Nuclear Magnetic Relaxation of ^{207}Pb in an Aqueous Medium

This communication reports some preliminary results concerning mechanisms of magnetic relaxation of the ^{207}Pb nucleus in aqueous electrolyte solution. In order that the present results should reflect, as far as possible, interactions between the lead nucleus and its unperturbed hydration sphere, we have chosen to study relaxation in acidic perchlorate solutions, in which ion association is generally regarded to be negligible (*1*).

A standard solution 3.5 M in $Pb(ClO_4)_2$ was prepared by dissolving reagent grade PbO in doubly distilled lead-free 70% $HClO_4$. The sample was degassed by a series of freeze–pump–thaw cycles and sealed under its own vapor pressure in a 10 mm o.d. tube. Relaxation times were measured using a Bruker B-KR 322S variable frequency (4–60 MHz) pulsed spectrometer at a fixed frequency of 10.431350 MHz operating in the triplet mode. The magnetic field was held constant by means of an external proton lock. The sample temperature was controlled within ±0.5°C with a Bruker B-ST 100/700 variable temperature accessory. Sampling techniques and other experimental details are described elsewhere (*2*).

The temperature dependence of T_1 is shown in Fig. 1. At least two distinct mechanisms dominate relaxation above and below the maximum at 35°C. The behavior of T_1 above 35°C is characteristic of either the spin–rotation interaction or of scalar coupling modulated by chemical exchange (*2*). A scalar interaction arises from coupling between lead nuclei and ^{17}O of water molecules surrounding the hydration sphere. An upper limit to this contribution to T_1 can be estimated from the theoretical relation:

$$(T_1)_{sc}^{-1} = \tfrac{2}{3} A^2 S(S+1) \frac{\tau_S}{1 + (\omega_I - \omega_S)^2 \tau_S^2} NC,$$

where A is the coupling constant, τ_S is the exchange time, N is the coordination number of lead and C the natural abundance (0.037%) of ^{17}O. No coupling constants between lead and oxygen have previously been measured, but Jameson and Gutowsky's (*3*) collection of coupling constants of directly bonded elements indicates that $A/2\pi$ does not exceed 1 KHz. Similarly the exchange time is unknown, but the value that gives the largest possible relaxation contribution is obtained when $(\omega_I - \omega_S)\tau = 1$. Assuming these values for A, τ_S and a primary hydration number of six, we find that $(T_1)_{sc}(^{207}$Pb$) \simeq$ 200 sec. This value is larger by an order of magnitude than the experimental relaxation times, and, therefore, an appreciable scalar contribution can be ruled out.

We are left with spin–rotation as the dominant relaxation mechanism above 35°C. The hydrated lead ion probably does not represent a well defined molecular species, and, thus, details of the motion that gives rise to this interaction are of special interest. Although the T_1 measurements appear not to provide an unambiguous description of the motion, calculation of the angular momentum correlation time suggests that relevant motions are not those for a rigid hydration sphere but rather pertain to

individual water molecules on the ionic surface. To examine this question we will use the measured spin–rotation component and Hubbard's (4) rate expression,

$$(T_1)^{-1}_{sr} = 2IkTC_0^2 \tau_{J/\hbar^2} \tag{1}$$

to compute τ_J assuming (1) that the hydration sphere of Pb^{+2} is rigid for times comparable to the angular momentum correlation time and (2) that the coordination sphere of Pb^{+2} is octahedral. The spin–rotation constant, C_0, for lead in a site of cubic symmetry
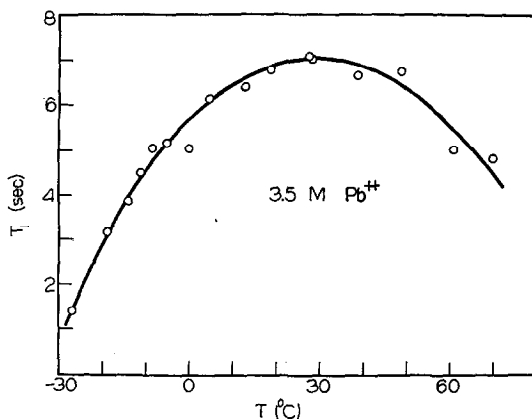

FIG. 1. T_1 of ^{207}Pb in 3.5 M $Pb(ClO_4)_2$ solution versus temperature.

can be determined directly from recent optical pumping data in conjunction with Flygare's (5) expression relating the scalar C_0 to the paramagnetic part of the shielding constant, σ_p,

$$C_0 = \left(\frac{e^2}{6mc^2}\right)^{-1} \left(\frac{\pi}{M_p \mu_N \gamma_{Pb}}\right)^{-1} \left(\frac{\sigma_p}{3I}\right) \tag{2}$$

[the symbolism is that given in Ref. (6)] $v_0 \sigma_p$ equals the chemical shift in hertz between resonances of the vapor phase diamagnetic lead atom and the hydrated lead ion. Optical pumping experiments (7) have determined that the effective ^{207}Pb magnetic moment in the vapor is 0.2049440 $\mu_N(^1H)$. From this value we compute a resonance frequency of 10.2484 MHz in the field maintained by our proton lock, for which v (^1H) = 50.00560 MHz. The hydrated lead ion was resonant at a frequency of 10.43135 MHz in the same field, giving $\sigma_p = -183$ kHz.

Before either the spin–rotation constant or τ_J can be calculated from Eqs. (1, 2), it is necessary to estimate the moment of inertia, I.

In accord with the assumptions stated above, we take the basic molecular unit to be the primary hydration sphere. The crystallographic radius for Pb^{+2}, $r_{Pb} = 1.2$ Å (8), and the crystallographic radius of oxygen, $r_0 = 0.66$ Å (8), are consistent with a distance of 1.95 Å between the lead nucleus and the center of mass of a water molecule. On this basis, I is computed to be 45.5×10^{-39} gm-cm^2 and a value of 41.1 kHz is obtained for $C_0/2\pi$.

The two unknown quantities in Eq. (1) are τ_J and the value of $(T_1)^{-1}_{sr}$ due to the spin–rotation interaction. If it is assumed that the spin–rotation contribution at 35°C is equal

to the contribution from the relaxation mechanism dominant below 35°C then $(T_1)_{sr} = 2(T_1)_{obs} = 14.2$ sec, which gives the value $(T_1)_{sr}^{-1} = 0.0705$ sec^{-1} at 35°C.

The resulting angular momentum correlation time predicted from this model is extraordinarily short: $\tau_J = 3.0 \times 10^{-16}$ sec. This time scale is short even relative to that of molecular vibrations. Although structured liquids can be expected to have very short angular momentum correlation times [values of shorter than 3.7×10^{-14} sec have, in fact, been measured for some simple liquids (9)], it is difficult to conceive of any rotational motion of a massive molecular unit that could correspond to this time scale. The fastest motion for a rigid hydration sphere is probably that in which the sphere breaks out of one hydrogen-bonded configuration and reorients into another. This motion probably has a duration longer than 10^{-14} sec. In view of the extreme shortness of our computed τ_J, it seems likely that the solvation sphere is nonrigid during intervals comparable to τ_J, in which case a spin–rotation constant based on the chemical shift is not applicable.

We have not commented on the mechanism of relaxation below 35°C. Detailed studies, involving isotopic substitution and variable frequency measurements are now in progress and should permit an unambiguous determination of the mechanism. If the low temperature measurements allow determination of the angular correlation time, an interesting comparison of τ_θ and τ_J [related by Hubbard's relation (4) for diffusive motions] may be possible.

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