ON THE LINE SHAPE PROBLEM OF PROTON RESONANCE SPECTRA OF HYDROXYL GROUPS ON SOLID SURFACES

D. FREUDE, D. MÜLLER and H. SCHMIEDEL
Sektion Physik der Karl-Marx-Universität Leipzig, NMR Labor,
Linnéstrasse 5, 701 Leipzig, D.D.R.

Received 17 September 1970

In this paper it is shown how, in contrast to the conventional method of moments, one can get detailed information about the geometrical arrangement of hydroxyl groups on solids by analyzing the nmr line shape. Generally the calculations of line shapes are very complicated. In the first part it is demonstrated that in some special cases the line shape function can be calculated exactly. Line shapes calculated according to a statistical distribution of the spins in a volume or on a plane are not in agreement with experimental results for silicagel and for decationated Y-zeolites. The modification of the statistical model proposed in this work allows one to explain the line shape of the structural hydroxyl groups of the zeolites satisfactorily. In the case of decationated Y-zeolite the analysis shows that the hydroxyl groups exist mainly in pairs with an inner proton-proton distance of 3.7 Å. The mean distance, calculated in the usual way from the second moment (2.7 Å), does not correspond to a geometrical structure.

1. Calculation of nmr-line shapes of solids

In stationary techniques without saturation the observed absorption signal of the nuclear magnetic resonance is described by a line shape function, \( f_0(\omega) \), which is the Fourier transform of the transverse relaxation function \( G_0(t) \):

\[
    f_0(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\omega t} G_0(t) \, dt. \tag{1}
\]

If the spins are fixed in space (i.e. \( \Delta \omega \tau_c \gg 1 \) with \( \Delta \omega \) as linewidth of the nuclear resonance absorption line and \( \tau_c \) as correlation time of the magnetic interaction energy of the nuclei) and exposed to a strong constant magnetic field \( \mathbf{H}_0 \), the relaxation function in the case of pure dipole-dipole interaction of the nuclei the expression

\[
    G_0(t) = \frac{1}{Z} \text{Tr}\{\exp(-it\mathbf{\mathcal{H}}) I_x \exp(it\mathbf{\mathcal{H}}) I_x^\dagger\} \cos(\omega_0 t) = G(t) \cos(\omega_0 t) \tag{2}
\]
results\textsuperscript{2}). \( I_x \) denotes the \( x \)-component of the operator of the angular momentum, \( \omega_0 = -\gamma H_0 \) the resonance frequency (\( \gamma \) is the gyromagnetic ratio), and
\[
\mathcal{H}_x = \sum_{j<k} B_{jk} (I_j I_k - \frac{1}{2} I_j I_k) \tag{3}
\]
is Van Vleck's truncated dipole operator with the structural parameters
\[
B_{jk} = (3\gamma^2 h^3 / 2r_{jk}^3) (1 - 3 \cos^2 \theta_{jk}).
\]
Here \( r_{jk} \) denotes the distance of the nuclei \( j \) and \( k \), and \( \theta_{jk} \) is the angle between the connecting vector \( r_{jk} \) of the nuclei and the magnetic field \( H_0 \). Thus the line shape function essentially depends on the quantities \( B_{jk} \) describing the geometrical arrangement of the nuclei. A calculation of the relaxation function according to eq. (2) is possible only in very simple cases. The structural parameters \( B_{jk} \) are proportional to \( r_{kk}^3 \), and therefore it is often sufficient to consider only the nearest environment in the calculation of the line shape function.

A good approximation for the relaxation function is (see e.g. ref. 3)
\[
G(t) = \frac{1}{N} \sum_{k \neq j} \prod_j \cos(\frac{1}{2} B_{jk} t), \tag{4}
\]
which follows from eq. (2) by neglecting the scalar terms in the operator of eq. (3).

Van Vleck's expression for the second moment is often used to get information about the geometrical arrangement of the nuclei from the measured nuclear magnetic resonance spectra. In the case of \( N \) protons this expression is
\[
M_2(G^2) = 358.1 \frac{1}{N} \sum_i \sum_{k \neq i} r_{ik}^{-6} (\AA^{-6}) \equiv 358.1 \ r_{m}^{-6} (\AA^{-6}), \tag{5}
\]
where \( r_{ik} \) are the distance of all neighbours of one spin \( i \). In this equation a mean distance between the spin is introduced. This mean distance can be interpreted by different models, and it is difficult to get detailed information about the geometrical arrangement of the nuclei from an analysis of the second moment only. Therefore a line shape analysis seems helpful to reduce the remaining models after using the method of second moments. For that purpose, however, it is necessary to calculate the line shape for the different models.

In some cases of practical interest this is indeed possible: Assuming for instance that the spins are quasi-independent from the orientations of the other spins [this case corresponds to neglecting the scalar terms in eq. (3)], and assuming that all distances from zero to infinity between one spin and
its nearest neighbours occur with the same probability, a Lorentzian line results (if very small distances are excluded, the line will decay faster on the tails) with a peak-to-peak line width

$$\delta H(G) = 123.8n(\text{Å}^{-3})$$

for protons: here $n$ denotes the spin density. With real systems a linear correlation between linewidth and spin density can be used as a condition for the validity of the assumptions. The calculation carried out in ref. 2 is valid for magnetically diluted systems with nuclei distributed at random, since in this case it is a reasonable approximation to take into account only the nearest neighbour of a spin and for a two spin system the scalar term in (3) is without influence.

If the spins are distributed at random in a plane (not in a volume) we get instead of a Lorentzian line the more complicated function

$$f_\theta(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \exp(i\omega t) \exp \left[ - n_\tau Z \alpha(\vartheta) t^4 \right],$$

with

$$Z = \frac{1}{4} \Gamma \left( \frac{1}{4} \right) \left( \frac{3}{2} \right)^{1/2},$$

$$\alpha(\vartheta) = 4 \int_0^{+n} d\varphi (1 - 3 \sin^2 \vartheta \cos^2 \varphi)^4,$$

and the plane density

$$n_\tau = n_\tau / F_v.$$

Here $n_\tau$ is the volume density and $F_v$ is the specific surface per unit volume; $\vartheta$ denotes the angle between the normal $n$ of the plane and the magnetic field $H_0$.

In order to see how, in this case, the line width depends on the density $n_\tau$ we note that the below relation follows from eq. (7)

$$f_\theta(\omega) = \left( 1/n_\tau^4 \right) f_\theta^{(1)}(\omega/n_\tau^4),$$

where $f_\theta^{(1)}(\omega)$ is the line shape for unit plane density. If $\Delta_1$ and $\Delta_{n_\tau}$ are the half widths of $f_\theta^{(1)}(\omega)$ and $f_\theta(\omega)$ respectively one gets from eq.(11) that

$$\Delta_{n_\tau} = n_\tau^4 \Delta_1.$$

This means that the line width increases with $n_\tau^4$.

If there are isolated two spin systems in the three-dimensional space, the resultant line shape results after averaging the orientations of the single pairs in the volume. Every single pair produces a doublet splitting with infinite
narrow lines. By considering the interaction of the pairs among each other these single lines are broadened.

Assuming a random, statistical distribution of the two spin systems with a mean distance of the pairs among each other, which is much greater than the distance between the protons of one pair, a calculation shows, that the single line of a doublet is approximately a Lorentzian line with the linewidth given by eq. (6) using \( n \) for the density of the spin pairs. The resulting line shape is given by the following equation:

\[
f(\omega) = \sum_k p_k(r_k) g(\omega, r_k),
\]

with

\[
g(\omega, r_k) = \int_0^\pi d\theta \left\{ \frac{\sin \theta}{1 + \left[ \omega - \omega_0 - \frac{1}{2}(\gamma^2 \hbar/r_k^2)(1 - 3 \cos^2 \theta) \right]^2 T_2^2} \right. \\
+ \left. \frac{\sin \theta}{1 + \left[ \omega - \omega_0 + \frac{1}{2}(\gamma^2 \hbar/r_k^2)(1 - 3 \cos^2 \theta) \right]^2 T_2^2} \right\}. 
\]

Here \( \theta \) denotes the angle between the vector describing the relative positions of the nuclei and the magnetic field, \( r_k \) is the distance between the nuclei of one pair, \( p_k \) is the relative number of two spin systems with a distance \( r_k \), and \( T_2 \) is the inverse linewidth of the single line of a doublet. \( f(\omega) \) in eq. (13) is not normalized. The integral can be solved analytically. By using assumed values of \( p_k(r_k) \) it is possible to calculate the values of the function \( f(\omega) \) for different \( \omega \).*

2. Experimental results and discussion

Hydroxyl groups occur on surfaces of silicagel, \( \gamma \)-alumina, in the lattice of decationated zeolites and other adsorbents. Decationated zeolites show an acidic catalytical activity. Therefore the structural hydroxyl groups of these zeolites are of special importance.

We studied the proton resonances on silicagel and on decationated Y-zeolites using a wide-line spectrometer of the bridge type (KRB 35, Akademiewerkstätten Berlin) at 21 MHz. To avoid saturation, only weak rf fields (0.1 to 0.3 mG) could be used since the longitudinal relaxation times of the hydroxyl groups were about 10 to 20 sec in our case. Due to the low signal-to-noise ratio for each curve several spectra with a sweep time of about 40 min per spectrum had to be accumulated for obtaining line- * Muromzev et al.*) calculated on a computer some esr-line shapes arising from a superposition of doublets of different distances. For the two spin distances a Gaussian distribution was assumed.
widths and intensities with an error of less than 5% and second moments with an error of less than 10%. Proton densities were determined by comparison with aqueous solutions of manganese. All samples were pumped down for 10 hr at the corresponding pretreatment temperature. As the line shape did not vary over the temperature range from liquid nitrogen to 100°C the measurements could be carried out at room temperature.

2.1. HYDROXYL GROUPS ON SILICAGEL

Samples of a porous silicagel (specific surface 600 m²/g) calcined at 500°C followed by rehydration at 100°C and evacuation at different temperatures showed line shapes, which can be described by Lorentzian lines within the interval of the threefold linewidth. Second moments were determined from the signal in the field range of a fivefold distance between slope extrema. At the boundaries of this range the signal had decayed to zero. Table 1 shows the dependence of the results on the pretreatment temperature of the samples: \( n_{\text{max}} \) is the maximum density of isolated hydroxyl groups (4.7 OH-groups per 100 Å²). This value results assuming that the OH-groups are attached to all points of a regular plane lattice of the surface silicon atoms, which consists of equilateral triangles with edges of 4.96 Å. Then \( n/n_{\text{max}} \) represents the relative number of surface silicon atoms connected to hydroxyl groups. \( r_m \) was calculated from eq. (5).

<table>
<thead>
<tr>
<th>Pretreatment temperature (°C)</th>
<th>Proton density ( n ) (protons/100 Å²)</th>
<th>Second moment ( W ) (G²)</th>
<th>( n/n_{\text{max}} )</th>
<th>( r_m ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>4.1</td>
<td>0.12</td>
<td>0.87</td>
<td>3.8</td>
</tr>
<tr>
<td>300</td>
<td>0.12</td>
<td>0.10</td>
<td>0.62</td>
<td>3.9</td>
</tr>
<tr>
<td>500</td>
<td>0.87</td>
<td>0.05</td>
<td>0.26</td>
<td>4.4</td>
</tr>
<tr>
<td>700</td>
<td>3.8</td>
<td>0.017</td>
<td>0.15</td>
<td>5.3</td>
</tr>
</tbody>
</table>

As the line width \( \delta H \) is proportional to the square root of the second moment, one can see from table 1 that \( \delta H \) is proportional to \( n^2 \). This is in contrast to the linear correlation between \( \delta H \) and \( n \) which was derived [cf. eq. (6)] for a three-dimensional statistical distribution of the spins. For a two-dimensional arrangement still worse agreement results. Therefore an arrangement of protons with spin-spin distances distributed at random does not exist for these hydroxyl groups. To interpret the \( r_m \) value from the second moment, we must use assumptions about the structure of the
silicagel surface. According to De Boer\(^5\) there are small regions where the surface silicon atoms build up a plane lattice consisting of equilateral triangles with edge lengths of 4.96 Å. Due to the Si–O–H angle of 113° according to Peri\(^6\) and an O–H distance of about 1 Å for the protons of OH-groups on two 4.96 Å distant surface silicon atoms, distances between 3.2 Å and 6.76 Å result. With the great number of allowed proton distances it is impossible to derive a specific model for the arrangement of the hydroxyl groups using only the value of the second moment. However, from the \(r_m\) distances in table 1 it can be concluded that only isolated hydroxyl groups exist (at most one OH-group on one surface silicon atom) and that the occupation density of the possible sites for isolated hydroxyl groups decreases with increasing pretreatment temperature.

It is possible that because of the high calcining temperature of the silicagel in spite of the rehydration no paired and neighboured hydroxyl groups exist\(^5\), which have a smaller distance than the isolated OH-groups and therefore a smaller \(r_m\) had to result.

### 2.2. Structural Hydroxyl Groups on Decationated Zeolites

Some results of proton resonance measurements on decationated Y-zeolites as a function of the degree of decationation are given in table 2: \(r_m\) denotes a mean distance calculated from the second moment according to eq. (5); \(r_n\) is the distance determined by the spin density assuming a regular cubic lattice.

<table>
<thead>
<tr>
<th>Degree of decationation (%)</th>
<th>Spin density (OH groups per cubo-octahedron)</th>
<th>(r_n) (Å)</th>
<th>(\delta H) (G)</th>
<th>(M_2) (G(^2))</th>
<th>(r_m) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.5</td>
<td>10.5</td>
<td>1.1</td>
<td>0.7</td>
<td>2.8</td>
</tr>
<tr>
<td>50</td>
<td>3.0</td>
<td>8.7</td>
<td>1.2</td>
<td>0.7</td>
<td>2.8</td>
</tr>
<tr>
<td>75</td>
<td>4.5</td>
<td>7.4</td>
<td>1.4</td>
<td>0.85</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The sodium form of the Y-zeolite (showing only a weak, negligible proton signal due to surface hydroxyl groups) was treated with ammonium ions. So the given degree of decationation represents the percentage of Na\(^+\)-ions replaced by NH\(_4^+\)-ions. By pretreatment of the samples at 300 °C, the ammonium ions decompose into NH\(_3\) and protons, the latter entering the lattice to form OH-groups. The linear correlation of eq. (6), between the experimental linewidths and the spin densities, does not occur. The same can be observed, if the spin density is varied by pretreatment temperature.
and not by the degree of decationation. As for silicagel it is not possible to draw further conclusions from the results shown in table 2. Therefore an analysis of the line shape is necessary. Regarding the structure of the zeolite and the values of $r_m$ and $r_n$, we conclude that there exist predominantly two spin systems. The influence of the remaining pairs on a two spin system can be approximated by a statistical broadening of the single lines of the doublet. According to eq. (6) the linewidths of the single lines were determined using the experimental spin densities. The line shape functions $g(\omega, r_k)$ were calculated according to eq. (14) for discrete $r_k$ (in steps of 0.3 Å from 2.0 to 5.1 Å).

Fig. 1 shows some doublet line shape functions for different values of $r_k$.

![Fig. 1. Calculated line shape functions $g(\omega, r_k)$ for different two spin distances $r_k$. Here $\omega = \gamma H$.](image)

The theoretical curves were fitted to the experimental line $G_{\text{exp}}$ using the method of least squares considering all the calculated $g(\omega, r_k)$:

$$\sum_{i=1}^{m} \left( \sum_{k=1}^{n} |c_k| g(\omega_i, r_k) - G_{\text{exp}}(\omega_i) \right)^2 \to \text{minimum},$$

whence $|c_k|$ can be determined. Fig. 2 shows the results for 75% and 25% exchanged Y-zeolites. For the 75% case the experimental curve can be explained assuming 94% two spin systems with a distance of about 3.7 Å and 6% of two spin systems with distance of 5.1 Å. For the 25% case we
have 87% two spin systems with a distance of 3.7 Å and 13% two spin systems with a distance of 5.1 Å. The error in determining the coefficients $|c_4|$ is about 5%. Since the line shape functions were calculated for discrete two spin distances only, a distribution of the radii around 3.7 Å cannot be excluded. However, the width of such a distribution must be less than 0.3 Å.

![Fig. 2. Line shape of hydroxyl groups in decationated Y-zeolites. (---) experimental curve for a 25% decationated Y-zeolite, (□) calculated curve fitted by the method of least squares. (—-) experimental curve for a 75% decationated Y-zeolite, (●) calculated curve fitted by the method of least squares.

The distances determined by this procedure essentially differ from the apparent distances $r_m$, which were derived from eq. (5) (see table 2). For instance for the 50% decationated sample an $r_n$ of about 9 Å results. Using distances distributed at random the probability of finding another proton in a volume with a radius of about 4.5 Å around the center of the two spin system is $(4.5/9)^3 = \frac{1}{6}$. This is the probability for the occurrence of three spin systems. Four spin arrangements are less frequent. Nevertheless they contribute more to the value of the second moment than the dominant two spin systems.

In contrast to other authors\(^8\)), we had no indications of different arrangements of hydroxyl groups or residual water. To separate the measured spectrum into a component resulting from the residual water and a component due to hydroxyl groups, it is necessary to assume that the magnetic interaction between the hydroxyl protons and the water protons is small compared with the interaction between hydroxyl–hydroxyl protons, and the interaction between protons of water. This is not correct, for instance, in the case of hydrogen bonding between water and a hydroxyl group. Moreover,
for such a separation there are experimental limits given by the accuracy of the measurement. Thus in the case of the simultaneous measurement of two line shape derivatives, with linewidths different, e.g., by a factor of 10, the modulation amplitude is limited by the demand for an unfalsified recording of the narrow line and the signal-to-noise ratio (SNR) is \[\text{hundred times worse for the broad line than for the narrow line.}\]

Unfortunately for the narrow line during a measuring time of one hour one only obtains a signal-to-noise ratio of less than 100 because of the long longitudinal relaxation times of the hydroxyl groups and their low density. Accumulation times in the order of days are necessary to obtain a SNR of 20 for the broad line, which is the minimum condition for an evaluation. Therefore a satisfactory separation of an ice line of residual water from a narrow line of hydroxyl groups is experimentally impossible.

A separation into different lines and attributing them to different regions of OH-groups, as was done in ref. 9, is not correct because there is no justification for assuming that the line shape of a single region is Gaussian. For instance, our experimental line shape can also be separated into two Gaussian lines, and from their second moments two apparent distances of 2.6 Å and 3.0 Å could be determined. These distances, however, have no geometrical significance.

Further details and a discussion concerning the nmr results on decationated Y-zeolites will be given in ref. 7.

Acknowledgments

We thank Prof. H. Pfeifer for his helpful discussions.

References

4) V. I. Muromzhev, V. V. Pomorzev and V. N. Kharitonova, Fiz. Tverd. Tela 10 (1968) 2462.
7) D. Freude, D. Müller and H. Schmiedel, in press.