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## ESR under UHV conditions on single crystal metal and metal-oxide surfaces

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Electron-Spin-Resonance (ESR) spectroscopy<sup>1-3/</sup>, routinely used in investigations on real catalysts, has high enough sensitivity to be applied to typical surface science experiments with single crystals. The limiting factor is the number of spins that lead to an acceptable signal-to-noise ratio, but its sensitivity is high enough to allow detection of a monolayer or even a fraction of a monolayer of molecules with unpaired electrons on a single crystal with a typical surface area of 1cm<sup>2</sup>. The disadvantages of this method are that it is exclusively applicable to systems which contain unpaired electrons, and, with respect to surface science, ESR is not inherently surface sensitive. But on the other hand ESR-spectroscopy is a powerful tool in the investigation of structure and dynamics of adsorbed molecules on single crystals, if the system is well chosen and prepared. In particular it is the aspect of dynamics of adsorbed molecules<sup>4/</sup> that renders this method interesting because there is a lack of methods in the field of surface science to study these aspects.

The present work contains results from ESR-measurements on following systems:

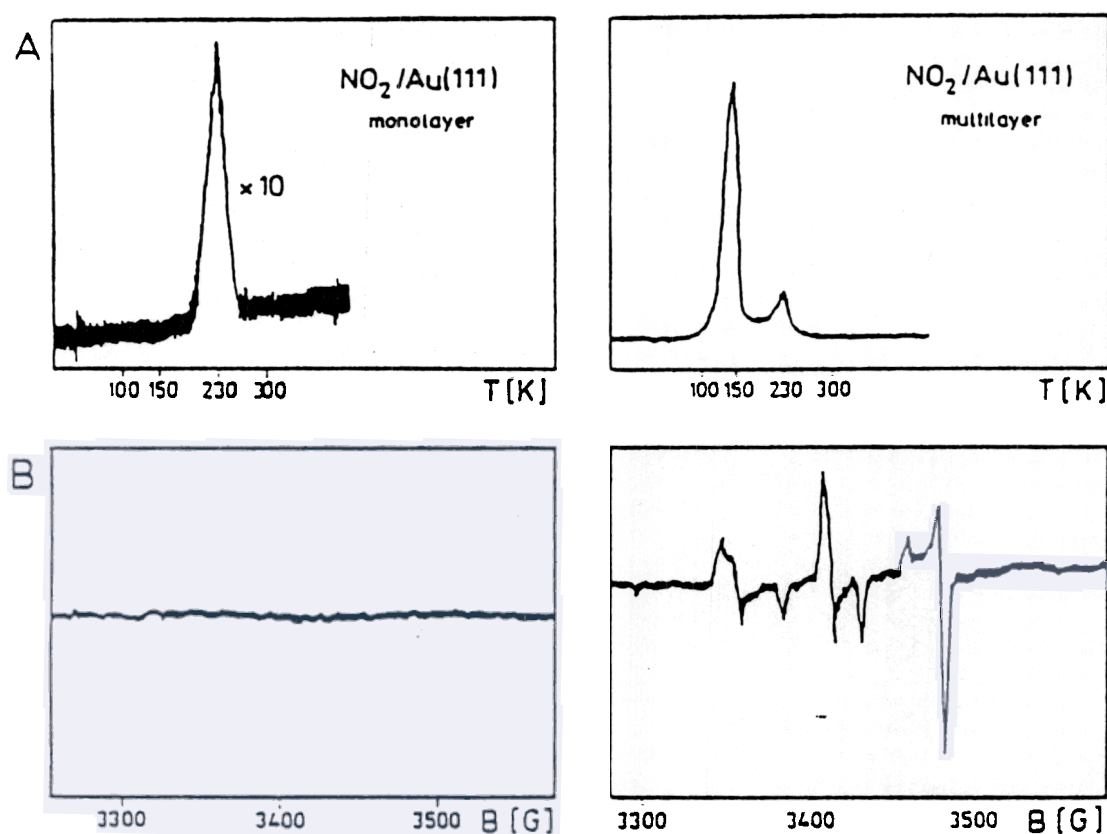
-NO <sub>2</sub> /Au(111)	-NO <sub>2</sub> /NiAl(110)
-NO <sub>2</sub> /NiO/Au(111)	-NO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> /NiAl(110)
-DTBN/NiO/Au(111)	(DTBN = Di-tert.-butylnitroxide)

The experiment combines the ultrahigh-vacuum-possibilities for preparation and characterisation (LEED, Auger, TDS) of adsorbates on single crystals with a standard electron-spin-resonance apparatus<sup>5/</sup>.

### NO<sub>2</sub>/Au(111) NO<sub>2</sub>/NiAl(110)

The system NO<sub>2</sub>/Au(111) exhibits a very clean and simple adsorption behaviour as revealed by the TPD data shown in Fig. 1a. We observe desorption peaks for the monolayer at T = 230 K and from the multilayer at T = 150 K in agreement with Bartram and Koel<sup>6/</sup>. In Fig. 1b the ESR spectra corresponding to the TPD spectra are shown. For the multilayer we observe a rather well resolved solid state spectrum of the NO<sub>2</sub> molecular solid. The monolayer shows no ESR signals above the background. The explanation for this latter result is simple. The interaction between the electrons at the Fermi energy of the metal substrate and the electron

spin on the molecule is so strong that the average residence time of the electron spin on the molecule is strongly reduced. This interpretation was given by Baberschke et al.<sup>[7-9]</sup>, who performed a similar experiment on a Ag surface. This effect, which is called Korringa-correlation<sup>[10]</sup>, leads to a strong increase of the line widths, so the spectrum disappears in the background noise. A thin oxide layer as surface spacer cancels this effect as we shall show. For a detailed discussion of the NO<sub>2</sub> multilayer spectrum one may refer to the papers of Schaafsma et al.<sup>[11-13]</sup>, who worked out the line shapes of NO<sub>2</sub> in a polycrystalline matrix of N<sub>2</sub>O<sub>4</sub>.



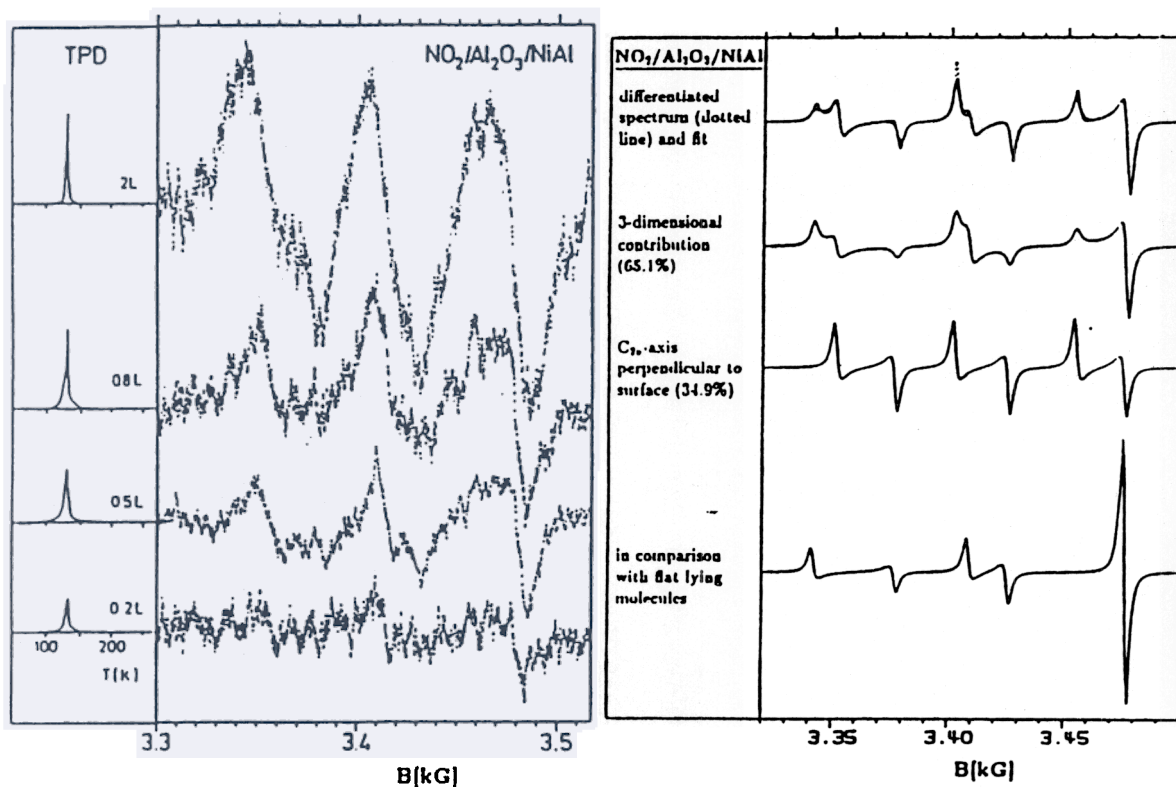
**Fig. 1:** Thermal desorption (TPD) and ESR spectra ( $T=35$  K) of NO<sub>2</sub>/Au(111); A) TPD signal for a monolayer NO<sub>2</sub> coverage (left panel), TPD signal for a multilayer coverage (right panel); B) ESR spectrum for a monolayer coverage (left panel), ESR spectrum for a multilayer coverage (right panel).

The comparison of an experimental spectrum with a computer simulated one under the assumption of random orientation reveals rather good agreement. The line width corresponds to non interacting NO<sub>2</sub> molecules.

The orientation of adsorbed molecules can be determined from angle dependent measurements. The angle dependent capabilities of the ESR experiment, where the angle between magnetic field and surface normal can be varied by turning the sample within the cavity can be demonstrated.

### $\text{NO}_2/\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$

The NiAl(110) surface was covered with  $\gamma\text{-Al}_2\text{O}_3(111)$  prepared according to a recipe by Jaeger et al/<sup>14/</sup>. Figure 2 shows a set of ESR spectra together with the corresponding TPD spectra starting with 0.2 L up to an exposure of 2 L of  $\text{NO}_2$ . The development of the spectra starts with rather poor signal to noise below 1 L. At 2 L the signal to noise has improved and the spectrum is characterized by a rather large line width, which may be a consequence of the strong intermolecular interaction. Figure 3 shows a spectrum recorded for a dose of 100 L. The fit to the data is a combination of a threedimensional random and a twodimensional oriented distribution. Below the combined fit the two composing distributions are shown



**Fig. 2:** ESR spectra as a function of  $\text{NO}_2$  coverage on  $\text{Al}_2\text{O}_3(111)/\text{NiAl}(110)$ . For each ESR spectrum the TPD spectrum is also shown. The spectra were taken at  $T = 35 \text{ K}$ .

**Fig. 3:** ESR spectrum at  $T = 35 \text{ K}$  of a thick  $\text{NO}_2$  layer (100 L) on  $\text{Al}_2\text{O}_3(111)/\text{NiAl}(110)$  fitted by a combination of a threedimensional random and a twodimensional (molecular plane perpendicular to surface) distribution. The decomposition is shown. For a comparison a twodimensional distribution with flat lying molecules is included.

seperately. The twodimensional distribution refers to  $\text{NO}_2$  molecules which are oriented with the molecular plane perpendicularly to the surface plane. For comparison a calculated distribution of molecules with their axis oriented parallel to the surface plane are shown. We attribute the existence of a superposition of a twodimensional and a threedimensional distribution of  $\text{NO}_2$  molecules to the coexistence of a physisorbed multilayer on top of a monolayer of molecules in direct contact with the  $\gamma\text{-Al}_2\text{O}_3(111)$  surface. We suspect the persisting deviations to be a consequence of molecular motion of the molecules in the system. Further computer simulations to incorporate this aspect are in progress.

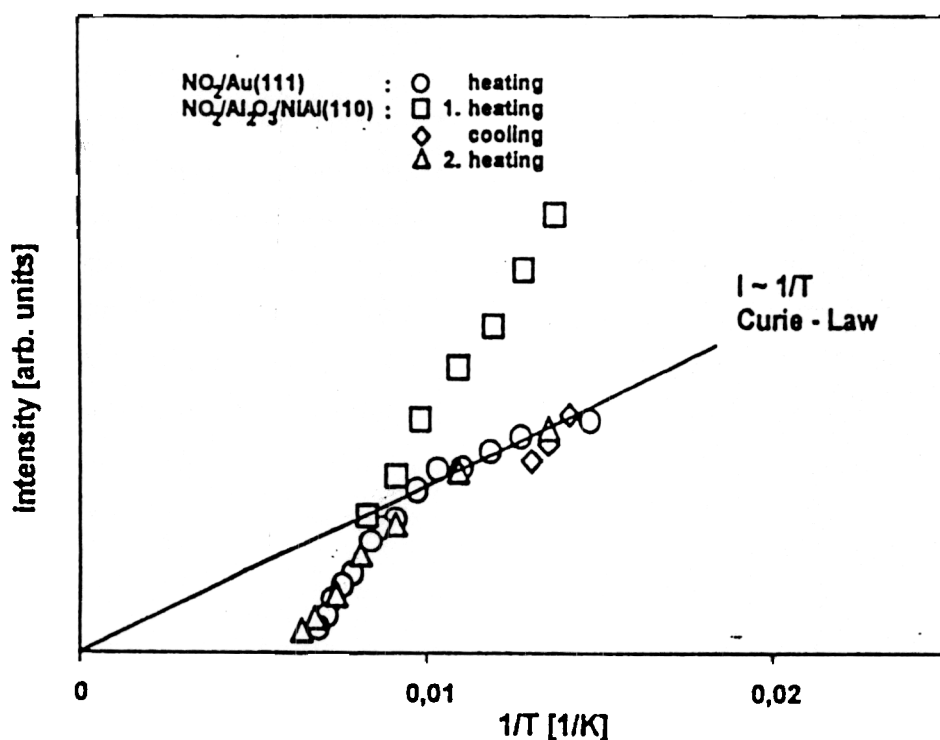


Fig. 4: Temperature dependence of the integrated intensity of  $\text{NO}_2/\text{Au}(111)$  and  $\text{NO}_2/\text{Al}_2\text{O}_3(111)/\text{NiAl}(110)$ . The temperature dependence expected from a Curie law is indicated by the solid line.

The change of the intensities of the spectra while varying the temperature is given in Fig. 4. The intensities are plotted versus the inverse temperature because we expect a Curie-type (straight line) behaviour for the resonance intensity of the paramagnetic  $\text{NO}_2$ . The  $\text{NO}_2$  overlayer on  $\gamma\text{-Al}_2\text{O}_3/\text{NiAl}(110)$  exhibits a temperature dependence different from the Curie behaviour. The signal decrease ( $\square$ ) is much faster upon heating the layer to a temperature close to desorption. If the process is stopped at this point and the sample is cooled down again ( $\diamond$ ) the data follow the straight line. We believe dimerization is taking place by allowing the  $\text{NO}_2$  molecules in the  $\text{N}_2\text{O}_4$  matrix or in the monolayer to move thus effectively removing the molecules from the spectrum. Upon recooling the adsorbate the expected  $1/T$  behaviour is found. If we perform

the same experiment again the datapoints ( $\Delta$ ) follow the Curie behaviour when heated, and the onset of desorption is indicated by the faster decrease of the signal intensity at  $0.01 \text{ K}^{-1}$  inverse temperature. The latter behaviour is also found for a  $\text{NO}_2$  physisorbate on  $\text{Au}(111)$  (o).

### $\text{NO}_2/\text{NiO}(111)/\text{Au}(111)$

The  $\text{NiO}(111)$  has been prepared according to a recipe described by Marre and Neddermeyer<sup>15/</sup>. Contrary to  $\gamma\text{-Al}_2\text{O}_3(111)/\text{NiAl}(110)$  which is sensitive to  $\text{NO}_2$ , loosing its long range order,  $\text{NiO}(111)$  appears to be inert. The LEED pattern remains unchanged upon adsorption. The adsorption behaviour is simple: There is a monolayer and a multilayer regime. The ESR spectrum of a multilayer of 100 L  $\text{NO}_2$  is similar to the spectrum of  $\text{NO}_2$  on  $\gamma\text{-Al}_2\text{O}_3/\text{NiAl}(110)$ . But on  $\text{NiO}(111)$  we could not obtain any signal when the coverage was less than 10 layers of  $\text{NO}_2$ . We have tried to insulate the  $\text{NO}_2$  from the substrate with a xenon interlayer as non-magnetic spacer. Figur 5 shows the spectra obtained from adsorbing 10 L  $\text{NO}_2$  on different amounts of pre-adsorbed Xe on the NiO. Between 0 and 20 layers of pre-

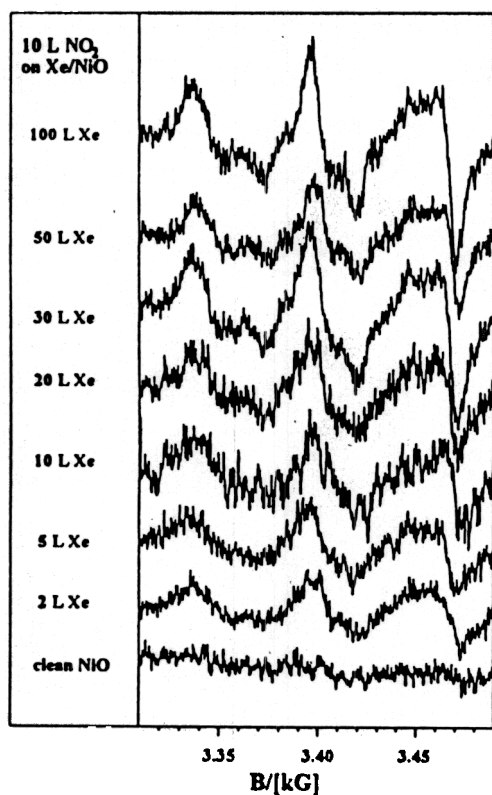


Fig. 5: ESR spectra of  $\text{NO}_2/\text{Xe}/\text{NiO}(111)$  depending on the thickness of the Xenon spacer.

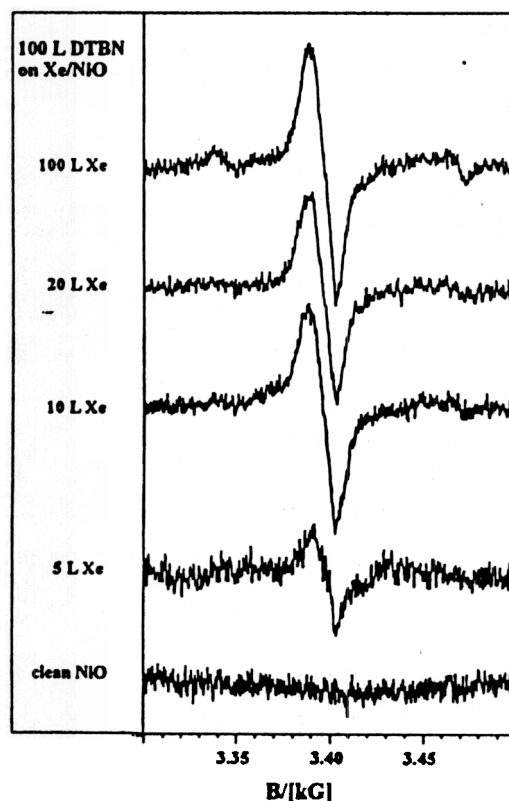


Fig. 6: ESR spectra of  $\text{DTBN}/\text{Xe}/\text{NiO}(111)$  depending on the thickness of the Xenon spacer.

adsorbed Xe the intensities of the lines increase and then reach a saturation value. The layer thickness had no influence on the linewidth.

A similar experiment with adsorbed DTBN/<sup>16</sup>,<sup>17</sup>/ yields qualitatively similar results, which are shown in Figur 6. The dosage of DTBN corresponds to about 25 layers. The hyperfine interaction cannot be seen due to the effect of exchange narrowing. Its remarkable that the saturation coverage of Xe is reached here with 10 layers.

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