Electron Spin Resonance Investigations of the Molecular Motion of NO_2 on $Al_2O_3(111)$ under Ultrahigh Vacuum Conditions

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We report on the first observation of electron spin resonance spectra of submonolayer coverages of small adsorbates on an epitaxially grown single crystal Al_2O_3 film under ultrahigh vacuum conditions. The spectra reveal a clear temperature and coverage dependence. The changes of linewidths and intensities as a function of surface temperature and coverage provide insight into diffusion processes on the Al_2O_3 surface.

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The properties of molecular adsorbates on ordered surfaces are of major interest in surface science, and there is a wide range of methods available to study them. But still information about molecular motion on well-ordered surfaces is hard to achieve. Fast infrared spectroscopy and nonlinear optical methods are now more and more used to study such processes [1]. In the time domain in which the elementary excitation for most spectroscopic methods, in particular electron spectroscopic methods, takes place, the adsorbate is almost immobile during interaction. Since time scales for molecular translational and rotational motions are the order of 10^{-6} to 10^{-10} s, it should be possible to detect molecular dynamics by electron spin resonance (ESR) which operates in this regime. It has already been applied for this purpose in the field of nitroxide spin labels in biological systems [2–4].

Although there are early reports on *in situ* cleaved semiconductor systems [5,6], the first ESR experiments on well-characterized single crystal surfaces have been performed by Baberschke [7–9]. They found that from submonolayers of paramagnetic molecules on a metal surface it was not possible to record an ESR spectrum since the coupling of the unpaired spin to the conduction electrons broadens the resonance line below the detection limit.

The present work deals with paramagnetic adsorbates on thin oxide layers which are of common interest in model catalyst investigations [10,11]. We report the first recording of ESR spectra in the submonolayer regime for a single crystal oxide surface under ultrahigh vacuum conditions. Details of the experimental setup have been described elsewhere [12]. In addition to the ESR spectrometer a quadrupole mass spectrometer, for performing temperature programmed desorption (TPD) spectroscopy, and a combined low energy electron diffraction–Auger system allow characterization of the substrate and adsorbate system in an attached preparation chamber. NO_2 dosing was performed through a capillary doser, which establishes a reproducible flux of pure NO_2 onto the Al_2O_3 surface. $Al_2O_3(111)$ was grown on a NiAl(110) single crystal as a well-ordered film of 5 Å thickness. The structure is of the γ-Al_2O_3 type. Details of preparation and properties of the film have been reported elsewhere [13].

Coverage calibration has been performed by means of TPD. In Fig. 1 TPD spectra for a variety of NO_2 doses are shown. The dosages given in Fig. 1 are expressed in terms of the rise of the base pressure for 10 s at a fixed distance between doser and surface. By multimass TPD measurements it has been checked that NO_2 is the only desorbing species. For small coverages a single desorption peak is found at 135 K which saturates at higher exposures. This first desorption peak can be assigned to isolated NO_2 molecules physisorbed to the oxide with

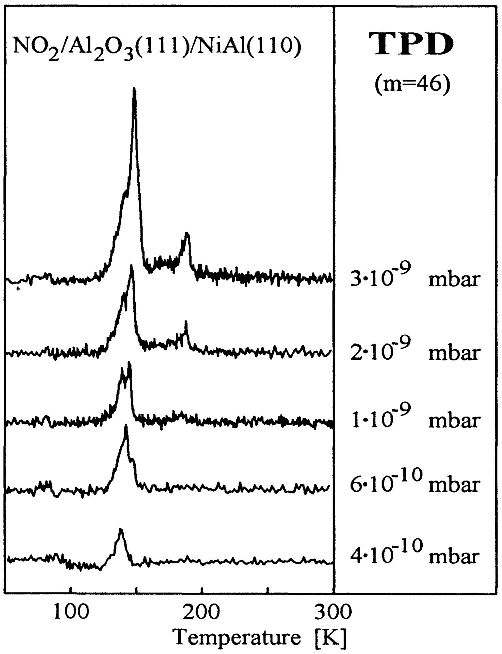

FIG. 1. TPD spectra of NO_2 on $Al_2O_3(111)$. The desorption feature at 135 K peak temperature saturates upon increase of dosage. A second feature overlapping the first one appears at a dosage of 10^{-9} mbar a slightly higher temperature, and does not saturate.

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a binding energy of 38 kJ/mol estimated according to Redhead's analysis [14]. At higher coverages a second desorption feature at nearly 10 K higher temperature appears. The observation of a TPD peak at higher temperature which does not saturate upon increase of exposure is quite unusual compared to the "normal" desorption behavior of, e.g., NO_2/Au(111) published by Bartram and Koel [15]. It indicates an intermolecular interaction energy larger than the binding energy from the molecule to the substrate. This desorption with higher binding energy may be due to two- and three-dimensional molecular aggregates, respectively. The desorption behavior at higher coverages becomes been more complicated and will be discussed elsewhere [16]. However, the main goal of calibrating submonolayer coverages has been achieved and was further confirmed by TPD of COS from the same substrate exhibiting a normal monolayer and multilayer desorption behavior and leading to the same coverage calibration.

Before we go into details of the spectra in Fig. 2 we try to explain the characteristics of the recorded ESR spectra. There are two main contributions to the habit of the spectra. First, the unpaired electron resides in a particular electron orbital of the molecule with a specific spatial orientation, which in turn leads to dependence of the electron spin resonance on the orientation of the molecule in the external magnetic field. In other words, the isotropic g value of the free electron is transformed into an anisotropic g tensor, which gives rise to a splitting of the resonance lines. The hyperfine interaction of the unpaired electron with the nuclear spin ($I = 1$) of the nitrogen atom as the second contribution may be described by the A tensor and finally leads to an appearance of the spectrum, exhibiting three well-separated parts. The spectra are presented as the first derivative of the microwave absorption as a function of the external field.

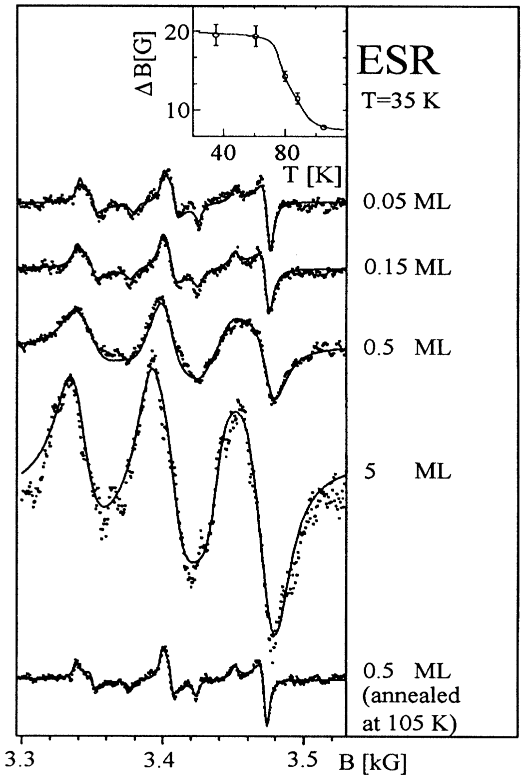

FIG. 2. ESR spectra for various NO_2 coverages at 35 K. The lowest spectrum shows the effect of annealing the sample at 105 K (see also the inset). The solid line represents the best computer simulation assuming a threedimensional random distribution.

In Fig. 2 coverage dependent ESR spectra of NO_2 on Al_2O_3(111) are shown. The main observation is the increasing linewidth ΔB of the spectra with increasing coverage. Assuming the linewidth to be due to dipolar interaction ($\Delta B \sim 1/r^3$) of the unpaired spins of neighboring molecules [17], it is obvious from the increase of the linewidth that the distance of the NO_2 molecules decreases. If the sample is annealed at different temperatures, as shown in the lowest spectrum in Fig. 2 and in the inset, a drastic decrease of linewidth and intensity after annealing to temperatures above 60 K is observed, although temperatures are well below the desorption temperature of 135 K. At about 100 K the decrease of intensity causes the spectrum to vanish below the detection limit within a few minutes. The decreasing of the concentration of NO_2 is caused by the reaction of paramagnetic NO_2 monomers to the diamagnetic N_2O_4 dimer ($2NO_2 \rightleftarrows N_2O_4$) [18]. Because at low temperatures the equilibrium of this reaction completely favors the dimer, there must be a kinetic restriction causing the molecule not to dimerize at low temperatures. We believe the onset of the reaction is coincident with the onset of translational diffusion of the NO_2 monomers on the surface. If the annealing procedure is repeated or continued over larger time intervals the decrease of the linewidth stops at a certain value (see the inset in Fig. 2), but the signal intensities continue to decrease below the limit of noise. At very low coverages no decrease of the linewidth can be observed, because it has reached its lower limiting value even after adsorption. This value may be assumed when intermolecular distances between the monomers become so large that the contribution of the dipolar interaction to the linewidth can be considered to be small as compared to other contributions. Then the only effect of the dimerization process is decreasing the spectral intensity. We compare computer simulations with the spectra in Fig. 2. The model for fitting these spectra is a three-dimensional random distribution of static molecules yielding a so-called powder pattern. A detailed description of the fitting procedure is given in [19,20]. The simulations match the experimental spectra except for some small differences; the nature of which becomes clear by considering the experimental results shown in Fig. 3.

ESR spectra of a submonolayer coverage of NO_2 were taken at different temperatures by warming the sample up step by step before recording the spectra. As mentioned above the signal intensity decreases within a few minutes at about 100 K, rendering it impossible to obtain spectra with a reasonable signal-to-noise ratio. However, it is possible to deduce an estimate for the diffusion coefficient D from this time behavior. Assuming the dimerization to be a diffusion controlled reaction, the theoretical investigation of Freemann and Doll [21] provides a relation between the rate constant observed and the diffusion coefficient. An evaluation in this framework yields a value of $D \sim 10^{-15}$ cm^2/s. The estimates based on coverage and spectral intensity versus time are quite crude; however, the calculated diffusion coefficient is remarkably small, compared to those measured, for example, for CO/Ni(100) [22] ($10^{-5}-10^{-7}$ cm^2/s).

The spectra at lower temperatures also give insight into dynamical processes on the surface. The simulations in Fig. 3 represent distributions of three-dimensional randomly oriented and static molecules. We find that the reproduction of the spectra becomes better for higher temperatures. This should not be the case if the deviations at lower temperatures corresponded to molecular motion not taken into account by the simulations. If a molecular rotational motion were unfrozen in the time window of the experiment, the deviation from a static distribution should become larger with increasing temperature eventually leading to the limit of motional narrowing. The high temperature spectra finally end up in a static and isotropic distribution. A possible explanation of this behavior can be given if we assume that a small fraction of the molecules adsorbs in an oriented geometry upon impact. This leads to deviations from a pure three-dimensional random distribution in the obtained ESR spectra. If the thermal energy of the system increases the molecules reorient themselves, and contributions due to oriented molecules are completely removed from the distribution. The change to an isotropic distribution is an irreversible process. By cooling down to 35 K again the three-dimensional randomly oriented and static distribution fits the spectrum quite well, as can be seen in the lowest spectrum of Fig. 2.

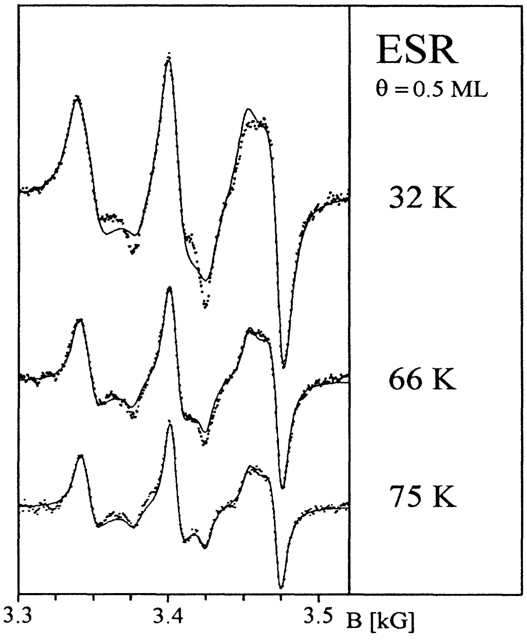

FIG. 3. Temperature dependent spectra including computer simulations (see Fig. 2) at a fixed coverage.

Two different forms of molecular motion are to be distinguished: First no rotational motion of the molecules could be detected below 100 K in the time window of the experiment. Taking into account uncertainties due to the signal noise and the linewidth one can estimate the rotational correlation time to be longer than 10^{-7} s. It should be noted that especially no indication for motional narrowing could be observed, which would be expected for rotational correlation times as short as 10^{-9} s. The second type of motion influencing the ESR spectra most drastically is the translational diffusion of the NO_2 monomers on the surface. The surface diffusion directly leads to dimerization and therefore to a complete loss of the ESR spectrum.

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