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Wide-Band Proton NMR Study of a New Hydrate $WO_3 \cdot \frac{1}{3}H_2O$ in the Powder Form

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The proton NMR of a new hydrate $WO_3 \cdot \frac{1}{3}H_2O$ as a powder was studied between −140 and 100°C. The lattice can be considered as "rigid" at temperatures below −80°C. The structural water corresponding to the above formula is coordinated in the form of water molecules. Above −80°C it undergoes thermally activated hindered rotation. The compound also retains adsorbed surface "water," partly in the form of strongly bonded OH groups, partly in the form of water molecules. Degassing at 175°C and 10^{-4} Torr removes the adsorbed molecular water but leaves OH groups bonded to the surface.

Introduction

One of us recently prepared a new hydrate of tungsten oxide, of general formula $WO_3 \cdot \frac{1}{3}H_2O$. This was characterized by various methods and an X-ray diffraction study on the powder gave the mean structure (*1*). This study of $WO_3 \cdot \frac{1}{3}H_2O$ reveals a certain number of problems concerning the water: in addition to the structural water one observes large amounts of adsorbed water strongly bonded to the solid. It cannot be completely desorbed even by vacuum treatment at 175°C nor in a current of inert gas at 200°C, which makes it difficult to obtain dry $WO_3 \cdot \frac{1}{3}H_2O$. Moreover, the compound may be assigned the formula $H_2W_3O_{10}$ or $WO_3 \cdot \frac{1}{3}H_2O$; ir study tends to show that the latter is more likely (*1*).

For these reasons we undertook the NMR study of this compound in order to obtain additional information about the structural and adsorbed water.

Experimental Section

Two types of $WO_3 \cdot \frac{1}{3}H_2O$ samples were studied (*1*): first, a powder consisting of microcrystals in the form of aggregates of fine needles about 200 nm long and 20 nm wide, with a specific area of 22 $m^2\ g^{-1}$; second, a sample consisting of octagonal platelets measuring about 1 nm, with a specific area of 3.5 $m^2\ g^{-1}$. The samples will be denoted A and B, respectively.

NMR spectra were recorded on samples submitted to desorption treatment or not. The untreated sample A will be denoted A_n and more generally the temperature at which the sample was degassed under a vacuum of 10^{-4} Torr will be indexed. The sample compositions are given in Table I.

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TABLE I

NUMBER OF TOTAL H_2O EQUIVALENTS PER WO_3 GROUP CONTAINED IN THE SAMPLES FROM THERMOGRAVIMETRIC MEASUREMENTS

A_n	A_{20}	A_{175}	B_{160}
0.6	0.45	0.36	0.34

The apparatus used was a Bruker CXP operating at 95 MHz. The signal was obtained from 100 free induction decays accumulated every 0.7 sec with a dead-time of 10 μsec. The Fourier transform spectrum was recorded without saturation. The powder samples were contained in 10-mm-diameter tubes. The probe signal was subtracted.

The experimental spectra are simulated by calculated spectra. In this work the spectra are calculated on the basis of two models whose normalized and weighted contributions are summed.

The first of these models is the magnetic configuration with two $\frac{1}{2}$ spins "in a rigid lattice" calculated by Pake (*2*) and denoted D. If R is the distance between these two spins, the interaction $\alpha = 3\mu/2R^3$, where μ is the magnetic moment of the proton, defines the scale of the abscissa of the spectrum calculated for this configuration. An NMR absorption of the D configuration, assuming these two spins groups to be isolated and oriented isotropically, is broadened by a gaussian function with a parameter β to allow for magnetic interactions between spins belonging to different groups. We shall write β in a form analogous to α, i.e., $\beta = 3\mu/2X^3$; X then gives an idea of the value of the shortest distances between spins not belonging to the same group. Clearly X must be greater than or at least equal to R for the model to have any physical meaning.

The second model used here is that of an absorption of Lorentzian form, denoted L. This absorption is characterized by the half-width of the absorption curve at the half-height; ΔH.

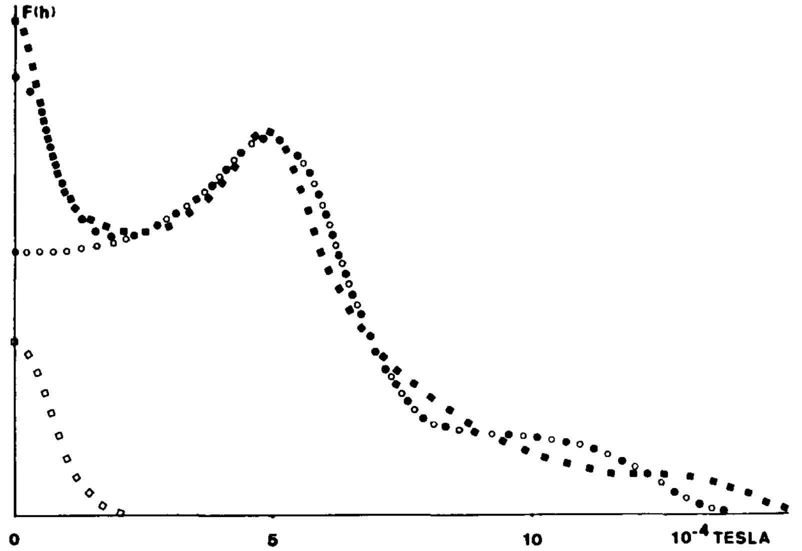

FIG. 1. Absorption curves for A_{175} sample at −90°C; solid squares: experimental spectrum; solid dots: computed curve; open dots: weighted computed contribution of configuration D_1; open squares: weighted computed contribution of configuration D_2.

The weighing coefficient of the *i*th model is given as w_i, where $\Sigma w_i = 1$.

In the most complicated cases considered here the calculated spectra involve two types of D configurations and one L form; the whole requires seven independent parameters including two weighing coefficients.

The calculated spectrum describing an experimental spectrum corresponds to least-squares minimization of the differences between the spectra (Newton coefficients method). The figures show only half of the curves thus obtained, the small errors in the symmetry of the experimental spectra being averaged.

Results

Sample A_{175} was studied by NMR at temperatures between −140 and 100°C. Between −140 and −80°C the same type of spectrum is observed and it can be assumed that the "rigid lattice" approximation is valid; Fig. 1 gives this "rigid lattice" spectrum of A_{175}. It can be described in terms of two configurations, D_1 and D_2. The corresponding values of the parameters are given in Table II. Ninety-three percent of the protons are in D_1 groups, where the distance $R_1 = 0.152$ nm is characteristic of water molecules, X_1 being about 0.30 nm. The contribution to the spectrum of the remaining 7% of the protons is no longer a doublet but a singlet that we describe with a D configuration as did Porte *et al.* for this type of contribution (*3–6*). The parameter values R_2 and X_2 found for this D_2 configuration lie between 0.33 and 0.4 nm. The "rigid lattice" condition being fulfilled, such large values show that the corresponding protons belong unambiguously to OH groups. What are then the relative positions of the water molecules and the OH groups between which the protons of A_{175} are distributed? Comparison of the β parameters of the gaussian broadening functions gives some

TABLE II

PARAMETER VALUES FOR THE CALCULATED SPECTRA

			D_1					D_2					D'_1				L	
Sample	Temperature (°C)	Model	w_{D_1} ±0.01	R_1 (nm) ±0.003	X_1 (nm) ±0.01	α_1 (10^{-4} Tesla)	β_1	w_{D_2} ±0.01	R_2 (nm) ±0.01	X_2 (nm) ±0.01	α_2 (10^{-4} Tesla)	β_2	$w_{D'_1}$	R'_1 (nm)	X'_1 (nm)	α'_1 (10^{-4} Tesla)	w_L ±0.01	ΔH (10^{-4} Tesla) ±0.03
A_{175}	−140	D + D	0.93	0.152	0.30	6.02	0.78	0.07	0.34	0.40	0.54	0.33						
A_{175}	−122	D + D	0.94	0.153	0.29	5.90	0.87	0.06	0.39	0.39	0.36	0.36						
A_{175}	−90	D + D	0.93	0.151	0.28	6.14	0.96	0.07	0.33	0.365	0.59	0.43						
A_{175}	−80	D + D	0.93	0.152	0.265	6.02	1.14	0.07	0.345	0.395	0.51	0.34						
A_{175}	−50	D + D + L	0.78	0.157	0.30	5.47	0.78						0.14	0.215	0.29	2.13	0.08	0.4
A_{175}	20	D + D + L	0.70	0.156	0.295	5.56	0.82						0.22	0.215	0.29	2.13	0.08	0.3
A_{175}	100	D + D + L	0.60	0.156	0.31	5.56	0.71						0.33	0.20	0.305	2.64	0.07	0.25
A_{20}	−140	D + D	0.95	0.154	0.26	5.79	1.20	0.05	0.325	0.325	0.62	0.62						
A_{20}	20	D + D + L	0.56	0.152	0.29	6.02	0.87						0.15	0.25	0.28	1.35	0.29	0.38
A_n	−140	D + D	0.97	0.154	0.233	5.79	1.67	0.03	0.325	0.325	0.62	0.62						
B_{160}	−140	D + D	0.97	0.155	0.31	5.68	0.71	0.03	0.39	0.39	0.36	0.36						

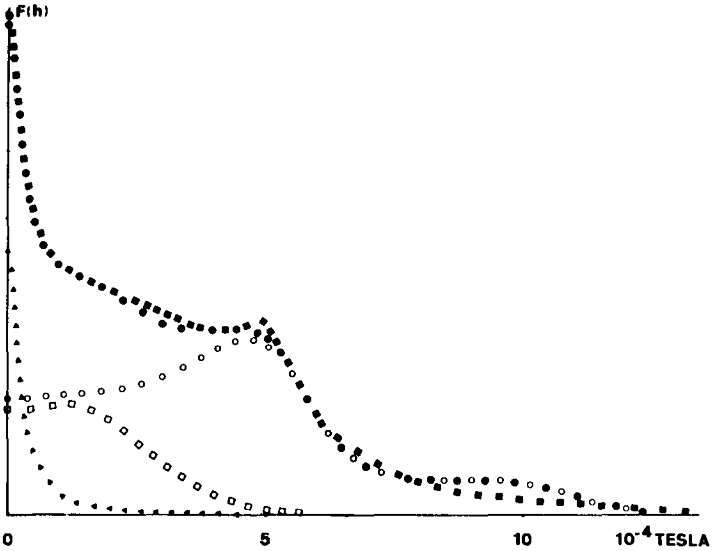

FIG. 2. Absorption curves for A_{175} sample at +20°C; solid squares: experimental spectrum; solid dots: computed curve; open dots: weighted computed contribution of configuration D_1; open squares: weighted computed contribution of configuration D_1'; solid triangles: weighted computed Lorentzian absorption curve.

indications as to the answer to this question. In fact, if the OH groups were situated among the water molecules on some of the latter's sites, the values of β_1 and β_2 should be similar. This is not the case: the ratio β_1/β_2 is about 2 (Table II). Consequently, the water molecules and the OH groups are generally not close neighbors.[1] The results on the other samples confirm this interpretation.

Above −80°C the spectrum of A_{175} changes progressively with the temperature; the results are interpreted as the sum of the contributions of two D configurations and an L curve (model $D_1 + D_1' + L$). The spectrum recorded at 20°C is shown in Fig. 2 and the numerical values of the parameters for each temperature are listed in Table II. The contribution of the signal D_1' to the spectrum increases with the temperature, whereas that of the signal L is constant (7–8%). However, the width of the latter decreases when the temperature is raised. The motion of the spins induced by increase in temperature leads generally to a modification of the corresponding spectrum. This modification maintains or reduces the spectral width (*10, 11*), but does not increase it; moreover, the spectrum can become Lorentzian. Consequently, the signal D_1', which is broader than D_2, can on no account arise from the latter; it is formed therefore from D_1. Furthermore, the change in the D_2 signal leads to the L signal. Both of them correspond to the same number of protons (6 to 8%) (Table II).

The spectra of samples A_{20}, A_n, and B_{160} at −140°C are, as that of A_{175}, interpreted in terms of two configurations, D_1 and D_2. The values of the parameters are similar for these different samples and to those of A_{175} (Table II). The protons of these samples are

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[1] One of us has proposed that a magnetic configuration with three ½ spins at the corners of an isosceles triangle be used for the interpretation of the spectra of compounds containing both water molecules and OH groups (*7–9*). There is no need for it here.

therefore mainly in the form of molecular water. The significant differences are in the weighing coefficients: A_{20}, A_n, and B_{160} all have relatively fewer OH groups than A_{175}: 5% for A_{20}, 3% for A_n and B_{160}. Moreover, the value of β_1 close to 0.78 $10^{-4}T$ is similar for B_{160} and A_{175} but larger for A_{20} and, especially, for A_n (1.74 $10^{-4}T$). We shall discuss the meaning of this modification later.

Discussion

To interpret the results it is necessary to recall the structure of $WO_3 \cdot \frac{1}{3}H_2O$ (*1*). This compound crystallizes in the orthorhombic system with a = 0.7359, b = 1.2513, c = 0.7704 nm, and Z = 12. The basic structural element consists of a layer of octahedra (WO_6) which share their corners and form six-membered rings (Fig. 3). The complete structure can be described as a stacking of layers of this type along the c axis, every second layer being shifted by $a/2$. Each tungsten atom is bonded to six O atoms in a slightly distorted octahedral coordination. $W_{(1)}$ is bonded to two $O_{(1)}$ atoms, two $O_{(2)}$ atoms, and two $O_{(3)}$ atoms. The $W_{(1)}$ octahedra share their $O_{(1)}$ and $O_{(2)}$ atoms with their neighboring octahedra in the same layer and the $O_{(3)}$ atoms with the adjacent $W_{(1)}$ octahedra in the layer above and below. The $W_{(2)}$-type octahedra are bonded to four $O_{(2)}$ atoms and to atoms $O_{(4)}$ and $O_{(5)}$ (Fig. 3). $O_{(2)}$ atoms are shared with the neighboring $W_{(1)}$ octahedra but atoms $O_{(4)}$ and $O_{(5)}$ are bonded to $W_{(2)}$ only. Measurement of the interatomic W–O distances gives a rather large $W_{(2)}$–$O_{(4)}$ distance of 0.21 nm; this indicates that $O_{(4)}$ could belong to a water molecule. Moreover, the $W_{(2)}$–$O_{(5)}$ distance is relatively short (0.18 nm) and can be attributed to a $W_{(2)}$–$O_{(5)}$ bond with a certain double bond character. If the stoichiometric compound were a hydrate each $O_{(4)}$ or $O_{(5)}$ would be the oxygen atom of a water molecule; if it were hydroxy compound all $O_{(4)}$ and $O_{(5)}$ atoms would belong to OH groups. These results therefore support a model in which the structural water of $WO_3 \cdot \frac{1}{3}H_2O$ is present as molecular water ($W_{(2)}$–$O_{(4)}$ bond) rather than as two OH groups.

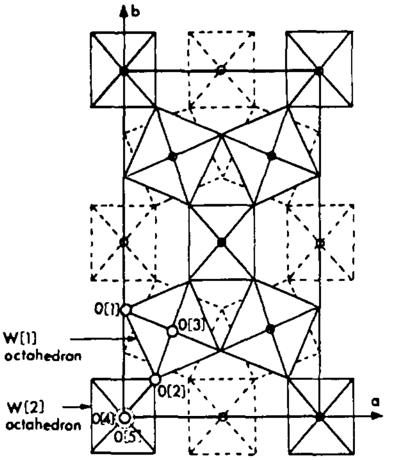

FIG. 3. Schematic projection of the crystal structure of $WO_3 \cdot \frac{1}{3}H_2O$ parallel to [001].

The interpretation of the low-temperature NMR spectra confirms this model: molecular water, representing 93% of the protons in A_{175}, corresponds to the structural water. However, the localization of the O atoms of the water molecules at $O_{(4)}$ leads to a difficulty in that it implies a distance of about 0.5 nm between protons belonging to distinct neighboring water molecules as against 0.3 nm measured by NMR (X_1, Table II). A distance compatible with that measured by NMR can be calculated by assuming that the position of the water molecules is modified from one plane to another: some of the $O_{(4)}$ and $O_{(5)}$ sites would be inverted. This localization of the water molecules is, however, incompatible with the chosen space groups. Alternatively, the water molecules could randomly occupy sites described as $O_{(4)}$ and $O_{(5)}$ in the structure, which would lead to a distance compatible with the NMR results. It is nevertheless impossible to overcome this difficulty as the structure obtained is a mean structure based on X-ray powder diffraction data, since a monocrystal could not be prepared.

We have already observed at temperatures below −80°C that the OH groups are remote from the water molecules. We assume that these OH groups are located on the sample surface. Under these conditions one can calculate that the surface coverage of A_{175} by OH groups is 0.7 if the OH group occupies 0.127 nm^2 (*12*). This localization of the OH groups is in agreement with the fact that sample B_{160}, which has a smaller specific area than A_{175}, contains fewer OH groups.

Another hydrated tungstic oxide, the yellow tungstic acid $WO_3 \cdot H_2O$ has been studied previously by rigid lattice proton NMR by Kabanov and Chuvaev (*13*). Their qualitative results are in agreement with ours on $WO_3 \cdot \frac{1}{3}H_2O$: both compounds are hydrates but contain a small amount of hydroxyl groups.

The thermogravimetric analysis results (*1*) show that the composition of the untreated sample A_n is about $WO_3 \cdot (H_2O)_{0.6}$ (Table I). During the degassing treatment at 175°C 45% of the total A_n water is desorbed, but the NMR study shows that only 3% of the A_n protons are in the form of OH groups. The molecular water detected by low-temperature NMR on A_n consists therefore of the structural water and adsorbed molecular water. Assuming that this adsorbed water is distributed homogeneously on the surface (22 m^2 g^{-1}) and that a water molecule covers 0.16 nm^2, we can calculate from the thermogravimetric results that A_n is covered by four to five layers of water molecules. This value is in reasonable agreement with that obtainable from the NMR results. The composition of the sample degassed at 20°C, A_{20}, is about $WO_3(H_2O)_{0.45}$ (Table I). In the same way as for A_n, we calculate that A_{20} is covered by about two layers of adsorbed molecular water. Small values of X are probably associated with the adsorbed molecular water detected at low temperature; but as this molecular water is not distinguishable from the structural water, the values of X_1 obtained for A_n and A_{20} are lower than that for A_{175} (Table II).

The Lorentzian form of the spectra of A_{175} when the experimental temperature is above −80°C reveals the movement of the OH groups. Following a method used by Paré (*14*) and Buigues (*15*) we find that an Arrhenius model, log (ΔH) proportional to $1/T$(T the temperature in degrees Kelvin), appears to describe the linewidths of this spectrum. The corresponding activation energy would be less than 1 kcal/mole; such a low value would correspond to rotations. In A_n and A_{20} at ambient temperature all the surface "water" is in motion.

The signal D_1' which develops from D_1 when the temperature increases can, *a priori*, be attributed to OH groups formed by dissociation of water molecules, or to these same water molecules in hindered rotation. The formation of OH groups supposes the migration of a proton from a water molecule at $O_{(4)}$ to a neighboring $O_{(5)}$. However, the fact that the distance between these oxygen atoms (0.38 nm) excludes the possibility of hydrogen bonds between them makes this theory very unlikely. Moreover, Gutowsky and Pake (*11*) have shown that the hindered rotation of water molecules about an axis perpendicular to the proton–proton direction reduces the abscissa scale of the spectrum, the value of the parameter α being multiplied by 0.5 theoretically; we find a value of about 0.4 (Table II) (in this case R_2 does not represent a real distance). For a thermally activated rotation,

$$H_2O_{(1)} \text{ (rigid)} \rightleftarrows H_2O_{(1')} \text{ (rotating)},$$

log w_1'/w_1 should be proportional to $1/T$. There is only a small number of measurements on A_{175} and A_{20} but the activation energy in the corresponding temperature range would be about 1.2 ± 0.25 kcal/mole.

Comparable activation energies (0.9 and 1.8 kcal/mole) have been attributed to the hindered rotations of water molecules (*15, 16*) or H_2O^+ groups (*17*), but also to proton jumps across potential barriers (*18*) in a hydrogen bond (*19*). It should be noted that the "flip" movements of water molecules, which, according to Holcomb and Pedersen (*10*), do not cause a decrease in the linewidth such as we observe here, generally require a greater activation energy (about 6 kcal/mole).

Conclusion

Wide-band ^1H NMR study of tungsten oxide hydrate $WO_3 \cdot \frac{1}{3}H_2O$ confirms that the bulk water is in the form of coordinated H_2O molecules. What remains of the surface water after desorption of the solid at 160–175°C and 10^{-4} Torr is exclusively in the form of OH groups strongly bonded to the surface, which explains why desorption is difficult.

The lattice can be considered as rigid below −80°C. Each water molecule is probably attached by its oxygen atom to a W atom (at $O_{(4)}$), the W–O bond being relatively long in the deformed WO_6 octahedron. To account for the distances between protons in neighboring water molecules we are led to imagine that there is a random distribution of $O_{(4)}$ and $O_{(5)}$ sites in the structure: NMR shows that the mean structure obtained from the X-ray powder diffraction data do not locate the water precisely.

At temperatures above −80°C the water molecules of the structure probably undergo thermally activated rotation, the corresponding activation energy being 1.2 ± 0.25 kcal/mole. Furthermore, the OH groups on the surface of the most desorbed sample are also subject to thermally activated movement; the low value of the associated energy could also correspond to a rotation.

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