ESR Studies of NO₂ Adsorbed on Surfaces. Analysis of Motional Dynamics

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ESR spectra of NO₂ adsorbed on crushed Vycor glass and on a zeolite were observed in the temperature range 4.8-221 K. Based upon spectral simulations using the slow-motional ESR theory for different models of rotational diffusion, we found that for NO₂ motion on the Vycor surface the following occurs: (1) At 4.8 K, NO₂ still shows residual motional effects. (2) Below 77 K the rotational motion of NO₂ is axially symmetric about the y axis (i.e. parallel to the O-O internuclear axis) such that \( N = R_l / R_\perp = 10 \). The parallel component of the diffusion tensor, \( R_p \), increases with temperature, e.g., \( R_p = 5 \times 10^9 \) and \( 1 \times 10^7 \) s⁻¹ at 4.8 and 77 K, respectively (based on a Brownian diffusion model). (3) Above 77 K, \( R_p \) increases with temperature so that almost isotropic rotational diffusion is estimated at 185 K (i.e., \( R_p = 1 \times 10^7 \) s⁻¹ and \( N = 1.3 \)), presumably due to a translational diffusion mechanism. (4) There are discrepancies between the observed and calculated line shapes especially for \( T \geq 77 \) K. None of the models used could improve the agreement, and possible improvements of the models are outlined. A quantum mechanical analysis of the 4.8 K spectrum implies either a renormalized moment of inertia for NO₂ that is orders of magnitude greater than that in the gas phase and/or a strong orientation-dependent interaction potential with the surface. In either case it is suggested that the y axis should be parallel to the surface. Additional line broadening probably due to an exchange process modulated by translational diffusion rapidly increases with temperature above 77 K, even though the NO₂ surface concentration decreases with increasing temperature. Distinct differences in motional dynamics are observed for NO₂ on the zeolite support.

Introduction

Nitrogen dioxide, NO₂, a stable paramagnetic gaseous molecule has been studied by a number of investigators using ESR. The ESR parameters and their relation to the electronic structure have been well established from single-crystal studies and molecular orbital calculations. The ESR parameters reported are summarized in Table I and the molecular coordinates related to the magnetic parameters are shown in Figure 1. Thus, NO₂ has potential as a "spin probe" for the study of molecular dynamics at the gas–solid interface by ESR.

In the course of our recent study of reactions between NO₂ and Cu–metal supported on porous Vycor glass, it was also found that the NO₂ adsorbed on the Vycor gave strongly temperature-dependent ESR spectra. We therefore decided to study NO₂ on the pure Vycor for a molecular-dynamics study in order to eliminate the background signal from the Cu²⁺–NO₂ complexes.

Although there have been ESR studies of molecular motion of NO₂ in the adsorbed state and in solid media, most of these studies were limited to qualitative analysis of the spectra. Only one paper, on the motional dynamics of NO₂ in synthetic zeolites, by Pietrzk and Wood attempts a quantitative analysis. They analyzed their temperature-dependent ESR line shapes using an early approximate theory and concluded that there was no preferred axis of rotation for the NO₂. However, our temperature-dependent NO₂ spectra are considerably different in appearance from those of the NO₂/zeolite system, but very similar to those from NO₂/silica gel.

In our laboratory, the theory for slow-motional ESR spectra has been extensively developed and has been applied successfully to ESR line shapes of nitroxides and the VO²⁺ ion in isotropic and anisotropic liquids. Recently, the theory was applied to the analysis of the temperature-dependent ESR line shapes of O₂⁻ adsorbed on Ti ions supported on Vycor glass, and it was concluded that the motion of O₂⁻ on the surface was highly anisotropic, consisting essentially of planar rotation about the axis perpendicular to the internuclear axis of O₂⁻ and parallel to the normal to the surface. We thus showed that our theory for slow-motional ESR spectra is very useful in the study of molecular dynamics at the gas–solid interface.

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(15) R. S. Mulliken, Rev. Mod. Phys., 14, 204 (1942).
The motion of NO\textsubscript{2} is primarily a rotation about the y axis (i.e., parallel to the internuclear axis between the oxygen atoms), but above 77 K the motion becomes nearly isotropic.

### II. Experimental Section

**A) Sample Preparation.** The porous Vycor quartz glass (Corning Code No. 7930, controlled pore size of 40 Å) was supplied in a crushed form by Dr. Jan Schreurs, Corning Glass Works. The crushed Vycor was cleaned and activated in the manner described previously.\textsuperscript{29-30}

The NO\textsubscript{2} used was obtained commercially (Madison Gas Products) and was purified by vacuum distillation. This gas gave the same results as NO\textsubscript{2} that was further purified by mixing with oxygen to remove NO. The equilibrium for the reaction \( \text{NO}_2 = \text{NO} + \frac{1}{2}\text{O}_2 \) is such that small amounts of NO and O\textsubscript{2} are always present in NO\textsubscript{2} and ESR signals due to O\textsubscript{2} gas are clearly observed at room temperature \((K_{288\,\text{K}} = 7.2 \times 10^{-7}).\textsuperscript{31}

The Vycor was exposed to about 10 torr of NO\textsubscript{2} (actually an equilibrium mixture of NO\textsubscript{2}) at room temperature for several hours and then degassed briefly (ca. 1 min) to remove nonadsorbed NO\textsubscript{2} at the same temperature. The adsorbed NO\textsubscript{2} is physisorbed, since pumping for about 30 min results in a complete loss of ESR signal. Na–Zeolon (Norton)\textsuperscript{32} was supplied by Dr. Paul H. Kasai, IBM. The zeolite was activated at 550 °C for 12 h under vacuum of \( P = 10^{-6} \) torr. About 500 torr of NO\textsubscript{2} was admitted to the zeolite at room temperature, and ESR spectra were recorded for the sample without degassing. Such high pressures were required in order to obtain an ESR signal, thus clearly demonstrating that the NO\textsubscript{2} is very weakly adsorbed on the zeolite.

### Table 1: ESR Parameters of NO\textsubscript{2} in Various Media

<table>
<thead>
<tr>
<th>medium</th>
<th>( g_x )</th>
<th>( g_y )</th>
<th>( g_z )</th>
<th>( g_{\text{iso}} )</th>
<th>( A_x )</th>
<th>( A_y )</th>
<th>( A_z )</th>
<th>( a_{\text{iso}} )</th>
<th>ref</th>
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<tr>
<td>NaNO\textsubscript{a} (77 K)</td>
<td>2.0057</td>
<td>1.9910</td>
<td>2.0015</td>
<td>1.9994</td>
<td>138.4</td>
<td>130.9</td>
<td>190.2</td>
<td>153.2</td>
<td>1</td>
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<tr>
<td>NaNO\textsubscript{a} (293 K)</td>
<td>2.0059</td>
<td>2.0052</td>
<td>2.0055</td>
<td>2.0055</td>
<td>102.2</td>
<td>92.7</td>
<td>140.3</td>
<td>111.7</td>
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<td>AgNO\textsubscript{a} (77 K)</td>
<td>2.0090</td>
<td>1.9978</td>
<td>2.0039</td>
<td>2.0086</td>
<td>143.1</td>
<td>135.1</td>
<td>195.3</td>
<td>157.8</td>
<td>3</td>
</tr>
<tr>
<td>KNO\textsubscript{2} (77 K)</td>
<td>2.0055</td>
<td>1.9832</td>
<td>1.9996</td>
<td>1.9994</td>
<td>136.6</td>
<td>141.1</td>
<td>176.3</td>
<td>151.3</td>
<td>4</td>
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<tr>
<td>ice (77 K)</td>
<td>2.0066</td>
<td>1.9920</td>
<td>2.0022</td>
<td>2.0003</td>
<td>141.6</td>
<td>139.6</td>
<td>196.8</td>
<td>159.3</td>
<td>5</td>
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<tr>
<td>CH\textsubscript{3}NO\textsubscript{2} (77 K)</td>
<td>2.0047</td>
<td>1.9915</td>
<td>2.0011</td>
<td>1.9991</td>
<td>132.6</td>
<td>124.3</td>
<td>182.4</td>
<td>146.4</td>
<td>6</td>
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<tr>
<td>N\textsubscript{2}O\textsubscript{5} (77 K)</td>
<td>2.0054</td>
<td>1.9913</td>
<td>2.0015</td>
<td>1.9994</td>
<td>140.9</td>
<td>134.8</td>
<td>188.2</td>
<td>154.6</td>
<td>7</td>
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<td>neon (4 K)</td>
<td>2.0062</td>
<td>1.9920</td>
<td>2.0030</td>
<td>2.0004</td>
<td>145.2</td>
<td>127.7</td>
<td>173.0</td>
<td>148.6</td>
<td>8</td>
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<tr>
<td>zeolite (Ca-X)\textsuperscript{b} (114 K)</td>
<td>2.0051</td>
<td>1.9921</td>
<td>2.0017</td>
<td>1.9996</td>
<td>145.7</td>
<td>133.3</td>
<td>189.4</td>
<td>161.1</td>
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<tr>
<td>zeolite (Na-X)\textsuperscript{b} (77 K)</td>
<td>2.0043</td>
<td>1.9922</td>
<td>2.0015</td>
<td>1.9993</td>
<td>143.8</td>
<td>137.2</td>
<td>189.1</td>
<td>156.5</td>
<td>9</td>
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<tr>
<td>ZnO\textsubscript{a} (77 K)</td>
<td>2.007</td>
<td>1.994</td>
<td>2.003</td>
<td>2.001</td>
<td>146.1</td>
<td>132.0</td>
<td>181.1</td>
<td>153.1</td>
<td>10</td>
</tr>
<tr>
<td>silica gel\textsuperscript{a} (77 K)</td>
<td>(2.004)\textsuperscript{c}</td>
<td>1.9907</td>
<td>(2.004)\textsuperscript{c}</td>
<td>1.9996</td>
<td>(165.7)\textsuperscript{c}</td>
<td>137.0</td>
<td>(165.7)\textsuperscript{c}</td>
<td>156.1</td>
<td>11</td>
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<tr>
<td>MgO (93 K)</td>
<td>2.005</td>
<td>1.9915</td>
<td>2.002</td>
<td>1.9995</td>
<td>148</td>
<td>137.0</td>
<td>189.0</td>
<td>158.0</td>
<td>13</td>
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<tr>
<td>NO\textsubscript{2} \textsuperscript{d} (gas) (283 K)</td>
<td>2.006178</td>
<td>1.991015</td>
<td>2.00199</td>
<td>1.9997</td>
<td>127.8</td>
<td>126.0</td>
<td>185.0</td>
<td>146.5</td>
<td>12</td>
</tr>
<tr>
<td>Vycor\textsuperscript{a} (4.8 K)</td>
<td>2.0051</td>
<td>1.9913</td>
<td>2.0017</td>
<td>1.9994</td>
<td>140.3</td>
<td>128.2</td>
<td>183.5</td>
<td>150.7</td>
<td>/</td>
</tr>
<tr>
<td>zeolite (Na–Zeolon (Norton))\textsuperscript{b} (4.8 K)</td>
<td>2.0051</td>
<td>1.9913</td>
<td>2.0017</td>
<td>1.9994</td>
<td>140.3</td>
<td>128.2</td>
<td>183.5</td>
<td>150.7</td>
<td>/</td>
</tr>
</tbody>
</table>

\( a \) Single-crystal studies. \( b \) Adsorbed state. \( c \) Averaged value of \( x \) and \( z \) components. \( d \) Microwave study. \( f \) The \( x \), \( y \), and \( z \) components of the quadrupole coupling tensor were found to be 0.9, 1.62, and 2.6 MHz or of negligible importance for ESR spectra. \( f \) Present work.

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![Figure 1](attachment:image.png)

**Figure 1.** (a) Structure of \(^{15}\text{N}\)NO\textsubscript{2}. (b) Illustration of the geometry for NO\textsubscript{2} showing the case in which the principal diffusion axis is not necessarily coincident with the principal axes of the NO\textsubscript{2} g and A tensors.
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**Experimental Results and Analysis**

(A) **Determination of A and g Tensor Components.** A number of ESR studies on NO\textsubscript{2} have been reported and the assignment of A and g tensor components has been well established by comparison with molecular orbital calculations.\textsuperscript{16-17} However, the numerical values of A and g are considerably shifted from medium to medium as seen in Table I. Thus, in order to simulate slow-motional spectra of NO\textsubscript{2}, one must first know the precise value of the A and g tensor components in the rigid limit for the present system.

The lowest temperature of our measurements was 4.8 K and the spectrum obtained is shown in Figure 2A. The simulation was carried out to accurately determine the ESR parameters of the spectrum at 4.8 K by using a rigid-limit simulation program. The best-fit theoretical spectra are shown in parts B and C of Figure 2, the difference between two theoretical spectra being only the intrinsic Lorentzian line width, $1/T_2^0$, used for the calculation. We show with a dotted line in Figure 2A that, to simulate the line shape corresponding to the experimental line width of the y component at $M_I = 0$ is well simulated by using $1/T_2^0 = 0.4$ G. Moreover, it is seen from Figure 2A that the experimental line width of the y component at $M_I = -1$ is less than that of the $x$ and $z$ components at $M_I = 1$, $1/T_2^0 = 1.6$ G is needed, but the line shape at $M_I = 0$ is well simulated by using $1/T_2^0 = 0.4$ G. Moreover, it is seen from Figure 2A that the experimental line width of the y component at $M_I = -1$ is less than that of the $x$ and $z$ components at $M_I = 1$, i.e., close to $1/T_2^0 = 0.4$ G. Thus, we find that the spectrum at 4.8 K cannot be simulated by a single line width, but the line width depends considerably on both the orientation and the value of $M_I$.

However, as shown in parts A and B of Figure 3, the spectrum of NO\textsubscript{2} adsorbed on zeolite at 4.7 K is simulated satisfactorily by use of a single line width and the same A and g tensor components as those of the NO\textsubscript{2}/Vycor system.

These results indicate that even at 4.8 K the NO\textsubscript{2} on Vycor is not in the true rigid limit, but rather in an incoherent slow-motional state. Nevertheless, the measured A and g tensor components should be very close to the rigid-limit values because of the following reasons. (1) The variation of the measured A and g components vs. temperature is shown in Figure 5. From this plot one can see that, below 11 K, the components no longer shift with temperature. (2) The greater sensitivity of the line widths, vs. the shifts in position, to motional effects is well-known in magnetic resonance (NMR and ESR) spectra,\textsuperscript{30} since the lines first broaden before they shift.

Thus, we will use the A and g tensor components $A_x = 140.3$ MHz (50.0 G), $A_y = 128.2$ MHz (46.0 G), $A_z = 183.5$ MHz (100.0 G), $g_x = 2.0051$, $g_y = 1.9913$, and $g_z = 2.0017$. These tensor components are essentially the same as those of NO\textsubscript{2} in liquid nitrogen, as expected, since NO\textsubscript{2} is a weak exchange interaction system.

(B) **Measurement of ESR Spectra.** ESR spectra were recorded at X-band with a Varian E-12 ESR spectrometer by employing 100-kHz (or 10-kHz when needed) field modulation at a low enough amplitude that no line shape distortion was observed. Microwave power was always adjusted so that no saturation occurred.

The sample temperature above 77 K was controlled by a Varian E-257 variable-temperature unit and measured with a copper-constantan thermocouple placed just above the sample. Moreover, the temperature of the sample was regulated within ±0.5 K between 4.2 and 80 K by means of an Oxford Instrument, ESR 9 continuous He gas flow cryostat.

The magnetic field was measured and calibrated with a Harvey-Wells gauss meter. The microwave frequency was measured with a Systron Donner electronic counter.

Relative spin concentrations at the different temperatures were determined by double integration of the experimental spectra after checking that the sensitivity remained unchanged. A Curie-Weiss law was assumed for the paramagnetic susceptibility.

***III. Experimental Results and Analysis***

**Figure 3.** Experimental spectrum of NO\textsubscript{2} in zeolite (Na-Zeolon) at 4.7 K (A) and best fitting one (B) calculated by using the rigid-limit program. The A and g tensor components used are the same as those of NO\textsubscript{2}/Vycor, but a Lorentzian line width of $1/T_2^0 = 1.2$ G was used.

Figure 4. Temperature-dependent ESR spectra of NO2/Vycor: (A) below 42.2 K; (B) above 77 K.

MHz (65.5 G), \( g_x = 2.0051, g_y = 1.9913, \) and \( g_z = 2.0017 \) for NO2 at 4.8 K as the rigid-limit values in the following calculations.

The following three points should be noted about the present values of ESR parameters. (1) Schaafsma et al.\(^7\) have pointed out that the contribution of the nonsecular terms of the spin Hamiltonian cannot be neglected because of the magnitude of the \( ^{14}\text{N} \) hyperfine splitting (i.e., second-order effects amount to a correction of about 0.5 G in the resonance position of the spectral lines and to about \( 5 \times 10^{-4} \) in \( g \) values).\(^7\) Therefore, second-order perturbation effects were taken into account in the spin Hamiltonian. It was found from the simulation that, although the line positions were shifted by the second-order contribution, the line shape was essentially unaffected when a line width larger than 0.4 G was used. (2) The present \( g \) components are very close to those reported for NO, trapped in a single crystal of NaN02 and in N2O4 medium\(^7\) (see Table I). However, the \( A \) components are slightly different from the values reported for the above two studies. This might be explained by the NO2 geometry, e.g., the bond angle of ONO, might be modified by the surface.\(^34\) These and related matters are discussed more fully in section IV.

(B) Temperature-Dependent Spectra of NO2 on Vycor Surfaces. The observed spectra in the temperature range from 4.8 to 221 K are shown in Figure 4. One can see that the line shape of the spectra depend strongly on temperature. In this section, we summarize the main characteristics of these spectra (cf. parts A and B of Fig 4). The graph of resonance line position vs. temperature Figure 5). (1) Below 11 K, no line positions are shifted, but the line shape changes significantly between 4.8 and 11.0 K, i.e., the relative heights for the \( y \) components at \( M_I = -1 \) and 0 and for all components of the \( M_I = 0 \) band become weaker at 11 K. This change can be interpreted as a motional effect as noted in the previous section. (2) With further increase in temperature, the \( x \) and \( z \) components are gradually shifted toward their common center for all three \( M_I \) bands and then they collapse to one broad band at about 77 K. Below 77 K, although the line positions corresponding to the \( y \) component are also shifted from the original position toward the position corresponding to rapid isotropic motion (giving averaged values of \( A \) and \( g \) components), the degree of shift is much less than that of the \( x \) and \( z \) components (see especially, the \( M_I = -1 \) band). This fact indicates that the rate of rotational diffusion about the \( y \) axis (\(-\text{O}--\text{O} \) direction, cf. Figure 1) is much greater than that about \( x \) and \( z \) axes in this temp-

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(34) The ONO angle can be calculated by use of Coulson's relationship (C. A. Coulson, Victor Henri Commemoratif, Contribution a l'Etude de la Structure Moleculaire, 1945, p 15). The estimated bond angles are given in ref 7 for the NO2 in a variety of matrices. The estimated angle (of 129°) for the present NO2 adsorbed on vycor is slightly smaller than that for the gas phase (134°).

(35) (a) We also note the ESR signal due to gaseous \( \text{O}_2 \) at \( g = 1.9758 \) shown in Figure 4B (cf. ref 13). This identification was clearly confirmed by observation of an identical signal after admitting pure \( \text{O}_2 \) gas into a blank ESR sample tube. Nonobservation of this signal below around 100 K is probably due to either adsorption of \( \text{O}_2 \) onto the vycor or a shift of the equilibrium constant for \( \text{NO}_2 = \text{NO} + \frac{1}{2}\text{O}_2 \) to the left. The same \( \text{O}_2 \) signal appears in the NO2/MgO system reported by Lunsford\(^1\) although he did not point it out (cf. the \(-180^\circ \) C spectrum in Figure 4a of ref 13). (b) Note also that the line shape of NO2 on MgO (at \(-190^\circ \) C)\(^1\) is close to the one we observed at 23.1 K on Vycor.
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Figure 5. Plot of experimental resonance positions vs. temperature. \( H_2 \) stands for a magnetic field strength of 3241.0 G. A microwave frequency of \( \nu = 9.070 \text{ GHz} \) was used. The lines (-----) and (-..-) stand for the resonance line positions corresponding to the rigid limit and to the fast isotropic motion, respectively (see the text for details).

temperature range. (3) Above 77 K, the positions of the collapsed lines from the \( x \) and \( z \) components are almost unchanged, but the \( y \) components (at the \( M_2 = -1, 0 \) bands) are seen to shift to the central part. This fact indicates that, in this temperature range, the rotational motion about the \( y \) axis increases significantly. (4) The \( M_2 = +1 \) band is not consistent with the observations on the \( M_2 = -1 \) and 0 bands. That is, the \( y \) component for \( M_2 = +1 \) is not visible, while the position of the \( z \) component for \( M_2 = +1 \) appears to be almost constant with temperature. (5) The line positions of the \( y \) component gradually become more diffuse with increasing temperature and are undetectable above 153 K. This may reflect increased rotational motion about the \( x \) and \( z \) axes and also the increased line width with temperature. The increase of the observed line width can be explained partly by the increase of rotational motion, but another mechanism for line broadening should also be considered. These matters will be discussed in detail in section D. (6) Another important observation is that the signal intensity of NO₂ determined by double integration decreased considerably with increasing temperature. For example, the concentration of NO₂ at 221 K is about 4% that at 77 K.

Finally, it should be noted that the present spectra of NO₂ observed over a wide temperature range are completely different from those in the gas phase, but characteristic of adsorbed species on the solid surface or trapped species in the solid matrix.

(C) Spectral Simulations. The spectral simulations of the temperature-dependent ESR spectra were carried out by using our slow-motional ESR simulation theory (programmed for a PDP-11 computer), for the rotational models, Brownian diffusion, jump diffusion (from weak to strong jump), and approximate free diffusion.

Figure 6. Theoretical spectra of NO₂ rotating about its \( x \) axis (B), \( y \) axis (C), and \( z \) axis (D). The spectra were calculated for Brownian rotational diffusion model by using \( R_1 = 1 \times 10^4 \text{ s}^{-1}, R_\perp = 5 \times 10^8 \text{ s}^{-1} \), and \( 1/3T_\perp = 0.4 \text{ G} \). For isotropic rotation (E), \( R_1 = R_\perp = 1 \times 10^4 \text{ s}^{-1} \) was used.

Note that for anisotropic rotational diffusion, the eigenvalues \( E_{L,K} \) of the diffusion operator are given by the expression

\[
E_{L,K} = R_1 B_{L-K} (L + 1) + (R_1 B_{K} - R_\perp B_{K}) K^2
\]

where \( B_{L-K} = [1 + R_\perp (L + 1)]^p \) and \( B_{K}^p = [1 + R_\perp K^2]^{p/2} \) for \( p = 1 \) for jump diffusion and \( p = 1/2 \) for approximate free diffusion. The definitions of \( L, K, \tau_1, \) and \( \tau_\perp \) are given elsewhere, but we note that the magnitude of \( \tau_1 \) or \( \tau_\perp \) is a measure of the mean jump size (or approximate inertial effect). Simple Brownian diffusion is obtained by letting \( R_1 \tau_1 \) and \( R_\perp \tau_\perp \rightarrow 0 \) so \( B_{L-K} = B_K = 1 \). In the present paper, for the purpose of comparing different models, anisotropic rotational correlation times, \( \tau_{R_{L-K}} \), and isotropic rotational correlation time \( \tau_R \) are defined as

\[
\tau_{R_{L-K}} = \left( 4 R_1 B_{L-K} \right)^{-1} \quad \tau_R = \left( \tau_R \left( \tau_{R_{L-K}} \right) \right)^{1/2}
\]

(36) The equilibrium constant \( K_p = 0.14 \) has been measured by Nordstrom and Chen [J. Phys. Chem., 89, 847 (1976)] for \( \text{NO}_2 \) = \( 2 \text{NO}_2 \). This is very close to the value 0.146 calculated in the ideal gas approximation where \( \Delta G_{298}^o = 1.14 \text{ kcal/mol} \). While at pressures below 1 torr and 298 K nearly all the NO₂ in the gas phase is dissociated, at 1 atm only about 1/3 mole fraction is. Enhanced dimerization on the Vycor surface.

RIII, which is reasonable since the Brownian diffusion model is considered. Theoretical analysis of the collapsed line width becomes narrower with further increase in peak heights at different increases for $83,525$ of the $y$ component is almost negligible with increasing $\gamma$ and $25,169$ of the doublet of $11$ are summarized as follows. (1) First, we note that, for $R_1 \| x$ and $y$ components are again averaged out, but the degree of broadening of the collapsed line is seen to be different at each $M_I$ band. The latter can be understood by recognizing that the degree of line broadening is related to $R_1$ and the separation frequency between the two components. In the case of $R_1 \| x$ (Figure 6C), the same type of argument again applied. The experimental spectra are clearly consistent with the case that $R_1 \| y$, especially in the lower temperature region.

Changes in the theoretical line shape occurring as a function of $R_1$ are shown in Figure 7. The sensitivity of the ESR line shape to molecular motion is seen from close to the rigid limit to the motional region, and with $R_1$ held constant at a small (rigid-limit) value.

The characteristics derived from the theoretical spectra are summarized as follows. (1) First, we note that, for $R_1 \leq 2.5 \times 10^8$ s$^{-1}$ and $R_1 \leq 2.5 \times 10^8$ s$^{-1}$, the position of each line is found to be essentially unshifted, but the line shape is changed slightly with decreasing $R_1$. (2) In the slow-motional region ($R_1 = 2.5 \times 10^8$ s$^{-1}$), the lines due to $A$ and $g$ anisotropies are well separated. With increasing $R_1$, the doublet of $x$ and $y$ components is shifted to the common center. Around $R_1 = 1 \times 10^8$ s$^{-1}$, the doublet at the $M_I = 0$ band becomes one broad line, whereas those at the $M_I = \pm 1$ bands are still separated. The doublets at the $M_I = -1$ and $+1$ bands collapse around $R_1 = 2.5 \times 10^8$ s$^{-1}$ and $R_1 = 5 \times 10^8$ s$^{-1}$, respectively. (3) It is also seen that the collapsed line width becomes narrower with further increase in $R_1$, i.e., the relative peak height compared with that of the $y$ component is greater. The line broadening of the $y$ component is almost negligible with increasing $R_1$, which is reasonable since $R_1 \| y$ axis. (4) Another important feature of the theoretical spectrum is the relative peak heights at different $M_i$ bands, i.e., the peaks of the $y, z$ components at the $M_I = \pm 1$ bands are the highest for $R_1 \leq 1 \times 10^7$ s$^{-1}$, but that at the $M_I = 0$ band gradually increases for $R_1 \geq 1 \times 10^7$ s$^{-1}$ and becomes greater than the one at the $M_I = \pm 1$ for $R_1 = 5 \times 10^8$ s$^{-1}$.

Next, the contribution of $R_1$ to the line shape for the Brownian diffusion model is considered. Theoretical spectra were calculated as a function of $R_1$. A value of $R_1 = 1 \times 10^5$ s$^{-1}$ was used (corresponding to intermediate slow motion), while $R_1$ was varied from $R_1 = 2.5 \times 10^5$ to $1 \times 10^8$ s$^{-1}$. For $R_1 \leq 1 \times 10^8$ s$^{-1}$, the line shape remains unchanged. For $R_1 \geq 1 \times 10^8$ s$^{-1}$, the line position of the $y$ component shifts to the lower field and at the same time they broaden. Furthermore, in this region, the $x$ and $z$ lines at the $M_I = 1$ band start to shift and become a broad singlet at $R_1 = 1 \times 10^8$ s$^{-1}$. Note that this value of $R_1 = 1 \times 10^8$ s$^{-1}$ is not enough to average out the $x$ and $y$ components at the $M_I = +1$ band. These simulations do demonstrate how the subtle features of the slow-motional spectra are affected by the details of the motions. This will provide helpful in the next section.

Another important parameter affecting the predicted line shape of the slow-motional ESR spectra is the residual line width, $1/T_2$. In order to see the sensitivity to $1/T_2$, of the slow-motional spectra for anisotropic Brownian diffusion, we calculated theoretical spectra as a function of $1/T_2$ for several cases of $R_1$ and $R_1$. It was found that the line shape changes considerably with a small variation of $1/T_2$, especially in the slow-motional region of $R_1$, $R_1 \leq 1 \times 10^8$ s$^{-1}$, which corresponds to our experiments. Thus, one has to be very careful in choosing $1/T_2$ to simulate the experimental spectra. The methods we used will be discussed in the following section.

(D) Comparison between Experimental and Theoretical Spectra. (1) NO$_2$ on Vycor. The experimental spectra are compared in Figure 8 with the best simulations obtained with a Brownian diffusion model. We make the following points: (1) Below 42.2 K, the calculated spectra correspond fairly well to the experimental ones at the central band $(M_I = 0)$, but they deviate considerably from...
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Figure 8. (A, B) The best-fitting theoretical spectra (Brownian rotational diffusion) compared with the experimental spectra of NO$_2$-Ycor in the temperature range between 4.8 and 185 K. The line widths used are given in Table I.

the experimental ones at the $M_f = \pm 1$ bands. Thus, the $x$ and $z$ components at the $M_f = \pm 1$ bands are collapsed into one broad line in the experimental spectra at 23.1 and 42.2 K, but they are still split in the calculated ones. Note that while the doublet (due to the $x$ and $z$ components) at the $M_f = \pm 1$ bands in the theoretical spectra can be averaged to one line by using higher values of $R_{\perp}$, the fit to the relative peak heights at each of the $M_f$ bands becomes worse. This disagreement cannot be improved by using any of the other models, as described below. 

(2) In order to simulate the spectra, a broader $1/T_{\perp}^0$ was required with increasing temperature. For example, $1/T_{\perp}^0 = 1.0$ G was needed for the spectrum at 11.0 K, whereas $1/T_{\perp}^0 = 2.5$ G and $1/T_{\perp}^0 = 7.0$ G were required for the spectra at 77 and 185 K, respectively. The line widths used in the simulation are given in Table I together with the $R_{\perp}$ and $R_{||}$ used. (Note that the theoretical spectra are not very sensitive to the $R_{\perp}$ and $R_{||}$ so their precision is about ±50%).

(3) The present simulations indicate that there are two distinct sets of spectra: i.e., those below 77 K and those above 77 K. Below 77 K, the rotational motion of NO$_2$ is quite anisotropic ($N = R_{\perp}/R_{||} \approx 10$) with both $R_{\perp}$ and $R_{||}$ increasing with temperature. At about 77 K, $R_{||}$ reaches a plateau in its value, while $R_{\perp}$ increases from $1 \times 10^6$ s$^{-1}$ (77 K) to $7.5 \times 10^6$ s$^{-1}$ (at 185 K) with further increase in temperature. Thus, the rotational diffusion approaches isotropic motion above 77 K. These features are clearly seen in Figure 9. Also, for $T > 77$ K, the line width rapidly becomes broader while the total intensities of the spectra decrease sharply with temperature as mentioned previously. (4) Although the line shapes cannot be accurately reproduced, the components of the diffusion tensor, $R_{\perp}$ and $R_{||}$, can be estimated from the theoretical spectra which give the same line positions as the experimental ones and are given in Table I.

We now discuss how we choose the value of $1/T_{\perp}^0$. In Figure 10 we show simulations carried out to fit the experimental spectrum recorded at 42.2 K. One sees that a change of $1/T_{\perp}^0$ from 1.0 to 3.0 G results in a considerable change in the relative peak heights at the $M_f = \pm 1$, 0 bands as well as in line shape. (Note that the maximum peak height of the theoretical spectrum is normalized to that of experimental one.) In the present studies, the $1/T_{\perp}^0$ giving the same spectral peak heights as those of the $x$ and/or $z$ components at the $M_f = \pm 1$, 0 bands was considered the optimum choice, e.g., $1/T_{\perp}^0 = 2.0$ G is a good choice at 42.2 K, as seen in the figure. Indeed, this line width gives the best fit among the spectra calculated.

We next examine how the line shapes change with the orientation of the axis about which the motion occurs. We calculated spectra as a function of the polar and azimuthal angles ($\theta$ and $\phi$) between the orientation of the principal coordinate system of the $g$ and $A$ tensors. We found from our calculations that the line shape is quite insensitive to the tilt angle, for $\theta \leq 45^\circ$, in the range of $R_{\perp} \approx 1 \times 10^7$ s$^{-1}$ and $R_{||} \approx 1 \times 10^6$ s$^{-1}$. When spectra were calculated as a function of $\phi$ as well, sensitivity of the line shape was greater than in the case of only changing $\theta$. However, the
jump diffusion model
jump models offer no significant improvement in the line
motional spectra (corresponding to the experimental spectrum at
two models as seen from the table. The reason the line
trends are found to be in the direction of worsening the
for
K)
Figure
TABLE 11: Best-Fitting Parameters for Slow-Motional Spectra

| $T$, K | $R_{||}$, s$^{-1}$ | $1/T_{||}$, s | $R_{\perp}$, s$^{-1}$ | $1/T_{\perp}$, s | $\tau_{R||}$, s | $\tau_{R\perp}$, s | $1/2T_{\perp}$, G |
|-------|-----------------|--------------|-----------------|--------------|-----------------|-----------------|------------------|
| 4.8   | BD$^a$          | $5 \times 10^3$ | $<1 \times 10^3$ | $5 \times 10^{-7}$ | $N > 5^b$ | $<1.7 \times 10^{-6}$ | 1.0 |
| 11.0  | JD$^b$          | $1 \times 10^6$ | $<1 \times 10^6$ | $1.3 \times 10^{+6}$ | $N \approx 10$ | $<1.7 \times 10^{-6}$ | 1.0 |
| 23.1  | JD$^b$          | $2.5 \times 10^6$ | $4 \times 10^{-7}$ | $5 \times 10^{-8}$ | $N = 10$ | $3.8 \times 10^{-7}$ | 1.5 |
| 42.2  | BD$^a$          | $7.5 \times 10^6$ | $7.5 \times 10^{-1}$ | $3.3 \times 10^{-4}$ | $N = 10$ | $2.2 \times 10^{-7}$ | 2.0 |
| 77    | BD$^a$          | $1 \times 10^7$ | $1 \times 10^{-7}$ | $1.3 \times 10^{-7}$ | $N = 10$ | $1.7 \times 10^{-7}$ | 2.5 |
| 106   | BD$^a$          | $2.5 \times 10^7$ | $2.5 \times 10^{-8}$ | $5 \times 10^{-8}$ | $N = 4$ | $6.7 \times 10^{-6}$ | 4.0 |
| 139   | BD$^a$          | $2.5 \times 10^7$ | $2.5 \times 10^{-8}$ | $5 \times 10^{-8}$ | $N = 2$ | $3.8 \times 10^{-6}$ | 5.0 |
| 185   | BD$^a$          | $1 \times 10^7$ | $1 \times 10^{-7}$ | $2.5 \times 10^{-8}$ | $N = 1.3$ | $2.2 \times 10^{-4}$ | 7.0 |

$^a$ BD = Brownian diffusion.  $^b$ JD = jump diffusion ($R_{||}/R_{\perp} = 1$).  $^c$ $\tau_{R||} = 1/4R_{||}$ for BD; $\tau_{R\perp} = 5/4R_{\perp}$ for JD.  $^d$ $\tau_{R\perp} = 1/6R_{\perp}$ for BD.  $^e$ $N = R_{||}/R_{\perp}$.

- BD = Brownian diffusion.
- JD = jump diffusion ($R_{||}/R_{\perp} = 1$).
- $\tau_{R||} = 1/4R_{||}$ for BD; $\tau_{R\perp} = 5/4R_{\perp}$ for JD.  $\tau_{R\perp} = 1/6R_{\perp}$ for BD.  $N = R_{||}/R_{\perp}$.

Figure 10. Theoretical spectra illustrating the sensitivity of slow-motional spectra (corresponding to the experimental spectrum at 42.2 K) of anisotropic Brownian rotational diffusion to the line width $1/T_{||}$ for $R_{||}$ (parallel to y axis) = $7.5 \times 10^{-6}$ s$^{-1}$ and $R_{\perp} = 7.5 \times 10^{-6}$ s$^{-1}$.

trends are found to be in the direction of worsening the agreement between experimental and theoretical spectra.

Theoretical spectra were calculated by using a moderate jump diffusion model ($R_{||}/R_{\perp} = 1$)$^{25,29}$ and the best-fitting parameters are given in Table II. In contrast to the cases of $O_2^{29}$ and the nitroxide radicals,$^{29}$ the theoretical line shape was not significantly changed from that of Brownian diffusion, although the $R_{||}$ obtained was different for the two models as seen from the table. The reason the line shape is not sensitive to the model is probably due to the particular values of the magnetic parameters for NO$_2$.

In fact, when $R_{||}$ was varied from 0.1 (weak jump) to 10.0 (strong jump) keeping $R_{\perp}$ constant, no significant differences could be seen in the simulations. Thus, these jump models offer no significant improvement in the line shape over the use of a Brownian diffusion model (cf. Figure 8A). The same comments apply to the approximate free diffusion model.

(2) NO$_2$ on Zeolite (Na–Zeolon). We have already noted that for this case the 4.7 and 77 K spectra can be satisfactorily simulated as being in the rigid limit, i.e., frozen on the ESR time scale. Motional effects on the spectrum are observed for $T \geq 120$ K. At 120 K, the NO$_2$ motion appears axially symmetric with the molecular y axis again the axis of faster motion, but the spectra become nearly isotropic with $1/2\tau_{R\perp}$ (based on a Brownian diffusion model). Also $1/2\tau_{R\perp}$ is already quite large at 250 K ($T_{\perp}^{-1} \approx 4$). No significant change of the line shape was observed for temperatures $T \geq 250$ K, but the intensity of the spectrum becomes weaker with increasing temperature, until it is no longer observable above 300 K.

IV. Discussion

We believe that our results for NO$_2$ dynamics on Vycor surfaces can best be understood in terms of two types of motions. The low-temperature motion (below 77 K) is dominated by anisotropic rotational motion of the NO$_2$ at a single surface site. The preferred axis for rotation is the molecular y axis. We estimate an “activation energy” (see below) for this motion to be $\approx 50 \pm 15$ kcal/mol for both $\tau_{R||}$ and $\tau_{R\perp}$ obtained from the Brownian rotational diffusion model. Above 77 K, the observed isotropic rotational motion is dominated by translational diffusion of the NO$_2$ to surface sites of different orientation (either by diffusion on the surface, or by gaslike “hops” between sites, or by collisions with NO$_2$O$_4$, cf. discussion below). We estimate an activation energy for this process to be $\approx 0.5 \pm 0.1$ kcal/mol from $\tau_{R\perp}$ (which, according to our model, must be decreasing more rapidly with increasing $T$ than $\tau_{R||}$ until both $\tau_{R\perp}$ become equal by the translational mechanism). Such a low activation energy for the translational diffusion process appears consistent with our observation that the NO$_2$ is only weakly physisorbed to the Vycor surface. In the case of NO$_2$ on Na–zeolon, rotation about the y axis appears only by 120 K, but by 250 K the rotation appears as isotropic implying the translational mechanism sets in at much higher temperatures and is consistent with NO$_2$ being more strongly physisorbed than on Vycor.

This interpretation is consistent with the observation of significant intrinsic line broadening as the temperature is raised especially since the broadening becomes less pronounced for the Na–Zeolon support at lower temper-
may be a primary source of broadening. The loss in [NO₂] adsorbed on the surface with increased temperature would imply that either dimerization to N₂O₄ is enhanced by increasing temperature and/or a reduced adsorption of NO₂ at the higher temperatures (which would be typical behavior).³⁶

We have found that the higher temperature spectra on Vycor can be satisfactorily simulated by an exchange mechanism replacing the increasing intrinsic T₂-E. We estimate an activation energy for such a process of about 0.4 ± 0.15 kcal/mol with an exchange rate of (1.0 ± 0.2) × 10⁵ s⁻¹ at 130 K. This activation energy is approximately the same as that obtained from the higher temperature rotational correlation times, and could imply that the NO₂, N₂O₄ exchange process is diffusion controlled.

This analysis implied that the exchange of NO₂ is with a species (e.g., N₂O₄) whose concentration remains substantially unchanged with temperature, or else one must correct the observed line broadening for the linear dependence of exchange on concentration. In the case of NO₂ on Vycor, if we assume a monolayer coverage of NO₂ and N₂O₄ on the surface, then even as [NO₂] is decreasing substantially with increasing temperature, it may be that the combined effects of (diffusion controlled) dimerization and the chemical exchange lead to approximately constant numbers of particles on the surface with which NO₂ can interact. Clearly further work is required to understand these matters.

We do wish to point out that the NO₂, N₂O₄ exchange process could be effective translation-collision mechanism for inducing what appears to be isotropic rotational reorientation.

Piaterak and Wood³ studied NO₂ on zeolites: Linde Type 10X (Ca²⁺ with ca. 9-Å channel size and Na⁺ with ca. 10-Å channel size). These also required high NO₂ pressures (>250 mmHg) in order to get appreciable ESR signals consistent with our Na-Zeolon results. Their conclusion on the observed motional dynamics analyzed by the older Monte-Carlo method can in current terms be stated as characteristic of isotropic Brownian diffusion. It is likely that they were observing the translational-type of mechanism discussed above, but further study is called for.

We come now to the discrepancies between theoretical and observed ESR spectra at the lower temperatures. These discrepancies are somewhat similar to those we previously observed in our study of O₂ adsorbed on Ti-Vycor surfaces, viz. the outer spectral lines in the slow-motional region were observed to be broader with unresolved detail compared to theoretical predictions.⁵⁹ The O₂ spectrum is, however, just a g tensor, but the loss in detail for our NO₂-Vycor spectra relate to averaging of the gₓ and gᵧ components. Thus it may be that a similar explanation, based on motional dynamics, could resolve the discrepancy for both cases. The possibilities mentioned for O₂ that should be considered here are as follows: explicit inclusion into the model of a surface-induced potential barrier to reorientation of the NO₂ and/or inclusion of coupling of the NO₂ motions to surface modes, i.e., surface polarization effects due to the van der Waals interactions of NO₂ with a local surface site. Also, to the extent that the electronic structure of NO₂ is modified by the surface, and this modification is modulated by the reorientation of NO₂ on the surface, one should consider how the values of the components of the g and A tensors (in the molecular frame in which they are defined) might change as a function of the orientation of NO₂ relative to the surface. We discuss below the extent to which the surface does modify these tensors. Last of all we recall that in our classical models we did not consider inertial effects, because previous work has indicated that they would lead to a pronounced sharpening of spectral features, which is the opposite of our observed discrepancies.

It was also pointed out in our O₂ study that it might be important to consider quantum mechanical effects on the motional dynamics of small molecules on the surface. These remarks are certainly appropriate for NO₂. The relevant gas-phase rotational constants, (i.e., A₁ = h²/2I₁) are well-known for NO₂ and are¹² 12.30 GHz (0.593 K) for Aₓ, 239.9 GHz (11.56 K) for Aᵧ, and 13.00 GHz (0.626 K) for A_z. These values, especially that for Aₓ, are much larger than the g and A tensors, so that a low-pressure gas-phase spectrum, even in magnetic fields of 3 kG and at 9-GHz frequencies, is dominated by the "quantum-mechanical averaging" of the g and A tensor anisotropies along lines we have already outlined for the simpler case of O₂. Also, the high-pressure, averaged ESR spectrum of gaseous NO₂ is well-known to be a simple triplet (with spacing of 132 MHz).⁴¹ Neither of these two limits is appropriate for the analysis of NO₂ surface spectra, especially those observed at low temperature, which are (nearly) rigid-limit results.

Instead, we proposed in our O₂ work that one should rewrite the quantum mechanics for rotational motion in terms of a "renormalized" moment of inertia tensor: 1 (and a corresponding Ḡ) as well as an effective potential V(0) in terms of the Euler angles 1 relating the orientation of the principal axes of inertia of NO₂ relative to the surface so that the rotational motion is described by an effective Hamiltonian yielding

\[ \sum_{i=x,y,z} \frac{L_i^2}{2I_i} + V(0)\Psi = E\Psi \]

in the absence of thermal relaxation with L_i the ith component of the angular momentum operator. In order to illustrate how significantly the interaction with the surface must modify the gas-phase constants we first consider the case of V(0) = 0, so the surface motion is free. Let us also consider just rotation about the molecular y axis since this corresponds to a very small moment of inertia (see above) and is the primary motion observed at low temperatures. In order to prevent complete quantum mechanical averaging of Aₓ with A₁ and gₓ and gᵧ we require a much increased Iᵧ (or decreased Aᵧ). Since gₓ - gᵧ is the smaller, we require, in order that these components not be averaged for the Mₓ = 0 band at 4.8 K that Aᵧ < βB₀(1/4)gₓ - gᵧ \approx 4.5 × 10⁻⁴ K, or Aᵧ must be at least 10⁴ times smaller than Aₓ. If we introduce a large barrier V(0) to rotation about the molecular y axis, then we would only require that Δₒ, the "tunneling" splitting of torsional sublevels of the ground torsional level, obeys nΔₒ < Iᵧ(1/2)(3/2)²/² for V(0) ≈ cos np. This may be more reasonable physically, although no ESR spectral evidence has been obtained for the classical-limiting model of coherent n-fold rotational jumps (cf. ref 26).

Either limiting surface quantum mechanical model could "explain" the residual motional effects detected at 4.8 K for NO₂-Vycor. In the case of free motion but a greatly reduced Aₓ there would be many thermally accessible

rotational $J$ levels each with its own effective $(g_y - g_z)$ and $(A_y - A_z)$ (actually the situation is even more complex, cf. ref 29), so there would be inhomogeneous broadening of the respective spectral regions. In the case of strongly hindered motion, $\Delta g_\| \parallel \frac{2\phi}{2\pi}$ would be very sensitive to local variations in surface-induced potential $\psi(\phi)$, and this can lead to site-to-site variation in apparent $(g_y - g_z)$ and $(A_y - A_z)$. Again this would be inhomogeneous broadening. The distinction between inhomogeneous vs. homogeneous broadening can, in principle, be made with electron spin-echo experiments and preliminary results do appear to be consistent with an inhomogeneous mechanism.42

The higher temperature onset of thermal relaxation can also be analyzed from a quantum mechanical approach.29 In summary, our point of view is that the ESR spectra are much closer to those characteristic of classical models than of gaslike quantum models, so that quantum corrections, if required, must be relatively small.

On the other hand, we do note that observations made by Brailsford and Morton21 on NO2 in alkali-halide crystals and Bojko and Silshee22 on NO2 in KCl showed quantum mechanical averaging about the molecular y axis even at 2 K. This is necessarily due to a vacancy site in the crystal with little effective rotational hindrance about this axis from the crystal potential. Our results for surface NO2-vycor are not of this type, although these previous observations suggest the possible importance of residual quantum effects. Bojko and Silshee22 find that the spin-rotational coupling is important in analyzing their ESR spectrum, but it is significantly reduced from the free molecule value probably due to the hindering potential. We now wish to consider any residual effects of the spin-rotational coupling on the surface NO2-vycor.

The spin-rotational interaction may be written as $J_{CS}$ where C is the spin-rotational coupling tensor which is quantized in the molecular frame $(x,y,z)$ and is accurately known for gaseous NO2.15 In the limiting case where only rotation about the molecular y axis is allowed it becomes $J_{CSy}$, with $C_{yyy} = 5.412$ GHz for the gas molecule, clearly a large interaction for 9-GHz spectroscopy. The dominant portion of C is known to result from the second-order perturbation cross term between the spin-orbit coupling $\lambda L$ and the electronic orbital-rotation coupling $L \cdot \mathbf{A} \cdot \mathbf{J}$, which leads to the relation $C = -2\Delta g g_y - \Delta A_{y}$. [In fact $(g_{yy} - g_{zz}) = -0.0113$ while $C_{yy}/2A_{yy} = -0.01128$ for the gas molecule, or especially good agreement.]43 If we use the limiting surface model of a free rotor ($\Psi_{\infty} = 1/(2\pi)^{1/2}e^{i\phi}$) with renormalized $\mathbf{A}$, then the free rotor states will have a diagonal contribution: $mC_{yy} \cos \theta \mathbf{S}_y$ (and nonsecular term: $mC_{yy} \sin \theta \mathbf{S}_y$) where $\theta$ is the angle between the z axis and molecular y axis. However, we must use a reduced $C_{yy} \approx -2\Delta g g_y \leq 0.2$ MHz (or $1 \times 10^{-5}$ K) due to the surface renormalization of $\mathbf{A}$, and it becomes of negligible importance to the ESR spectrum. In a similar manner, one may consider the other limiting case of a highly hindered rotor (i.e., a large $V_J/(2\hbar^2)$). Here $J_{CSy}$ can only connect different torsional levels separated by $\Delta E_\| \approx nh \langle V_a \rangle^{1/2} (since J_y = i-(\hbar/\partial \phi))$, so it will be unimportant for $\Psi_{\infty}(\phi)$ very large. Also, the secular term (which must be at least as important as the nonsecular term) is unimportant for $\theta = \pi/2$, which corresponds to the excessively broadened x and z components.

Finally, we note that the spin-rotation mechanism is independent of nuclear-spin quantum number, so that it cannot explain the low temperature discrepancies most prominent for the $M_I = \pm 1$ bands.44

It would be of interest to know the orientation of the NO2 on the surface, i.e., is the molecular y axis perpendicular or parallel to the surface, when rotation is largely about the y axis? Based upon our results we favor the parallel orientation. This is because the y axis perpendicular to the surface (i.e., NO2 “standing up” but weakly bonded via a single oxygen atom) would present a minimum of surface hindrance to reorientation about this axis (viz. only a small increase in $I_y$) while for y parallel to the surface there should be considerable interference of the surface with the motion, since a rotation about $\phi$ would alternately bring NO2 flat on the surface and either the N atom or the two O atoms nearer the surface. Thus, for the perpendicular orientation a gaslike rotation would be expected and is contrary to our above discussion, while for a parallel orientation that motion is likely to be dominated by surface interactions and is more consistent with our discussion.

Clearly studies with 18O-labeled NO2 would be helpful in distinguishing the two possibilities (Brailsford and Morton21 did find equivalent 17O’s for NO2 in KCl) as would studies on oriented single-crystal surfaces.

We note that Iwaisumi et al.11 have observed similar temperature-dependent ESR line shapes for NO2 adsorbed on a silica gel surface above 77 K, and they concluded from their axially symmetric A and g tensors at 77 K that NO2 rotates about the y axis, consistent with our observation. They infer from this that $\psi$ is perpendicular to the surface, since that would allow rotation about this axis. Our analysis, as we have discussed, suggests that the motion would then be too unrestricted! There is, in fact, some indirect evidence for a preferential orientation of NO2 such that the plane of the molecule is parallel to the surface. Kasi et al.45 have found that when NO2 is trapped in a Neon matrix at 4 K formed by depositing the neon on a flat rod, the NO2 tends to align parallel to the surface. They suggest that the surface of the oriented matrix might “dictate the orientation of planar molecules impinged upon it.” If we compare the $\Delta A_y \approx A_y - a_{yy}$ given in Table I for neon matrix vs. the gas (for which $\Delta A_y \approx \Delta A_y$), then we find $\Delta A_y$ remains virtually unchanged while $\Delta A_y$ and $\Delta A_z$ are reduced in magnitude from $-18.7$ to $-3.4$ MHz (for $A_z$), and from $+38.5$ to $24.4$ MHz (for $A_y$). We take this as the effect of van der Waals forces of the neon layers above and below

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(44) The effect of spin rotation in the “classical” limit may also be considered. It seems appropriate to consider a model of slow rotational reorientation, but where angular momentum relaxation can still occur. In the case of unhindered axial rotation about the molecular y axis the expressions of Goldman et al. [J. Chem. Phys, 58, 3071 (1973)] become

$$T_{1,\text{SR}}^{18\text{N}} = T_{1,\text{SR}}^{(\text{sec})} + \frac{\gamma}{4} T_{1,\text{SR}}^{18\text{N}}$$
$$T_{1,\text{SR}}^{14\text{N}} = \frac{kT}{A_{yy} C_{yy} \sin^2 \theta \tau_{xy} (1 + \omega_{xy}^2 \tau_{yy}^2)^{-1}}$$

which are seen to be independent of $I$ for a Brownian model where the angular momentum relaxation time $\tau_{xy} = I_{zz}/\tau_\|$, with $\omega$ the friction coefficient (provided $\omega_{xy}^2 \tau_\| < 1$ or else $\omega_{xy}^2 \tau_\| > 1$ to $T_{1,\text{SR}}^{18\text{N}} \ll T_{1,\text{SR}}^{(\text{as})}$). Again we see that $T_{1,\text{SR}}^{18\text{N}}$ can only significantly broaden the y components of the spectrum and $T_{1,\text{SR}}^{14\text{N}}$ is nuclear spin independent, both inconsistent with “explaining” our discrepancies. [Note also, the quantum-classical correspondence for spin-rotational motion may have to be fully explored.] However, the $M_I$ independence of $T_{1,\text{SR}}^{18\text{N}}$ is not inconsistent with the higher temperature broadening observed, which we believe is more likely due to chemical or spin exchange.

(45) Preliminary efforts using NO2 prepared from N16O and O18 enriched with approximately 20% 18O yielded a spectrum with broader widths and no 18O label could be clearly distinguished at 77 K. It seems clear that NO2 highly enriched with 18O should be used in any future work.
the NO$_2$ plane. For NO$_2$-vycor, $\Delta A_y$ is again virtually unchanged while $\Delta A_z = -18.7$ and $\Delta A_y = +32.8$, or the same trends as for neon but less pronounced. This is to be expected for NO$_2$ above the surface rather than sandwiched between layers. (We note that the molecular orbital analyses rely on configuration interaction to interpret the inequality of $\Delta A_y$.) Last of all, we wish to comment that, as the NO$_2$ molecule adsorbed on Vycor displays a predominantly axial rotation about the y axis (parallel to the O–O internuclear axis) below 77 K but above this temperature the motion becomes more nearly isotropic probably due to a translational diffusion mechanism. The line shape analysis is reasonably consistent with this picture, except for some discrepancies in detail for 77 K and below, which are worthy of further study. From consideration of quantum models for the rotation, it is suggested that this y axis aligns parallel to the surface, but further work with $^{18}$O labeling is recommended.

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Temperature and Density Dependence of the Proton Lifetime in Liquid Water

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The NMR $T_{1p}$ technique is developed to determine the average residence time, $\tau_w$, of a proton on a water molecule in liquid water. The temperature and density dependence of $\tau_w$ is measured in the range 0–100 °C and at densities up to 1.25 g cm$^{-3}$ (pressure range, 1 bar to 5.6 kbar). The $T_{1p}$ technique is compared to other NMR methods such as the $T_1$ and $T_2$ techniques also used to determine $\tau_w$. The anomalous behavior of $\tau_w$ with compression at temperatures below 40 °C parallels changes in other physical properties of liquid water.

Introduction

Ever since Meiboom's original paper, there has been considerable effort to determine the rate constants governing proton transfer between H$_2$O$^+$ ($k_1$) and OH$^-$ ($k_2$) ions and neutral water molecules. However, a review of the literature since 1961 reveals that the values of $k_1$ and $k_2$ and the corresponding activation energies for these rates are still in dispute. More recently, work has centered on the measurement of the average time that a proton spends on a water molecule ($\tau_x$) in bulk neutral water and in occluded water. Woessner$^7$ has measured $\tau_x$'s for preferentially ordered water molecules in minerals and porous clays. Pintar et al.$^8$ have determined $\tau_x$ values for bulk neutral water from NMR spin–spin relaxation ($T_2$) measurements, and Noack et al.$^9$ have determined $\tau_x$ by using the field-cycling technique to measure spin–lattice relaxation ($T_1$) at very low $H_2$O fields. In this work we present the first direct application of NMR spin–lattice relaxation measurements in the rotating frame ($T_{1p}$) to determine the temperature and density dependence of $\tau_w$.

Meiboom$^1$ has shown that the Bloch equations modified for proton exchange may be solved provided certain assumptions are made. For our experimental conditions these assumptions are valid, and the expression relating the proton lifetime to the difference in relaxation rates is

$$\frac{1}{T_{1p}} - \frac{1}{T_1} = \tau_x \sum_i \frac{P_{ij}^2}{1 + \tau_x^2 (\delta_{ij}^2 + \omega_i^2)}$$

(1)

where $\tau_w$ is the average time that a proton is bonded to a given oxygen atom, $P_{ij}$ is the relative intensity of the $i$th