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

G. Illing, T. Porwol, H.-J. Freund Physikalische Chemie I, Ruhr-Universität Bochum, 4630 Bochum, FRG

H. Kuhlenbeck, M. Neumann Fachbereich Physik, Universität Osnabrück, 4500 Osnabrück, FRG

S. Bernstorff

BESSY GmbH, Berlin, FRG

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'. In other words, instead of observing only one inner valence ion state, for example, the 3g ion state in CO, a whole series of ion states, due to shake-up satellites is found experimentally'2'. These shake up satellites partly borrow their intensity from the outer valence ionizations/3/. 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/6-12/: 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 hy we can put photoemission and autoionisation spectra on a common binding energy scale relative to Er. 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-TGmonochromator at the BESSY storage ring.

The lowest spectrum shows for comparison the spectrum of a clean Ni(110) surface taken with hy=288eV. 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 50/1n- and 40-features at -8 eV and 11 eV, as expected, but hardly any structure below 15eV binding energy. If the photon energy is increased to 288.0 eV, an energy for which the clean Ni(110) spectrum is shown below, we are in resonance with the lowest energy $C1s \rightarrow 2\pi$ excitation, which decays into the valence ion states and leads to the observed intense adsorbate spectrum with six features as indicated. The intensity of these features is drastically attenuated if we change from near-normal to near-grazing light incidence. This attenuation documments the dipole selection rules for the initial C1-2n excitation: The CO molecules are titled only slightly from normal orientation (-20°) so that a Cls+2n-excitation exhibits its highest oszillator strength for near (20*)normal light incidence, because the polarization vector should be oriented perpendicular to the C-Oband 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 Cls-or-shape resonance excitation, which is a core-to-continuum excitation/11/. 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 KVV-transitions appear as low intense features at higher binding energy, because they stay fixed in kinetic energy while the photemission peaks shift. This is documented by the spectrum taken with hv=320 eV. With this photon energy one is well above the core-ionization threshold. The Auger peaks are shifted with respect to the previous spectrum by the difference in photon energy. Finally, we reach the



Fig.1. Normal emission electron spectra¹²⁷¹ for various photon energies as indicated. Those spectra taken in resonance with a core-to-bound excitation are marked.

 $01s \rightarrow 2\pi$ resonance, and we observe resonance enhanced features at the same binding energy position as in the case of the $C1s \rightarrow 2\pi$ induced spectrum.

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

I $a \mid \langle v_f \mid p \mid v_i \rangle \mid^2$ (1) in photoemission with respect to a radiationless transition

I a $|\langle v_f | 1/r_{11} | v_i \rangle|^2$ (2) in autoionization. It has been shown numerically¹⁴/ that this accounts for the experimental observations in gas phase CO¹¹³⁻¹⁴/. 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 existance of such states¹¹⁹/.

Fig.2 shows an autoionization spectrum in comparison with a calculated photoemission spectrum of a Niz-CO cluster. The character of the states, as given by the calculation is indicated. In the photoelectron spectra the $5\sigma/1\pi$ and 4σ ionization are most intense. These states are partially screened/19-23/, and they correspond to configurations $N^{-1}5\sigma^{-1}(1\pi^{-1})2\pi$ and $N^{-1}4\sigma^{-1}2\pi$ of the adsorbate where M denotes a metal level. In order to deduce from this calculation how the relative intensities of the various states change when going from photoionization to autoionization we resort to the qualitative discussion of autoionization matrix elements outlined in ref./14/. In general, the intensity of an autoionization decay is given by equation (2). A more detailed analysis¹¹⁴ shows that the calculation can, under certain approximations, be reduced to matrix elements of the type:

< Φin,Φv |1/rij | ΦvΦis >

where the Φ_1 are one-electron levels and the index v stands for valence. The autoionization intensity for the screened $5\sigma/1\pi$ and 4σ states is small because it is governed by matrix elements of the type

(\$\$\$\$\$ 1/rij \$\$\$\$\$

where ϕ_{1n} is the continuum orbital of the outgoing electron charactized by the angular momentum quantum numbers 1 and n. This has to be compared with matrix elements of type

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 form the molecule reducing the coulomb matrix element considerably. A different situation is expected for the uncreened state, i.e. configurations of type $5\sigma^{-1}$, $4\sigma^{-1}$ or $1\pi^{-1}$. Their intentsity 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 presented calculation places the lines involving the 50⁻¹ unscreened states at little lower binding energies as compared with the $M^{-1}4\sigma^{-1}2\pi$ screened ion state. However, the shake-up states involving the $4\sigma^{-1}$ configuration are situated several eV below those involving the 50-1 shake-ups. We expect the 50-1 shake up states to exhibit larger intensities as compared with the $4\sigma^{-1}$ shake up states for the Cls $\rightarrow 2\pi$ decay because of the preferential localization of the 50⁻¹ configuration on the carbon atom. We identify peak (1) in Fig.2 as a $5\sigma^{-1}$ shake-up state, because its intensity is attenuated in the $01s \rightarrow 2\pi$ decay spectrum. The calculation places the 40⁻¹ shake-up states into the flank of the most intense peak. The most intense peak appears to be a superposition of states mainly due to 50-11n-12n, and 1n- $^22\pi$ configurations which is consistent with its large intensity in both the Cls+2 π and Ols+2 π decay spectra. In the region below the most intense peak, the situation becomes rather complicated, because many configurations start to mix and an assignment has to await more detailed explicite calculations of the autoionization intensities. However, there is reason to believe, that we can also achieve more detailed experimental information. As Umbach and Hussain^{/26/} demonstrated, electron emission via



Fig.2. Assignment²⁷ of the CO(2x1)P2mg/Ni(110) autoionization spectrum after C1s+2m excitation on the basis of a Ni₂-CO cluster calculation¹⁹.

radiationsless 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

Fig.3 shows an autoionization spectrum from a $CO_2/Ni(110)$ adsorbate prepared at a surface temperature of T=80 K in comparison with a CO_2 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 CO_2 . In photoemission there is a oneto-one correspondence between the spectra of the gas and the condensed molecular solid^{40/}. Since the gas phase photoelectron spectrum has been recorded throughout the full outer and inner valence electron region^{41/} we compare in Fig.3 this photoelectron spectrum with the autoionzation spectrum. The binding energy scale is referenced to the vaccum level. The difference in the selection rules is particularly impressive in the region of the outer valence levels. While the ionization probability to the $2\pi_g$ ion state is particularly large, the probability for autoionization into this state vanishes for C1s+2



Fig.3. Normal emission autoionization spectrum of a $CO_2/Ni(110)$ adsorbate (difference between adsorbate spectrum and free surface spectrum) in compariosn with the CO_2 gas phase spectrum/^{41/}.

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.

- 1. L.S. Cederbaum, W. Domcke, Adv. Chem. Phys. <u>36</u>, 205 (1977).
- 2. S. Krummacher, V. Schmidt, F. Wuilleumier, J.M. Bizeau, D. Ederer, J. Phys. B16, 1733 (1983).
- 3. J. Schirmer, O. Walter, Chem. Phys. 78, 201 (1983).
- 4. J.N. Miller, D.T. Ling, I. Lindau, P.M. Stefan, W.B. Spicer, Phys. Rev. Lett. , 1419 (1977).
- 5. H.-J. Freund, F. Greuter, D. Heskett, B.W. Plummer, Phys. Rev. B28, 1727 (1983).
- 6. C.T. Chen, Thesis, University of Pennsylvania (1985), unpublished.
- E.W. Plummer, C.T. Chen, W.K. Ford, W. Eberhardt, R.P. Messmer, H.-J. Freund, Surf. Sci. 158, 58 (1985).
- 8. C.T. Chen, R.A. DiDio, W.K. Ford, E.W. Plummer, Phys. Rev. B32, 8434 (1985).
- 9. D. Menzel, P. Feulner, R. Treichler, E. Umbach, W. Wurth, Phys. Scri. 717, 166 (1987).
- 10. G. Loubriel, T. Gustafsson, L.I. Johansson, S.J. Oh, Phys. Rev. Lett. 49, 571 (1982).
- 11. W. Wurth, R. Treichler, E. Umbach, D. Menzel, Phys. Rev. B35, 7741 (1987).
- 12. W. Wurth, C. Schneider, R. Treichler, D. Menzel, E. Umbach, Phys. Rev. to be published.
- 13. J.L. Dehmer, D. Dill, Phys. Rev. Lett. 35, 213 (1975).
- 14. H.-J. Freund, C.-N. Liegener, Chem. Phys. Lett. 134, 70 (1987).
- 15. L. Ungier, T.D. Thomas, Chem. Phys. Lett. 96, 247 (1983).
- 16. L. Ungier, T.D. Thomas, Phys. Rev. Lett. 53, 435 (1984).
- 17. L. Ungier, T.D. Thomas, J. Chem. Phys. 82, 3146 (1985).
- U. Becker, R. Hölzel, H.-G. Kerkhoff, B. Lander, D. Szosak, B. Wehlitz, Phys. Rev. Lett. 56, 1458 (1986).
- 19. D. Saddei, H.-J. Freund, G. Hohlneicher, Surf. Sci. 95, 257 (1980).
- 20. K. Hermann, P.S. Bagus, C.R. Brundle, D. Menzel, Phys. Rev. B24, 7025 (1981).
- 21. R.P. Messmer, S.H. Lamson, Chem. Phys. Lett. 65, 465 (1979).
- 22. H.-J. Freund, E.W. Plummer, Phys. Rev. B23, 4859 (1981).
- 23. K. Schönhammer, O. Gunnarsson, Sol. State Commun. 26, 399 (1978).
- 24. G. Wendin "Structure and Bonding" Vol. 45 (Springer Verlag, Berlin (1981)).
- 25. D. Saddei, Thesis, Universität Köln (1982).
- 26. E. Umbach, Z. Hussain, Phys. Rev. Lett. 52, 754 (1984).
- 27. G. Illing, T. Porwol, H.-J. Freund, H. Kuhlenbeck, M. Neumann, S. Bernstorff, to be published.
- B. Bartos, H.-J. Freund, H. Kuhlenbeck, M. Neumann, H. Lindner, K. Müller, Surf. Sci. 179, 59 (1987).
- G. Illing, D. Heskett, E.W. Plummer, H.-J. Freund, J. Somers, Th. Lindner, A.M. Bradshaw, U. Buskotte, M. Neumann, U. Starke, K. Heinz, P. de'Andres, D. Saldin, J.B. Pendry, Surf. Sci. to be published.
- 30. J.-H. Pock, H.-J. Lau, E.E. Koch, Chem. Phys. 83, 377 (1984).
- 31. H.-J. Freund, H. Kossmann, V. Schmidt, Chem. Phys. Lett. 123, 463 (1986).