

Dynamics of the Stable Radical Di-*tert*-butyl Nitroxide on an Epitaxially Grown Al₂O₃ Film

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Received: October 9, 1996; In Final Form: January 21, 1997[⊗]

The molecular dynamics of one monolayer adsorption species of di-*tert*-butyl nitroxide (DTBN) adsorbed on a thin film of γ -Al₂O₃(111) grown on a NiAl(110) single crystal has been studied via ESR line-shape analysis. Below 200 K a rigid limit spectrum is found, above this temperature the changes in line shape are consistent with slow motions of the molecule. Best agreement between the experimental spectra and simulations is obtained using a “moderate jump” model with both Brownian diffusion and jump type contributions to the molecular dynamics. The motional processes have an activation energy of about 9 kJ/mol.

Introduction

The study of the elementary steps in molecular adsorption is still on the agenda of many research groups. While in the past the aspects of geometric and electronic structure have been the center of interest, more and more the dynamics of the systems are being examined. Numerous systems have been explored applying surface science methods in the past years with respect to a variety of different scientific aspects: desorption processes have been studied in many cases¹ as well as vibrations of adsorbed molecules.² Surface diffusion has been investigated employing laser desorption methods.^{3,4} Unfortunately, there are only a few techniques suitable for the study of dynamics of adsorbed molecules on their adsorption sites, especially on single crystal surfaces: Hofmann and Toennies⁵ reported about frustrated translations and activation barriers for diffusion in different systems studied with inelastic helium scattering. Haglund⁶ and Detje et al.⁷ described nuclear magnetic resonance (NMR) experiments using atomic beam methods to study the diffusion of alkali atoms on hot and cold surfaces. These experiments appear to be limited to rather special cases, while NMR in general, which cleared up many questions involving molecular dynamics in the liquid and solid phase as well as on polycrystalline surfaces, is not sufficiently sensitive to be applied to adsorbates on single crystal surfaces: 10¹⁷ nuclear spins are needed to obtain a sufficient signal-to-noise ratio compared to 10¹⁴ adsorption sites on a single crystalline surface of 1 cm². Electron spin resonance (ESR) spectroscopy, on the other hand, has the advantage of a 10⁶ times greater sensitivity compared with NMR and can detect submonolayer coverages on single crystal surfaces. Changes in the line shape of ESR spectra caused by molecular motion cover a broad range of motional frequencies and allow studies on various modes of motion;⁸ its disadvantage is that only paramagnetic molecules can be used as adsorbates. The spectrum may also contain more information about the interaction between adsorbate and substrate and between the adsorbed molecules.

A second limitation of the ESR experiments exists with respect to the choice of substrates: It has not been possible to detect signals from monolayer coverages of paramagnetic molecules adsorbed on metal surfaces.^{9,10} An interaction between the unpaired electrons of the molecules and the conduction electrons in the metal leads to a drastic increase of

line widths. Baberschke and co-workers¹¹ found in the case of NO₂/Ag(110) that a preadsorbed noble gas layer shields the paramagnetic molecules from the conduction electrons, and a detectable ESR spectrum is recovered. Adsorption on dielectric oxide films grown on metal substrates has been used as well¹² and has the advantage that the thermal range for studying molecular dynamics is limited only by the desorption temperature of the adsorbate. Schlienz et al.¹³ studied submonolayer coverages of NO₂ adsorbed on an Al₂O₃(111) film. The problem in this study was the complete dimerization of the NO₂ molecules to diamagnetic N₂O₄ caused by the onset of lateral diffusion well below the desorption temperature of NO₂. From the time dependence of the signal intensity the diffusion coefficient of the NO₂ molecules on the surface was estimated. Beckendorf et al.¹⁴ showed that an analysis of the molecular motion is possible in the case of mixed NO₂/N₂O₄ multilayers where dimerization is suppressed. Risse et al.¹⁵ studied the dynamics of self-assembled films: stearic acid molecules, spin-labeled at certain positions, form a stable bond to an Al₂O₃(111) film, and the motion of these molecules could be studied over a wide temperature range.

The present study reports ESR line-shape analysis in the system DTBN adsorbed on the same thin film of γ -Al₂O₃(111) grown on a NiAl(110) single crystal.¹⁶

Experimental Section

The ESR measurements were performed in a specially designed UHV-ESR chamber;¹² careful sample design and a liquid helium cryostat allow the crystal to reach 40 K. The ESR spectrometer (Bruker B-ER 420) has been improved by building in a new X-band microwave bridge (Bruker ECS 041 XK) and lock-in amplifier (Bruker ER 023 M). This modification led to a clear increase of the signal-to-noise ratio. The ESR-UHV chamber is equipped with a quadrupole mass spectrometer that allowed the registration of multimass TPD spectra and with a combined LEED/Auger unit for substrate characterization. The base pressure is better than 1×10^{-10} mbar.

The γ -Al₂O₃(111) film was prepared on a NiAl(110) single crystal (orientational deviation <1%) according to the recipe of Jaeger et al.¹⁷ The substrate was cleaned by sputtering with Ar ions and then heated to 1000 °C; the crystal was oxidized and then completely covered with a well-ordered oxide film. Whether the Al₂O₃ film covers the NiAl substrate completely was checked with CO titration.¹⁸ This oxide layer, studied

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[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

thoroughly by electron spectroscopy, LEED,¹⁹ and scanning tunneling microscopy,²⁰ shows long-range order with a structure based on slightly distorted hexagonal oxygen layers with a packing of aluminum ions, as in γ -alumina. The thickness of the oxide film is only about 0.5 nm. Adsorption of small molecules on this film has also been studied.¹⁹

DTBN was purchased commercially (Lancaster), carefully degassed to its vapor pressure, and used without further purification. It was stored in glass bottles attached to a dosing valve, which led into the UHV chamber. Before dosing the storage was warmed to approximately 50 °C to increase the vapor pressure. The chamber atmosphere was then flooded with DTBN. The exposures are given in langmuirs (\equiv Torr s).

Modeling

The program for simulating and fitting the experimental spectra was written by Beckendorf;²¹ the calculation of molecular motion was based on a program package developed by Freed and co-workers.²² It describes dynamic processes using the stochastic Liouville equation for the dynamic processes.²³ The resonance position of a DTBN molecule is a function of its orientation relative to the static magnetic field **B**. This orientation dependence is described by the **g** tensor, which mediates the interaction between the electron spin **s** and the magnetic field **B**. DTBN molecules, which contain the magnetic active ¹⁴N nucleus, show an additional interaction between the electron spin **s** and the nuclear spin **I**, which is described by the **A** tensor. The Hamiltonian used to describe the ESR spectra then takes the form

$$H = \mathbf{s} \cdot \mathbf{g} \cdot \mathbf{B} + \mathbf{s} \cdot \mathbf{A} \cdot \mathbf{I}$$

The simulations are performed assuming a statistical distribution of the molecular orientations,¹⁶ Lorentzian line shapes, and axial symmetry of **g** and **A** tensors ($g_{xx} = g_{yy}$, $A_{xx} = A_{yy}$). A full parameter set consists of two *g* values, two *A* values, a line width assumed to be constant over the whole spectrum (no function of the nuclear spin state), the line intensity, and the parameter describing the dynamics. It is known from experimental data that a distribution of the motional states for adsorbed molecules may exist.²⁴ The simulations reported here often consist of two parts: a rigid limit spectrum representing static molecules and a spectrum simulated with a definite parameter set for molecular motion, both with same *g* and *A* values and line width. The additional fit parameter is the relative fraction of both parts contributing to the simulated spectrum.

Results and Discussion

Figure 1a shows structure and size of the DTBN molecule.^{25,26} The unpaired electron is located in an antibonding π^* orbital at the NO group, but the magnetic properties can be approximated by assuming that the unpaired electron occupies a *p*_z orbital at the nitrogen atom.²⁷ This is illustrated in Figure 1b, where also the standard coordinate system for the nitroxide group is defined. This assignment will be important in the discussion of the model for the molecular dynamics.

DTBN on Al₂O₃(111)/NiAl(110) reveals a complex adsorption behavior with three different binding modes in the monolayer regime, which has been discussed in detail elsewhere.¹⁶ The results presented here are concerned with the adsorption species identified with a DTBN molecule bound via donation of a lone pair orbital of oxygen to an aluminum as acceptor center at the surface (species I in ref 16). This bond is remarkably strong, since a binding energy of 120 kJ/mol has been estimated from the desorption temperature of 440 K

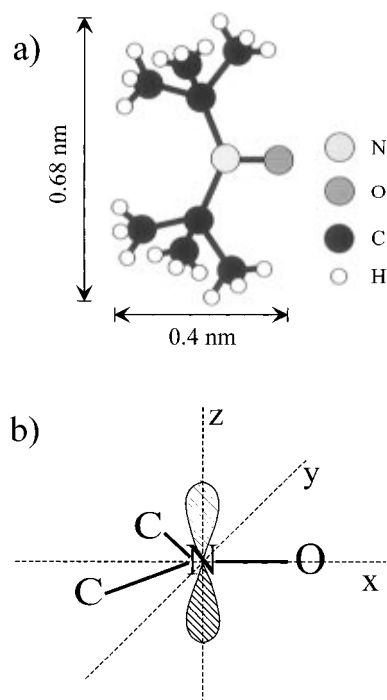


Figure 1. (a) Structure and magnitude of the DTBN molecule. (b) Standard coordinate system for the nitroxide group.

observed in the thermal desorption spectra (see arrow in the inset in Figure 2).

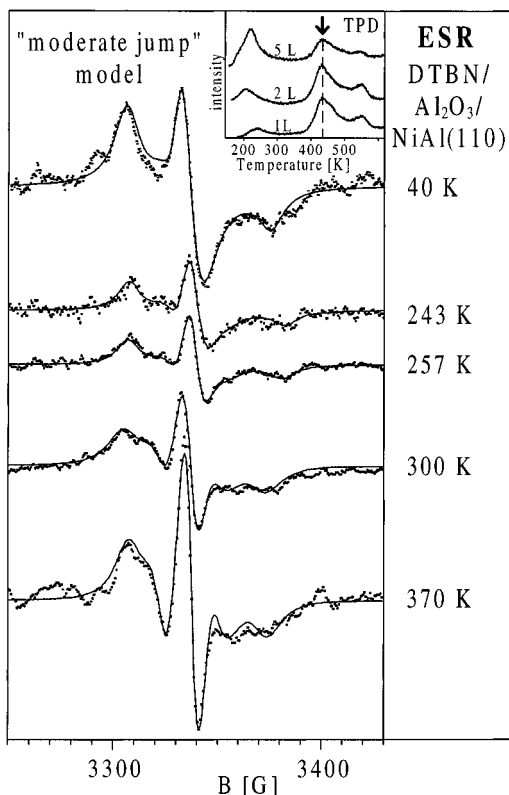
Full monolayer coverages were prepared by heating adsorbed multilayers well above the desorption temperature of the multilayer. After equilibration, less than 10% of the adsorbed molecules in the remaining monolayer are in the ESR-active adsorption state mentioned above. The majority of the DTBN molecules is doubly bound to the surface (via both nitrogen and oxygen atoms) and ESR-inactive (species II in ref 16). Therefore, the ESR-active molecules show spectra which are well resolved and not broadened by exchange interactions. These have been studied in the temperature range from 40 to 370 K accessible with the present sample holder design.

Below 200 K a rigid-limit ESR spectrum as shown in Figure 2 at 40 K is obtained. The parameters gained from these spectra (**g** and **A** tensor components) form the basis for the simulation of spectra measured at higher temperature which includes effects of molecular dynamics. Since the **A** tensor components are very sensitive to the chemical environment of the molecule,^{28,29} their values have to be evaluated separately from the effects of molecular dynamics. The first row of Table 1 shows the results. The absolute *g* values have not been referenced to a standard and are thus not significant, but their splitting Δg , the difference between g_{zz} and $g_{xx} = g_{yy}$, is consistent with that reported before from DTBN adsorbed on polycrystalline Al₂O₃.³⁰ Additionally, the *A* values are close to those reported therein.³⁰ The line width (full width at half-maximum) is about 17 G and may contain some contributions from dipolar interaction between the ESR-active molecules.

Above 200 K changes in line shape as shown in Figure 2 reveal the onset of molecular dynamics. (The simulations (solid lines) are carried out assuming a particular motional model, the "moderate jump" model, which is discussed below.) The line width has dropped to about 12 G, which is known to result from intramolecular interactions manifested as unresolved proton hyperfine splittings.³¹ The dipolar interactions are now averaged out by the molecular dynamics. The remarkable intensity behavior (increasing intensity at higher temperature) is caused

TABLE 1: Fitting Parameters for the Rigid Limit and the "Moderate Jump" Model

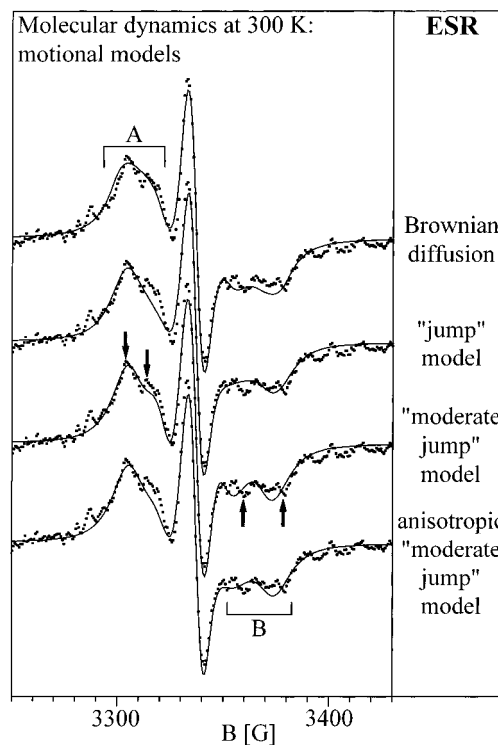
T (K)	$g_{xx} = g_{yy}$	g_{zz}	Δg	$A_{xx} = A_{yy}$	A_{zz}	ΔB (G)	% dyn	D (s ⁻¹)	τ^a (s)
40	2.0046	2.0001	0.0045	8.2	38.5	17.3	0		
243	2.0055	2.0012	0.0043	8.2	38.5	12.1	51.3	9.72×10^6	1.0×10^{-7}
257	2.0054	2.0016	0.0038	8.2	38.5	11.5	54.7	1.21×10^7	8.3×10^{-8}
300	2.0046	2.0024	0.0022	8.2	38.5	11.5	100	1.76×10^7	5.7×10^{-8}
370	2.0035	2.0003	0.0032	8.2	38.5	8.0	100	2.12×10^7	4.7×10^{-8}

^a $\tau = 1/D$.**Figure 2.** ESR spectra of DTBN monolayers on Al₂O₃(111)/NiAl(110) at different temperatures. Simulations including molecular dynamics are done with the "moderate jump" model which is described in the text. The inset shows TPD spectra, in which this ESR-active adsorption state is marked with an arrow.

by the reversible conversion of DTBN molecules from the ESR-inactive to the ESR-active state and is discussed elsewhere.¹⁶

Four different models for the molecular dynamics have been tested to simulate the experimental spectra. Brownian rotational diffusion and jump type diffusion^{32,33} have been used for this analysis, both in their pure forms and in two mixed models. Brownian rotational diffusion is characterized by the rotational diffusion constant D and jump type motion by a residence time τ . The motions have been assumed to be isotropic. In the "moderate jump" model,³³ both Brownian and jump type contributions to the motion are coupled via the condition $D\tau = 1$. Since in the present case the molecular adsorption site has a 6-fold symmetry,¹⁷ the jump angle has been fixed to integer multiples of 60°. The fourth model is a modification of the "moderate jump" model. Brownian rotational diffusion is restricted only to rotations around the molecular N–O axis (x axis, see Figure 1b), which is the binding axis to the substrate. In contrast to the "moderate jump" model an independent variation of D ($=D_{xx}$) and τ is possible.

Figure 3 shows a comparison of the fits based upon the four different models for the spectrum measured at 300 K of Figure 2. The ranges in the ESR spectra that are sensitive to the fit models⁸ are labeled A and B. The decision between the models is made according to the agreement in those ranges. In

**Figure 3.** Comparison of different models for the molecular dynamics shown for the ESR spectrum measured at 300 K. Explanations are given in the text.

particular, the choice of the best model results from how the splittings in both areas (marked with arrows) have been reproduced. The problems connected with base-line subtraction have been carefully dealt with, and only features that are present in the spectra independent of background have been considered.

The most reasonable agreement is obtained with the "moderate jump" model. In the pure "jump" model as well as in the "moderate jump with anisotropic Brownian diffusion" the splittings in regions A and B are not obtained simultaneously. With pure Brownian diffusion the splitting seems to be reproduced on the high field side but only a broadening is seen on the low field side. This high field splitting is induced by a fraction of static molecules of about 30% contributing to the fit. In the "moderate jump" model 100% of the molecules are in motion at 300 K, and both splittings are reproduced by the fit on the low field side very well and on the high field side slightly exaggerated and energetically slightly closer to the center region of the spectrum. Nevertheless, the overall agreement is best between the given alternatives. The parameters used for the simulations with the "moderate jump" model (Figure 2) are shown in Table 1. The line width drops below 10 G at 370 K, which may be a hint that internal rotations of the *tert*-butyl groups are activated, beginning to average out the interactions between the unpaired electron and the methyl protons.

A serious problem in the fits is the variation of Δg : from the rigid limit to 300 K it decreases and then increases again toward 370 K. Since the g values are almost invariant against

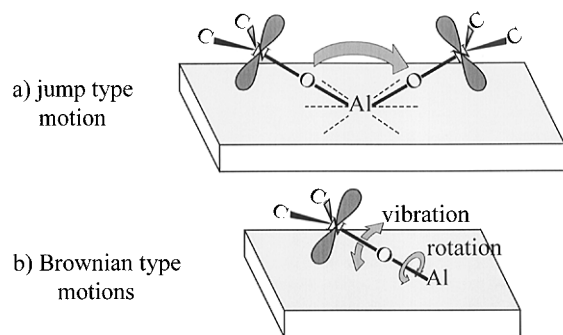


Figure 4. Sketch of the different motion types contained in the "moderate jump" model: (a) jump type motions; (b) Brownian rotational diffusion which can be interpreted as low-amplitude vibrations and hindered rotations.

changes in the molecular surroundings,³⁴ this variation is likely to be an imperfection in the fitting procedure. It concerns all four models which tried to simulate the experimental spectra. Therefore, the imperfection does not depend on the model for the molecular dynamics itself. It is possible that the **A** tensor components, which are known to be sensitive to the chemical surroundings, are changed by the onset of molecular dynamics, e.g., by a loosening of the bond to the surface. Such an effect cannot be separated at present from line-shape changes due to molecular motion. Since the **A** tensor components have been fixed in the simulations to their rigid limit values, an artificial shifting of the *g* values may be induced by this effect. Consequently, the quantitative results for the motional parameter will be questionable, but the qualitative modeling of molecular motion gives at least insight into the motion of the adsorbed DTBN molecules. The use of perdeuterio-DTBN in an adsorption experiment would reveal more details in its ESR spectrum caused by smaller line widths, but this experiment remains to be done. The results will be discussed keeping this in mind.

The dynamics of the adsorbed DTBN molecules have two components: first, the jump contribution, which may be taken to represent the fast switching between the six equivalent positions around an aluminum binding center at the surface as shown in Figure 4a; second, an additional tumbling contribution which cannot be caused from collisions with gas phase molecules, since the experiment takes place under UHV conditions. The high stability of the adsorbate under UHV conditions also rules out a translational diffusion of the DTBN molecules. The tumbling involves two other motional degrees of freedom for the DTBN molecule as a whole: a rotation around the binding axis and a vibration against the surface. If both motions are of low amplitude, they may be reflected in the additional Brownian contribution to the jumping motion. The low-amplitude tumbling is traceable to the bulky *tert*-butyl groups which interact via van der Waals forces with the surface and restrict both movements to small angles. The distribution of the unpaired electron in the molecular frame exhibits axial symmetry with respect to the *z* axis ($g_{xx} = g_{yy}$, $A_{xx} = A_{yy}$; see Figure 1b). Therefore, the value of D_{zz} does not influence the simulated spectrum. D_{xx} and D_{yy} , on the other hand, may correspond to the low-amplitude motions. The rotation around the binding axis (*x* axis) can be easily identified with the contribution from D_{xx} , as illustrated in Figure 4b. If only the D_{xx} contribution is taken into account the "anisotropic moderate jump model" applies. The fits, however, indicate that this does not lead to an improved simulation of the data. In fact, D_{yy} has to be considered. The vibration of the molecule against the surface can be seen as a hindered rotation of the molecule around the aluminum center (in direction of the surface normal) as also shown in Figure 4b. A decoupling of D_{xx} and D_{yy} leads to no

further improvement in the simulation. It may be concluded that the imperfections of the simulations that are manifested in the *g* value shifts may be due to the fact that the models used in the present paper are developed for the description of molecular motion in the liquid phase. The application to the dynamics of adsorbed molecules may require changes in the future.

An Arrhenius plot of the temperature dependence of the correlation time τ_c reveals an activation energy of about 9 kJ/mol. Lozos and Hoffman,³⁰ who found *pure* Brownian motion for DTBN adsorbed on polycrystalline Al₂O₃, reported a value of 7.9 kJ/mol. The difference in the results may be taken as an indication that on the polycrystalline substrate different types of binding sites with different possibilities for motional freedom must exist as compared with the model system studied here.¹⁶

Summary and Conclusions

The dynamics of one ESR-active adsorption form of DTBN on Al₂O₃(111)/NiAl(110) has been analyzed by temperature-dependent line-shape changes in the measured ESR spectra. The results are interpreted at the molecular level. The dynamics consists of three contributions: a jump type motion between the six equivalent positions at each adsorption site, a hindered rotation around the N–O binding axis, and a low-amplitude vibration of the molecule against the surface. It should be noticed that the simulations used contain imperfections which have to be overcome in the future.

Acknowledgment. The authors are grateful to the Deutsche Forschungsgemeinschaft, the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, the Bundesministerium für Bildung und Forschung, and the Fonds der Chemischen Industrie for financial support. T. Risse and T. Klüner thank the Studienstiftung des Deutschen Volkes for financial support.

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