(7) P. A. Yeats, B. F. E. Ford, J. R. Sams, and F. Aubke, *Chem. Commun.*, 791 (1969).
(8) P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **11**, 2634 (1972).
(9) M. Schmeisser, P. Sartori, and B. Lippsmeier, *Chem. Ber.*, **103**, 868 (1970).
(10) P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, **10**, 1877 (1971).
(11) H. Roesky and H. Wiezer, *Chem. Ber.*, **104**, 2258 (1971).
(12) H. Schmidt, C. Blohm, and G. Jander, *Angew. Chem.*, **59**, 233 (1947).
(13) A. Henderson and A. K. Holliday, *J. Organomet. Chem.*, **4**, 344 (1965).
(14) D. F. Shriver, "The Manipulation of Air-sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(15) F. B. Dudley and G. H. Cady, *J. Am. Chem. Soc.*, **79**, 513 (1957).
(16) R. E. Noftle and G. H. Cady, *Inorg. Chem.*, **4**, 1010 (1965).
(17) H. A. Carter, C. Milne, and F. Aubke, *J. Inorg. Nucl. Chem.*, **37**, 282 (1975).
(18) R. K. Ingham, S. D. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 478 (1960); D. Seyferth, *J. Am. Chem. Soc.*, **79**, 2133 (1957).
(19) M. F. Dove, R. King, and T. J. King, *J. Chem. Soc., Chem. Commun.*, 944 (1973).
(20) P. F. R. Ewings, P. G. Harrison, T. J. King, and A. Morris, *J. Chem. Soc., Chem. Commun.*, 53 (1974).
(21) H. Bürger, K. Burczyk, and A. Blaschette, *Monatsh. Chem.*, **101**, 102 (1970).
(22) P. G. Harrison, *Coord. Chem. Rev.*, **20**, 1 (1976).
(23) C. Stepien, H. A. Carter, and F. Aubke, unpublished results, as quoted by J. R. Dalziel and F. Aubke, *Inorg. Chem.*, **12**, 2707 (1973).
(24) P. J. Rentzeperis, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **117**, 431 (1962).
(25) D. Potts, H. D. Sharma, A. J. Carty, and A. Walker, *Inorg. Chem.*, **13**, 1205 (1974).
(26) J. Lees and P. A. Flinn, *Phys. Lett.*, **19**, 186 (1965).
(27) J. D. Donaldson and B. J. Senior, *J. Chem. Soc. A*, 1796 (1966).
(28) F. Feigl, "Spot Tests", Vol. 1, Elsevier, Amsterdam, 1954, p 107.

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New Interpretation of Proton Magnetic Resonance Powder Spectra of the Sodium Silicates $Na_2O{\cdot}SiO_2{\cdot}5H_2O$ and $Na_2O{\cdot}SiO_2{\cdot}9H_2O$

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Proton magnetic resonance powder spectra at 85 K of sodium silicates $Na_2O{\cdot}SiO_2{\cdot}5H_2O$ and $Na_2O{\cdot}SiO_2{\cdot}9H_2O$ have been reinterpreted using a model of three spin $^1/_2$ nuclei located at the apexes of an isosceles triangle. The findings confirm that these solids are hydrogenomonosilicates with the formula $Na_2(SiO_2(OH)_2){\cdot}(n-1)H_2O$ (n = 5 and 9). However, the occurrence of distorted H_3O^+ ions cannot be ruled out in the nonahydrate.

Introduction

The dipolar interaction of nuclei with spin $^1/_2$ is the main effect observed from the magnetic resonance of these nuclei in solids. Interaction models must be used to interpret the experimental spectra with precision by calculating shape functions. The number of nuclei taken into account in these models and their relative geometric positions should represent, as closely as possible, the actual patterns formed by the resonating nuclei in the solids studied.

When studying monocrystals we noticed that these patterns have only a limited number of orientations in relation to the applied magnetic field. On the contrary, all orientations must be considered for powdered samples. Furthermore, to take into account interactions between patterns, a Gaussian broadening is superposed on the absorption of supposedly isolated patterns.

The proton magnetic resonance (^{1}H NMR) study of hydrates was initiated by Pake.[2] The two-spin model proposed by this author agrees with the fact that the distance R between the two H atoms of a given water molecule is distinctly less than the shortest distances between two H atoms not belonging to the same water molecule (the effect observed is proportional to $\alpha = 3\mu/2R^3$, where μ is the proton magnetic moment).

Gutowsky et al.[3,4] have tried to interpret the ^{1}H NMR spectra of hydrated hydrogeno salts by taking the weighted sum of the contributions of two two-spin patterns; one pattern represents the H atoms of water molecules and the other pattern represents the "acidic" H atoms considered two by two (the values of R in the two patterns are then very different). This method leads to good results if the two types of patterns are actually far enough from each other in the compounds being analyzed, but it cannot be generalized without caution. In practice, the interactions between H atoms belonging either to one or more water molecules of hydration or to one or more neighboring "acidic" H atoms are seldom weak enough to be neglected to the required level of approximation.

The model formed by three spin $^1/_2$ nuclei located at the apexes of an equilateral triangle has been proposed by Andrew and Bersohn[5] and reexamined by Richards and Smith.[6] This model can be used, in particular, for the salts of the H_3O^+ ion.[7,8] It can be applied to monocrystalline and powdered samples.

Table I. Model Proposed to Interpret the ^{1}H NMR Spectra of Powder Solid Hydrates

No. of H in pattern	Parameters involved	Ref
2	$\alpha = 3\mu/2R^3$; R = HH distance in the pattern $\beta = 3\mu/2X^3$; X = lowest averaged distance between H of different patterns	2
2	Two distinct patterns: four parameters $\alpha_1, \alpha_2, \beta_1, \beta_2$; $+\omega$ weighting factor defining the proportion of H atoms in the two patterns	3, 4
3	Pattern: equilateral triangle α, β	5, 6
3	Isosceles triangle $\alpha = 3\mu/2R_{23}{}^3$; R_{23} = base of triangle $\lambda = R_{12}/R_{23}$; $R_{12} = R_{13}$ = equal sides of triangle β	9

Andrew and Finch[9] have proposed a model with three spin $^1/_2$ nuclei located at the apexes of an isosceles triangle. This model has been used to interpret the ^{1}H NMR spectrum of $H_2(AlP_3O_{10}){\cdot}2H_2O$.[10] The two H atoms of a water molecule would define the base of the triangle, an "acidic" H atom being located at the opposite apex.

Pedersen and Håland[11] used a scalene triangle model to interpret the ^{1}H NMR spectra of monocrystalline dihydrated oxalic acid, but these authors did not generalize the use of their model to powder spectra.

The different models used and the parameters they involve are summarized in Table I.

Purpose of the Study

In a preceding article,[12] we undertook the interpretation of the ^{1}H NMR spectra (at 85 K) of sodium silicates $Na_2O{\cdot}$

$SiO_2 \cdot nH_2O$, $n = 5$ and 9. The properties of these silicates show that they are actually hydrogenomonosilicates[13,16] and their formula is $Na_2(SiO_2(OH)_2) \cdot (n-1)H_2O$. The shape functions were computed from the models we were considering at that time, i.e., a two-spin model and a three-spin model, with the spins being located at the apexes of an equilateral triangle. We found that Gutowsky's method, in which two different two-spin patterns are considered,[3] completely failed. Indeed the weighting coefficients—considered as variable parameters—that must be applied to the two contributions to fit the computed spectra to the experimental spectra of each of the two hydrates were not compatible with the formula $Na_2(SiO_2(OH)_2) \cdot (n-1)H_2O$. The agreement was not satisfactory either when computing the spectrum of $Na_2O \cdot SiO_2 \cdot 5H_2O$ on the basis of the formula $Na_2(H_3O)_2SiO_4 \cdot 2H_2O$. However the agreement was rather good for $Na_2O \cdot SiO_2 \cdot 9H_2O$ on the basis of the formula $Na_2(H_3O)_2SiO_4 \cdot 6H_2O$.

The agreement between experimental and computed spectra for pentahydrate and nonahydrate should be improved when using a model with three spins of $^1/_2$ at the apexes of an isosceles triangle—instead of an equilateral triangle—together with a two-spin model. The weighting coefficients in agreement with such an overall model correspond to the formula $Na(HH_2O)_2SiO_4 \cdot (n-3)H_2O$, for which only $n - 3$ H_2O groups are represented by a two-spin model.

Our purpose is to determine, as far as possible, the nature of the chemical groups to which the "acidic" H atoms are attached from the values of the above parameters giving the best simulations of the experimental spectra.

Experimental Section

The conditions for obtaining and using spectra have already been described.[10,12,17] A CII Iris 80 computer was used. Six independent parameters define the two types of patterns used, their relative number, and their interactions with the external patterns. (i) For the three-spin patterns we have $\alpha = 3\mu/2R_{23}{}^3$, $\beta = 3\mu/2X^3$, and $\lambda = R_{12}/R_{23} = R_{13}/R_{23}$. The absorption derivative is given by

$$(\mathrm{d}f/\mathrm{d}h)_3 = (2\pi)^{-1/2}\beta^{-3}\int_{-\infty}^{+\infty}(h-h_0)[\mathrm{G}_3(h_0)] \times \exp[-(h-h_0)^2/2\beta^2]\,\mathrm{d}h_0$$

where h_0 is the value of the magnetic field for a given line; this line is broadened so that it contributes to the magnitude of absorption at another value h of the magnetic field. $\mathrm{G}_3(h_0)$ is a complicated function of h_0, α, and λ. (ii) For the two-spin patterns we have $\alpha' = 3\mu/2R'^3$ and $\beta' = 3\mu/2X'^3$, and

$$(\mathrm{d}f/\mathrm{d}h)_2 = (2\pi)^{-1/2}\beta'^{-3}\int_{-\infty}^{+\infty}(h-h_0)[\mathrm{G}_2(h_0)] \times \exp(-(h-h_0)^2/2\beta'^2)\,\mathrm{d}h_0$$

where

$$\mathrm{G}_2(h_0) = C_1/(h_0-\alpha)^{1/2} + C_2/(h_0+\alpha)^{1/2}$$

$C_1 = 1$ for $-2\alpha \leq h_0 < \alpha$, $C_1 = 0$ for $h_0 \leq -2\alpha$ and $h_0 > \alpha$; $C_2 = 1$ for $-\alpha < h_0 \leq 2\alpha$, $C_2 = 0$ for $h_0 < -\alpha$ and $h_0 \geq 2\alpha$. We use a weighting coefficient ω such that

$$\mathrm{d}f/\mathrm{d}h = \omega(\mathrm{d}f/\mathrm{d}h)_3 + (1-\omega)(\mathrm{d}f/\mathrm{d}h)_2$$

Here we have $\omega = {}^2/_3$ for the pentahydrate and $\omega = {}^1/_3$ for the nonahydrate.

Because of the complicated expression of $\mathrm{G}_3(h_0)$ very large computation times would be required to find the values of the five remaining parameters by a least-squares procedure. Though we are trying at present to develop a program for such a procedure, a less precise method was used in this study. The parameters were systematically varied so as to find the set of parameters giving the best fit. λ being chosen, the shape of the curves representing the absorption derivative depends in a simple manner on the different parameters: (i) the abscissas of the maxima are determined mainly by the values of α and α'; (ii) the sharpness of these maxima is defined by β and β'. Furthermore the following conditions can be introduced a priori: (i) first we state $1 \leq \lambda \leq X/R_{23}$. $\lambda \geq 1$ for R_{23} is the H–H distance in an H_2O molecule, the third H being an "acidic" H from an OH group; thus $R_{12} = R_{13} \geq R_{23}$. $\lambda > X/R_{23}$ would mean that the interaction between patterns is stronger than the interaction between H atoms inside the patterns and the model should then be rejected. (ii) For the two-spin patterns representing water molecules we impose a priori $X' \gtrsim 1.25R'$, that is to say $\beta'/\alpha' < 0.5$. Thus the choice of the five parameters is highly restricted.

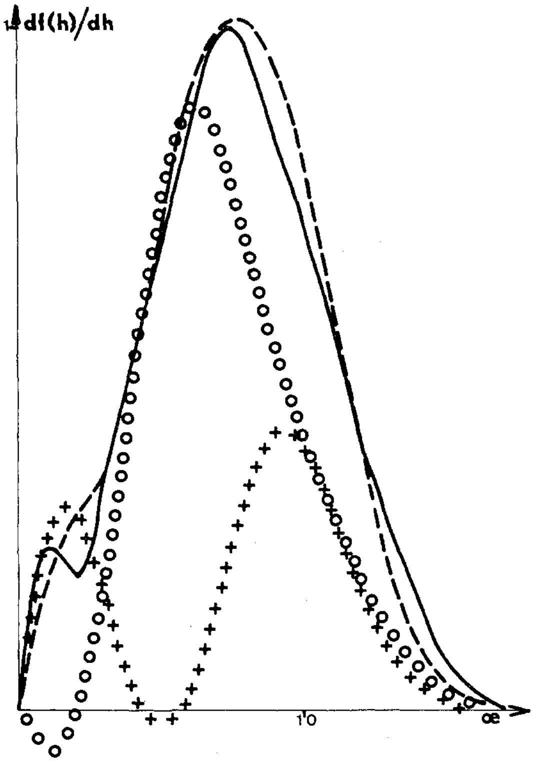

Figure 1. Derivatives of the powder absorption curves for $Na_2O \cdot SiO_2 \cdot 9H_2O$ at 85 K (half-curves are shown): —, experimental curve; – – –, computed curve; +++, weighted computed contribution of isosceles-triangle patterns; ∘∘∘, weighted computed contribution of two-spin patterns; λ = 1.10.

Table II. Parameters of Computed Spectrum for $Na_2O \cdot SiO_2 \cdot 9H_2O$ at 85 K[a]

Isosceles-triangle pattern	Two-spin pattern
$\omega = {}^3/_9$	$1 - \omega = {}^6/_9$
$R_{23} = 1.60$ Å	$R' = 1.60$ Å
$R_{12} = R_{13} = 1.76$ Å	
$\lambda = 1.10$	
$\beta = 1.91$ Oe	$\beta' = 2.38$ Oe
$\alpha_{23} = 5.16$ Oe	$\alpha' = 5.16$ Oe
$\beta/\alpha_{23} = 0.37$	$\beta'/\alpha' = 0.46$
$X = 2.23$ Å	$X' = 2.07$ Å

[a] Experimental second moment 31.2 Oe^2; total computed second moment 29.1 Oe^2.

Since the curves representing the absorption derivative as a function of the external magnetic field have a center of symmetry, we have drawn only half of the curves in the figures.

Results and Discussion

The experimental spectrum and the computed spectra for $Na_2O \cdot SiO_2 \cdot 9H_2O$ at 85 K are given in Figures 1–3. For each value of λ the other four parameters have been optimized so as to obtain the best fit with the experimental spectrum. It is clearly evident from the figures that the fit is best for λ = 1.10. The parameters corresponding to the computed spectrum for λ = 1.10 are indicated in Table II together with the experimental and computed values of the second moment. The description of the spectrum is only slightly improved compared

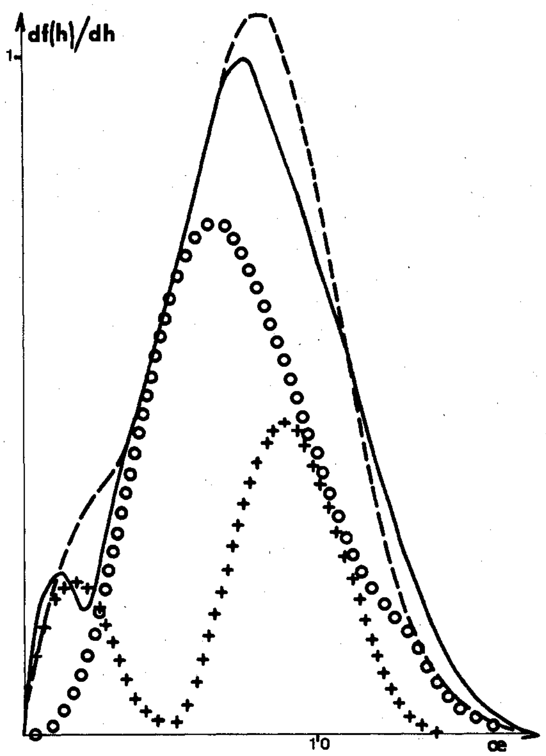

Figure 2. Derivatives of the powder absorption curves for $Na_2O \cdot SiO_2 \cdot 9H_2O$ at 85 K: —, experimental curve; - - -, computed curve; +++, weighted computed contribution of isosceles-triangle patterns; °°°, weighted computed contribution of two-spin patterns; $\lambda = 1$.

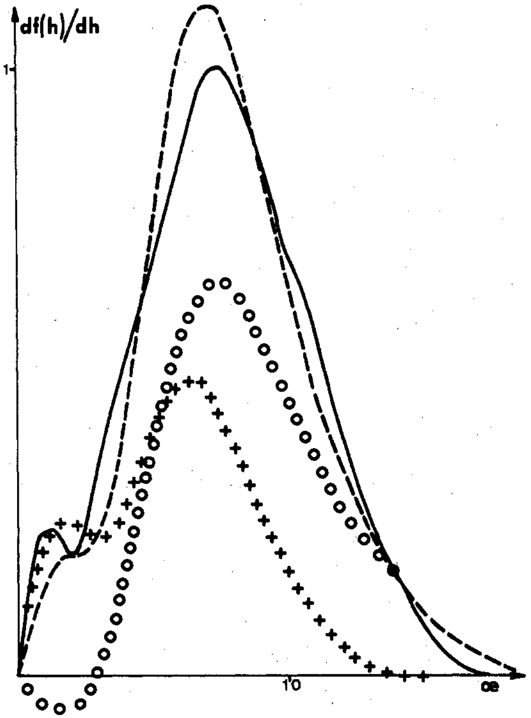

Figure 3. Derivatives of the powder absorption curves for $Na_2O \cdot SiO_2 \cdot 9H_2O$ at 85 K: —, experimental curve; - - -, computed curve; +++, weighted computed contribution of isosceles-triangle patterns; °°°, weighted computed contribution of two-spin patterns; $\lambda = 1.27$.

with the result obtained with a pattern consisting of an equilateral triangle[12] and the main defect still appears; i.e., the maximum of the half-curve located at 1.35 Oe, which is very apparent on the experimental spectrum, can be represented only by a shoulder on the computed spectrum. The accuracy of the values of R_{12} and R_{23} is difficult to estimate and is not excellent because of the symmetry adopted for the model, but the difference between R_{23} and R_{12} (or R_{13}) is significant. The value obtained for R_{23} is compatible with the atoms 2 and 3 belonging to a water molecule. On the contrary, the lengths R_{12} and R_{13} are not. Their value is slightly higher than some values indicated in the literature[7] for the length of the sides of the equilateral triangle formed by the three H atoms of an H_3O^+ ion (1.72 Å). More recent experimental determinations[18] yield 1.65–1.67 Å for this length in an isolated ion and an ab initio computation[19] indicates 1.67 Å. From these comparisons we cannot conclude for sure as to the chemical nature of the oxyhydrogenated group to which the "acidic" H atom belongs and in particular whether or not this atom is linked to a water molecule so as to form a distorted H_3O^+ ion. In a compound so rich in water, the second hypothesis seems to us more likely, because of a comment by Lundgren and Williams,[18] according to whom the H_3O^+ ion is considerably distorted and may even lose its "identity" when in the presence of one or more water molecules. A scalene triangle model might enable us to reach a conclusion. In any case, the value of X is significantly larger than R_{12} so that the interaction approximation of a three-spin pattern seems reasonable.

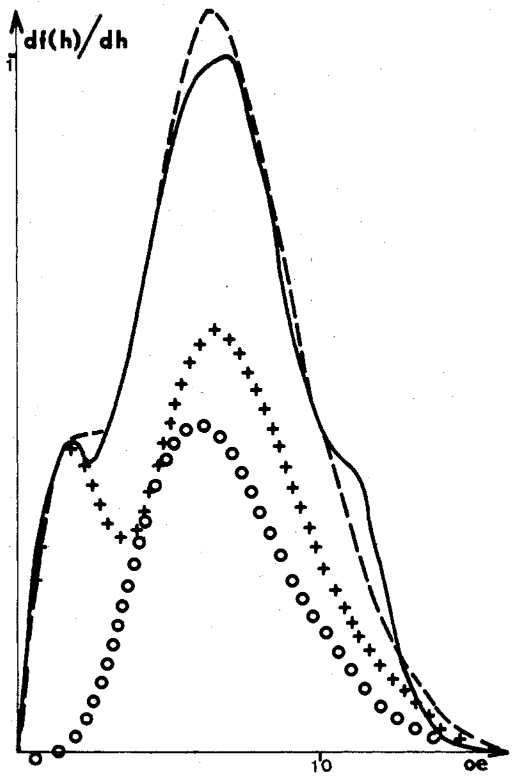

Figure 4. Derivatives of the powder absorption curves for $Na_2O \cdot SiO_2 \cdot 5H_2O$ at 85 K: —, experimental curve; - - -, computed curve; +++, weighted computed contribution of isosceles-triangle patterns; °°°, weighted computed contribution of two-spin patterns; $\lambda = 1.36$.

The experimental spectrum and the best computed spectra for $\lambda = 1$, 1.36, and 1.5 for $Na_2O \cdot SiO_2 \cdot 5H_2O$ at 85 K are given in Figures 4–6. The value of $\lambda = 1.36$ was found to give the best fit. The parameters corresponding to this computed spectrum are given in Table III. The experimental spectrum is correctly described, as opposed to what was observed with the equilateral-triangle model.[12] Three small defects are still apparent on the computed spectrum: (i) the maximum of the half-curve located at 1.7 Oe should be more marked; (ii) the amplitude of the main maximum located at 6.8 Oe is a little too large; (iii) a shoulder of the experimental curve located

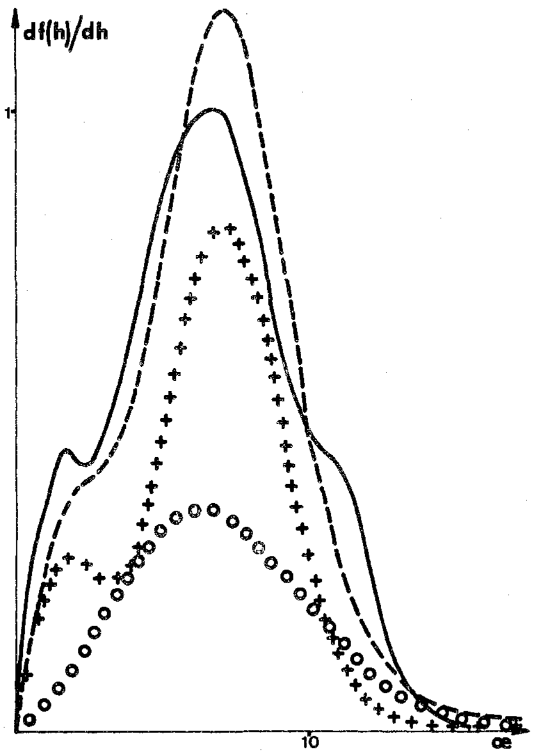

Figure 5. Derivatives of the powder absorption curves for $Na_2O\cdot SiO_2\cdot 5H_2O$ at 85 K: —, experimental curve; - - -, computed curve; +++, weighted computed contribution of isosceles-triangle patterns; ∘∘∘, weighted computed contribution of two-spin patterns; λ = 1.

Table III. Parameters of Computed Spectrum for $Na_2O\cdot SiO_2\cdot 5H_2O$ at 85 K[a]

Isosceles-triangle pattern	Two-spin pattern
$\omega = {}^3/_5$	$1 - \omega = {}^2/_5$
$R_{23} = 1.56$ Å	$R' = 1.65$ Å
$R_{12} = R_{13} = 2.12$ Å	
$\lambda = 1.36$	
$\beta = 1.86$ Oe	$\beta' = 2.45$ Oe
$\alpha_{23} = 5.57$ Oe	$\alpha' = 4.71$ Oe
$\beta/\alpha_{23} = 0.33$	$\beta'/\alpha' = 0.52$
$X = 2.25$ Å	$X' = 2.05$ Å

[a] Experimental second moment 23.8 Oe^2; total computed second moment 24.2 Oe^2.

at 11.1 Oe is missing. Furthermore the value of X is only slightly larger than R_{12} (because of the high value of λ) so that the approximation of a three-spin pattern may not be justified. The value of R_{23} indicates that atoms 2 and 3 belong to the same water molecule. Hence within the framework of this model we can conclude that the H atoms 1, 2, and 3 do not belong to the same oxyhydrogenated group. R', the distance between the two H atoms of a two-spin pattern, is equal to 1.65 Å. This value is near the upper limit of what can be admitted for a water molecule. In this case, the use of models with a larger number of spins, or at least less symmetrical ones, would probably be required to improve the coincidence between experimental and computed spectra. On the whole, however, our results are in complete agreement with the chemical formula $Na_2(SiO_2(OH)_2)\cdot 4H_2O$ proposed by Thilo[13,14] and Jost[16] for $Na_2O\cdot SiO_2\cdot 5H_2O$.

Williams and Dent Glasser[20] have recently located the H atoms in $Na_2O\cdot SiO_2\cdot 6H_2O$ by neutron diffraction. The hydration level of this compound is intermediate between those of the two salts for which we are interpreting the ^1H NMR spectra. The findings of these authors confirm the formula $Na_2(SiO_2(OH)_2)\cdot 5H_2O$. The shortest distance between an "acidic" H atom and an H atom of a water molecule is 2.15 Å. It is 2.10 Å between H atoms of different water molecules.

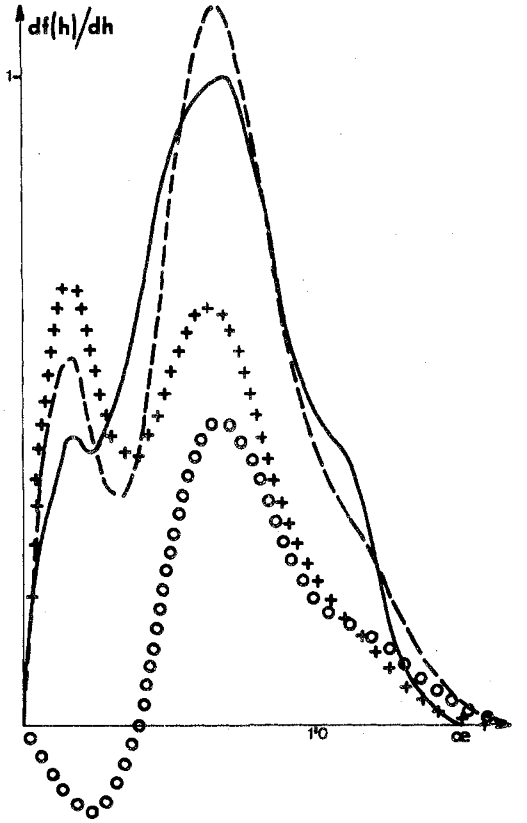

Figure 6. Derivatives of the powder absorption curves for $Na_2O\cdot SiO_2\cdot 5H_2O$ at 85 K: —, experimental curve; - - -, computed curve; +++, weighted computed contribution of isosceles-triangle patterns; ∘∘∘, weighted computed contribution of two-spin patterns; λ = 1.5.

There is no apparent crystallographic relationship between the different hydrates in this family of compounds. However, and though only indicative, the numerical values of the parameters presented in Tables II and III are acceptable when compared with the distances directly determined by neutron diffraction. Thus the interpretation method we propose here is at least an interesting way to eliminate some wrong hypotheses, for instance nonstoichiometry or the presence of H_3O^+.

Conclusion

The interpretation, by simulation, of ^1H NMR powder spectra of $Na_2O\cdot SiO_2\cdot 5H_2O$ and $Na_2O\cdot SiO_2\cdot 9H_2O$ has been improved by using an isosceles-triangle model, such that the two H atoms of a given water molecule are at the apexes of the base and that an "acidic" H atom is located at the opposite apex. The formula $Na_2(SiO_2(OH)_2)\cdot 4H_2O$ is valid for the pentahydrate. A similar formula is probably also valid for the nonahydrate, though the presence of a distorted H_3O^+ ion cannot be ruled out in the latter salt.

Registry No. $Na_2O\cdot SiO_2\cdot 9H_2O$, 14691-76-0; $Na_2O\cdot SiO_2\cdot 5H_2O$, 13812-77-6.

References and Notes

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(2) G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).
(3) A. L. Porte, H. S. Gutowsky, and G. M. Harris, *J. Chem. Phys.*, **34**, 66 (1961).
(4) A. L. Porte, H. S. Gutowsky, and J. E. Boggs, *J. Chem. Phys.*, **36**, 1695 (1962).
(5) E. R. Andrew and R. Bersohn, *J. Chem. Phys.*, **18**, 159 (1950).
(6) R. E. Richards and J. A. S. Smith, *Trans. Faraday Soc.*, **48**, 675 (1952).
(7) R. E. Richards and J. A. S. Smith, *Trans. Faraday Soc.*, **47**, 1261 (1951); J. A. S. Smith and R. E. Richards, *ibid.*, **48**, 307 (1952).
(8) Y. Kakiuchi, H. Shono, H. Komatsu, and K. Kigoshi, *J. Chem. Phys.*, **19**, 1069 (1951); *J. Phys. Soc. Jpn.*, **7**, 102 (1952).

(9) E. R. Andrew and N. D. Finch, *Proc. Phys. Soc., London, Sect. B*, **70**, 980 (1957).
(10) C. Dorêmieux-Morin, *J. Magn. Reson.*, **21**, 419 (1976).
(11) K. Håland and B. Pedersen, *J. Chem. Phys.*, **49**, 3194 (1968).
(12) C. Dorêmieux-Morin and E. Freund, *Bull. Soc. Chim. Fr.*, 418 (1973).
(13) E. Thilo and W. Miedreich, *Z. Anorg. Allg. Chem.*, **267**, 76 (1951).
(14) E. Thilo, W. Wieker, and H. Stade, *Z. Anorg. Allg. Chem.*, **340**, 261 (1965).
(15) P. B. Jamieson and L. S. Dent Glasser, *Acta Crystallogr.*, **20**, 688 (1966).
(16) K.-H. Jost and W. Hilmer, *Acta Crystallogr.*, **21**, 583 (1966).
(17) C. Dorêmieux-Morin, M. Krahe, and F. d'Yvoire, *Bull. Soc. Chim. Fr.*, 409 (1973).
(18) J.-O. Lundgren and J. M. Williams, *J. Chem. Phys.*, **58**, 788 (1973).
(19) M. D. Newton and S. Ehrenson, *J. Am. Chem. Soc.*, **93**, 4971 (1971).
(20) P. P. Williams and L. S. Dent Glasser, *Acta Crystallogr. Sect. B.*, **27**, 2269 (1971).

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Electronic Structure of Organosilicon Compounds. 2. Maximum Overlap Approximation Calculations of Hybridization in Some Silanes

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The electronic structure of some silanes is discussed in terms of the hybridization parameters obtained by the application of the MOA method. The calculated J(Si–H) spin–spin coupling constants and bond angles are in fair agreement with available experimental data. The predicted heats of formation reproduce nicely several experimentally observed features. It was found that the hybrid orbitals describing similar chemical environments are to the high degree transferable. Therefore, the calculated hybridization parameters can serve for an approximate description of higher silanes.

Introduction

Although silicon is in the same column of the periodic system as carbon, the properties of the two elements differ widely. For example, silanes are extremely air sensitive. On the other hand, the Si–O–Si linkage is particularly strong, being one of the most important inorganic structural groups. It is therefore not surprising that in the last two decades considerable attention has been paid to the synthesis and investigation of physical and chemical properties of silicon compounds and particularly of silanes.[1-3] A direct comparison of C–C with Si–Si bonds requires a detailed knowledge of their electronic properties. It is the aim of this paper to report on maximum overlap approximation (MOA) calculations performed on some silanes. Their electronic structure is discussed in terms of the local hybrid orbitals and compared with that of the corresponding hydrocarbon compounds.

Outline of the Calculation

A variable-hybridization model of covalent bonding calculated by the maximum overlap method proved very useful in describing properties of hydrocarbons characterized by localized bonds.[4] Recently, the method was successfully extended to encompass conjugated molecules such as polyenes and their alkylated derivatives.[5] The prerequisite for application of the MOA method is an absence of bonded atoms exhibiting widely different electronegativities. Since the electronegativities (on Pauling's scale) of H, C, and Si are 2.1, 2.5, and 1.8, respectively, one can anticipate that MOA hybrid orbitals will give a fair description of bonding in silanes. It should be also mentioned that the orbital electronegativities of hydrogen, carbon, and silicon, where the latter are in sp^3 hybridization states, are proposed to be 2.21, 2.48, and 2.25, respectively.[6] Furthermore, the group electronegativities of CH_3 and SiH_3 groups are practically the same (vide infra), a fact giving additional justification for the maximum overlap calculations.

The details of the MOA method are given elsewhere.[4] Briefly, the method is based on the intuitive idea that an atom retains its identity within a molecule. Therefore, it is assumed that electronic states of an atom are slightly disturbed and the influence of the neighboring atoms is reflected in mixing of the nearly degenerate atomic levels. Thus hybrid orbitals are formed which possess desirable directional properties. The general form of the hybrid orbital centered on the nucleus A is

$$\Psi_{Ai} = a_{Ai}(ns) + (1 - a_{Ai}^2)^{1/2}(np)_i \qquad (1)$$

where n stands for the principal quantum number and a_{Ai} denotes a mixing parameter ranging from 0 to 1. The hybrid orbitals placed on the same atom are orthogonal according to the Pauli principle. This condition imposes a set of equations which determine interhybrid angles

$$a_{Ai}a_{Aj} + (1 - a_{Ai}^2)^{1/2}(1 - a_{Aj}^2)^{1/2}\cos\theta_{ij} = 0 \qquad (2)$$

where θ_{ij} is an angle between the symmetry axes of the hybrids Ψ_{Ai} and Ψ_{Aj}. The hybridization parameters a_{Ai} (eq 1 and 2) are not, strictly speaking, determined by the application of the variational theorem. Instead, they are varied until maximum of the bond overlap integrals is achieved

$$E_b = \sum_{A-B} k_{AB}S_{AB} \qquad (3)$$

where the summation is extended over all bonds in a molecule. The constant k_{AB} is a weighting factor which takes into account the difference in bond energy for different bonds. Expression 3 deserves some more comments. It is based on Mulliken's analysis of the resonance energy term $-2\beta/(1 + S)$ appearing in the LCAO–MO treatment of simple diatomics.[7] Mulliken has shown that the heats of atomization can be calculated with a good accuracy if the resonance integral is equal to

$$\beta = -(1/2)PSI \qquad (4)$$

where P is an adjustable empirical parameter, S is the overlap integral between appropriate atomic orbitals participating in a bond formation, and I is their average ionization potential. Then the quantity

$$E_{AB} = P_{AB}S_{AB}I_{AB}/(1 + S_{AB}) \qquad (5)$$

is a good measure of the A–B bond energy if the intramolecular charge transfer is not highly pronounced. It turns out that the parameter P does not vary too much being roughly 1 for most σ bonds. If we write the product $P_{AB}I_{AB}$ as a new