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NMR Chemical Shift of the Hydroxyl Ion

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The proton magnetic screening constant for the OH^- ion has been calculated. In the used method [11] the electronic ground state is represented by an unsymmetrized product of one-electron wave functions. The origin of the magnetic potential is chosen at the center of gravity of the electron under consideration. The result $\sigma = 3.2 \times 10^{-5}$ means that the low apparent screening constant found experimentally in the study of dilute solutions of bases [1] can hardly be explained without considering the environment of the ion. For its first hydration shell a model is discussed with the aid of which the experimental results can qualitatively be understood.

INTRODUCTION

The existing experimental data concerning the proton magnetic resonance in the hydroxyl ion have been obtained by extrapolation to the limit of zero concentration of results from NMR measurements on dilute solutions of bases.[1,2] The chemical shift obtained in this way is about −10 ppm (parts per million) related to the resonance in liquid water.

This surprising shift to low field has been discussed in the literature,[2–4] where it has been put in relation to the chemical shift — about −11 ppm — of the hydronium ion H_3O^+ in dilute solutions of acids. With the use of a rough picture of the H_3O^+ ion its screening constant can be expected to be low because of the small electron charges on its hydrogen atoms.[6,7] A corresponding picture of the OH^- ion would, however, involve a positive shift relative to water because of the excess electron of OH^-.

The foundations for discussions of the magnetic shielding in OH^- have been very weak as there has been no knowledge of the charge distribution in the ion. Musher [4] has started from the assumption that in OH^- and H_3O^- the excess respectively lack in electron charge relative to water should be located at the oxygen atoms. With this assumption he explained the observed shifts without considering other molecules or ions in the liquids.

Kresge [3] has considered also the shift in the shielding of water protons, which is caused by the positive counterions, Na^+ and K^+, of OH^-. By comparing with an analogous system — ammonium and amide ions in liquid

ammonia — he corrected for such effects of counterions. The remaining shift arising from OH^- is estimated to ~ -4.4 ppm relative to liquid water.

Kresge has also pointed out that this shift probably does not correspond to a "free" OH^- ion but also involves additional effects from shifts in water molecules in the hydration shell of OH^-. (See further under "Discussion").

Now there are available theoretical data of the atomic charges in H_3O^+ [6,7] as well as in OH^-.[9,10] In contradiction to Musher's assumption these data imply, that the whole electron charge lack in H_3O^+ is located at the hydrogen atoms while only 45 % of the excess charge in OH^- is located at the oxygen atom.

The aim of the present study is to find the proton magnetic screening constant in OH^- without considering adjacent molecules or ions. To do this we use the existing electron wave function for the hydroxyl ion.[10] The screening constant calculated in this way will then be a basis for discussions of the NMR effects in solutions.

CALCULATION OF THE SCREENING CONSTANT

The method has earlier been described [11,12] in detail. For molecules, where comparison with experimental values of screening constants is possible, the method has predicted values within about 15 % from the experimental ones. Therefore its accuracy should be sufficient for answering the question if a "free" OH^- complex has properties, which alone can be responsible for the observed downfield shift.

We first briefly describe the general method.

a. The Hamiltonian

In the presence of the applied magnetic field **H** and the magnetic field from the proton magnetic dipole $\boldsymbol{\mu}$ the Hamiltonian $\mathscr{H}$ to be considered can be written [8]:

$$\mathscr{H} = \mathscr{H}_0 + \mathscr{H}_\mu + \mathscr{H}_H + \mathscr{H}_{\mu H} + \mathscr{H}_{HH} + \mathscr{H}_{\mu\mu} \tag{1}$$

Here $\mathscr{H}_0$ is the zero-order Hamiltonian of the electrons in the absence of magnetic fields. In the remaining parts of $\mathscr{H}$ we only consider terms giving contributions to the screening constant: [8,12]

$$\begin{aligned} \mathscr{H}_\mu &= -\frac{e\,i\,\hbar}{mc}\boldsymbol{\mu}\sum_i \frac{\mathbf{r}_i \times \nabla_i}{r_i^3} \\ \mathscr{H}_H &= -\frac{e\,i\,\hbar}{2mc}\mathbf{H}\sum_i \mathbf{r}_{Oi} \times \nabla_i \\ \mathscr{H}_{\mu H} &= \frac{e^2}{2mc^2}\sum_i \frac{(\mathbf{H}\times\mathbf{r}_{Oi})\cdot(\boldsymbol{\mu}\times\mathbf{r}_i)}{r_i^3} \end{aligned} \tag{2}$$

i denotes the electrons, $\mathbf{r}_i$ has its origin at the proton under consideration and $\mathbf{r}_{Oi}$ has its origin at some arbitrary point O.

The energy part being of interest consists of those energy terms, which are proportional to the products $\mu_\alpha H_\beta$ between $\boldsymbol{\mu}$- and **H**-components. The

proportionality constants $\sigma_{\alpha\beta}$ in these terms form the screening tensor σ. The screening constant σ for a rapidly rotating molecule is then given by

$$\sigma = \tfrac{1}{3}\,\mathrm{tr}\,\sigma = \tfrac{1}{3}\,(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) \tag{3}$$

b. Wave function

The total electron wave function is formed as a direct product of four doubly occupied one-electron wave functions ("orbitals") ψ_i. The oxygen $1s$ electrons are thereby not considered.

In principle the ψ_i's are calculated with the variation method and are constructed according to

$$\psi_i = \psi_i^0\,(1 + \boldsymbol{\mu}\cdot\mathbf{f}_i + \mathbf{H}\cdot\mathbf{g}_i) \tag{4}$$

Here the ψ_i^0's are the corresponding functions in the absence of magnetic fields and $\mathbf{f}_i$ and $\mathbf{g}_i$ are functions containing parameters to be varied.

If $\mathbf{f}_i$ and $\mathbf{g}_i$ are formed as linear functions of the coordinates of the i:th electron it can be shown[11] that the contribution $\sigma_{i,\alpha\alpha}$ to a diagonal element of $\boldsymbol{\sigma}$ from an electron pair described by ψ_i is

$$\sigma_{i,\alpha\alpha} = \frac{e^2}{mc^2}\langle\psi_i^0\,|\,r^{-3}\,|\,\mathbf{r}(\mathbf{r}-\langle\mathbf{r}\rangle_i)-r_\alpha(r_\alpha-\langle r_\alpha\rangle_i)\,|\,\psi_i^0\rangle \tag{5}$$

$\langle\mathbf{r}\rangle_i$ is the position vector of the center of gravity of the considered electron. Summing over i we see that (5) gives the diamagnetic screening term arising from the expectation value of $\mathscr{H}_{\mu H}$ in the ground state if the origin O of the magnetic potential is chosen at $\langle\mathbf{r}\rangle_i$.

In the earlier applications of the method the oxygen lone-pair orbitals ψ_{Li} were assumed to be $s-p$ hybrids. The bonding orbitals ψ_B were constructed in the way[11,12]

$$\psi_B = \{(1-\gamma)\,(1s_H)^2 + \gamma\Phi_B^{\,2}\}^{1/2} \tag{6}$$

where $\Phi_B = (1+\lambda^2)^{-1/2}\,(\lambda\cdot 2s + 2p)$ is the bonding hybrid of oxygen. Here γ and λ are determined by the geometry and the dipole moment of the molecule.

c. Application to OH^-

To determine γ and λ in the present case we have to start from the "bond-orbital" wave functions calculated in.[10] These original one-electron orbitals are three equivalent lone-pair orbitals λ_i and one orbital b describing the bond.

These orbitals are linear combinations of the oxygen atomic orbitals (AO's) $1s$, $2s$, $2p_x$, $2p_y$, $2p_z$ (Slater orbitals) and the hydrogen AO $1s_H \sim \exp(-r_H)$.

We mix the functions λ_i with b by a transformation, which gives the three equivalent nonbonding orbitals A_i and the bonding orbital B, where A_i is orthogonal to B and has no contribution from the hydrogen AO $1s_H$. In

this way all the $1s_H$ content in the total wave function has been transformed to B.

As lone-pair orbital ψ_{Li} we use A_i, which is given by

$$A_i = 0.5587 \times 2s - 0.1906 \times 2p_h + 0.8072 \times 2\,p\pi_i \tag{7}$$

h represents the O—H direction and π_i a direction perpendicular to h. The original λ_i contained the oxygen AO $1s$, the coefficient of which is negligible in A_i.

B is given by

$$B = 0.7075 \times 1s_H - 0.0430 \times 1s - 0.0895 \times 2s + 0.5431 \times 2p_h \tag{8}$$

In order to identify B with ψ_B as far as possible the parameter λ in Φ_B is put equal to the quotient between the coefficients of $2s$ and $2p$ in B. This condition gives $\lambda = -0.1648$. Generally γ in (6) will be given by the experimental value of the dipole moment of the molecule. For OH^- we have no such experimental value. Therefore we give γ such a value that the center of gravity of the $\psi_B{}^*\psi_B$ electron distribution coincides with that of the B^*B distribution.

With the wave functions ψ_{Li} and ψ_B calculated in this way the contributions σ_B and σ_{Li} to the screening constant are obtained from (3) and (5).

The numerical calculations are made with the aid of an expansion of r^{-1} and $\mathbf{r}/r^3$ in spherical coordinates with the oxygen nucleus as a center (see Refs. 11 and 12).

The total screening constant $\frac{1}{2}$ is given by

$$\sigma = 3\,\sigma_{Li} + \sigma_B \tag{9}$$

σ, σ_{Li} and σ_B are tabulated in Table 1 together with quantities discussed under b in Discussion.

DISCUSSION

a. The method

It may be argued that the method used for construction of the wave function is somewhat arbitrary. However, in his study of the hydrogen halides [11] Fixman made the calculations both with tetrahedral hybridization and without hybridization in the oxygen part Φ_B of ψ_B (6) and in these two extreme cases the results differed from each other only in a few decimals $\times\ 10^{-5}$. It is further probable that the adjustment of γ in (6) to give the experimental value of the

Table 1. Values of the theoretically obtained screening constant σ and its parts σ_{Li} and σ_B, together with the "observed" value [5] σ_{obs}, the value σ_{hydr} remaining after correction for counterions [3] and the value $\sigma_{H\text{-bond}}$ estimated here for the H bonds in the hydration shell of OH^- (in ppm units). See also under "Introduction" and "Discussion". Chemical shifts with respect to liquid water are obtained if the σ value 25.2 for water [18,19] is subtracted from the tabulated values.

σ_{Li}	0.9	σ_{obs}	15
σ_B	29.4	σ_{hydr}	20.8
σ	32.2	$\sigma_{H\text{-bond}}$	21.4

dipole moment is important. In our case we have no such experimental value. Instead we have to determine γ with the aid of the charge distribution given by our originally calculated wave functions.[10] As such functions usually give reasonable values of dipole moments we may expect them to be acceptable even for the determination of γ.

Another parameter which affects the screening constant is the exponent ζ of the hydrogen AO $1s_H \sim \exp(-\zeta r_H)$. As pointed out by Fixman it has been found by variational calculation on molecules that ζ should be greater than 1.0. In, for example, HF ζ is equal to 1.32.

We mean, that such large ζ values are not the best ones for screening constants even if they give the lowest total molecular energies. The most important region for the σ values is the region near the proton because σ is given by an integral containing $1/r_H$. The nearer the proton we get, the better the free hydrogen atom wave function $1s_H \sim \exp(\sim r_H)$ should be. We have used the value $\zeta = 1.0$ for this reason and also because of the fact that the higher ζ value in Fixmans applications does not seem to give better results.

b. The obtained results

Regarding the results given in Table 1 it seems very difficult to explain the low apparent screening constant of OH^- without taking the environment of the ion into consideration. Therefore we introduce the effects of counterions and water molecules in the hydration shell. In the following we will discuss a model, which qualitatively describes the observed shift.

Let us, according to Kresge,[3] assume the downfield shift -4.4 ppm (see Introduction) to be assigned to the OH^- ion and its hydration shell. This shell has been discussed by Ackermann [13–15] and by Busing and Hornig.[16] Ackermann has proposed a model with the OH^- ion fitted into an ice-like lattice. Along one of the four tetrahedral directions from the oxygen atom its "own" H atom is situated. In the three remaining tetrahedral directions there are three oxygen atoms belonging to adjacent water molecules. Because of the strong negative charge (~ -0.8 a.u.) of the OH^- oxygen atom it seems very reasonable to assume that each one of the three mentioned O...O lines contains an H atom belonging to the adjacent water molecule. The three hydrogen bonds formed in this way should be very strong. Such bonds with a length of 2.69 Å have also been found in X-ray studies of $LiOH \cdot H_2O$.[17] From the results of Raman spectroscopical studies performed by Busing and Hornig [16] it is further concluded that the hydrogen atom in OH^- does not take part in any essential hydrogen bonding.

The apparent shift, -4.4 ppm, can be regarded as the sum of the shifts of the proton in OH^- and the protons in the three strong hydrogen bonds. The screening constant in liquid water, which is referred to here, is 25.2 ppm.[18,19] The screening constant of OH^- calculated by us here is 32.2 ppm. This means, that the shift of the proton in the "pure" OH^- ion should be $\sim +7$ ppm. In order to get the sum -4.4 ppm from this shift and the shifts in the three strong H bonds we have to assume each of the latter shifts to be ~ -3.8 ppm (Table 1).

It does not seem unlikely, that the difference between the proton screening constant of the actual strong H bonds and the constant of a normal water-water H bond is of this order of magnitude. For comparison we mention the H bond shift in hydrogen fluoride, which is −2.1 ppm with respect to water.[18]

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