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ENERGY LEVEL SHIFTS OF CO CHEMISORBED AND CONDENSED ON RH(111)

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Energy level shifts of CO in different phases, gas, solid and chemisorbed on Rh(111) are compared. Between gaseous and solid CO a shift of the 4 σ and 5 σ derived molecular orbitals of about 2.7 eV to lower binding energies due to polarization is observed. A larger 1 π - 4 σ separation of the CO molecules condensed and chemisorbed on Rh(111) is observed with respect to the gas phase. A comparison of the binding energies of the three molecular orbitals in the different phases allows to estimate the bonding shift of the 5 σ level to 2.7 eV.

Since the pioneering work of Eastman and Cashion¹, photoelectron spectra of CO molecularly adsorbed on a large variety of transition metals have been reported.² All these measurements show energy level shifts of the molecular orbitals in the chemisorbed phase with respect to the gas phase. Different mechanisms have been invoked for the origin of these shifts.³⁻⁵ A consistent interpretation of these effects on the basis of the experimental work performed until now is difficult. More detailed information is expected by comparing the spectra of chemisorbed molecules with those of the gas as well as the solid.⁶ As the photoelectron spectra of the molecules condensed on the same substrate usually do not exist, the energetic position of the molecular orbitals in the chemisorbed phase is discussed in comparison with the gas phase and theory. In this letter we present a comparison of the energy levels of CO chemisorbed and condensed on the Rh(111) surface with those of gaseous CO. Synchrotron radiation was used as a light source for performing UPS-measurements in the photon energy range 15 eV to 27.5 eV. The photoelectrons were energy analysed with a Physical Electronics doublestage cylindrical mirror analyser. The resolution was 0.5 eV. Preparation and cleaning of the sample was achieved by standard UHV techniques. The Rh(111) sample was attached to a liquid Helium flow cryostat. During the measurements on solid CO the temperature of the sample was in the 10-20 K range, well below the boiling point of CO ($T_b=20$ K) at 10^{-8} Pa. Further details of the experiment will be presented in a forthcoming paper.⁷

Photoelectron spectra of 2.7×10^{-2} Pa sec CO condensed on the Rh(111) surface are shown in fig. 1 for different excitation energies. We estimate the thickness

of the film to be about 15 nm. Structure observed in the low binding energy range is due to photoemission from the Rh 4d bands. Thus the Fermi level E_F can be determined. The vacuum level has been found to lie 5.1 eV above the Fermi level. The three peaks denoted 4σ , 1π and 5σ are derived from the corresponding molecular orbitals of gaseous CO. Positions, relative separations and relative intensities of these peaks vary with photon energy. The half width of the peaks is 1 eV to 2 eV, much broader than the experimental resolution of 0.5 eV. With this resolution we could not resolve molecular vibrational modes. Thus it is not possible to distinguish whether the peaks are smeared out due to resolution only or due to the excitation of phonon sidebands as discussed by Gadzuk et al.⁸ With increasing photon energy the peak maxima move to higher as well as to lower binding energies. In addition the relative peak separation changes. The peak position varies by up to + 0.4 eV. This value is reasonable for the dispersion of energy bands in van der Waals solids.⁹

As can be seen from fig. 1 the emission intensity due to direct electrons is attenuated if the kinetic energy of the photoelectrons exceeds a threshold energy of 8 eV with respect to the vacuum level. The arrows indicate the onset of this scattering mechanism, when the photoelectron can be scattered to the bottom of the conduction band and a second electron is excited simultaneously to a localized state (Frenkel exciton within the band gap). The lowest excitation energy to localized states in solid CO is 7.9 eV as obtained from ultraviolet transmission¹⁰ and electron energy loss measurements.¹¹ This excitation energy together with the threshold energy yields a band gap of 11 ± 0.5 eV. This scattering mechanism can influence

the apparent peak position, when its onset falls in the range of a CO emission band (see e.g. the spectrum for $h\nu=25.0$ eV in fig. 1).

In fig. 2 photoemission data of CO in different phases are compared. The binding energy is referred to the vacuum level taking into account the measured workfunctions of CO chemisorbed ($\phi=5.5$ eV) and condensed ($\phi=5.1$ eV) on the Rh(111) surface. The difference spectrum (fig. 2a) recorded with $h\nu = 27.5$ eV was obtained after admission of 1.3×10^{-4} Pa sec CO onto the clean Rh(111) surface at room temperature. For clarity only the region of the CO induced extra emission is shown. The spectrum shows two main peaks, similar to those observed in photoelectron spectra of CO chemisorbed on other transition metals (see e.g. Ref. 3 and 12 and References cited therein). The structure at lower binding energies can be deconvoluted in two peaks by exploiting the photon energy dependence of the peak intensity in a similar way as for CO chemisorbed on Ir.¹³ The energies of the resulting three peaks are 16.7 eV, 13.8 eV and 13.3 eV with respect to the vacuum level. The peaks observed in our spectra at binding energies of 16.7 eV and 13.8 eV increase with photon energy whereas the peak at 13.3 eV decreases.⁷ The energy dependence of the CO induced extra emission observed for CO chemisorbed on Ni¹⁴ has recently been explained as due to a resonance in the photoionization cross section by comparison with measurements¹⁵ and calculations¹⁶ for the partial photoionization cross sections for CO in the gas phase. We identify the peaks at higher binding energies as due to the 4σ and 5σ molecular orbitals. These levels have the same symmetry and thus their photoionization cross sections should show in a first approximation a similar behavior.

We note however, that angular emission effects may influence the behavior of the emission intensities from the different levels, if the molecule is oriented on the surface as discussed e.g. in Ref. 7. The structure at 13.3 eV is mainly derived from the 1π molecular orbital. In fig. 2b the photoelectron spectrum of solid CO with background subtracted as indicated in fig. 1 is shown. For a complete comparison of CO in its different phases two photoelectron spectra of gaseous CO are reproduced in fig. 2c.^{15,17} In order to align the 4σ levels the energy scales of the spectra of CO chemisorbed and condensed on Rh(111) have been shifted by 3.0 eV and 2.7 eV, as indicated in fig. 2 respectively. The mean peak separation between the 1π and 4σ level is 0.65 eV and 0.9 eV larger in the chemisorbed and solid phase than in the gas phase, respectively. The 5σ level lies 2.8 eV closer to the 4σ level in the chemisorbed phase than in the solid or gas phase.

Discussing the observed level shifts we have to consider different effects. These shifts originate from both the initial and the final state of the photoexcitation process. Two kinds of mechanisms can contribute to the initial state shift, the bonding and the chemical shift. The former describes the lowering in binding energy when a chemical bond is formed. The latter is caused by a change of the chemical environment. The final state shift is due to the difference in relaxation energy in the different phases. This difference is expected to lower the observed binding energies of corresponding levels of CO chemisorbed and condensed on solids with respect to the gas phase.^{4,5} The difference in relaxation energy originates from the dielectric screening of the hole created in the photoexcitation process and will be denoted in this discussion as polarization shift. Experimentally it is not possible to separate the level shifts discussed. Only the sum of these shifts can be observed. However, it is possible to estimate the main contri-

butions by a comparison of the experimental data together with theoretical arguments.⁵

In solids composed of homonuclear molecules like N_2 or O_2 a reduction in binding energy of the molecular orbitals up to 1.7 eV with respect to the gas phase has been observed and interpreted as due to dielectric screening.¹⁸ We ascribe the shifts of 2.7 eV and 3.0 eV indicated in fig. 2 as being mainly due to polarization effects. Even if we take into account chemical shifts of -1.0 eV to -1.2 eV for the different levels in the chemisorbed phase as calculated for Ni_2CO ^{4,5} we obtain a polarization shift which is still reasonable. Polarization energies up to 4 eV have been theoretically predicted when comparing gas phase data to those of chemisorbed species.¹⁹

After taking into account the polarization shift the peak maximum of the 1π level in solid CO lies still at lower binding energy with respect to gaseous CO. This shift of 0.9 eV is larger than the difference in energies between peak maximum (vertical transition) and the low energy onset (adiabatic transition) of the observed peaks in gaseous CO. Thus a possible change of the Franck-Condon factors in going from gaseous to solid CO cannot fully explain this shift. In addition, the dispersion of the energy bands in solid CO would also be too small. This shift can most likely be explained by an interaction between the CO molecules. A similar shift of the 1π level is observed in the chemisorbed phase resulting in a larger peak separation of the 4σ and 1π levels. Within experimental error we have found no clear evidence for bandstructure effects for CO chemisorbed on Rh(111) although bandformation has been predicted²⁰ and observed for CO on Ni(100) recently.²¹

For CO chemisorbed on Fe(100) the $4\sigma - 1\pi$ separation was found to be larger than in the gas phase, too, and was ascribed to a stretching of the CO molecules, because the strong bonding interaction of the 5σ molecular orbital with metal d-states may weaken the carbon-oxygen bond.²² Provided the carbon-oxygen separation is increased the orbital overlap will decrease causing a decrease in binding energy of the bonding levels. The 1π level has more bonding character than the 4σ level and is therefore expected to show the strongest peak shift resulting in an increase of the $4\sigma - 1\pi$ peak separation. In solid CO the intermolecular interaction may also weaken the carbon-oxygen bond. However, a strong weakening of this bond in the condensed phase is rather unlikely due to the very weak intermolecular interactions. Thus different polarization shifts for the individual molecular orbitals seem to be responsible for changes in relative peak separations. Different polarization energies may also be important for the chemisorbed phase.

A shift of 2.7 eV is observed for the 5σ level when comparing CO chemisorbed and condensed on Rh(111) demonstrating that the strong chemisorption bond is formed by an overlap of the 5σ molecular orbital with d-orbitals of the metal. Hermann and Bagus calculated an initial state shift for the 5σ -level of -3.42 eV for Ni_2CO^5 with respect to the gas phase. Keeping in mind that possible chemical shifts are not included in the relative shifts of the spectra in fig. 2 an excellent agreement between theory and experiment is obtained. The strong bonding interaction of the 5σ level with

the orbitals of the metal yields a weakening of the molecular bond. We observe a peak separation between the 4σ and 1π level of CO chemisorbed on Rh(111) which is nearly the same as in solid CO. This would suggest a stretching of the CO molecule in accordance with infrared measurements on $\text{Rh}_2(\text{CO})_6$ ²³ and CO chemisorbed on Rh^{24} which show a lowering of the vibrational stretching frequency with respect to gaseous CO.

In summary, we have shown that initial and final state effects contribute to the energy level shifts of CO in different phases. The importance of comparing the dependent spectra from chemisorbed CO to both the gas phase and the solid phase spectra has become evident. In particular, we have estimated shifts due to polarization and bonding of CO chemisorbed and condensed on Rh(111). Experimentally there is no rigorous way to separate chemical, bonding and polarization shifts. Therefore a quantitative determination of the different shifts is only possible together with theoretical arguments. Bandformation, change in Franck-Condon factors as well as phonon sidebands have to be considered in a thorough interpretation of photoemission data in the valence band region of condensed and chemisorbed molecules.

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Figure Captions:

Fig. 1: Photoelectron energy distributions for CO condensed on the Rh(111) surface obtained with different photon energies. The spectra are plotted on a binding energy scale with $E_p = 0$. They are displaced to each other proportional to the photon energies used (right scale). The arrows indicate the onset of electron exciton scattering (see text).

Fig. 2: Comparison of photoelectron spectra of CO chemisorbed on Rh(111) (Panel a), condensed on Rh(111) (Panel b) and of gaseous CO (Ref. 15,17) (Panel c). For each spectrum the binding energy is referred to the vacuum level. The energy scales have been shifted by 3.0 eV and 2.7 eV for the chemisorbed and condensed phase respectively in order to align the 4 σ -maxima.

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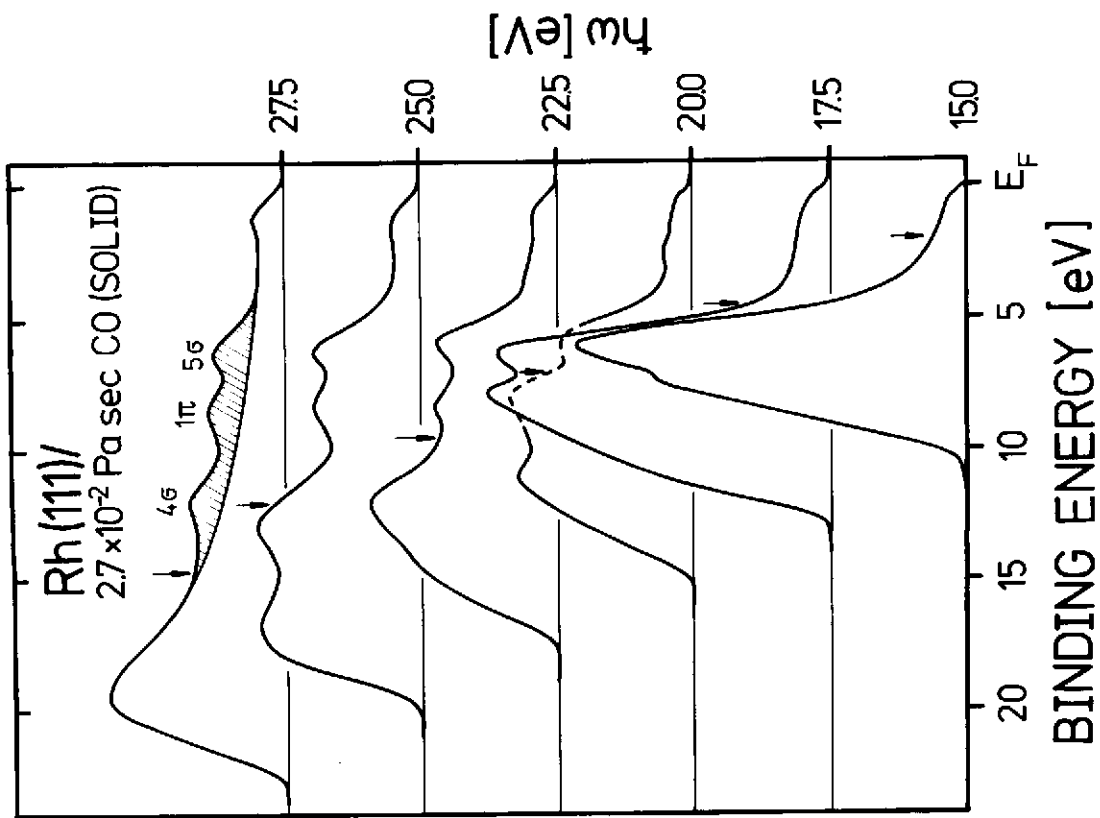


Fig. 1

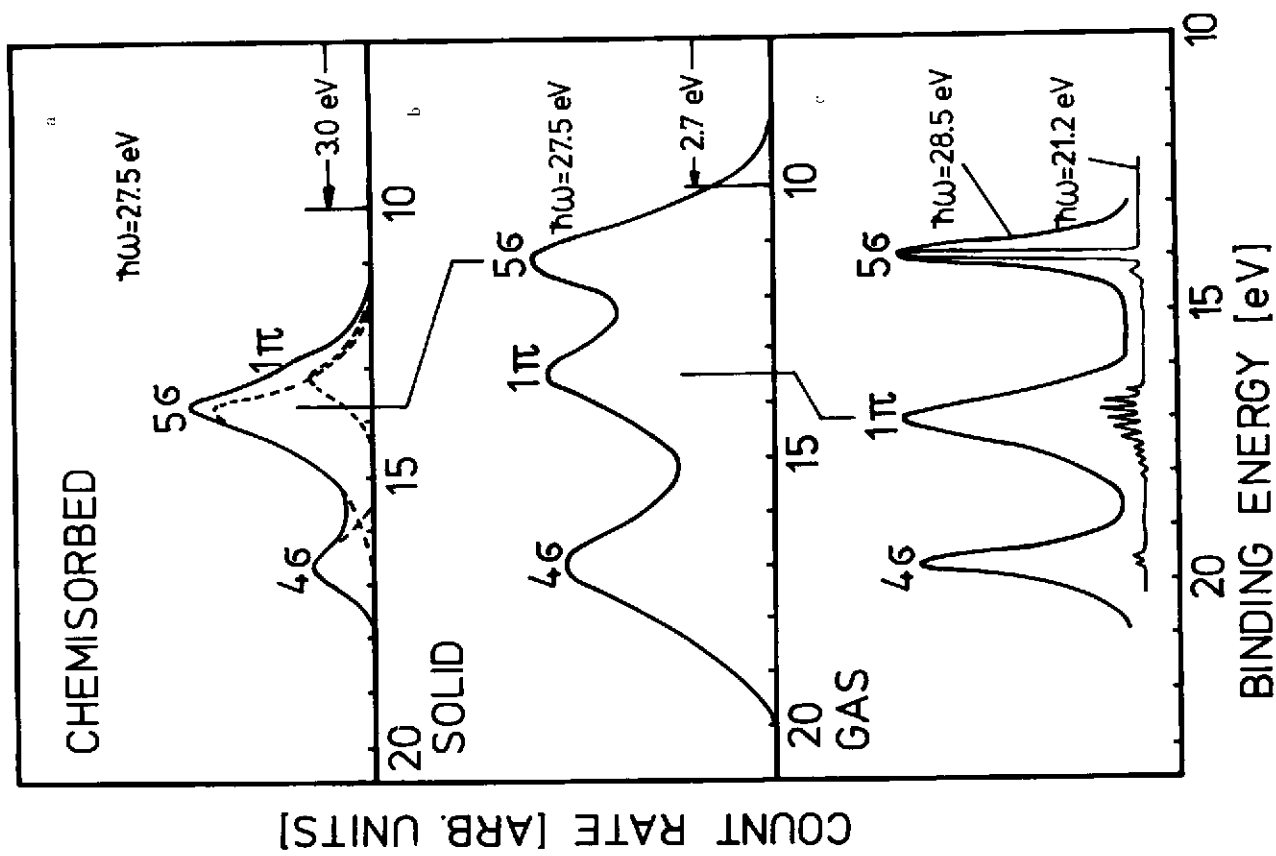


Fig. 2