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Abstract

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MAGNETIC RELAXATION OF PROTONS AND DEUTERONS IN AQUEOUS SOLUTIONS OF Cr^{3+} IONS

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Hausser and Laukien ([1]) found that the longitudinal time T_1 of nuclear magnetic relaxation of protons in "green" aqueous solutions of $CrCl_3$ becomes shorter upon heating in the temperature interval 0–20°C. Gutovsky et al. ([2]) obtained analogous results for "violet" solutions of $CrCl_3$ and suggested that changes in the structure of the solvation shells of Cr^{3+} ions may be responsible for this decrease. A different explanation of this fact was given by Bloembergen and Morgan ([3]). They believe that the shortening of T_1 is caused by a decrease in the residence time τ_H of protons in the first hydration shell of the Cr^{3+} ion.

It is known ([4]) that the rates of chemical exchange of protons and deuterons differ substantially. This difference should be reflected in the nuclear relaxation times if the latter are determined by the rates of hydrogen exchange. It therefore seemed of interest to carry out a comparative study of the magnetic relaxation of protons and deuterons in solutions of Cr^{3+} ions as a function of temperature and of the isotopic composition of the solvent (water).

The times T_{1D}, T_{2D}, T_{1H}, T_{2H} were determined by the spin-echo method. Proton resonance was observed at a frequency of 28.7 MHz, and deuteron resonance at 4.4 MHz, in the same constant magnetic field of strength 6730 oersteds. The transverse relaxation times were measured using 90–180°, and the longitudinal times using, respectively, 90–180°–90–180° sequences of radio-frequency pulses. The accuracy of the measurements was: $T_{1D} \pm 15\%$, $T_{2D} \pm 10\%$, $T_{1H} \pm 10\%$, $T_{2H} \pm 7\%$, temperatures ±2°C. Chromium nitrate of "chemically pure" grade and heavy water containing 99.5% deuterium were used for preparation of the samples. After preparation, the solutions were kept for several days at room temperature. It turned out that the influence of the temperature "prehistory" of the solution on T_{1H} and T_{2H}, which had been observed in ([2]) for "violet" solutions of $CrCl_3$, is also present in "violet" solutions of $Cr(NO_3)_3$. The values of the times T_{1H} and T_{2H} of samples kept for several hours at 90°C were 15% higher than T_{1H} and T_{2H} of samples not subjected to heating.

The results of measuring the temperature dependence of the relaxation times are given in Fig. 1. Heating of the solution causes an increase in T_{1D} in the temper-

Figure 1

Figure 1: Figure 1

ature interval 0-100°C, whereas T_{1H} first decreases, passes through a minimum, and only then begins to increase. An increase in temperature is accompanied by a slight increase in T_{2D}, while T_{2H} becomes much shorter. Apparently, such a difference in the relaxation characteristics of protons and deuterons can be explained only by taking account of the mechanism of hydrogen exchange. To interpret the results we use the formula ([3])

$$(T_1)^{-1} = (T_{1W})^{-1} + (Nn/N_n)(T_{1c} + \tau_n)^{-1}, \tag{1}$$

where T_1 is the measured nuclear relaxation time, T_{1W} is the nuclear relaxation time in the pure solvent, T_{1c} is the relaxation time of nuclei in the first hydration sphere of a paramagnetic ion, τ_n is the residence time of nuclei in the first hydration sphere, N is the concentration of paramagnetic ions, N_n is the concentration of nuclei in the solution, n is the number of nuclei in the first hydration sphere. Under the experimental conditions, $(N = 0.1M)$, the first term on the right-hand side of (1) is considerably smaller than the second. Denoting $(Nn/N_I) = Pb$, we write:

$$(T_1)^{-1} \simeq Pb\,(T_{1c} + \tau\,)^{-1}. \tag{2}$$

An analogous relation also holds for T_2

$$(T_2)^{-1} \simeq Pb\,(T_{2c} + \tau\,)^{-1}. \tag{3}$$

It may be assumed that Pb does not depend on the isotopic composition of the solvent.

Fig. 1. Temperature dependence of the relaxation times of protons and deuterons in an aqueous solution ($50\%\,H_2O$ + $50\%\,D_2O$) containing $0.1\,M$ chromium nitrate:
1—NT_{2H}; 2—NT_{1H}, 3—NT_{2D}, 4—NT_{1D}

The relaxation times T_{1c} and T_{2c} entering equations (1)–(3) are:

$$(T_{1c})^{-1} = (T_{1g.g})^{-1} + (T_1\ \ )^{-1}, \tag{4}$$

$$(T_{2c})^{-1} = (T_{2\,.}\,)^{-1} + (T_2\ \ )^{-1}. \tag{5}$$

In (4) and (5) the first terms on the right-hand sides denote the contribution of the dipole interaction, and the second terms that of the exchange interaction, to the relaxation times.

Let us first consider the behavior of the longitudinal times. Usually $(T_1\ )^{-1} \ll (T_{1\ .})^{-1}$. Then $(T_{1c})^{-1} \simeq (T_{1\ .})^{-1} \sim \gamma_I^2$. Here γ is the gyromagnetic ratio of the nucleus whose relaxation is being considered. Since $(\gamma_{\mathrm{H}}/\gamma_{\mathrm{D}})^2 = 6.53$, it may be expected that the time $T_{1\mathrm{D}\ .}$ should be 42.5 times longer than $T_{1\mathrm{H}\ .}$. The residence time of a deuteron, τ_{D}, in the first hydration shell of a Cr^{3+} ion should also be longer than τ_{H}, but only by a factor of 5–10 ([4]). Consequently, the assumed excess in (3) of τ_{H} over $T_{1c\mathrm{H}}$ at low temperatures should decrease or disappear entirely when the relaxation of deuterons is considered. This is indeed observed experimentally. The dependence of $T_{1\mathrm{D}}$ on temperature bears no traces whatever of the influence of τ_{D} and is determined mainly by the temperature dependence of the correlation time of the magnetic dipole interaction between the paramagnetic ion and the deuteron. To account for the possible shortening of the times $T_{1\mathrm{D}}$ due to quadrupole relaxation of deuterons, the temperature dependence of $T_{1w\mathrm{D}}$ in pure water was measured. It turned out that quadrupole relaxation contributes no more than $\sim 10\%$ to the measured $T_{1\mathrm{D}}$. Taking this contribution into account, it was found that $(T_{1\mathrm{D}\ .}/T_{1\mathrm{H}\ .}) = 36$ at 90°C, which is close to the theoretically expected value 42.5. The times $T_{1\mathrm{H}}$ were also measured in solutions of Cr^{3+} ions in 100% H_2O and in a mixture of 5% H_2O + 95% D_2O. The form of the curves obtained is similar to that shown in Fig. 1 for $T_{1\mathrm{H}}$ in a solution containing 50% H_2O and 50% D_2O, with the only difference that in the solution containing 95% D_2O the minimum is shifted toward higher temperatures, and in the 100% H_2O solution toward lower temperatures. The values of $T_{1\mathrm{H}}$ in the range 20—0°C increase as heavy water is added. At temperatures above ~ 60°C, the values of $T_{1\mathrm{H}}$ for all three solutions do not differ from one another within the limits of experimental error. Consequently, the correlation times of the dipole interaction cannot depend appreciably on the isotopic composition of the solvent. From the slope of the $T_{1\mathrm{H}}$ curves in the high-temperature region and of $T_{1\mathrm{D}}$ in the interval 0—100°C, we found the activation energy for reorientation of the hydrated chromium ion to be $V_c = 3.2$ kcal/mol.

and the dipole correlation time $\tau_c(300^\circ\mathrm{K}) = 10 \cdot 10^{-11}$ sec; the latter is in good agreement with the value $\tau_c(300^\circ\mathrm{K}) = 8 \cdot 10^{-11}$ sec obtained in [3]. In determining these quantities it was assumed that $\omega_s \tau_c \gg 1$ (ω_s is the Larmor precession frequency of the electron spins), and it was taken that $\tau_c = \tau_c^0 = \exp(V_c/RT)$. With the aid of formula (2), from the temperature dependence of $T_{1\mathrm{H}}$, the values of the residence times of protons τ_{H} in the first hydration sphere of Cr^{3+} ions were determined. They proved to be $3.6 \cdot 10^{-6}$ sec, $5.4 \cdot 10^{-6}$ sec, and $8.7 \cdot 10^{-6}$ sec at 300°K for 100% H_2O, 50% H_2O + 50% D_2O, and 5% H_2O + 95% D_2O, respectively. The temperature dependence of τ_{H} satisfies the condition $\tau_{\mathrm{H}} = \tau_{\mathrm{H}}^0 \exp(V_{\mathrm{H}}/RT)$ in the range 0-40°C, with an activation energy for proton exchange $V_{\mathrm{H}} = 10 \pm 0.2$ kcal/mole for all three solutions.

These quantities are in agreement with the values of τ_H and V_H obtained in [3].

The comparison made above between T_{1D} and T_{1H} is also valid for transverse relaxation times, since $(T_{2\,ex})^{-1} \sim \gamma_l^2$, according to [6], and $(T_{2\,d.d.})^{-1} = 1.16\,(T_{1\,d.d.})^{-1}$. T_{2D} is not affected by hydrogen exchange, and the weak increase of T_{2D} upon heating may be attributed to a decrease in the contribution from the dipole mechanism. On the contrary, the strong shortening of T_{2H} in the range 0-30°C is due to a decrease in τ_H. The values of T_{2H} increase upon addition of D_2O in the low-temperature region and prove to be independent of the isotopic composition of the solution at $t^\circ \gg 65$°C. Assuming that T_{2H} at high temperatures does not depend on τ_H, and that the time T_{2cH} changes upon heating in the same way as $T_{2cD} = (1/Pb)T_{2D}$, constants characterizing hydrogen exchange were found. These constants practically coincided with those calculated from the temperature dependence of the T_{1H} times. In the case where $\tau_s \ll \tau_H$, the exchange contribution to T_2 is expressed by formula (5):

$$(T_{2\,ex})^{-1} = (1/3)\,Pb\,S(S+1)(A/\hbar)^2\tau_s, \tag{6}$$

where $S = 3/2$ is the electron spin of the Cr^{3+} ion, A is the exchange-interaction constant, and τ_s is the electron relaxation time. Taking $\tau_s = 5 \cdot 10^{-10}$ sec [3], from the experimental data, with the aid of (6), we found*: $(A_H/h) = 3 \cdot 10^6$ Hz and $(A_D/h) = 4.3 \cdot 10^5$ Hz. The value of (A_H/h) found by us is greater than $(A_H/h) = 2 \cdot 10^6$ Hz, reported in [3]. According to the theory [6], $A_I \sim \gamma_I |\psi(0)|_I^2$; here $|\psi(0)|_I^2$ is the density of unpaired electrons of the ion at the nuclei of the hydrogen atoms in the hydration shell. Comparison of the quantities A_H and A_D gave: $|\psi(0)|_D^2 = 0.93|\psi(0)|_H^2$, i.e., the density of unpaired electrons at deuteron sites is somewhat lower than at proton sites. An analogous conclusion was made earlier for aqueous solutions of Mn^{2+} ions [7].

Fig. 2. Dependence of the relaxation times of protons and deuterons on the isotopic composition of the solvent (water) at a temperature of 0°C. Chromium nitrate concentration 0.1 M: 1–NT_{2H}, 2–NT_{1H}, 3–NT_{2D}, 4–NT_{1D}.

Figure 2 presents the dependence of the relaxation times of protons and deuterons in aqueous solutions containing 0.1 M chromium nitrate at 0°C on the isotopic composition of the solvent. T_{1H} and T_{2H} lengthen as D_2O is added, whereas the times T_{1D} and T_{2D} do not undergo changes exceeding the experimental errors. A weak ($\sim 30\%$) increase–

* Calculations were performed for a temperature of 90°C; there are grounds to believe that in the range $\sim$ 20-100°C the time τ_s for a 0.1 M solution of Cr^{3+} should not change substantially with temperature.

T_{1H} and T_{2H} upon addition of D_2O was found at room temperature. These results can be readily understood on the basis of the foregoing.

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Note: Figure translations are in progress. See original paper for figures.