Autoionization of the Systems P2mgCO/Ni(110) and CO2/Ni(110) after core-to-bound excitation

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Photoemission has failed so far to allow detailed spectroscopic investigations of the inner valence ionization region of adsorbed molecules. 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\(^{1/2}\). In other words, instead of observing only one inner valence ion state, for example, the \(\pi\) ion state in CO, a whole series of ion states, due to shake-up satellites is found experimentally\(^{1/2}\). These shake up satellites partly borrow their intensity from the outer valence ionizations\(^{1/2}\). 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\(^{4/5}\). Several groups have, recently, chosen a different approach\(^{4/5}\): Electron spectroscopy via autoionization of highly excited states of the adsorbate. These highly excited states are populated through core-to-bound excitations with synchrotron radiation, and decay radiationless into valence ion states of the adsorbate. If we record the photoelectron spectrum and the autoionization spectrum with the same photon energy \(h\nu\) we can put photoemission and autoionization spectra on a common binding energy scale relative to \(E_r\). Of course, for photon energies different from the resonance energies, 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.1 where electron spectra of a CO(2x1)/P2mg/Ni(110) adsorbate are plotted for different photon energies. The spectra were recorded in near normal incidence with (100) polarization 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 \(h\nu=288\) 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 5p/1m- and 4p-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 \(\text{C}1\sigma\rightarrow\text{2p}\) 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 near-normal to near-grazing light incidence. This attenuation documents the dipole selection rules for the initial \(\text{C}1\sigma\rightarrow\text{2p}\) excitation: The CO molecules are titled only slightly from normal orientation \(-20^\circ\) so that a \(\text{C}1\sigma\rightarrow\text{2p}\)-excitation exhibits its highest oscillator strength for near \((20^\circ)\)-normal light incidence, because the polarization vector should be oriented perpendicular to the \(\text{C}-\text{O}\)-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 C1s-\(\pi\)-shape resonance excitation, which is a core-to-continuum excitation\(^{1/1}\). Therefore, the dominant decay mechanism in the latter case is Auger decay, i.e. a radiationless transition from a core-hole state to a two-valence-hole state. In this case, the Auger-XVV-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 \(h\nu=320\) 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. Finally, we reach the
Fig. 1. Normal emission electron spectra for various photon energies as indicated. Those spectra taken in resonance with a core-to-bound excitation are marked.
01s-2n resonance, and we observe resonance enhanced features at the same binding energy position as in the case of the Cls-2n induced spectrum.

To interpret the autoionization spectra of the adsorbate, we have to consider the different matrix element, governing a photon induced dipole transition

\[
I \propto \left| \langle \psi_f | p | \psi_i \rangle \right|^2
\]

in photoemission with respect to a radiationless transition

\[
I \propto \left| \langle \psi_f | | r \rangle | \psi_i \rangle \right|^2
\]

in autoionization. It has been shown numerically \cite{1} that this accounts for the experimental observations in gas phase CO \cite{15,16}. It is therefore near at hand to try a corresponding interpretation in the adsorbate case in Fig.1. The bands at binding energies above the photoemission features at 8eV and 11eV 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 \cite{16}.

Fig.2 shows an autoionization spectrum in comparison with a calculated photoemission spectrum of a Ni-CO cluster. The character of the states, as given by the calculation is indicated. In the photoelectron spectra the 5s/1m and 4a ionization are most intense. These states are partially screened \cite{14,15}, and they correspond to configurations N'-5s'-(1m'-1j2n and N'-4a'-2n of the adsorbate where N denotes a metal level. In order to deduce from this calculation how the relative intensities of the various states change when going from photoionization to autoionization we resort to the qualitative discussion of autoionization matrix elements outlined in ref.\cite{14}. In general, the intensity of an autoionization decay is given by equation (2). A more detailed analysis \cite{14} shows that the calculation can, under certain approximations, be reduced to matrix elements of the type:

\[
\langle \phi_{1s}, \theta_{1s} | | \alpha | \phi_{1s}, \theta_{1s} \rangle
\]

where the \phi_i are one-electron levels and the index \nu stands for valence. The autoionization intensity for the screened 5s/1m and 4a states is small because it is governed by matrix elements of the type

\[
\langle \phi_{1s}, \theta_{1s} | | \alpha | \phi_{1s}, \theta_{1s} \rangle
\]

or

\[
\langle \phi_{1s}, \theta_{1s} | | \alpha | \phi_{1s}, \theta_{1s} \rangle
\]

where \theta_{1s} is the continuum orbital of the outgoing electron characterized by the angular momentum quantum numbers l and m. This has to be compared with matrix elements of type

\[
\langle \phi_{1s}, \theta_{1s} | | \alpha | \phi_{1s}, \theta_{1s} \rangle
\]

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 involved metal orbital 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 5s'-1m' or 4a'-1j'. Their 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 places the lines involving the 5s'-unscreened states at little lower binding energies as compared with the N'-4a'-2n screened ion state. However, the shake-up states involving the 4a'-1m' configuration are situated several eV below those involving the 5s'-shake-ups. We expect the 5s'-shake-up states to exhibit larger intensities as compared with the 4a'-shake-up states for the Cls-2n decay because of the preferential localization of the 5s'-configuration on the carbon atom. We identify peak (1) in Fig.2 as a 5s'-shake-up state, because its intensity is attenuated in the Ols-2n decay spectrum. The calculation places the 4a'-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 5s'-1m'-2n, and 1m'-2n configurations which is consistent with its large intensity in both the Cls-2n and Ols-2n 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 explicit calculations of the autoionization intensities. However, there is reason to believe, that we can also achieve more detailed experimental information. As Ubach and Hussain\cite{15} demonstrated, electron emission via
Fig. 2. Assignment of the CO(2x1)/P3mg/Ni(110) autoionization spectrum after C1s-2p excitation on the basis of a Ni-CO cluster calculation.
radiationless decay can 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/27/.

Fig. 3 shows an autoionization spectrum from a CO2/ Ni(110) adsorbate prepared at a surface temperature of T=80 K in comparison with a CO2 gas phase spectrum. This system has been investigated by several surface sensitive techniques/28,29/, and there is no doubt that under the chosen conditions the adsorbed molecular overlayer consists of dominantly physisorbed CO2. In photoemission there is a one-to-one correspondence between the spectra of the gas and the condensed molecular solid/30/. Since the gas phase photoelectron spectrum has been recorded throughout the full outer and inner valence electron region/31/ we compare in Fig.3 this photoelectron spectrum with the autoionization spectrum. The binding energy scale is referenced to the vacuum level. The difference in the selection rules is particularly impressive in the region of the outer valence levels. While the ionization probability to the 2p state is particularly large, the probability for autoionization into this state vanishes for C1s→2
core-to-bound excitation. The reason is that this state carries no electron density at the carbon atom due to the inversion symmetry which is not broken via the core-to-bound excitation. Again, similar to the case of the CO adsorbates, the inner valence shake up states gain most of the autoionization intensity.