polar angles is dominated by a δ channel only. The experimental angular dependence shows the same behaviour as the $5\sigma^{-1}$ state or the δ -type $1\pi^{-1}$ state.

Fig. 6(b) shows the angular dependence of the second peak located at 14 eV. As in the case of the first peak it is increasing, but it reaches its maximum much faster and ends in a kind of broad plateau. In addition to that, it is weaker than in the case of the first peak. The minimum intensity is \approx 70% of the maximum intensity. Compared with the dependence expected for the $4\sigma^{-1}$ state shown in Fig. 7(a), the overall behaviour is the same but the experimental curve is distinctly different from the calculated one. Obviously the maximum is reached much faster than expected from the calculation. This may be due to charge transfer processes from the NiO substrate.

The angular dependence of the third peak (20 eV) is reversed compared with the first two dependences shown. The intensity decreases nearly continuously but again it is only weakly

dependent on the angle. At its minimum it has $\approx 75\%$ of the maximum intensity. This is strikingly similar to the calculated dependences of the $5\sigma^{-2}\pi^*$ and the $4\sigma^{-1}5\sigma^{-1}\pi^*$ states shown in Fig. 7(c) and (d). The calculated dependences show the same shape and furthermore much smaller intensity variations than in the case of the single hole states. The dependences of the $1\pi^{-1}1\pi^{-1}2\pi^*$ and the $1\pi^{-2}2\pi^*$ states shown in Fig. 7(e) and (f), which dominate the satellite region in the metal spectra, show an entirely different angular dependence.

However, the angular dependence of the fourth peak at 25 eV does not reveal at all the expected behaviour of a $\sigma\sigma$ satellite. First of all its angular dependence is extremely weak, which may indicate a strong mixture of different states with different angular dependences. It fits with both a mixture of the $1\pi^{-2}2\pi^*$ and the $1\pi^{-1}1\pi^{-1}2\pi^*$ or the $5\sigma^{-1}4\sigma^{-1}2\pi^*$ and the $4\sigma^{-1}1\pi^{-1}2\pi^*$ states, but at the present no detailed assignment is possible for this peak.

Summarizing, in the case of the first three peaks the phenomenological assignment found before is



Fig. 7. Calculated angular dependences for gas phase CO. The calculation is done without any configuration interaction taken into account (pure configurations).

corroborated by the analysis of the angular dependences in the case of CO/NiO(100), but there are some uncertainties still remaining.

3.4. Angular dependence in the system CO/NiO(111)

All considerations stated above assume a static perpendicular orientation of the CO molecule. For tilted molecules the analysis of the angular dependence becomes much more involved. Maciejewski et al. reported an analysis of such a case for the first time [32]. They consider the case of CO/Ni(100) tilted to both sides containing the glide plane in CO(p2mg)/Ni(110).

According to NEXAFS measurements, CO is adsorbed on a NiO(111) surface with a tilt angle of about 45° , which results from the microfaceting of surface. A schematic drawing of the surface is shown in Fig. 8. The CO molecules are adsorbed on



Fig. 8. Model structure of the NiO(111) surface. The CO molecules (white) can be seen adsorbed on the NiO(100) microfacets in this figure.

the microfacets as if they were adsorbed on the NiO(100) surface, i.e. perpendicular to the microfacets but inclined at 45° with respect to the global surface plane. This explains why we detect an inclined geometry in the NEXAFS measurements. A detailed analysis has been reported elsewhere [28]. Because the faceting is connected with the considerable disordering on the surface, we must assume that there is no azimuthal ordering. Thus we employ the model sketched in Fig. 9 to represent



Fig. 9. Definitions of the angles used for the treatment of tilted molecules.

the angular dependence of the desired spectrum. This corresponds to an ensemble of CO molecules which rotate around the azimuthal angle φ , whereas the tilt angle δ is kept fixed at 45°.

We start our analysis by realizing that the probability for the excitation process preceding the deexcitation depends on the azimuthal angle φ . The intensity of exciting an electron from the 2s into a π -type orbital is given by

$$I_{\rm exc} \propto |\boldsymbol{E} - (\boldsymbol{E} \cdot \boldsymbol{M})\boldsymbol{M}| \tag{1}$$

where E is the electric field vector of the polarized light and M is the normalized vector of the molecular axis

$$\boldsymbol{M} = \begin{pmatrix} \sin \delta \cos \varphi \\ \sin \delta \cos \varphi \\ \cos \delta \end{pmatrix}$$
(2)

This leads to (see also [33,34])

$$I_{\text{exc}} = (|E_x|^2 + |E_y|^2 + |E_z|^2) - (|E_x|\sin\delta\cos\varphi + |E_y|\sin\delta\sin\varphi + |E_z|\cos\delta)^2$$
(3)

Introducing the degree of polarization P

$$|E_{x}|^{2} = P \cos^{2} \beta |E|^{2}$$

$$|E_{y}|^{2} = (1 - P)|E|^{2}$$

$$|E_{z}|^{2} = P \sin^{2} \beta |E|^{2}$$
(4)

where β is the angle of the spreading direction of the light and the surface. For the excitation of a molecule with a tilt angle δ and an azimuthal angle φ we obtain

$$I_{\text{exc}} \propto 1 - P\cos^2\beta\sin^2\delta\cos^2\varphi - 2\sqrt[3]{P}\sqrt[3]{1-P}\cos\beta\sin^2\delta\cos\varphi\sin\varphi - 2P\cos\beta\sin\beta\sin\delta\cos\delta\cos\varphi - (1-P)\sin^2\delta\sin^2\varphi - 2\sqrt[3]{P}\sqrt[3]{1-P}\sin\beta\sin\delta\sin\varphi\cos\delta - P\sin^2\beta\cos^2\delta$$
(5)

Furthermore, the angular dependence of the autoionization spectra itself depends on the deexcitation process. As already discussed in the preceding section, this intensity $I_{dec}(\gamma)$ depends on the angle γ between the molecular axis and the connection of the molecule and the analyser, and is given by

$$\cos\gamma = \frac{\boldsymbol{M} \cdot \boldsymbol{A}}{|\boldsymbol{M}| \cdot |\boldsymbol{A}|} \tag{7}$$

with

$$\boldsymbol{A} = \begin{pmatrix} r\sin\alpha\\0\\r\cos\alpha \end{pmatrix} \tag{8}$$

Because |M| = 1, it follows that

$$\cos\gamma = \sin\alpha\sin\delta\cos\varphi + \cos\alpha\cos\delta \tag{9}$$

Adopting the approximations of Maciejewski et al. [32], we can obtain an analytical form for the angular dependence of the decay as a function of the orbitals taking part. It can be stated that

$$I_{\sigma\sigma}^{\text{dec}} \approx |R_{00} Y_{00} + R_{20} Y_{20}|^2$$

= $[c_{00} + c_{20} (3\cos\gamma - 1)]^2$ (10)

$$I_{\sigma\pi}^{\text{dec}} \approx |R_{21}Y_{21} + R_{11}Y_{11}|^2$$

= $(c_{21}\cos\gamma\sin\gamma + c_{11}\sin\gamma)^2$ (11)

$$I_{\pi\pi}^{\text{dec}} \approx |R_{00} Y_{00} + R_{20} Y_{20} + R_{22} Y_{22}|^2$$

= $[c_{00} + c_{20} (3\cos\gamma - 1) + c_{22}\sin\gamma]^2$ (12)

These equations are identical to those of ref. [32] apart from the $R_{11}Y_{11}$ term in the $I_{\sigma\pi}$ case that is necessary to account for the 2s character of the 4σ and 5σ orbitals. The decay intensity for, e.g., a $\sigma\sigma$

satellite is given by

$$I_{\sigma\sigma}^{\text{dec}} \approx \left[1 + \frac{c_{20}}{c_{00}} [3(\sin\alpha\sin\delta\cos\varphi + \cos\alpha\cos\delta) - 1]\right]^2$$
(13)

Introducing now the probability of excitation and integrating over all possible azimuthal positions, it follows that

$$I_{\sigma\sigma l}^{\text{total}}(\beta, \alpha, \delta) = \int_{0}^{2\pi} I_{\text{exc}}(\beta, \delta, \varphi) I_{\sigma\sigma}^{\text{dec}}(\alpha, \delta, \varphi) d\varphi$$
(14)

The calculation of this integral is not difficult but is tedious, and will not be given in detail here. In the appendix the results for the special cases $I_{\sigma\sigma}^{\text{total}}(\alpha,\beta=45^\circ,\delta,P=0.8,c_{20}/c_{00}=1)$ and $I_{\sigma\pi}^{\text{total}}(\alpha,\beta=45^\circ,\delta d,P=0.8,c_{21}/c_{11}=1/3)$ can be found. The values of the parameters c_{20}/c_{00} and c_{21}/c_{11} were fitted to reproduce the angular behaviour of the corresponding peaks in the spectra of CO on NiO(100). In the case of the $\pi\pi$ satellite two parameters are necessary and the overall shape of the curve is dominated by those parameters. Therefore we did not perform further calculations for this case.

With such calculations it is possible to give a qualitative explanation of the angular dependence of the autoionization spectra of CO on NiO(111). The experimental results are shown in Fig. 10. The results of the estimations for a tilt angle of $\delta = 46^{\circ}$ are shown in Fig. 11 for the cases $\sigma\sigma$ and $\sigma\pi$. Again the first two peaks have to be compared with the dependence of the single hole states. In case of the $5\sigma^{-1}$ and $4\sigma^{-1}$ the $\sigma\pi$ case is relevant. Because the $\pi\pi$ case relevant for the $1\pi^{-1}$ state has not been calculated a comparison is not possible.

The experimental curves are both increasing with polar angle but the overall dependence is weaker than in the case of CO on NiO(100). This is in agreement with an expected weakening of the dependence from the azimuthal disordering. Both peaks seem to reveal a very broad maximum at $\approx 50-60^{\circ}$. The calculated curves show a maximum at $\approx 30-40^{\circ}$ but the overall shape is similar. The third peak shows a falling angular dependence (Fig. 10(c)) which can also be found in the estima-

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Fig. 10. Experimental angular dependences of the four main peaks in the autoionization of CO on NiO(111).

tion for the $\sigma\sigma$ satellite (Fig. 11, top). Again, however, the angular dependence of the fourth peak shown in Fig. 10(d) is still not comparable with the calculation (Fig. 11, bottom). Because the calculated dependences shown in Fig. 11 are only a rough estimate, it can be stated only that this is not in disagreement with the assignment for the CO autoionization on the transition metal oxide surfaces.

An attempt to carry out the same estimation for the case of $Cr_2O_3(111)$ shows distinctly different calculated and experimental dependences. However, the CO lies flat on the Cr_2O_3 surface $(\delta = 90^\circ)$ and more modelling is needed before a detailed analysis can be given.

3.5. Valence-CI calculations for the 1h and 2h1p cationic states

A rigorous assignment of the signals in the autoionization spectra requires detailed knowledge about the cationic states involved in the decay process. To this purpose, we performed ab initio CI calculations both for a CO gas phase molecule and

a CO molecule adsorbed on a NiO(100) surface. The calculations were carried out with the Bochum program package [35,36]. We utilized three different models for the NiO(100) surface in order to investigate separately the influences of the electrostatic field, the nickel 3d electrons, and the oxygen 2p electrons in the decay process. The first model was a simple Madelung field representing the pure electrostatic field of the ionic crystal. The second model was a NiO_5^{8-} cluster again embedded in a Madelung field. This model allows inclusion of the charge transfer (CT) states which are generated when electrons from the singly occupied eg-type Ni d-orbitals take part in the decay. We will refer to these orbitals in the following as metal d (Md) orbitals. Because the Pauli repulsion of the oxygen orbitals is necessary for the correct ligand field at the Ni atom [23], it needs at least this cluster for a reasonable description of the electronic structure at the NiO(100) surface. However, in this model we did not allow for a charge transfer from the oxygen atoms to CO. This is done in the third model, a MgO_5^{8-} cluster embedded in a Madelung field.



Fig. 11. Estimated angular dependence of the autoionization states of an azimuthally disordered molecule which is tilted by 46° from the surface normal.

The Ni atom was substituted by Mg because Mg does not contain 3d electrons, hence we can exclude charge transfer from the singly occupied nickel orbitals to CO. Because of the similarity between NiO and MgO, the MgO_5^{8-} cluster can represent the O2p orbitals of NiO reasonably well.

We used essentially the basis sets of ref. [23] (TZP basis for CO and DZ basis for the cluster models). The CI calculations were performed using the SCF orbitals of the ground state of CO or of the CO/NiO₅⁵⁻ or CO/MgO₅⁵⁻ cluster, respectively. The $2\pi^*$ orbital, unoccupied in the CO ground state, was optimized in the frozen core of a CO²⁺ ion. We included all configurations containing seven electrons in the 4σ , 1π , 5σ and $2\pi^*$ orbitals. Furthermore, we included all single excitations from the Ni d-orbitals for the NiO₅⁸⁻ cluster (model 2) and all single excitations from the O2p orbitals for the MgO₅⁸⁻ cluster (model 3).

In Table 2 we present the calculated energies of the 1h and 2h1p states as energy differences relative to the $5\sigma^{-1}$ state, which is set to 0 eV. In the first column of Table 2 the results for gaseous CO are shown. The second column contains the results for a calculation where the CO molecule is placed above the pure Madelung potential. In the third column the result of the calculation with the NiO_5^{8-} cluster is shown. The calculations with CO on the embedded MgO_5^{8-} cluster are not included in Table 2 because we obtained too many energetically very close states.

The calculated states for the gas phase CO are in total agreement with the experiment [20] and the assignment given by Freund and Liegener [21]. The comparison between the first two columns shows that the Madelung potential has almost no effect on the energetic order of the states. Because of the differences between the spectrum of CO on NiO(100) and that of gas phase CO discussed before, it can be stated that the electrostatic interaction is not a sufficient model for the adsorption. However, in the calculation for the NiO_{5|8-} cluster several differences arise. The energy difference between the $5\sigma^{-1}$ and $1\pi^{-1}$ states is considerably reduced, although it is not as small as expected from experiment [24].

In the low binding energy region two types of states are found. Between 0 and 4 eV there are only single hole states $(5\sigma^{-1}, 1\pi^{-1})$ with Md⁻¹ determinants mixing in). In the region between 4.5 and 5.2 eV, both the $4\sigma^{-1}$ single hole and the CT states can be found. The CT states have originally been assigned to too high energies, owing to a missing relaxation of the O2p orbitals upon the ionization of the nickel cation [37], and were shifted semiempirically by ≈ 6 eV to lower energies. Apparently the second peak (see Fig. 5) of the spectrum is formed by the charge transfer states together with the $4\sigma^{-1}$ state. This is consistent with the angular dependence of the second peak as discussed in Section 3.3. The assignment of the third peak as being dominated by $\sigma\sigma$ states is also corroborated by the present calculations. There are no $\pi\pi$ states in this energy region relative to the $5\sigma^{-1}$ state, thus our calculations predict no $\pi\pi$ influence on the third peak, corroborating the idea of a $\sigma\sigma$ -type structure.

The contribution of the charge transfer from the oxygen atoms can be estimated from the MgO_5^{8-} cluster calculations (model 3). They show a vast number of CT states in which excitations of the oxygen atoms to CO take place which form almost a continuum over the whole energy region. Because

Table 2

Valence-CI results for the energy level of the 1h and 2h1p states of CO

Energy (eV)	Isolated CO state	CO on Madelung potential state	CO on NiO ₅ ⁸ - cluster state
0	$5\sigma^{-1}$	$5\sigma^{-1}$	$5\sigma^{-1}$
2.2			$5\sigma^{-1}, Md^{-1}$
2.4			$1\pi^{-1}$
2.5			Md^{-1} , $5\sigma^{-1}$
2.8	$1\pi^{-1}$		
2.9			$Md^{-1}, 5\sigma^{-1}$
3.2			Md^{-1} , $5\sigma^{-1}$
3.3		$1\pi^{-1}$	3
4.8			$1\pi^{-2}2\pi^*$
4.9			$1\pi^{-2}2\pi^*$
5.0			4σ
≈5			$1\pi^{-2}C1$
5.2		a -1	$5\sigma^{-2}\pi^{*}$
5.8 4 1	51112-*	4 σ	
0.1	30^{-1}		
67		$5\sigma^{-1}1\pi^{-1}2\pi^*$	
6.8	$5\sigma^{-1}1\pi^{-1}2\pi^*$	50 IN 28	
7.2	••• •••		$5\sigma^{-1}1\pi^{-1}2\pi^*$
7.3			$5\sigma^{-1}1\pi^{-1}2\pi^*$
7.4			$4\sigma^{-1}$
			$5\sigma^{-1}1\pi^{-1}2\pi^*$
7.5			$4\sigma^{-1}$
			$5\sigma^{-1}1\pi^{-1}2\pi^*$
7.5			$1\pi^{-1}$
		1 1	$1\pi^{-2}2\pi^*$
7.9	- 1- 1	$5\sigma^{-1}1\pi^{-1}2\pi^*$	
8.1	$5\sigma^{-1}1\pi^{-1}2\pi^{*}$		c -ll. +
8.3			$5\sigma^{-1}\pi^{-2}\pi^{*}$
8.4		cl1_+l2_*	$5\sigma^{-1}\pi^{-2}\pi^{+}$
0.0	51110-*	$5\sigma 1\pi 2\pi^{-2}$	
9.0	$30 1\pi 2\pi^{-1}$	$3\sigma^{-1}5\sigma^{-1}2\pi^*$	
91	$5 \sigma^{-2} 2 \pi^*$	40 50 21	
2.1	$4\sigma^{-1}5\sigma^{-1}2\pi^*$		
9.2			$5\sigma^{-1}1\pi^{-1}2\pi^*$
9.3			$5\sigma^{-1}1\pi^{-1}2\pi^*$
9.5		$5\sigma^{-1}1\pi^{-1}2\pi^*$	
9.6	$5\sigma^{-1}1\pi^{-1}2\pi^*$	$5\sigma^{-1}1\pi^{-1}2\pi^*$	$5\sigma^{-1}1\pi^{-1}2\pi^*$
9.7	$5\sigma^{-1}1\pi^{-1}2\pi^*$		$5\sigma^{-1}1\pi^{-1}2\pi^*$
9.8			$5\sigma^{-1}1\pi^{-1}2\pi^*$
9.8			$5\sigma^{-2}2\pi^{*}$
			$4\sigma^{-1}5\sigma^{-1}2\pi^*$
9.8			$5\sigma^{-1}1\pi^{-1}2\pi^*$
9.9			$5\sigma^{-1}1\pi^{-1}2\pi^*$
10.1			4σ
10.2		1-15-12-*	$5\sigma 1\pi^{-2}\pi^{-2}$
10.2	40-150-170*	40 30 ZT	
10.5	-TU JU Z/		

Energy (eV)	Isolated CO state	CO on Madelung potential state	CO on NiO ⁸ 5 cluster state
10.4		$5\sigma^{-1}1\pi^{-1}2\pi^*$	
10.5	$4\sigma^{-1}5\sigma^{-1}2\pi^{*}$		
10.6	$5\sigma^{-1}1\pi^{-1}2\pi^*$ $4\sigma^{-1}$		
10.7			$4\sigma^{-1}5\sigma^{-1}2\pi^{*}$
10.7			$5\sigma^{-1}1\pi^{-1}2\pi^*$
10.7			$4\sigma^{-1}5\sigma^{-1}2\pi^{*}$
10.9			$5\sigma^{-1}1\pi^{-1}2\pi^{*}$
11.2			$5\sigma^{-1}1\pi^{-1}2\pi^{*}$
11.7		$5\sigma^{-1}1\pi^{-1}2\pi^*$	
11.9	$5\sigma^{-1}1\pi^{-1}2\pi^*$		
12.3		$5\sigma^{-1}1\pi^{-1}2\pi^*$	
12.4	$5\sigma^{-1}1\pi^{-1}2\pi^*$		
13.2		$1\pi^{-1}1\pi^{-1}2\pi^*$	
		$5\sigma^{-1}1\pi^{-1}2\pi^*$	
13.6	$1\pi^{-1}1\pi^{-1}2\pi^*$		
14.0		$5\sigma^{-2}2\pi^*$	
		$4\sigma^{-1}5\sigma^{-1}2\pi^*$	
14.2	$4\sigma^{-1}5\sigma^{-1}2\pi^*$		
	$5\sigma^{-2}2\pi^*$		
14.4		$1\pi^{-1}5\sigma^{-1}\pi^{*2}$	
14.6		$1\pi^{-1}1\pi^{-1}2\pi^*$	
		$1\pi^{-2}2\pi^{*}$	
14.7	$\pi^{-3}\pi^{*}$	$4\sigma^{-1}5\sigma^{-1}2\pi^*$	
14.9	$4\sigma^{-1}5\sigma^{-1}2\pi^*$		
	$1\pi^{-1}1\pi^{-1}2\pi^*$		
15.5		$4\sigma^{-1}1\pi^{-1}2\pi^*$	
15.6		$1\pi^{-2}2\pi^{*}$	

of mixing with the CO states, these charge transfer states can be expected to gain intensity in the autoionization process. Thus they lead to broadened signals. This is in accord with the rather broad experimental signals.

To summarize, our calculations show that the relative energetic positions of the electronic states reached in the autoionization process can be represented reasonably well by CI calculations with local cluster models for the NiO(100) surface. However, the Madelung potential alone is not sufficient to describe the difference between the autoionization spectra of the gas phase and the adsorbed CO. Because the electronic states being populated in the deexcitation process are known to be localized near the core hole, these cluster models can be expected to yield an adequate description. However, especially if oxygen charge transfer is taken

Table 2

Continued

into account, a more thorough theoretical analysis of the intensities which allows for a rigorous comparison between calculated and experimental spectra is necessary. Such an analysis is currently in progress and will be published in a forthcoming paper [38].

4. Conclusions

To summarize, we find that the autoionization of CO on the different oxide surfaces proves to be very dependent on the substrate. In the case of CO/ $Al_2O_3/NiAl(110)$, the C1s autoionization spectrum is nearly identical to that of free CO, but a small broadening caused by the substrate appears to be present. The Auger spectrum clearly indicates a strong influence of the substrate, leading to a broad, featureless structure. In order further to elucidate this behaviour, studies using other core level spectroscopies need to be performed.

For CO adsorbed on the transition metal oxide surfaces, the autoionization spectrum differs significantly from the gas phase spectrum. In order to assign the individual spectral features, the angular dependence was found to be useful, but more detailed calculations and simulations are necessary. The valence-CI calculations presented here can provide only a first hint towards an assignment. A calculation of intensities and energies taking into account both the charge transfer from the metal ion and the charge transfer from the surface oxygen simultaneously appears to be necessary. The results are comparable with those for the proposed electrostatic bonding mechanism discussed previously.

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Appendix

$$\begin{aligned} & I_{\text{total}}^{\sigma\sigma}(\alpha,\beta=45^{\circ},\delta,P=0.8,c_{20}/c_{00}=1) \\ &= -148.4402529\cos(\alpha)^{2}\cos(\delta)^{4} \\ &- 137.8\cos(\alpha)^{4}\cos(\delta)^{2} + 165.4\cos(\alpha)^{2}\cos(\delta)^{2} \\ &+ 9.9\cos(\delta)^{6}\cos(\alpha)^{2} + 173.2\cos(\alpha)^{4}\cos(\delta)^{4} \\ &- 14.8\cos(\delta)^{6}\cos(\alpha)^{4} - 0.7\cos(\delta)^{6} \\ &+ 135.7\cos(\delta)^{4}\cos(\alpha)\sin(\alpha) - 67.9\cos(\delta)^{6} \\ &\times \cos(\alpha)\sin(\alpha) - 67.9\cos(\delta)^{2}\cos(\alpha)\sin(\alpha) \\ &+ 67.9\cos(\delta)^{2}\cos(\alpha)^{3}\sin(\alpha) - 27.6\cos(\delta)^{2} \\ &+ 13.4 + 14.8\cos(\delta)^{4} - 26.9\cos(\alpha)^{4} \\ &+ 13.4\cos(\alpha)^{4} + 158.3\cos(\delta)^{6}\sin(\alpha)\cos(\alpha)^{3} \\ &- 226.2\cos(\delta)^{4}\sin(\alpha)\cos(\alpha)^{3} \end{aligned}$$

$$\begin{split} I_{\text{total}}^{\sigma\pi}(\alpha,\beta &= 45^{\circ}, \delta, P = 0.8, c_{21}/c_{11} = 1/3) \\ &= 15.3\cos(\alpha)^4\cos(\delta)^2 - 10.4\cos(\alpha)\cos(\delta) \\ &+ 0.1\cos(\delta)^6 + 25.1\cos(\delta)^4\sin(\alpha)\cos(\alpha)^3 \\ &- 17.6\cos(\delta)^6\sin(\alpha)\cos(\alpha)^3 + 47.8\cos(\delta)^2 \\ &\times \sin(\alpha)\cos(\alpha) - 55.3\cos(\delta)^4\sin(\alpha)\cos(\alpha) \\ &- 1.1\cos(\delta)^6\cos(\alpha)^2 + 67.9\cos(\delta)^3\sin(\alpha) \\ &\times \cos(\alpha)^2 - 56.5\cos(\delta)^5\sin(\alpha)\cos(\alpha)^2 \\ &- 3.8\cos(\delta)\sin(\alpha) - 7.5\cos(\delta)^3\sin(\alpha) \\ &+ 1.6\cos(\delta)^6\cos(\alpha)^4 + 36.8\cos(\alpha)^3\cos(\delta) \\ &+ 22.8\cos(\delta)^4\cos(\alpha)^2 - 11.3\cos(\delta)\sin(\alpha) \\ &\times \cos(\alpha)^2 + 11.3\cos(\delta)^5\sin(\alpha) + 35.8\cos(\delta)^3 \\ &\times \cos(\alpha) + 19.3\cos(\alpha)^2 + 6.6\cos(\delta)^5\cos(\alpha)^3 \\ &- 71.2\cos(\alpha)^2\cos(\delta)^2 - 2.8\cos(\delta)^5\cos(\alpha) \end{split}$$

+
$$7.5\cos(\delta)^6\cos(\alpha)\sin(\alpha) - 7.5\cos(\delta)^2\cos(\alpha)^3$$

× $\sin(\alpha) + 21.8 - 1.5\cos(\alpha)^4 - 2.9\cos(\delta)^4$
- $66.0\cos(\alpha)^3\cos(\delta)^3 + 15.0\cos(\delta)^2$
- $19.2\cos(\alpha)^4\cos(\delta)^4$ (A2)

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