

Orientation and Dynamics of NO₂ in a N₂O₄ Host Matrix Prepared on a Plane Surface Investigated by ESR Line Shape Analysis

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Received: August 4, 1995; In Final Form: January 24, 1996[⊗]

Thick films (approximately 100 μm) of NO₂/N₂O₄ were prepared in a combined ultrahigh-vacuum ESR apparatus by adsorption of gaseous NO₂ through a dosing system on a single-crystal surface (NiAl(110)). The adsorption temperature was in the range from 35 to 65 K. The line shapes of the ESR spectra are dependent on the adsorption conditions and show remarkable changes in heating processes. These observations can be explained in terms of geometrical rearrangements and molecular dynamics of the NO₂ monomers. The line widths vary from 2 to 10 G depending on the concentration of ESR-active molecules through magnetic dipolar interactions. In all cases the observed line shape itself cannot be described by a simple distribution of randomly oriented molecules. The analysis of the spectra indicates a preferred molecular orientation with the NO₂ C₂ axis perpendicular to the surface plane of the substrate. The spectra are fitted by computer simulation using a line width that depends on the *z* component of the nuclear spin as well as on the orientation of the NO₂ molecules relative to the external magnetic field. The latter is thought to be needed according to effects of molecular motion. The line shape of a sample annealed to 110 K is very well described by a statistical distribution of the molecules. The computer simulations are based here on a mixture of rigid particles and molecules undergoing rotational diffusion. The spectra recorded in the temperature range from 48 to 150 K indicate that the principal axis perpendicular to the molecular NO₂ plane is the axis of rotation. Rotational constants are found to be in the range from 1.6×10^7 to 5.8×10^7 s⁻¹.

Introduction

NO₂ molecules in different matrices have been investigated by electron spin resonance (ESR) spectroscopy for more than 35 years.¹ NO₂ as a radical contains an odd number of electrons resulting in a total spin of $S = 1/2$. Due to the fact that the spin underlies an anisotropic spatial distribution (the electron occupies a 6a₁ molecular orbital²), the resonance positions (values of the swept external magnetic field **B** for a fixed value of the microwave frequency ω) are strongly dependent on the molecule's orientation relative to the direction of the applied magnetic field. As a consequence, the line shape of an ESR spectrum is a representation of the distribution of the paramagnetic particles in space.

Molecular motion results in a continuous loss of the anisotropy of spin density in the time domain of the experiment. If the correlation time of this motion is much smaller than the microwave frequency, motional narrowing results; i.e., the anisotropy is completely washed out. For the simulations reported in this paper the correlation times are in a range called the slow tumbling region.³ In this region the interactions of the unpaired spin, which determine the shape of the EPR spectrum, are modulated through molecular dynamics giving rise to typical differences from spectra in the rigid limit. The slow tumbling region is described by a theory developed in the group of Freed.³ The spectral simulations are based on a stochastic approach of rotational diffusion.⁴

For NO₂ in rare gas matrices at 4 K preferred molecular orientations investigated by ESR are reported.^{5–7} Preferential orientations were obtained by deposition of the gases on flat surfaces, e.g., of a sapphire rod^{5,7} or a copper target.⁶ In these studies the spectra were recorded as a function of the angle between the surface plane and the magnetic field. The analysis showed (qualitatively) that a large majority of the molecular

planes of the NO₂ molecules were oriented parallel to the substrate surfaces. In contrast, in this paper a preferential orientation of molecular planes of NO₂ in a N₂O₄ matrix perpendicular to the orienting plane will be reported.

Molecular dynamics of NO₂ within an adsorbate were investigated by Shiotani and Freed⁸ for the first time systematically. They adsorbed NO₂ on crushed Vycor and zeolite. In the temperature range from 4.8 to 77 K a rotation around the O–O axis was suggested. Above 77 K rotations around the other axes become important, resulting in an isotropic rotation at about 185 K. In this analysis there were still significant discrepancies between the experimental CW ESR spectra and the computed line shapes. A later investigation utilizing new developed pulse ESR methods⁹ showed that in this system two different species of adsorbed NO₂ were present at low temperatures, but only one of them showed molecular motion. The qualitative model of this motion (preferred rotation around the O–O axis) was maintained. Also, Adrian¹⁰ (NO₂/Ar) and Adrian et al.¹¹ (NO₂/CH₄) assumed a rotation around the O–O axis for NO₂ in different matrices. Myers et al.⁷ (NO₂/Ar, NO₂/Ne) interpreted their spectra further by a hindered rotation around the C₂ axis. In the present paper the quantitative and satisfactory analysis of ESR spectra demonstrates that on our substrates rotation around the axis perpendicular to the molecular plane of NO₂ in a N₂O₄ matrix takes place. No extra peaks in the spectra as detected by Schaafsma and Kommandeur¹² after photolysis of ground state N₂O₄, which have been assigned to a rotation around the O–O axis, have been observed.

Very rarely investigations of NO₂ on single-crystal surfaces^{13,14} have been reported. Unfortunately, the resolution of the observed spectra is relatively poor in the regime of submonolayer coverage of radicals as NO₂ (compared with the spectra in this paper). Due to the large line width, effects resulting from a preferential orientation are not very well distinguishable from effects of molecular motion. In ref 13 in

[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1996.

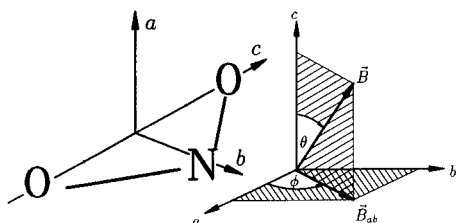


Figure 1. Molecular coordinate system and the molecular orientation relative to the external magnetic field **B**.

a submonolayer coverage NO₂ was found to lie flat on a monolayer of preadsorbed rare gas. But adsorption of NO₂ onto a rougher rare gas film leads to a random molecular distribution. On an oxide film the nonequilibrium conditions for adsorption of half a monolayer NO₂ at low temperatures also result in a spectrum which is not describable by a random distribution of molecules.¹⁴ Only after annealing the ESR spectra show an isotropic molecular distribution. In the present study as UHV ESR setup previously build to investigate submonolayer coverages is used to prepare the thicker films reproducibly.

Experimental Results and Analysis

The ESR measurements reported here were carried out in a ultrahigh-vacuum system designed to study the interaction of adsorbates with ordered single-crystal surfaces in the monolayer regime. These facilities are described elsewhere.^{15,16} In this paper a report of the measurements done on thick films of adsorbed NO₂ is given. The preparation of such samples requires dosing of relatively large amounts of gas to the single-crystal surface.

ESR spectra taken immediately after the dosing procedure show line shapes which depend on several parameters like substrate temperature or rate of adsorption. The sample was prepared via background dosing using a doser consisting of a gold-coated stainless steel tube. The dosage given here is defined by the pressure per time the gas inlet is opened.

Independent of the fact that a prediction of line shape direct after exposure was not possible, all spectra show the same features. NO₂ monomers are distributed with a preferred orientation of the molecular C₂ axis (Figure 1) parallel to the surface normal. The degree of orientation and the line width are functions of the uncontrolled parameters of the dosing procedure.

To describe the molecular distribution in space, a relation between the molecule's coordinate system and the laboratory coordinate system is needed. In the left part of Figure 1 the notation for the principal axis system of the NO₂ molecule is illustrated. In the following the axis perpendicular to the molecular plane is referred to as *a*. *b* is the C₂ axis and *c* the internuclear O–O axis. In the right part of Figure 1 the orientation of the molecule's coordinate system relative to the external magnetic field **B** is described by the two angles θ and ϕ . The direction of **B** defines the *z* direction of the laboratory coordinate system.

Preferred Molecular Orientation. Figure 2 demonstrates the effects of some different spatial distributions of NO₂ molecules in the EPR spectra. The simulations are based on the solution of the spin Hamiltonian

$$H = \mu_B \hat{S} \hat{g} \mathbf{B} + \hbar \hat{S} \hat{A} \hat{I}$$

up to second-order perturbation theory.¹⁷ Resonance positions are functions of the Euler angles between the molecular principal axis system and the laboratory coordinate system.¹⁶ For a single

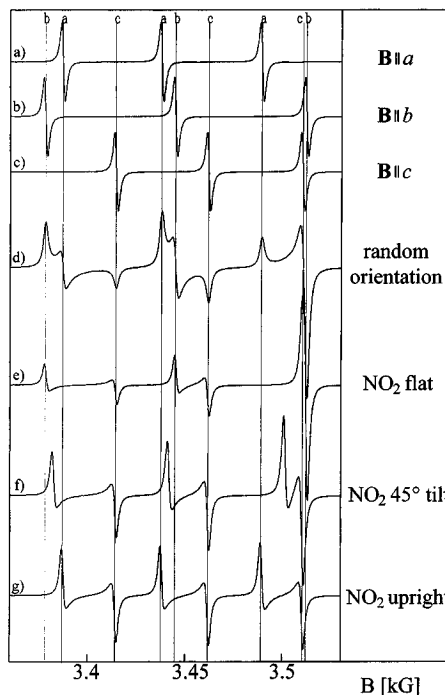


Figure 2. Effects of different molecular distributions onto NO₂ ESR line shapes: (a–c) all molecules are oriented in the same way; (d) simulation for a statistical distribution; (e–g) the angle between the C₂ axis of the molecule and the surface normal was varied. A line width of 3 G was used for all simulations.

molecular orientation a triplet of (Lorentzian-shaped) lines due to the interaction with the nuclear spin $I = 1$ of ¹⁴N nucleus is obtained (Figure 2a–c). If the molecules are randomly distributed, triplets of all possible orientations have to be summed up to give the corresponding EPR spectrum (Figure 2d). Figure 2e–g shows ESR line shapes resulting from molecular distributions where the O–O axis lies in the plane and the C₂ axis has different angles with respect to the surface normal for the case of an orienting plane (with **B** lying in this plane).

The spectrum of NO₂ in a N₂O₄ matrix at 35 K (Figure 3) can easily be identified as a mixture of the simulations in Figure 2d,g. The decomposition is shown in Figure 4. For the simulations (solid lines in Figures 3 and 4) a more sophisticated model was developed. The part describing the oriented molecules (at the bottom of Figure 4) was simulated by a probability distribution of tilt angles (angle between C₂ axis and surface normal) decaying exponentially with larger angles. In the fitting procedure the molecules had the degree of freedom to orient themselves with the O–O axis out of the surface plane by introducing virtual planes tilted with an angle to the surface. The probability of finding such a virtual plane also decreases exponentially. Molecules having an angle less than 10° between the C₂ axis and the surface normal are intensified by a factor of 5.6 (fit at the bottom of Figure 4) in comparison with a hypothetical spectrum (in the center of Figure 4) derived from statistical orientation.

The sample was annealed by stopping the helium flux of the cryostat. The ESR spectra in Figure 3 were transiently recorded while the temperature slowly changed from 35 to 150 K during 120 min. The vertical lines in Figure 3 indicate the resonance positions (gained from fitting) for the molecule's principal axes lying along the magnetic field. No significant changes occur in the spectrum up to 125 K. Above this temperature the resonance positions belonging to the *b* and *c* axis start to shift to their averaged value. This is thought to be an effect of

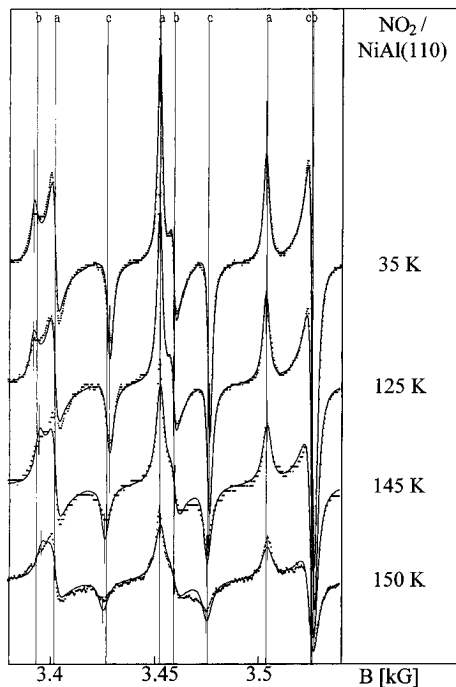


Figure 3. NO₂ ESR spectra (**B** oriented within the substrate surface) of a molecular distribution with a preferred orientation of the molecules perpendicular to the surface. The following parameters are used for the simulation at 35 K: $g_a = 2.0050$, $g_b = 2.0012$, $g_c = 1.9909$, $A_a = 50.8$ G, $A_b = 67.5$ G, and $A_c = 48.7$ G. Line widths of the different values for m_l are (from the left to the right) 3.7, 3.0, and 3.5 G.

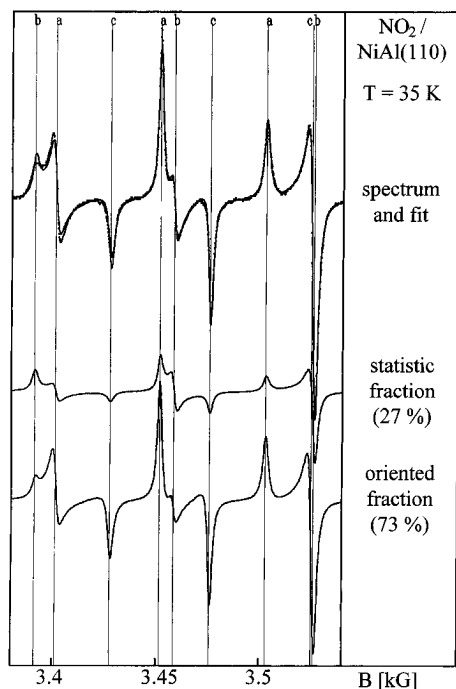


Figure 4. Spectrum on top of Figure 3 as superimposed from a partial distribution of molecules with a three-dimensional statistic orientation and another partial distribution of molecules with preferential orientation.

rotational diffusion around the a axis and will be discussed later. Simultaneously (Figure 3, 150 K), the fit is too sharp in the b and c component while it is too broad in the a component. Above 150 K the ESR signal decreases very fast. This is caused by two processes: Desorption takes place while at the same time monomers react by translational diffusion to diamagnetic dimers.¹⁵ This model of the molecular distribution could be verified by angle-dependent measurements (not shown here).

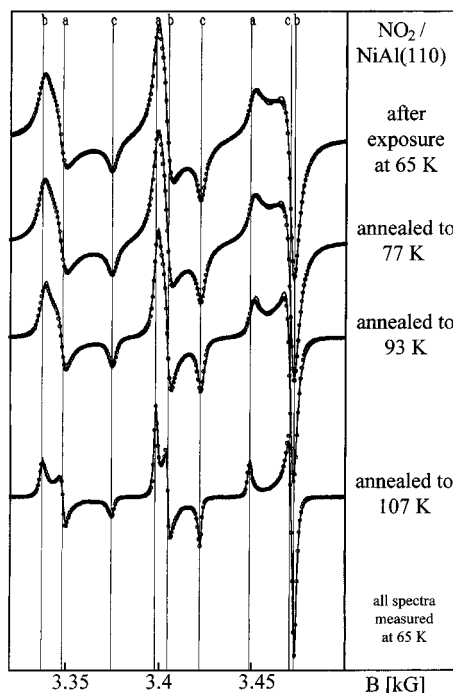


Figure 5. Steps necessary to prepare a state of randomly oriented molecules. Tempering reduces the line width by dimerization. Simultaneously, the molecular orientation becomes statistical as indicated in Figure 6.

To simulate these spectra, only the angle between the surface plane and the direction of **B** has additionally been considered.

Molecular Dynamics. Figure 5 shows the steps to prepare a state of randomly oriented NO₂ monomers. This is necessary to divide clearly the effects of preferred orientations and molecular dynamics. The spectrum on top of Figure 5, measured directly after adsorption, is fitted on the basis of a preferred orientation of the molecules (10%) as mentioned above (line width 8 G). Annealing the sample to 77 K and cooling to 65 K induces no change in line shape. A further annealing procedure to 93 K results in a spectrum very well describable just by a random distribution and a line width of 5.5 G. At 93 K molecular motions are clearly observable (see Figure 7). This motion results in a random distribution of the molecules which can be frozen by cooling to 65 K shown in the third spectrum in Figure 5. Warming to 107 K leads to a further reduction of the line width (to approximately 2.5 G). Now the simulation to the spectrum at the bottom of Figure 5 includes a part of molecules in motion (details in Figure 7) not seen before because the line width was relatively large. The variation of the angle between the magnetic field and the orienting surface is proof for the random distribution of NO₂ monomers: The perfect independence of the ESR line shape from this variation is shown in Figure 6. Note that in the spectra discussed before (see Figure 3) effects of dynamics are initially observed at 125 K. This indicates that the highly oriented phase is hindered in motion.

To take the effects of molecular motions to ESR line shape into consideration, a program package developed by Freed and co-workers^{3,4} was integrated in the fitting routine. The dynamical process in the simulations has been assumed to be Brownian rotational diffusion. The fits in Figure 7 are based on a superposition from a part of rigid molecules with a part of molecules in motion. The line widths vary with the z component of the nuclear spin. The preferred axis of rotation can easily be deduced from the spectra by realizing that rotation around the a component leads to relatively sharp lines which do not change their positions with increasing temperature. Features

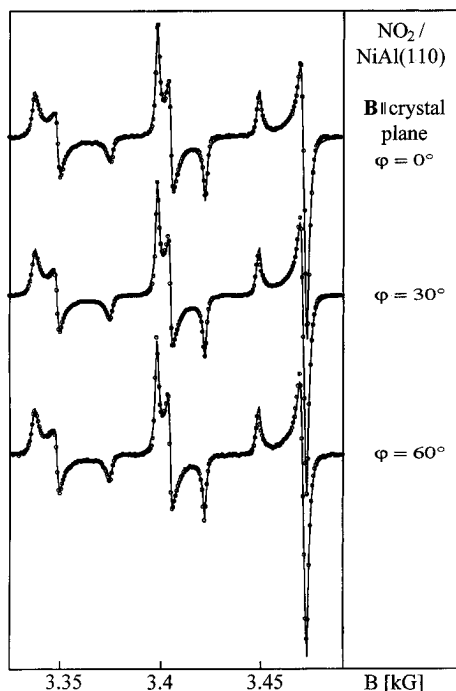


Figure 6. Angle-dependent measurements of the lowermost spectrum in Figure 5 demonstrating a completely statistical distribution of the molecular orientations.

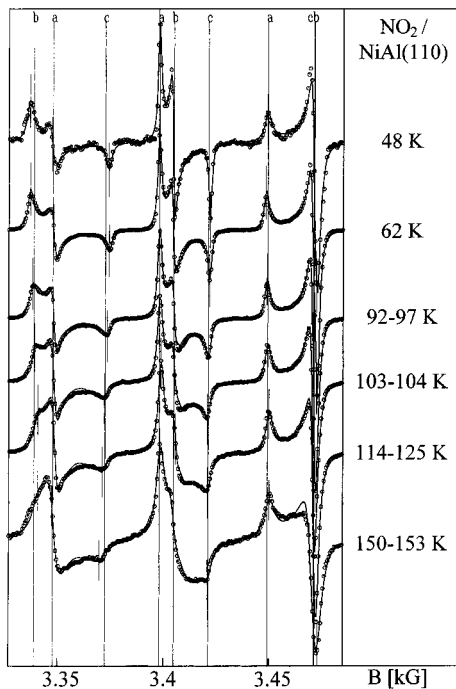


Figure 7. Rotational diffusion of the NO₂ molecules around the axis perpendicular to the molecular plane. Simulations are based on a superposition of a fraction of rigid molecules with a fraction of molecules in motion. ESR parameters are given in Table 1.

belonging to the *b* and *c* components broaden and shift to their averaged values by rotation around the *a* axis. So the *a* axis has to be the axis of rotation. ESR line shapes resulting from rotations around *b* and *c* as well as from isotropic rotation lead to quite different spectra and are discussed in ref 8.

Besides this motion, described by the rotational constant R_{\parallel} , a second, perpendicular rotational constant R_{\perp} , describing a rotation around *b* and *c*, was considered. The complete set of parameters to fit the spectra in Figure 7 are given in Table 1. The range in temperatures assigned to the spectra is a conse-

quence of the difficult temperature control by varying the helium flux and simultaneously heating the cryostat. The effects of motions of the NO₂ molecules to the ESR line shape increase with increasing temperature. This is indicated by the growing R_{\parallel} and the simultaneous growing of the fraction of molecules in motion. R_{\perp} shows no significant variations (see Table 1). Because the program package⁴ used in the simulations is not suited to simulate rigid limit spectra, these values of R_{\perp} have to be interpreted as upper limits.⁸ Due to this fact, the spectrum on top of Figure 7 was simulated by allowing the line width ΔB to vary analogously to g^{16} with the orientation relative to the magnetic field **B**:

$$\Delta B(\theta, \phi) = (\Delta B_a^2 \cos^2 \phi \sin^2 \theta + \Delta B_b^2 \sin^2 \phi \sin^2 \theta + \Delta B_c^2 \cos^2 \theta)^{1/2}$$

θ is the angle between the O—O axis *c* and **B**; ϕ is the angle between the *a* axis and the projection of **B** along the molecular mirror plane *ab* (see Figure 1). ΔB_a (ΔB_b , ΔB_c) are the values of the line widths assigned to **B** parallel to *a* (*b*, *c*). To simulate axial symmetric motion as above the parameter $\Delta B_{\perp} = \Delta B_b = \Delta B_c$ was used. In this manner a sharpening of the features in the spectrum belonging to *a* could be obtained while the others are broadened. Averaged values for the line width are given in Table 1.

Discussion

The simulations still show some imperfections, although they were made on a relatively sophisticated level. With increasing temperature the features belonging to the *a* axis are not well reproduced. This is a consequence of the model of superimposing a fraction of rigid molecules with dynamic particles characterized by only one set of rotational constants. Instead of this, a distribution for R_{\perp} and R_{\parallel} would be more appropriate.¹⁸ To predict such quantities, it would be necessary to have more information on the relation between energetics and dynamics. Unfortunately, in the simulation procedure molecular motion is supposed to be a stochastic process.³ Therefore, the energy of a molecule subjected to rotational diffusion is not well-defined.

Another imperfection would be corrected using a distribution of rotational constants. The resonance positions assigned by vertical lines to the principal values of the **g** and **A** tensors listed in Table 1 show a shift as a function of temperature. But as long as the molecule's shape is not modified by the motion or the chemical environment, the *g* and *A* values should be temperature-independent parameters. A better model of molecular motion should contain *g* and *A* values as parameters for a whole temperature series of spectra instead of a set for every single spectrum. For this reason the spread in the principal tensor components must be considered as a lower limit of the real values even at lowest temperatures.

Directly after adsorption there are strong orientational effects in the ESR spectra. One possibility to explain this is a preferred orientation of the N₂O₄ matrix crystallites, in which the NO₂ monomers exist as defects. These crystallites could be oriented by the substrate surface during the preparation procedure. But in this case tempering procedures should result in an increase of orientational effects by increasing order through further crystallization. The opposite is observed. Another model is favorable: The NO₂/N₂O₄ molecules form glasslike aggregates in two dimensions with a layered morphology after exposure at low temperatures. (It is known that via adsorption at low temperatures N₂O₄ dimer structures different from the most stable symmetrical geometry (planar O₂NNO₂) are formed.¹⁹)

TABLE 1: ESR Parameters for the Simulations in Figure 7^a

T/K	g tensor			A tensor/G			line width/G			fraction/%		rotation	
	g_a	g_b	g_c	A_a	A_b	A_c	l	c	r	rig	mo	R_{\perp}/s^{-1}	R_{\parallel}/s^{-1}
48	2.0046	2.0010	1.9905	50.91	67.73	48.45	3.43	1.70	3.39	100.0			
62	2.0047	2.0009	1.9906	50.20	67.68	47.96	2.97	1.98	2.53	75.0	25.0	5.08×10^5	1.58×10^7
92–97	2.0046	2.0007	1.9909	50.52	66.89	48.35	3.23	2.22	2.78	52.2	47.8	1.61×10^5	1.87×10^7
103–104	2.0045	2.0006	1.9912	50.70	65.98	49.21	3.68	2.63	3.39	40.9	59.1	1.80×10^5	2.17×10^7
114–125	2.0042	2.0002	1.9911	50.96	65.06	50.32	4.22	2.94	3.84	41.8	58.2	2.50×10^5	2.71×10^7
150–153	2.0044	2.0008	1.9912	51.42	64.17	51.65	6.41	4.44	5.87	41.7	58.3	2.50×10^5	3.34×10^7

^a Abbreviations: l = left, c = center, r = right, rig = rigid molecules, mo = molecules in motion.

The planes of these aggregates are oriented preferentially parallel to the substrate plane. These layers form a phase with a larger inner surface between the layers. NO₂ monomers find enough space to “adsorb” with their C₂ axis pointing perpendicular to the aggregate planes, i.e., in a preferred upright geometry with respect to the substrate plane. This assumption of inner surfaces parallel to the substrate surface was introduced by an exponential decay of the probability of virtual planes in our model for simulations. NO₂ monomers in the highly oriented phase are therefore hindered in motion (see Figure 3, spectrum at 125 K). Tempering results in the formation of planar N₂O₄ dimers¹⁹ and a simultaneous loss of inner surface. The remaining monomers are located in cavities of a disordered N₂O₄ matrix and are partly subjected to rotational diffusion even at lowest temperatures.

Conclusions

It was demonstrated that the possibilities of ESR spectroscopy provide quantitative insight into anisotropies in spatial distributions of paramagnetic adsorbates. The analysis of spectra recorded as a function of temperature indicates that the process of rotational diffusion is of importance down to 35 K. For the first time it is shown that NO₂ stands preferentially upright relative to an orienting plane, and rotation around the axis perpendicular to the molecular plane takes place. The information gained from the well-resolved spectra presented here may help in the analysis of poorer resolved spectra of submonolayer coverage of NO₂ on ordered surfaces as recorded in ref 14. Such investigations are in progress.

References and Notes

- (1) Jen, C. K.; Foner, S. N.; Cochran, E. L.; Bowers, V. A. *Phys. Rev.* **1958**, *112*, 1169.
- (2) Jackels, C. F.; Davidson, E. R. *J. Chem. Phys.* **1975**, *63*, 4672.
- (3) Freed, J. H. In *Spin Labeling: Theory and Applications*; Berliner, L. J., Ed.; Academic Press: New York, 1976; Vol. 1, Chapter 3, pp 53–132.
- (4) Schneider, D. J.; Freed, J. H. In *Spin Labeling: Theory and Applications*; Berliner, L. J., Reuben, J. Eds.; Plenum Press: New York, 1989; Vol. 8, Chapter 1, pp 1–76.
- (5) Kasai, P. H.; Weltner, Jr., W.; Whipple, E. B. *J. Chem. Phys.* **1964**, *42*, 1120.
- (6) McDowell, C. A.; Nakajima, H.; Raghunathan, P. *Can. J. Chem.* **1970**, *48*, 805.
- (7) Myers, G. H.; Easley, W. C.; Zilles, B. A. *J. Chem. Phys.* **1970**, *53*, 1181.
- (8) Shiotani, M.; Freed, J. H. *J. Phys. Chem.* **1981**, *85*, 3873.
- (9) Millhauser, G. L.; Gorchester, J.; Freed, J. H. In *Electron Magnetic Resonance of the Solid State*; Weil, J. A., Ed.; Canadian Society for Chemistry: Ottawa, 1987; p 571.
- (10) Adrian, F. J. *Chem. Phys. Lett.* **1962**, *36*, 1692.
- (11) Adrian, F. J.; Kim, B. F.; Bohandy, J. *J. Chem. Phys.* **1985**, *82*, 1804.
- (12) Schaafsma, T. J.; Kommandeur, J. *Mol. Phys.* **1968**, *14*, 517.
- (13) Zomack, M.; Baberschke, K. *Phys. Rev. B* **1987**, *36*, 5756.
- (14) Schlienz, H.; Beckendorf, M.; Katter, U. J.; Risse, T.; Freund, H.-J. *Phys. Rev. Lett.* **1995**, *74*, 761.
- (15) Katter, U. J.; Schlienz, H.; Beckendorf, M.; Freund, H. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 340.
- (16) Beckendorf, M.; Katter, U. J.; Schlienz, H.; Freund, H.-J. *J. Phys.: Condens. Matter* **1993**, *5*, 5471.
- (17) McClung, R. E. D. *Can. J. Phys.* **1968**, *46*, 2271.
- (18) Mailer, C.; Hoffman, B. M. *J. Phys. Chem.* **1976**, *80*, 842.
- (19) Bolduan, F.; Jodl, H. J.; Loewenschuss, A. *J. Chem. Phys.* **1984**, *80*, 1739.

JP9522627