

## Vibrational structure of excited states of molecules on oxide surfaces

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A more detailed knowledge of excited states of molecules adsorbed on solid surfaces is interesting from various points of view. To understand, for example, photochemistry at surfaces, the lifetimes of excited states are important parameters.

We report ELS spectra showing vibrational structure for CO on a thin (thickness: 5 Å)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(111) film grown on a NiAl(110) surface. The molecules desorb from the surface in the range 35 K < T < 75 K and thermal desorption spectroscopy (TDS) allows us to differentiate between monolayer and multilayer regimes. Two species exist in the monolayer. From the observed line widths of the vibrational sub-bands in electron energy loss spectroscopy (ELS) life times are estimated. For O<sub>2</sub> on the same surface, TDS also indicates the presence of monolayer and multilayer adsorption. With ELS, sharp signals from two excited states, known from the gas phase to be spin flip excitations, are observed. This indicates that there is no strong spin coupling between the O<sub>2</sub> molecules and the metal substrate underneath the oxide film. Angle resolved ELS data reveal no pronounced angle dependent cross section effects.

### 1. INTRODUCTION

Photochemical processes on solid surfaces have gained increasing interest in recent years [1-5]. Often, excited states of adsorbed molecules are involved in these processes. A detailed study of the excited states with appropriate spectroscopic techniques is difficult because the life times of the states are short and the corresponding line widths are large [6-8]. In fact, within the monolayer observations of molecular excited states on metal surfaces are rather the exception than the rule [7,9]. The main factor is the energy dissipation from the molecule in the excited state into the solid which may be induced through electron-hole pair creation at the Fermi energy of the metal [10]. On solid surfaces of substrates with considerable band gaps, however, chances to observe molecular excited states with reasonable resolution are much better [11]. Recently, we have reported preparation and characterization of a thin, long range ordered  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(111) film on a NiAl(110) surface [12].  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(111) has a band width of 9.5 eV [13] in the bulk, and is therefore well suited for a study of excited states in molecular adsorbates [11]. We report in this contribution a systematic study of two small

molecules, CO and O<sub>2</sub>, on this surface. We have also studied other molecules, for example, CO<sub>2</sub>, NO, NO<sub>2</sub>, and H<sub>2</sub>O [14]. We shall show that for CO and O<sub>2</sub>, excited states may be studied on the oxide surface. These states are reasonably long lived and allow pronounced vibronic structure to be observed. This allows us to estimate, among other physical quantities, the life times involved.

### 2. EXPERIMENTAL

The experiments have been performed in two magnetically shielded UHV systems. One is designed for angle resolved photoelectron spectroscopy (ARUPS) and for angle resolved electron energy loss spectroscopy (ELS). The other one is designed for spot profile analysis low energy electron diffraction (SPA-LEED). In the ARUPS system the electron energy analyser is mounted on a goniometer allowing for angular resolved electron detection in two orthogonal planes. For the ELS experiments the overall resolution of analyser plus electron monochromator was set to 50 meV. In the SPA-LEED system the transfer width was approximately 800 Å.

The NiAl(110) crystal was mounted on a liquid He flow cryostat which allowed for cooling to about 25 K. Heating was possible by electron impact on the reverse side of the crystal. After cleaning the sample using sputtering and annealing cycles, the oxide film was prepared by admitting 1200 L ( $1 \text{ L} = 10^{-6} \text{ Torr s}$ ) of oxygen at elevated temperature (550 K) into the chamber, and subsequent annealing to 1200 K as described in more detail elsewhere [11,14]. The quality of the resulting oxide film was documented by a set of sharp LEED spots with low background intensity. Films prepared in this way have a thickness of about 5 Å.

To avoid contamination of the adsorbate layer from the residual gas atmosphere during the measurements, it was flashed off every 20 minutes and the adsorbate was prepared anew.

### 3. RESULTS AND DISCUSSION

In previous work the geometric and electronic structure of the  $\gamma\text{-Al}_2\text{O}_3(111)$  film on a NiAl(110) surface has been studied in detail applying ARUPS [12,15,16], HREELS [12,15,16], XPS [12], LEED [12,17], XPD [18], STM [15,19], and ISS [12,19]. It was found that the film has a uniform

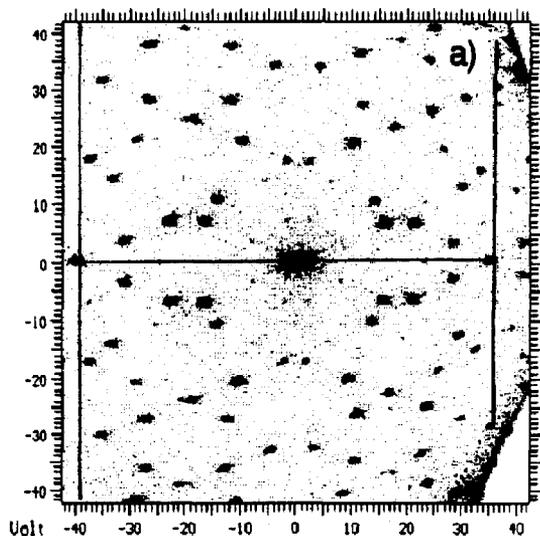
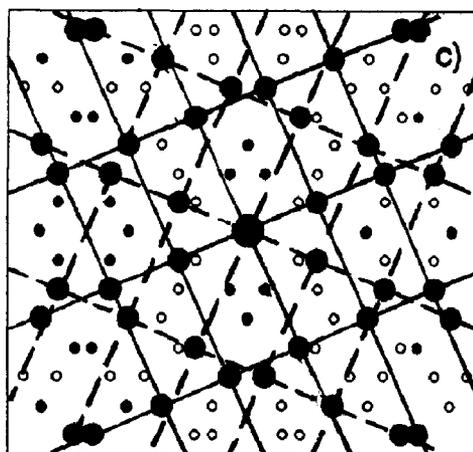
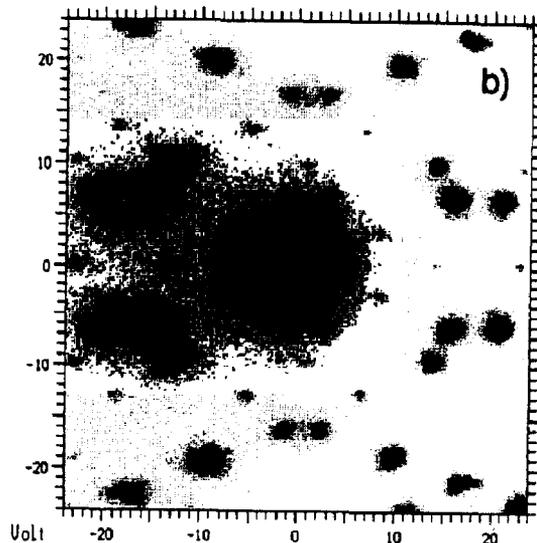


Fig. 1.a) Wide scan SPA-LEED pattern of the  $\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$  system.



●: (0,0)-spot    ●:  $\text{Al}_2\text{O}_3$ -spot  
 Double diffraction spots with respect to NiAl-spots of first order:  
 ●: observed    ○: not observed

Fig. 1.b) Enlarged view in the range of the (0,0)-reflex of the  $\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$  SPA-LEED pattern.

c) Schematic representation of single and double diffraction spots for comparison with Fig. 1a and 1b

thickness of 4-5 Å and is smooth with terrace widths of 200-300 Å. Photoemission suggests that the film has a stoichiometry of Al:O = 2:3 with no Ni in the film. Also, an interfacial layer with higher Ni concentrations appeared to be very unlikely. HREELS suggests, through the recorded phonon spectrum, that the film does not exhibit an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> but rather a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structure with Al atoms occupying tetrahedral as well as octahedral sites. The surface is oxygen terminated as revealed through ISS. Conventional LEED has shown that the unit mesh is very large in real space, i.e. 10.6 Å x 17.9 Å, and that there are two domains. We have undertaken a SPA-LEED study [20], the details of which shall be reported elsewhere [21]. Here we only want to note the observation of double diffraction spots, which so far had not been observed for the film [12,17]. Fig. 1a shows a SPA-LEED pattern of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> film. The spots from the NiAl substrate are indicated in the figure through the large unit mesh in reciprocal space. There is a wealth of Al<sub>2</sub>O<sub>3</sub> induced spots of which only the most intense ones are visible in the figure.

A more enhanced pattern of a close up near the (0,0) spot, shown in Fig. 1b, also exhibits the less intense features. In Fig. 1c a schematic diagram allows the assignment of the features to the two domain structures. The spots that are not part of the two-domain lattice are due to double diffraction with respect to NiAl spots of first order. The ones observed are shown as filled circles. Their intensities are very small, and that is the reason why they have not been observed in the earlier LEED experiments.

### 3.1 CO adsorbates

Fig. 2 shows TDS spectra for different exposures. There are four features discernable in the data. The monolayer saturates at about 1 L. There are two different features in the monolayer regime with desorption maxima at 67 K and at 58 K. This corresponds to adsorption enthalpies of 0.17 eV and 0.14 eV, respectively. A typical adsorption enthalpy of the same order of magnitude for a CO-metal adsorbate, i.e. CO/Ag(111), has been determined

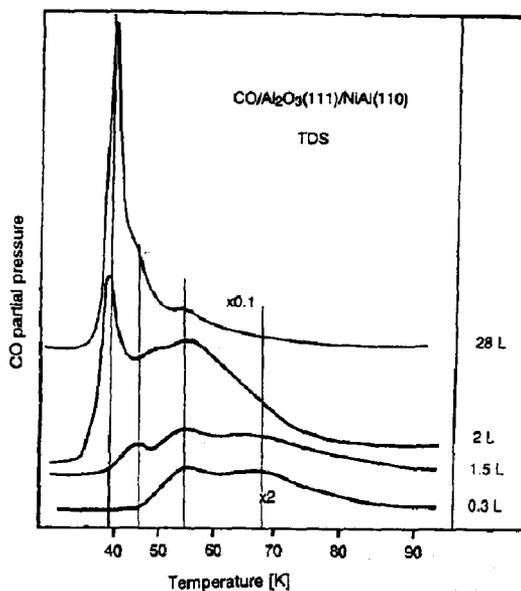


Fig. 2. Thermal desorption spectra of the system CO/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(111)/NiAl(110) after dosing varying amounts of CO at T = 35 K.

to be 0.17 eV [22]. Before the multilayer desorption peak at 38 K appears there seems to exist a fourth feature with maximum desorption temperature around 45 K. It is not clear at present whether the latter feature corresponds to a bilayer or another intermediate state of the adsorbate. The multilayer adsorption enthalpy of 0.08 eV is close to the heat of condensation [23].

Knowing these TD spectra we can ask what is the relation between temperature and CO pressure to maintain the CO coverage as found in the UHV experiment, even at elevated temperature? Take for example the most strongly bound species in the monolayer. A simple estimate shows [14,15] that for T = 500 K the most strongly bound species needs a CO pressure of about 1 bar. To keep the other species, desorbing at 58 K, at the surface we would have to increase the CO pressure to 290 bar. We note in passing that such estimates may be interesting with respect to certain questions in catalysis.

In Fig. 3 we show the ELS spectrum ( $E_p = 18$  eV) of a CO multilayer on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(111)/NiAl(110) substrate. In the lowest trace we see on the left the

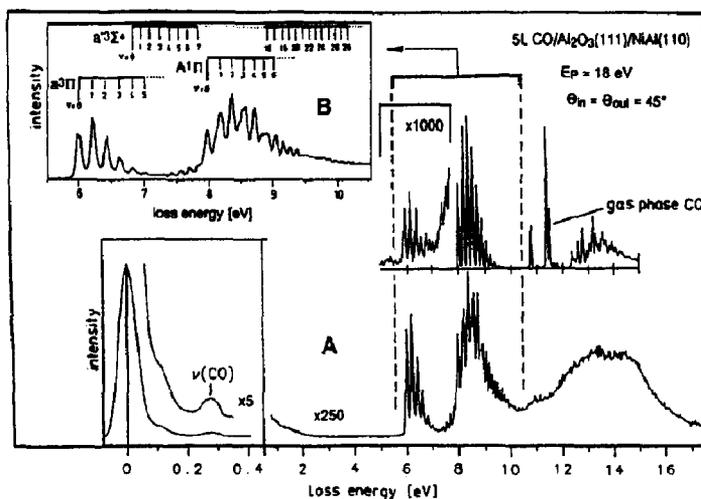


Fig. 3. Electron energy loss spectra at  $T = 35$  K of a CO multilayer on  $\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$  in comparison with the gas phase [24]. An enlarged view of the vibrational progressions are shown in the top inset. Note, that the vibrational loss part is plotted on a larger energy scale.

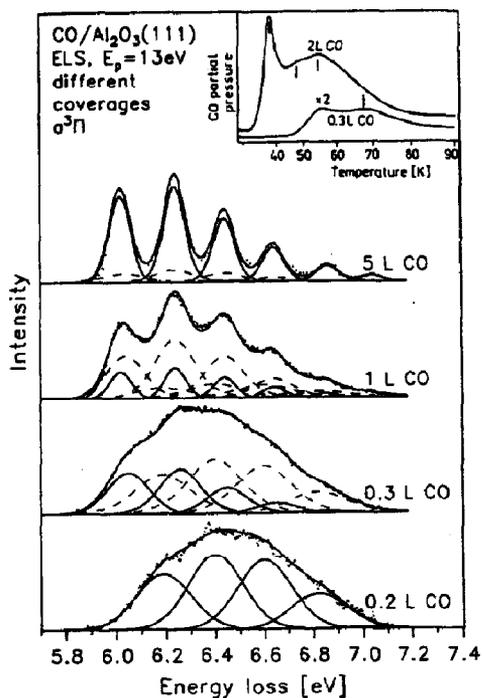


Fig. 4. Electron energy loss spectra at  $T = 35$  K in the range of the  $a^3\Pi$  excitation as a function of coverage. Relevant TD spectra are shown in the inset.

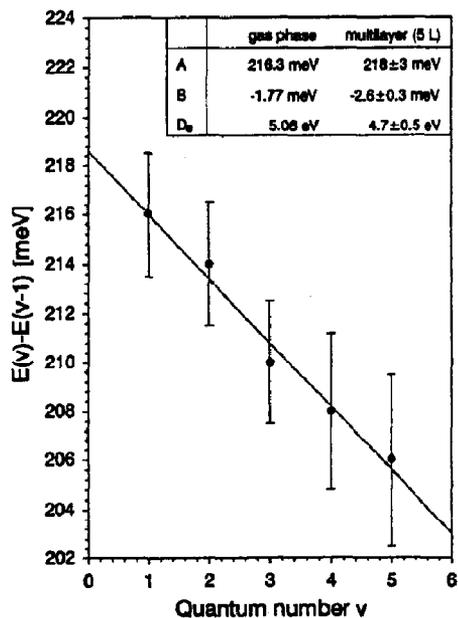


Fig. 5. Birge-Spencer analysis to determine the  $a^3\Pi$  dissociation energy. The inset shows the results in comparison with the gas phase [26].

elastic peak, and, due to the relatively low resolution, only a slight indication of the  $\text{Al}_2\text{O}_3$  phonons (see ref. [12] for a well resolved phonon spectrum) followed by the CO vibrational stretch loss in the ground state. At 6 eV (note the change in energy scale) losses due to excited states start. The assignment of the spectrum is rather straightforward for the adsorbate because it compares favourably with the gas phase, shown for comparison [24]. A detailed assignment of the progressions is shown in the inset. In the following we shall consider in more detail the optically forbidden (but in electron scattering allowed) progression of the  $a^3\Pi$  state. The population of the  $a^3\Pi$  state involves primarily the excitation of a  $5\sigma$  electron into the  $2\pi$  orbital.

Fig. 4 shows a set of ELS spectra of this excitation as a function of coverage. Clearly, as has been discussed in detail in a previous paper [11], there is a pronounced intensity of this excitation visible in the monolayer regime. The line width at 0.2 L exposure is rather large but the remaining structure allows us to fit (least square) a single Franck-Condon distribution to the peak. The TD spectra at this dose suggest the presence of a single species. Increase to 0.3 L leads to the appearance of a peak at 58 K desorption temperature in the TD spectra. This new state should have its own characteristic Franck-Condon distribution. The fit therefore shows two distributions: one due to the one determined from the 0.2 L exposure, which was then fixed as far as parameters are concerned, and a second one which was optimized to fit the total progression at 0.3 L exposure. This second progression is clearly shifted with respect to the first one by 170 meV as indicated by the line. At 1 L exposure the multilayer progression starts to contribute. It is only shifted by 25 meV with respect to the second progression. In total, the multilayer signal is shifted with respect to the most strongly bound excitation by 195 meV.

This leads to the following immediate conclusions: The ground state of the most strongly bound state is stabilized through interaction with the substrate by 0.19 eV, i.e. with respect to the multilayer by 0.11 eV. Since the excitation energy for the monolayer species is by 0.195 eV larger

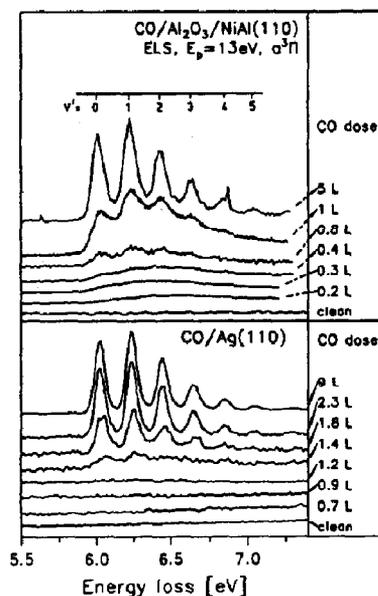


Fig. 6. Comparison of EL spectra ( $a^3\Pi$ ) of CO on  $\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$  with spectra of CO on  $\text{Ag}(110)$  at  $T = 35$  K as a function of exposure.

compared with the multilayer the excited state must be destabilized by 0.085 eV. One reason for this destabilization may be the expected stronger repulsion between molecule and substrate because population of the  $2\pi$  orbital increases the average size of CO and leads to a more pronounced Pauli repulsion between CO and the top oxygen layer of the substrate which behaves electronically like a layer of rare gas atoms ( $\text{Ne} \Leftrightarrow \text{O}_2^-$ ). Since the CO molecule is physisorbed on  $\text{Al}_2\text{O}_3$  we have assumed in this case that the potential energy well of the  $a^3\Pi$  state is very similar to the gas phase. We can provide evidence for this by performing a Birge-Sponer analysis for the multilayer progression. This is done in Fig. 5, where the spacing between neighbouring vibrational quanta is plotted as a function of the vibrational quantum number. From the fit we can determine the dissociation energy and the anharmonicity. The inset shows the result of the fit and the comparison with the gas phase. The well depths are the same within the experimental error while the anharmonicity seems to be slightly increased with respect to the gas phase [26].

species	adsorption enthalpy [meV]	FWHM [meV]	$E(v'=0)$ [eV]	$E(v'=1)-E(v'=0)$ [meV]	lifetime [ $10^{-15}$ s]
$T_{des} = 67$ K	-170	260	6.19	210	2.5
$T_{des} = 55$ K	-140	190	6.04	200	3.5
multilayer	-88	70	6.02	200	9.4
gas phase			6.02	202	some ms
1 ml CO/Ag(110)	$\approx -150$	large	?	?	small

Table 1. Experimentally determined molecular parameters of three different CO species on  $\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$ .

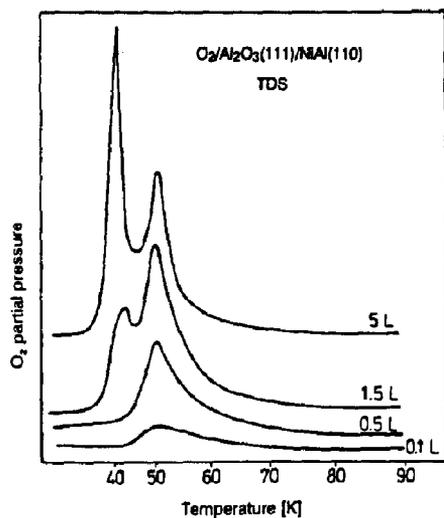


Fig. 7. Thermal desorption spectra of the system  $\text{O}_2/\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$  after dosing varying amounts of  $\text{O}_2$  at  $T = 35$  K.

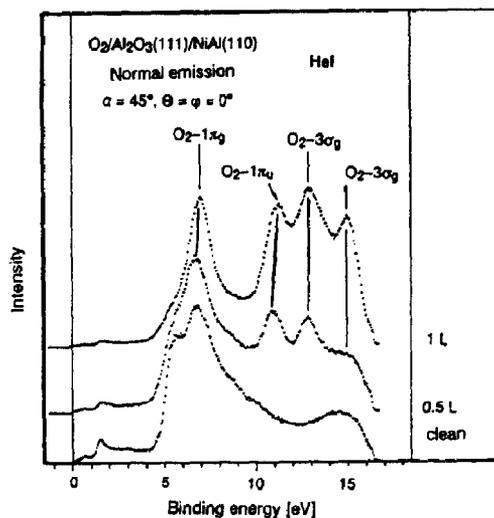


Fig. 8. ARUP spectra (He I) taken at normal emission of molecular oxygen on  $\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$  as a function of exposure.

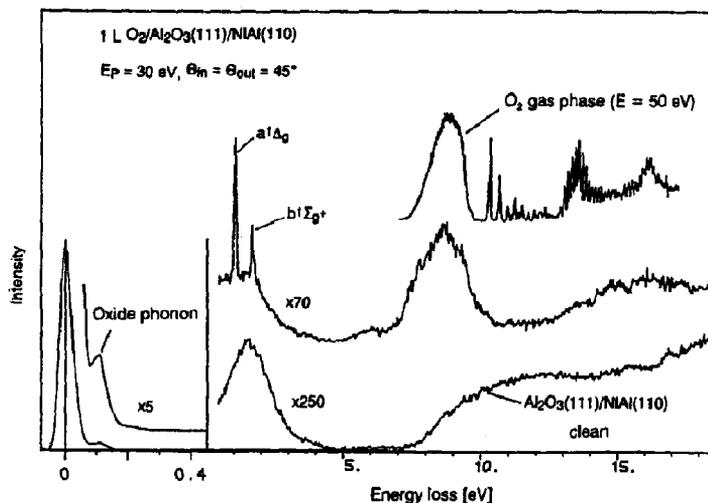


Fig. 9. Electron energy loss spectra of  $\text{O}_2/\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$  over a wide range energy range in comparison with the clean surface and the gas phase spectrum [28].

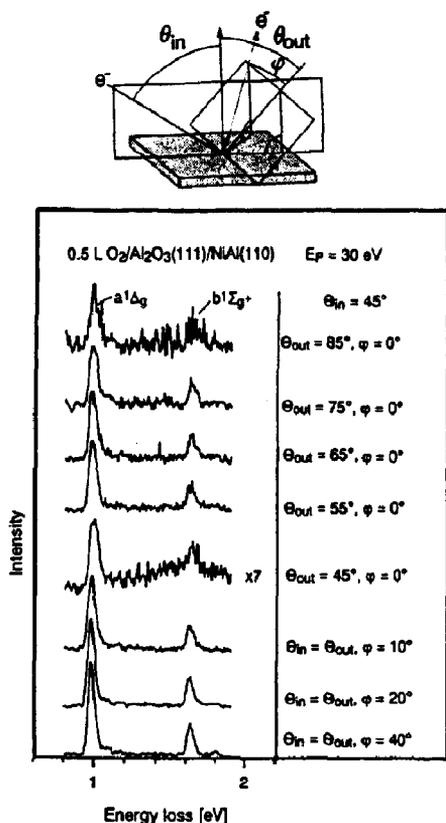


Fig. 10. Angle resolved electron energy loss spectra of  $O_2/\gamma\text{-Al}_2O_3(111)/\text{NiAl}(110)$  for different scattering geometries as indicated in the inset.

Next, we consider the line widths of the observed spectra. Table 1 collects the important information. We have discussed this in detail in ref. [11] and will not repeat the rather involved discussion. We want to comment that the observed life times are rather large compared to the time electronic excitations need to occur. The reason may be that the energy of the  $a^3\Pi$  state is not sufficient to excite electron-hole pairs in the substrate considering the large gap size of 9.5 eV. The situation is very different on a metal surface. In Fig. 6 we compare the set of spectra on the  $\gamma\text{-Al}_2O_3(111)$  substrate with a set of spectra of CO on Ag(110) [9]. While in the multilayer on the metal surface we observe spectra comparable with those on the oxide surface, it is clear that in the monolayer regime below 1.2 L exposure there is no

excitation discernable from the background in the case of the metal substrate. The reason appears to be rather obvious: There is no band gap in a metal, energy dissipation through electron hole pair creation is not hindered and the line widths are very large.

### 3.2 $O_2$ adsorbates

Fig. 7 shows the TD spectra of  $O_2$  on  $\gamma\text{-Al}_2O_3(111)/\text{NiAl}(110)$ . The spectra are simpler as compared with CO. Clearly, the monolayer ( $T_{des} \approx 52$  K) saturates around 1 L exposure and already at 1.5 L exposure a clear multilayer desorption signal ( $T_{des} \approx 40$  K) can be observed. The adsorption enthalpies correspond to 0.12 eV and 0.11 eV, respectively. The photoelectron spectra (Fig. 8) taken in normal emission with unpolarized He I light clearly reveal the features typical for molecular  $O_2$ . There have been some preliminary angle resolved photoelectron spectra taken with unpolarized light indicating that the  $O_2$  molecules may be oriented parallel to the surface. However, a definite conclusion must await a detailed synchrotron study.

Fig. 9 shows a wide scan of the EL spectra of the  $O_2$  adsorbate. Here we have included for comparison the spectrum of the clean substrate and the gas phase spectrum. In the spectrum of the clean substrate there is a peak around 1.5 eV excitation energy which is not typical for pure  $Al_2O_3$  but probably due to an excitation between the  $Al_2O_3$  film and the NiAl(110) substrate. Directly on top of this feature there are two very sharp features observed in the adsorbate. These are due to the  $a^1\Delta_g$  and  $b^1\Sigma_g^+$  states of  $O_2$  as observed for  $O_2$  on graphite by Palmer and co-workers [27]. The higher energy features are relatively broad already in the gas phase [28] or are broadened by interaction with the substrate so that we cannot resolve vibrational structure at present. The lines connected with Rydberg excitations are quenched, as was also the case for CO (but not discussed). The important observation is the small widths of the low energy states. They are indicative of the persistence of the

spin coupling in the O<sub>2</sub> molecule as it is adsorbed on the oxide surface. Even though the oxide film is very thin there appears to be no significant coupling of the molecular spin with the Fermi sea of the alloy substrate.

We have studied the angular dependence of the two excited states and show in Fig. 10 a set of spectra taken with a primary energy of 30 eV, an angle of incidence of  $\theta_{in} = 45^\circ$  and various scattering geometries. There is no strong angular dependence observed. This is in contrast to reports for O<sub>2</sub> on graphite [27] where a pronounced angular dependence has been observed. However, the data on the O<sub>2</sub>/graphite system have been taken within a negative ion resonance of O<sub>2</sub> which occurs between 6 eV and 8.5 eV. In the present case the data were taken way off resonance.

#### 4. CONCLUSIONS

We have shown that molecular adsorbates on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(111)/NiAl(110) are useful systems to study the properties of excited states weakly interacting with solid surfaces. CO and O<sub>2</sub> adsorbates have been studied in particular.

For CO adsorbates we have found via ELS measurements vibrationally resolved excitations even in the submonolayer regime. The life time of the vibrational components can be estimated to be around to  $5 \times 10^{-15}$  s. A comparison with corresponding adsorbates on a metal surface, e.g. Ag(110) [9], shows that the metal surfaces quench the excited states with high efficiency. Consequences for photochemical processes at surfaces are briefly mentioned.

For O<sub>2</sub> adsorbates we have found very sharp spin-flip excitations within the adsorbate indicating that the coupling between the open shells of O<sub>2</sub> with the Fermi sea of the alloy substrate is rather small.

We mention how the low temperature data can be used to estimate the coverage of a particular weakly bound state under high pressure and high temperature conditions.

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