

Physical aspects of relaxation and shake-up effects in x-ray photoemission spectroscopy and core $\rightarrow 2\pi^*$ absorption spectra of CO chemisorbed on Ni(111)

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The physical origin of the peculiar relaxation shifts and spectral shapes appearing in x-ray-induced core-to-valence excitation and core-level photoemission spectra (XPS) of CO chemisorbed on Ni(111) are discussed and interpreted within a unified framework. Within the model presented, the electronic transitions in core-to-valence excitation spectroscopy and XPS are shown to give rise to drastic electronic rearrangements within the adsorption system and to the charge shake-up in the CO $2\pi^*$ derived resonance partly filled via the back-donation mechanism. Such singular relaxation processes, common to both spectroscopies, are closely related and can be treated on the same footing. This makes it possible to establish unified relaxation shifts and spectral characteristics for two seemingly different experimental situations. The use of this formalism in analyzing the experimental data enables one to estimate and distinguish between the extra-adsorbate (image or nonbonding) and intra-adsorbate (chemically induced) screening of the core holes created either by x-ray-induced core-to-valence electronic transitions or core-level photoionization in CO/Ni(111).

I. INTRODUCTION

Photoelectron spectroscopies utilizing x-ray (XPS) and ultraviolet (UPS) radiation, and more recently inverse photoemission, have provided valuable information on the electronic structure of CO adsorbed on transition and noble metals.¹⁻¹⁹ The data acquired by these techniques contain the information about the adsorbate electronic structure in the final ionized state which may differ con-

siderably from the initial ground state of the system.

The desire to probe the electronic configurations of adsorbed species in a neutral state initiated the utilization of the high-resolution core-to-valence excitation spectroscopy in the studies of chemisorption on metals.²⁰⁻²³ This method leaves the investigated adsorbates neutral in the final, albeit excited state, thereby making the results of the measurements much less affected by large screening relaxation effects otherwise characteristic of photoemis-

TABLE I. Energetics for chemisorbed, physisorbed, and free CO (Ref. 22). Energy levels given relative to the vacuum level, Γ is the full width at half maximum.

| | CO chemisorbed on Ni(111) | | CO physisorbed on noble metals | | CO free molecule | |
|---------------------------|--|--------------------|-----------------------------------|-------------------|--|---|
| | ϵ (eV) | Γ (eV) | ϵ (eV) | Γ (eV) | ϵ (eV) | Γ (eV) |
| O $1s \rightarrow 2\pi^*$ | 532.4 | 3.5 | 534.1 | 1.15 ^a | 534.1 ^b 534.1 ^c 534.0 ^d | 1.15 ^a 1.3 ^{a,c} |
| O $1s$ | -536.7 ^e -536.8 ^f | <2.1 ^f | -538.3 ^g | 1.5 ^g | -542.6 ^h -542.1 ^j | |
| C $1s \rightarrow 2\pi^*$ | 287.0 | 2.2 | 287.3 | <0.18 | 287.3 ^c 287.4 ^k 287.3 ^d | 0.095 ^c 0.10 ^k |
| C $1s$ | -291.2 ^e -291.2 ^f | <1.85 ^f | -292.1 ^g | 1.5 ^g | -296.2 ^h -295.9 ^j | |
| $2\pi^*$ | -2.8 ^l | 3.1 ^l | +1.3 ^m | 0.6 ^m | +1.9 ⁿ | 1.1 ^{a,n} |

^aReference 30.

^bReference 21.

^cReference 24.

^dReference 27.

^eReference 3.

^fReference 4.

^gReference 29.

^hReference 25.

ⁱReference 2.

^jReference 28.

^kReference 26.

^lReference 17.

^mReference 31.

ⁿReference 32.

sion and inverse photoemission experiments.¹⁻¹⁹ The method has recently been applied by Jugnet *et al.*^{21,22} to the study of soft x-ray-induced core-to-valence electronic transitions in three different phases of CO, viz., gaseous, condensed (physisorbed) on noble metals, and chemisorbed on Ni(111) surface. The adsorption spectra of the electronic transitions from both O 1s and C 1s into the $2\pi^*$ -derived valence levels (with respect to adsorbate-substrate interaction) of chemisorbed CO when compared and correlated with the corresponding photoemission and inverse photoemission spectra showed a dramatic change regarding the position and the shape of the $2\pi^*$ -derived resonance. These changes, which are shown in Figs. 1 and 3 of Ref. 21 and compiled in Table I,²² may be summarized as follows.

(i) The transition energy $\epsilon_{1s-2\pi^*}$ of core-to-valence transitions in chemisorbed CO exhibits a (downward) relaxation shift with respect to the gaseous and condensed CO. On the other hand, the transitions in the condensed phase do not exhibit any relaxation shift at all with respect to the gaseous CO. This has to be correlated with the relaxation shifts of the 1s core levels which show up in XPS of physisorbed and chemisorbed CO. These are notably larger, particularly in the latter case, and in accordance with the expectation of large relaxation energies of final ionized states (cf. Table I).

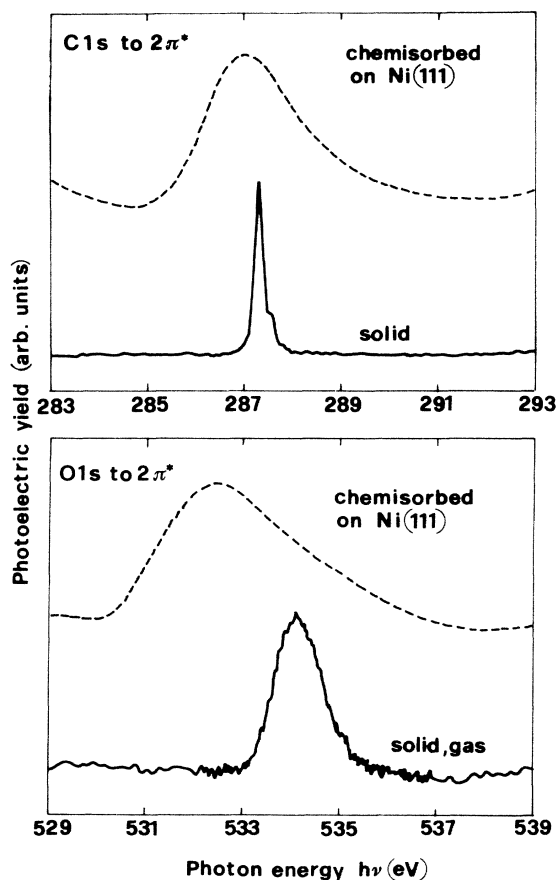


FIG. 1. Core-level excitation spectra for solid CO and chemisorbed CO on Ni(111). Vibronic fine structure is resolved for the C 1s excitation in solid CO but unresolved for the O 1s excitation (after Ref. 21).

(ii) The shape (spectral density) of the $2\pi^*$ -derived resonance as measured by the core-to-valence transition rate is notably asymmetric, with a sharp drop of the spectral density near the threshold energy $\epsilon_T = \tilde{\epsilon}_{1s} - \phi_{\text{Ni(111)}}$ (cf. Fig. 1). Here $\tilde{\epsilon}_{1s}$ is either the O 1s or C 1s core-level energy with respect to the vacuum level, ϕ is the work function of the substrate and the authors^{21,22} identified the resonance maximum with $\epsilon_{1s-2\pi^*}$. Again, a correlation has to be made between the shapes of these spectra and the XPS spectra of O 1s and C 1s core levels which exhibit pronounced asymmetric broadening of the threshold line and tailing off toward the higher binding energy side of the spectrum⁴ (cf. Fig. 2).

The origin of the majority of these features has still remained unexplained. Recently, Avouris, Bagus, and Rossi³³ discussed the energetics and the electronic structure of the Cu_5CO excited and ionized clusters which they used as a prototype of CO/Cu adsorption. Within their approach they were able to demonstrate and explain both qualitatively and quantitatively several trends of CO adsorption on copper as well as some static properties of the adsorbate spectra. Since dynamic features of the adsor-

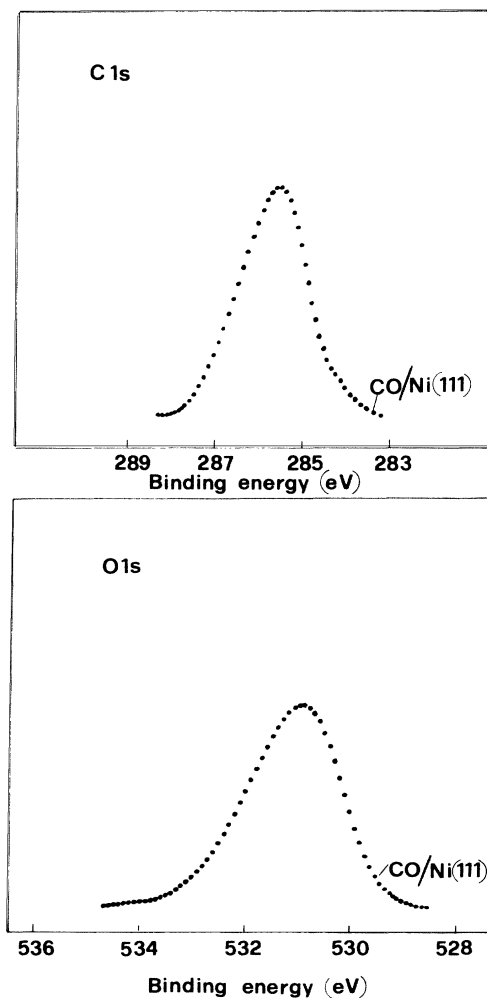


FIG. 2. XPS (Al $K\alpha$) spectra of C 1s and O 1s core levels of CO adsorbed on Ni(111). Binding energies measured relative to the Fermi level (after Ref. 4).

bate spectral properties cannot be obtained within such an approach, we present here a unified theoretical description of the dynamics of x-ray-induced core-to-valence electronic transitions and photoionization in adsorbates. We give a qualitative explanation of the origin of the features (i) and (ii) using the concepts of extra- and intra-adsorbate relaxation and shake-up processes. The model interprets rather successfully these peculiar effects in terms of a specific nondiabatic response of the adsorption system to the perturbations imposed by the spectroscopic techniques employed in the experiments.

II. MODEL DESCRIPTION OF SHAKE-UP AND RELAXATION PROCESSES IN THE SPECTRA OF ADSORBED CO

The interaction of the electronic charge of adsorbed CO with the x-ray electromagnetic field which gives rise to core-valence transitions is described by a perturbation:^{34,35}

$$H_x = \sum_{m,\sigma} f_{1s,m\sigma} c_{m\sigma}^\dagger c_{1s\sigma} e^{-i\omega_x t} + \text{H.c.} \quad (1)$$

Here $c_{m\sigma}$ and $c_{1s\sigma}$ are the particle-field operators for the electrons in the $2\pi^*$ and $1s$ orbital of CO, respectively, σ is the spin index, and m is the appropriate quantum number which describes the electronic states in the unperturbed $2\pi^*$ orbital (in the case of a system rotationally invariant around the axis of CO, which adsorbs perpendicularly onto a jelliumlike surface, m will denote the z component of the orbital angular momentum). $f_{1s,m\sigma}$ is the probability amplitude of a particular core-to-valence transition, and ω_x is the frequency of the applied radiation.

The experimentally measured absorption rate for such

transitions as a function of energy ϵ is proportional to³⁴⁻³⁸

$$S_{1s-2\pi}(\epsilon) = \frac{1}{\pi} \text{Im} \int_{-\infty}^{\infty} e^{i\epsilon t} R(t) dt, \quad (2a)$$

where the response function of the system is defined as

$$R_{1s-2\pi}(t) = -i \langle 0 | T[H_x(t)H_x(0)] | 0 \rangle. \quad (2b)$$

Here $|0\rangle$ denotes the initial (ground) state of the system consisting of the adsorbate in interaction with the substrate, T is the chronological operator, and the time evolution of H_x is governed by the full Hamiltonian of the system.

The x-ray photoemission spectrum of the CO $1s$ core levels is to a good approximation proportional to the core level density of states $\rho_{1s\sigma}(\epsilon)$. The latter is obtained as the imaginary part of the Fourier transform of the corresponding core-level propagator:³⁸⁻⁴¹

$$\rho_{1s\sigma}(\epsilon) = \frac{1}{\pi} \left| \text{Im} \int_{-\infty}^{\infty} dt e^{i\epsilon t} G_{1s\sigma}(t) \right|, \quad (3a)$$

where

$$G_{1s\sigma}(t) = -i \langle 0 | T[c_{1s\sigma}(t)c_{1s\sigma}^\dagger(0)] | 0 \rangle \quad (3b)$$

describes the core-hole propagation after the photoemission of the electron from the state $|1s\sigma\rangle$.

A convenient model for studying the bonding- and screening-induced dynamical relaxation processes in the spectra of adsorbates was developed a decade ago³⁶⁻³⁸ and here we shall adopt it to the case of electronic transitions in adsorbed CO. Assuming the hybridization of the CO $2\pi^*$ orbital with the s - p band states $|k,\sigma\rangle$ of the substrate only^{16,21} the Hamiltonian of the composite system may be written in the form

$$H = \sum_{k,\sigma} \epsilon_k n_{k\sigma} + \sum_{\sigma} \epsilon_{1s}^0 n_{1s\sigma} + \sum_{m,\sigma} \epsilon_{m\sigma} n_{m\sigma} + \sum_{k,m,\sigma} (V_{mk} c_{m\sigma}^\dagger c_{k\sigma} + \text{H.c.}) + \sum_{m,\sigma,m',\sigma'} U_{m\sigma,m'\sigma'} n_{m\sigma} n_{m'\sigma'} + \sum_{\mathbf{Q}} \omega_{\mathbf{Q}} a_{\mathbf{Q}}^\dagger a_{\mathbf{Q}} + \sum_{m,\sigma} n_{m\sigma} \sum_{\mathbf{Q}} \lambda_{\mathbf{Q}}^m (a_{\mathbf{Q}}^\dagger + a_{-\mathbf{Q}}) - \sum_{\sigma} (1 - n_{1s\sigma}) \sum_{\mathbf{Q}} \lambda_{\mathbf{Q}}^s (a_{\mathbf{Q}}^\dagger + a_{-\mathbf{Q}}) - \sum_{m,\sigma} U_{1s\sigma,m\sigma} n_{m\sigma} (1 - n_{1s\sigma}). \quad (4)$$

The first three terms on the right-hand side (rhs) of (4) describe the unperturbed states of the substrate ($|k,\sigma\rangle$) and the adsorbate ($|m,\sigma\rangle$ and $|1s,\sigma\rangle$), respectively, where $n_{k\sigma} = c_{k\sigma}^\dagger c_{k\sigma}$, $n_{1s\sigma} = c_{1s\sigma}^\dagger c_{1s\sigma}$, and $n_{m\sigma} = c_{m\sigma}^\dagger c_{m\sigma}$ are the corresponding electron number operators expressed through electron creation and annihilation operators c^\dagger and c , respectively. The fourth term describes the hybridization between the adsorbate $2\pi^*$ orbital and the substrate s - p band. It gives rise to the broadening of the $2\pi^*$ -derived level into a resonance of width $\Gamma_{2\pi^*}$. The fifth term describes two-body intra-orbital interactions among the electrons occupying the $2\pi^*$ -derived states. The next three terms describe the screening field of the substrate and the interaction of the electron and hole charge in the $2\pi^*$ and $1s$ core levels, respectively, with the screening field (i.e., the linear surface response of the substrate charge-density fluctuations) through the corresponding

coupling matrix elements $\lambda_{\mathbf{Q}}$. Here $\{\mathbf{Q}\}$ are the quantum numbers of the elementary excitations of energy $\omega_{\mathbf{Q}}$ characteristic of the substrate surface response and $a_{\mathbf{Q}}^\dagger$ and $a_{\mathbf{Q}}$ are the corresponding creation and annihilation operators, respectively. The last term describes the intra-adsorbate relaxation subsequent to the core hole creation in x-ray photoemission and in x-ray-photoabsorption-induced core-to-valence electronic transitions. The presence of this term in H is of crucial importance as it accounts for the dynamic relaxation and shake-up processes in XPS and core-to-valence transitions, i.e., it determines the shapes of the measured spectra. The physical process described by this term is the following. Sudden creation of a positive core hole charge either in the O $1s$ or the C $1s$ levels of adsorbed CO gives rise to a downward relaxation of the valence states within the $2\pi^*$ -derived orbital of the adsorbate through the in-

terorbital Coulomb integral $U_{1s\sigma, m\sigma}$ (hereafter sometimes to be referred to as $U_{1s, 2\pi}$). In XPS, where the photoemitted electron leaves the system, this interaction takes place first between the core hole and the electrons residing within the valence resonance, which is partly filled in the initial state via the back-donation mechanism. On the other hand, in core-to-valence transitions this interaction takes place both between the core hole and the valence electrons, as in XPS, and between the core hole and the electron that has made the transition into the unoccupied part of the valence resonance.

The many-body Hamiltonian (4) is rather complex and its complete solution is unattainable. Yet, some interesting aspects of the adsorbate spectral properties connected with the features quoted in (i) and (ii) in the Introduction may be inferred from (2) and (3) by studying the limiting regimes of the intra- and extra-adsorbate screening and relaxation processes.³⁶⁻³⁸

To this end, we first point out that, in general, one may consider two distinct types of screening processes subsequent to a core-level ionization of the adsorbate in either photoemission or core-to-valence transitions. The ionization of the core level gives rise to a sudden appearance of a localized positive hole charge which will strongly perturb the electrons in its vicinity. The effect of this perturbation, as described by the Hamiltonian (4) is twofold. The suddenly created hole charge will couple, first, to the electronic charge in the adsorbate valence orbitals through $U_{1s, m\sigma}$ and, second, to the dynamic surface response of the substrate through λ_Q . The interplay between these two transient perturbations will give rise to peculiar shapes in the measured spectra as well as to the relaxation shifts of the levels in the final state.

In a core-to-valence transition the total electronic charge is conserved and the core hole in the final state may be screened out either (a) locally, predominantly by the same electron that made the transition (intra-adsorbate screening or charge compensation⁴²) or (b) by the response of the substrate if the final electronic state is delocalized (extra-adsorbate relaxation). In this case the plasmons of the substrate may provide an efficient screening mechanism.⁴³ (a) is expected to be important for transitions in the threshold region, whereas (b) is likely to be more efficient away from the threshold, when the core electron makes a transition into an empty band of states high above the Fermi energy.^{37,38} In XPS, the photoemitted electron leaves the system and therefore the screening of the core hole must proceed either through the mechanism (b) or an additional charge transfer from the substrate into those adsorbate derived states which have been pulled below the Fermi level by the interaction $U_{1s\sigma, m\sigma}$.³⁸⁻⁴⁰

The charge transfer effects and partial occupation of the $2\pi^*$ resonances in the initial state make the situation for distinguishing between the roles of screening mechanisms (a) and (b) rather critical. However, some estimates can be made upon incorporating as much as possible the effects of mechanism (b) into some basic parameters of the model, viz., ϵ_{1s} , $\epsilon_{m\sigma}$, V_{km} , $U_{m\sigma, m'\sigma}$, and $U_{1s\sigma, m\sigma}$. To achieve this one introduces a canonical transformation of the Hamiltonian (4):

$$\tilde{H} = \hat{O}^{-1} H \hat{O}, \quad (5a)$$

with

$$\hat{O} = \exp \left[- \sum_{m\sigma} n_{m\sigma} \sum_Q \lambda_Q^m (a_Q^\dagger - a_{-Q}) / \omega_Q + \sum_{\sigma} (1 - n_{1s\sigma}) \sum_Q \lambda_Q^s (a_Q^\dagger - a_{-Q}) / \omega_Q \right], \quad (5b)$$

which removes the term linear in the substrate screening field operators a and a^\dagger from H , at the expense of modifying the energies of the localized states and the interactions U . The transformation \hat{O} generates also a more complicated hybridization (hopping) term in \tilde{H} .³⁶⁻³⁸ This rather lengthy procedure is described in detail in Ref. 38, Sec. 5 C, and here we generalize it to the situation in which the core hole and the valence electronic charge of the adsorbate may reside in the orbitals with different centers of gravity, as indeed is the case with CO. This procedure yields^{38,44} the following values for the basic parameters in \tilde{H} :

$$\tilde{\epsilon}_{1s} = \epsilon_{1s}^0 + v_{1s}, \quad (6a)$$

$$\tilde{\epsilon}_m = \epsilon_m - v_m, \quad (6b)$$

$$\tilde{U}_{m\sigma, m'\sigma} = U_{m\sigma, m'\sigma} - 2v_m, \quad (6c)$$

$$\tilde{U}_{1s, m\sigma} = U_{1s, m\sigma} - 2v_{1sm}. \quad (6d)$$

Here v_{1s} and v_m are the screening (image) relaxation shifts for the charge in the core $1s$ and the valence $2\pi^*$ adsorbate orbitals, respectively, and v_{1sm} is the interaction of the charge in the core state with the image of the charge in the $2\pi^*$ orbital. Note that in the present notation all $v > 0$ and that for spherical orbitals located at the same center farther outside the surface $v_{1s} = v_m = v_{1sm}$. Hence, the energy of the core-to-valence transition in the present system would be expressed as

$$\epsilon_{1s-2\pi} = \epsilon_{2\pi} - \epsilon_{1s}^0 - U_{1s, 2\pi} + (2v_{1s-2\pi} - v_{1s} - v_{2\pi}) + \Delta\epsilon_{\text{scr}} + \Delta\epsilon_{\text{chem}}, \quad (7)$$

where $\epsilon_{2\pi}$ incorporates the initial-state chemical shift $\Lambda_{2\pi}$ of the $2\pi^*$ -derived resonance,³⁸ $v_{2\pi} = v_m$, and $\Delta\epsilon_{\text{scr}}$ and $\Delta\epsilon_{\text{chem}}$ are the extra-adsorbate screening relaxation shift and the shift due to the relaxation of the charge within the $2\pi^*$ -derived resonance, respectively. Elaborate calculations yield³⁶⁻³⁸

$$\Delta\epsilon_{\text{scr}} \cong v_{2\pi} \left[\frac{\Gamma_{2\pi}}{W_{s-p}} \right]^2, \quad (8)$$

where $\Gamma_{2\pi}$ and W_{s-p} denote the widths of the adsorbate valence resonance and the substrate band which participates in chemisorption, respectively. Now, as $\Gamma_{2\pi} < W_{s-p}$, the magnitude of (8) is going to be very small, and this smallness is a manifestation of the charge conservation during the transition which holds within the characteristic resonance lifetime $\Gamma_{2\pi}^{-1}$.^{36,38} Also, in accordance with our assumption of the small initial ground-state occupation of the $2\pi^*$ -derived resonance, we have neglected in (7) a shift which would originate from the intra-orbital correlation

and exchange described by (6c). Thus the shifts due to both extra-adsorbate screening and correlation in (7) will be small.

On the other hand, inverse photoemission and core-to-valence transitions indicate that the resonant broadening of the $2\pi^*$ -derived level is rather large [> 1 eV (Refs. 16 and 21)], and hence points toward a possibly large participation of this orbital in the chemically induced relaxation and screening processes. An appreciable charge transfer from the metal into the $2\pi^*$ -derived *relaxed* (final) state could give rise to an appreciable chemical relaxation shift which, irrespective of means of excitation, may be expressed as^{35,38}

$$\Delta\epsilon_{\text{chem}} = - \sum_{m,\sigma} \int_{-\infty}^{\epsilon_F} \frac{\delta_{m\sigma}(\epsilon)}{\pi} d\epsilon. \quad (9a)$$

Here $\delta_{m\sigma}(\epsilon)$ is the effective phase shift for a single electron scattering of the $1s$ core hole in the (m,σ) th channel of the adsorbate valence resonance.^{38,40}

$$\delta_{m\sigma}(\epsilon) = \arctan \left[\frac{\pi \rho_{m\sigma}^0(\epsilon) \tilde{U}_{1s,m\sigma}}{1 + \tilde{U}_{1s,m\sigma} \gamma_{m\sigma}(\epsilon)} \right], \quad (9b)$$

where $\rho_{m\sigma}^0(\epsilon)$ is the effective one-electron density of states characterizing the (m,σ) th component of the $2\pi^*$ derived resonance *before* the creation of the core hole in the $1s$ state, $\gamma_{m\sigma}(\epsilon)$ is its Hilbert transform, and ϵ_F denotes the Fermi energy of the system.

The core level energy ϵ_{1s} as measured in XPS can be obtained from the core-level propagator (3b).³⁸ It comprises both image and chemically induced relaxation shift:

$$\bar{\epsilon}_{1s} = \epsilon_{1s}^0 + v_{1s} - \Delta\epsilon_{\text{chem}} = \epsilon_{1s}^0 - \Delta\epsilon_{1s}, \quad (10)$$

where the unperturbed gas-phase core-level energy ϵ_{1s}^0 is referred to the vacuum level. Hence, as is seen from (9a) and (10), the image and chemically induced relaxation mechanisms may play a more symmetric role in the case of core ionization of the adsorbate. Only in the case of complete hole charge compensation by the electrons transferred from the substrate into the localized adsorbate valence resonance in the final state, the image screening would become insignificant. However, as will be seen below, we do not impose from the very outset only this type of screening [which would lead to the Friedel sum rule imposed on the localized state phase shifts $\delta_{m\sigma}(\epsilon_F)$ only], but rather investigate the implications of both screening mechanisms.

III. RELAXATION SHIFTS IN XPS AND CORE-TO-VALENCE SPECTROSCOPY OF CO/Ni

The expressions (6)–(10) enable us now to comment on the nature of the relaxation process in the spectra of the CO/Ni(111) system. First of all, the image screening mechanism should affect the relaxation in both physisorbed and chemisorbed species. This may easily be deduced from the XPS spectra of core levels of physisorbed and chemisorbed CO (cf. Table I and Ref. 22). For CO physisorption on noble metals, the XPS core-level shifts $\Delta\epsilon_{1s}$ are almost equal and amount to ~ 4 eV, irrespective

of the core level involved, i.e.,

$$v_{O\ 1s} \cong v_{C\ 1s} \cong 4 \text{ eV}, \quad (11)$$

because one should have $\Delta\epsilon_{\text{chem}} \cong 0$ in the physisorption systems. Secondly, the XPS core-level shifts are notably larger (by ~ 1 eV) for a chemisorbed molecule. Depending on the core level considered, they may differ due to an additional chemical shift generated by the different interorbital interactions $U_{O\ 1s,m\sigma}$ or $U_{C\ 1s,m\sigma}$ appearing in (9b). Another particularly illuminating feature derives from the comparison of the transition energies $\epsilon_{1s-2\pi}$ (7), in the physisorbed and the gas phase [the latter case is described by the first three terms on the rhs of Eq. (7)]. Since in the case of physisorption $\Gamma_{2\pi} \rightarrow 0$ and consequently $\delta(\epsilon) \rightarrow 0$, the contribution of the last two terms on the rhs of (7) should, according to (8) and (9), be minimum. Now, as within the experimental error there is no difference whatsoever between the values of $\epsilon_{1s-2\pi}$ in the *physisorbed* and the *gas phase*,²¹ the bracket on the rhs of (7) which contains the image screening shifts v should also vanish. This immediately leads to a conclusion that the core charge and the electron charge after the core-to-valence transition would experience equivalent substrate induced image shifts, which is fully consistent with equally large core-level shifts $v_{C\ 1s}$ and $v_{O\ 1s}$ discussed above [Eq. (11)].

The comparison of core-level shifts and core-to-valence transition energies of physisorbed and chemisorbed CO offers yet further convincing evidence as to the role of the charge transfer-induced—versus—image-induced relaxation shifts. It should be noted that due to the fixed position of the substrate Fermi level the *same* formula for the chemical relaxation shift (9a) applies to the core-level photoemission (XPS) as well as to the corresponding core-to-valence transitions.^{35,38} Using the data of Table I and Ref. 22 for the O $1s$ core relaxation shift in chemisorbed and physisorbed CO, and identifying their difference with the charge transfer or chemically induced shift, we find

$$\Delta\epsilon_{\text{chem}} |_{\text{XPS(O } 1s)} = 1.55 \text{ eV}. \quad (12a)$$

On the other hand, by taking the difference of the O $1s$ core-to-valence excitation energies in the chemisorbed and physisorbed phases²¹ (cf. Table I) and neglecting $\Delta\epsilon_{\text{scr}}$ on the basis of (8), we find

$$\Delta\epsilon_{\text{chem}} |_{O\ 1s \rightarrow 2\pi} = 1.7 \text{ eV}. \quad (12b)$$

Within all the uncertainties involved and the neglect of $\Delta\epsilon_{\text{scr}}$, this gives practically the same value as (12a), as it indeed should do according to Eq. (9a). The merit of this result is that the relevant data have been extracted from completely independent measurements. This clearly reinforces the role of the chemically induced or charge transfer screening mechanism in the core-to-valence transitions. Analogously, we get from Table I for the C $1s$ levels:

$$\Delta\epsilon_{\text{chem}} |_{\text{XPS(C } 1s)} = 0.9 \text{ eV}, \quad (12c)$$

$$\Delta\epsilon_{\text{chem}} |_{C\ 1s \rightarrow 2\pi} = 0.3 \text{ eV}. \quad (12d)$$

Here the agreement between the magnitudes of the chemisorption-induced relaxation shifts observed by two different spectroscopic methods is less satisfactory than the one obtained for the O 1s level, but Eqs. (12c) and (12d) definitely indicate smaller chemically induced relaxation for electronic transitions out of the C 1s level of CO adsorbed on Ni(111). This is in accordance with the findings depicted in Fig. 2 or Ref. 21 which demonstrate that larger chemisorption shift should be expected in the case of O 1s \rightarrow $2\pi^*$ transitions.

To conclude the present discussion of the relaxation shifts in XPS and core-to-valence excitation spectroscopy of CO adsorbed on Ni(111), we may safely reiterate that the concept of screening of the core hole based on image relaxation and charge transfer (back donation) effects may provide a consistent and successful qualitative interpretation of the experimental findings and queries quoted in (i) in the Introduction.

IV. LINE SHAPES OF XPS AND CORE-TO-VALENCE ABSORPTION SPECTRA OF CO/Ni(111)

Common characteristics of the XPS core-level spectra of adsorbates, besides the already discussed upward relaxation shifts, is the asymmetric broadening of the threshold line [here corresponding to $\epsilon = \tilde{\epsilon}_{1s}$, cf. Eq. (10)] toward higher binding energies and a possible appearance of satellite features below the threshold.¹⁻⁵ Such additional spectral structures which originate from dynamic electronic relaxation processes following the sudden creation of the core hole in photoemission are usually termed as shake-up. They may involve various types of electronic excitations in the adsorption complex as intraband transitions within the adsorbate-induced resonances (soft electron-hole pairs), interband transitions both within the adsorbate and the substrate and charge transfer effects, surface plasmons, etc. The occurrence of each of these electronic excitations requires certain energy which in turn will give rise to a peculiar energy loss structure in the measured core-level XPS spectra of adsorbates.

A fact of major importance in studying the XPS core-level relaxation shifts and shake-up spectral features is the realization that they are connected through the "zero work sum rule."^{37,38,40} The latter states that the additional spectral weight accumulated in the shake up structures on the high-binding-energy side of the spectrum is exactly balanced by the upward relaxation shift of the threshold line. Mathematically speaking, the first moment of the spectrum must remain unchanged by the relaxation processes and hence any relaxation of the threshold implies automatically the existence of some shake-up features in the spectra, caused either by soft electron-hole pairs (asymmetric broadening) or interband transitions and plasmons (satellites). In this respect different chemisorption systems exhibit a large variety of different spectral characteristics.

Relaxation shifts, asymmetric threshold broadening, and plasmon satellites have been observed in the XPS spectra of 1s core levels of O/Al(111),⁴⁵ although some controversies may exist as to how much the surface-plasmon satellite would bear intrinsic (core-hole-induced)

versus extrinsic (photoelectron-induced) character. However, as the asymmetric threshold broadening can be of solely intrinsic origin, this reinforces the role of soft electron-hole pairs in the screening of the adsorbate core hole. Such intraband shake-up appears, for instance, as the only feature in the XPS spectra of 1s level of oxygen adsorbed on W(110).¹

In molecular adsorption, however, more complex shake-up processes may take place. A characteristic example is a triply peaked C 1s spectrum of CO/Cu(100),^{1,2} interpretable in terms of shake-up and charge transfer processes within the model outlined in Sec. II.⁴⁶ Here, besides the asymmetric threshold peak and the peak at the unrelaxed energy, where the latter would be the only spectral feature in the absence of the adsorbate-substrate coupling,⁴¹ a third peak appears. This is due to the presence of a relatively narrow copper *d* band below the Fermi level which may also participate in the charge transfer screening process.⁴⁶ On the other hand, in CO adsorption on W(110) and Ni(100), only the asymmetric threshold peak and the peak at the unrelaxed energy have been observed.¹ In CO adsorption on Ni(111) the only shake-up feature found in either the C 1s or the O 1s XPS spectrum was the asymmetric threshold peak⁴ (cf. Fig. 2). Such spectral shape, which is characteristic of a rather strong chemisorption (see below), arises from an interplay between the finite core hole lifetime and an infrared threshold singularity. The latter is generated by the emission of the soft electron-hole pairs within the $2\pi^*$ -derived resonance which respond to the sudden perturbation brought about by the localized core hole charge.^{39,40} The underlying physics is the following: Since the $2\pi^*$ -derived resonance in the CO/Ni(111) system is broad it may be partly filled by the back-donation mechanism also in the initial, ground state. Hence $\rho_{m\sigma}^0(\epsilon_F) \neq 0$ and consequently $\delta_{m\sigma}(\epsilon_F) \neq 0$. The core hole suddenly created in photoemission pulls the resonance down by the amount $\tilde{U}_{1s,m\sigma}$ in each relaxation or the scattering channel (m, σ) and thereby shakes up the electrons in the resonance states which were initially occupied. This gives rise to the creation of low-energy electron-hole pairs in the valence states that project into the resonance. Such emission of electron-hole pairs is a highly singular process³⁴ which may lead to the appearance of an infrared threshold singularity in the adsorbate core level spectra $\rho_{1s}(\epsilon)$.³⁹ Hence, in the absence of the lifetime broadening effects these spectra will no longer be represented by a δ function at $\tilde{\epsilon}_{1s}$, but rather by a totally asymmetric integrable threshold divergence.^{39,40}

$$\lim_{\epsilon \rightarrow \tilde{\epsilon}_{1s}} \rho_{1s}(\epsilon) \propto \Theta(\tilde{\epsilon}_{1s} - \epsilon) / (\tilde{\epsilon}_{1s} - \epsilon)^\alpha, \quad (13a)$$

with

$$\alpha = 1 - \sum_{m,\sigma} n_{m\sigma}^2, \quad (13b)$$

where $n_{m\sigma}$ is the number of extra electrons brought into each scattering channel (m, σ) to screen out the core hole.³⁵ This number is obtained by integrating up to the Fermi level the change in the adsorbate valence density of states generated in the (m, σ)th channel by the action of

$\tilde{U}_{1s\sigma,m\sigma}$. When this charge is expressed through the phase shifts (9b) which govern the valence resonance electron scattering off the core hole, one finds, analogously as in the formulation of the Friedel sum rule, that $n_{m\sigma} = \delta_{m\sigma}(\epsilon_F)/\pi$.

The completely asymmetric spectrum (12a) will in real systems be smeared out into an asymmetric Lorentzian-like structure,⁴⁰ by the finite core-hole lifetime, as indeed has been found for CO/Ni(111) (cf. Fig. 2 and Ref. 4). The absence of other shake-up structures and satellites from the 1s core-level XPS spectra of CO/Ni(111) signifies that $\tilde{U}_{1s,2\pi} \approx \Gamma_{2\pi} \approx \tilde{\epsilon}_m - \epsilon_F$, i.e., that the $2\pi^*$ -derived resonance does not shift down with respect to the Fermi level in the manner which would allow the formation of an unrelaxed peak. This is characteristic of the case of a relatively strong chemisorptive bonding.⁴¹ Therefore, since we are dealing with resonances located close to the Fermi level, we would have $\rho_{m\sigma}^0(\epsilon_F) \approx \Gamma_{2\pi}^{-1}$ and the magnitude of $\tilde{U}_{1s\sigma,m\sigma}\rho_{m\sigma}^0(\epsilon_F)$ should be of the order of unity, as indeed can be estimated from Figs. 1 and 3 of Ref. 21. Hence, the information about the strength of the CO-Ni(111) chemisorptive bond extracted from the shapes of the XPS core spectra and from the width of the valence $2\pi^*$ spectra as measured in core-to-valence spectroscopy and inverse photoemission are in conformity since large $\Gamma_{2\pi}$ implies strong hybridization of the $2\pi^*$ molecular level with the broad substrate *s-p* band.

The shape of the $2\pi^*$ -derived resonance spectrum in core-to-valence transitions caused by x-ray absorption would, in the one-electron picture, reflect the one-electron density of states extending from the Fermi level up to the resonance band edge^{34,38} (cf. Fig. 3). However, due to the relaxation effects which here manifest themselves as singular scattering of the localized core hole of both the electron excited into the resonance band and the electrons which were occupying the resonance in the *initial* state (shake-up processes), the spectral density which shows up experimentally will deviate substantially from the one-electron picture. Hence, the electronic relaxation event which takes place is the same as in the XPS, except for the photoemitted electron which is here excited to near the Fermi level in the resonance instead of having left the system entirely. By studying the x-ray absorption rate pertinent to the core-to-valence transitions we find^{38,39} that the x-ray absorption spectrum (2a) would in the threshold region behave as

$$\lim_{\epsilon \rightarrow \epsilon_T} S_{1s-2\pi}(\epsilon) = \sum_{m,\sigma} \frac{\rho_{m\sigma}^0(\epsilon_F)}{[\rho_{m\sigma}^0(\epsilon_F)(\epsilon - \epsilon_T)]^\alpha} \Theta(\epsilon - \epsilon_T), \quad (14)$$

where α is again given by (13b). However, since in core-to-valence transitions one electron is supplied by the core hole in the transition channel (*l,ν*), the numbers $n_{m\sigma}$ are here given by

$$n_{m\sigma} = \begin{cases} \delta_{m\sigma}(\epsilon_F)/\pi - 1, & (m,\sigma) = (l,\nu) \\ \delta_{m\sigma}(\epsilon_F)/\pi, & \text{all other channels.} \end{cases} \quad (15)$$

The absorption rate (14) may therefore be either singular ($\alpha > 0$) or zero ($\alpha < 0$), depending on the magnitude of the sum of the squares of the extra screening electrons in each channel. In both cases the measured absorption

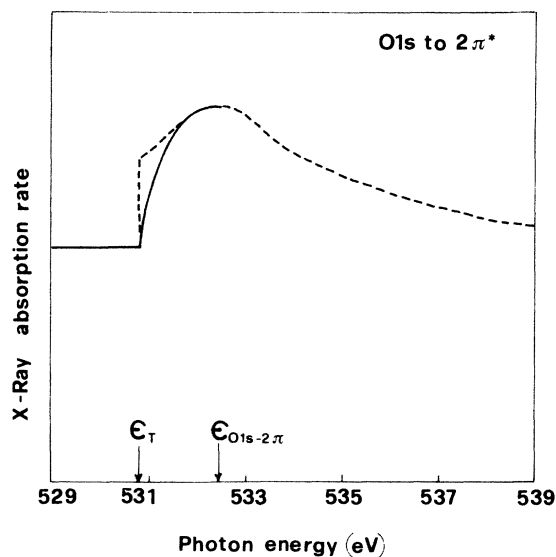


FIG. 3. Optical absorption rate [Eq. (2a)] for the O $1s \rightarrow 2\pi^*$ core-to-valence electronic transition. Dashed line: absorption rate in the one electron picture; solid line: threshold softening of the spectrum due to the shake-up relaxation processes for $\alpha < 0$ [cf. Eq. (14)].

spectrum will exhibit strong asymmetricity and the finite core-hole lifetime will act to round off and broaden the sharp edges of the spectra.⁴⁰ Here it is important to notice that the phase shifts (9a) may, in general, be either positive or negative. Namely, in spite of the fact that the empty $2\pi^*$ orbital of free CO is fourfold degenerate, its occupation in the adsorbed phase by the backdonation mechanism may lead to a removal of the degeneracy due to the action of different $\tilde{U}_{m\sigma,m'\sigma}$. A clear example of this effect is the O₂ molecule in which two electrons in the $2\pi^*$ orbital may give rise either to a singlet or a triplet state, the latter being the ground state of the molecule. Obviously, the electrons bound in these states or the resonances derived thereof would be subjected to different potentials. Hence, the electrons making core-to-valence transitions in chemisorbed CO may be subjected to unequal one-particle phase shifts $\delta_{m\sigma}(\epsilon_F)$, each depending on $\rho_{m\sigma}^0(\epsilon)$ and $\tilde{U}_{1s,m\sigma}$ through (9b), and *a fortiori* the many-body interactions $\tilde{U}_{m\sigma,m'\sigma}$.

In the present case of electronic scattering within the resonant broadened $2\pi^*$ -derived states the values of the phase shifts at the Fermi level may vary between $-\pi/2$ and $\pi/2$. Provided the intra-adsorbate screening is significant, and this should be so due to the observed large chemically induced relaxation shift [cf. (9a) and (12)], the sum of the squares of the numbers of electrons in the scattering channels in (12) may even exceed unity, thereby giving $\alpha < 0$. This would give rise to a *power-law quenching or softening* of the absorption spectrum (2a) at the threshold, a situation shown by a solid line in Fig. 3. Such a behavior of the spectrum indeed seems to have been detected experimentally for both O $1s \rightarrow$ and C $1s \rightarrow$ valence transitions in the CO/Ni(111) system, (cf. Fig. 1), with different corresponding softening intervals ($\epsilon_T < \epsilon < \epsilon_{1s-2\pi}$), but each exceeding 1 eV. This effect of the threshold softening can hardly be ascribed to the

core-level lifetime broadening as the natural width of, e.g., C $1s \rightarrow 2\pi$ transition is around 0.2 eV (Refs. 21 and 22) in the gas phase. Neither can this arise from the low resolution as the latter was of the order of 0.05 eV.²¹ Therefore, the shake-up relaxation mechanism offers itself as an explanation for the threshold softening of the absorption spectrum in much the same manner as in the interpretation of the asymmetry of the adsorbate core-level XPS spectra. It also enables a unified interpretation of the bonding-induced relaxation shifts of the core levels encountered in both core-to-valence transitions and photoemission from adsorbed CO.

In summary, within the model presented, the interpretation of the features (i) and (ii) quoted in the Introduction is unified and rests on the assumption of a partial filling of the $2\pi^*$ -derived states of chemisorbed CO in the ground state via the so-called back-donation mechanism.⁴⁷

Such effects of backdonation and relaxation are in a strong correlation with other peculiar aspects of CO adsorption on metals, particularly with those discussed in connection with inverse photoemission⁴⁸ and beam scattering experiments.⁴⁹

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