

OBSERVATION OF PULSED NUCLEUS-NUCLEUS POLARIZATION

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Submitted to JETP editor April 27, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) **49**, 760-764 (September, 1965)

Experiments on double nuclear magnetic resonance in a flowing liquid are described. The work was carried out with aqueous solutions of hypophosphates at different concentrations and temperatures. With a change in the intensity of the solvent line, the hypophosphate proton line intensities increase greatly, sometimes by a factor of three. It is shown experimentally that polarization of the hypophosphate protons does not result from relaxation processes but appears at the instant of radio-frequency resonant action on the solvent protons, the characteristic time for the appearance of polarization being much shorter than the transverse relaxation times of the solvent and hypophosphate protons. Polarization of the hypophosphate protons by the solvent protons is attributed to molecular association based on the hydrogen bond. The mechanism of the observed polarization is not elucidated.

WE have investigated the structure of concentrated hypophosphate solutions by the method of transient dynamic polarization^[1,2] using a flow-through measuring head.^[3] The experimental arrangement is shown schematically in Fig. 1. The solution flows successively through a strong polarizing magnetic field H_p and two NMR detectors L_1 and L_2 located in a weak magnetic field. The flow time from H_p to L_2 is shorter than the spin-lattice relaxation time of protons in the solvent and hypophosphate.

As the solution flows through L_1 , which is connected to an rf oscillator, the nuclei are acted upon by an rf field pulse of duration τ_n , which is the time required for flow through L_1 . (The pulsed rf action results from the limited time spent by the nuclei within the space of L_1 .) The small gradient of the external magnetic field H_n is perpendicular to the liquid's direction of motion. Because of the pulsed rf field action the magnetization direction of a nucleus upon leaving the detector forms the angle $\theta = \gamma H_1 \tau_n$ with H_n , where H_1 is the resonant rf field strength in L_1 .

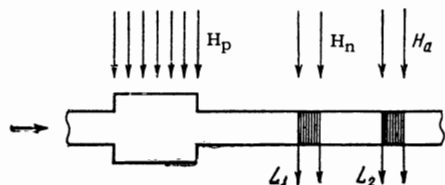


FIG. 1. Experimental arrangement for studying the spin-spin interaction between different nuclei in a moving liquid. H_p - magnetic field of polarizing magnet; H_n - magnetic field in the region of the nutation detector L_1 ; H_a - magnetic field in the region of the detector L_2 (analyzing field).

Thus by selecting the resonant frequency the detector L_1 enables us to rotate the nuclear magnetization direction for an individual NMR line through any angle θ .

In the segment of the liquid's course through the inhomogeneous magnetic field between L_1 and L_2 the transverse magnetization component of the affected line, $M_{\perp} = M_0 \sin \theta = M_0 \sin \gamma H_1 \tau_n$, disappears rapidly, and the line intensity in L_2 is determined only by the longitudinal component $M_{\parallel} = M_0 \cos \gamma H_1 \tau_n$. The detector L_2 is used to observe the entire NMR spectrum and its evolution following the rf field action on individual lines. The magnetic field in which L_1 and L_2 were located considerably exceeded the rf field but remained small enough to obviate appreciable polarization of the liquid. The flow was turbulent, with a Reynolds number $Re \sim 8000$. The transitions between the fields H_p , H_n , and H_a (the field at L_2) were adiabatic.

The working solutions were concentrated solutions of sodium, potassium, and calcium hypophosphates etc. The proton spectrum of an aqueous hypophosphate solution in the field $H_a = 35$ Oe contains three lines - a strong line of the protons in water and two weaker lines representing the hypophosphate protons and separated 257.5 cps from the former on both sides.^[3,4] The hypophosphate proton doublet results from a pseudo-exchange interaction between the protons and phosphorus nuclei. Because of the rapid relaxation of phosphorus, rapid equalization of the hypophosphate proton lines is observed when one of these lines is rotated through some angle θ .

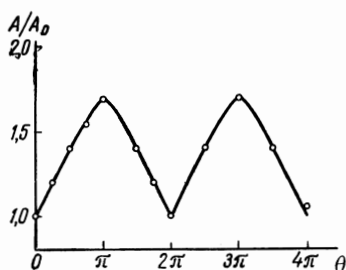


FIG. 2. Experimental relative growth of signal intensity, A/A_0 , from sodium hypophosphate protons vs. rotational angle θ of water proton magnetization. The magnetic field at L_1 was ~ 3.5 Oe; the temperature of the solution was 27°C .

When the two side lines were saturated by applying a rectangular pulse to one of them in L_1 and their growth in time resulting from the relaxation of water protons was observed by means of L_2 (the time of flow between L_1 and L_2 being varied by increasing the length of the pipe), it was found that a pseudo-exchange interaction between protons of the salt and of the solvent is dominant in aqueous hypophosphate solutions. Transition probabilities were computed, considering that the external field does not polarize protons of both the salt and the water, from the equation [1]

$$(d\mathbf{I}/dt)_{t \rightarrow 0} = -\sigma\mathbf{S}, \quad (1)$$

where \mathbf{I} is the magnetization of protons in the salt, \mathbf{S} is the magnetization of solvent protons, $\sigma = W_2 - W_0$, W_2 is the probability of $(+ \rightarrow -)$ transitions, and W_0 is the probability of $(+ \rightarrow -)$ transitions. The experimental result $\sigma \approx -0.23 \text{ sec}^{-1}$ (i.e., $\sigma < 0$)¹⁾ was obtained for a $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ solution containing 10 moles in 1000 g H_2O . The sign of σ indicates the dominance of the pseudo-exchange interaction over the dipole-dipole interaction.^[1,2]

We could expect, because of the sign of σ , that when the solvent proton line is saturated in L_1 the salt proton line in L_2 would become weaker than when the lines of the spectrum are in thermal equilibrium. However, when the solvent proton line was saturated or inverted in L_1 , the hypophosphate proton lines were strengthened considerably in L_2 . For example, with a $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ solution having 10 moles in 1000 g H_2O at 12°C the hypophosphate proton lines became three

times stronger when a rectangular pulse was applied to the solvent line.

We shall now point out some characteristics of the observed polarization. Figure 2 shows the experimental dependence of the relative nuclear polarization on the angle θ of the water-proton magnetization direction. (θ was varied by changing H_1 .)

Figure 3 shows the experimental relationship between the relative growth of nuclear polarization and the rate of liquid flow with a constant rotational angle $\theta = \pi/2$ of the water proton magnetization, for a $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ solution having 10 moles in 1000 g H_2O at two temperatures. The greatest growth of polarization is associated with an optimum flow rate. A constant angle $\theta = \pi/2$ was maintained by varying H_1 in L_1 . The angle θ was calibrated in advance as a function of H_1 and of the flow rate for a weakly relaxing substance (distilled water).

Figure 4 shows the experimental dependence of the amplification factor on the concentration of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ for $\theta = \pi$ at 22°C . With increasing concentration the amplification also increases. In performing these nucleus-nucleus polarization experiments the water-proton signal amplitudes in both the normal and inverted states were monitored for the purpose of registering a possible transfer of polarization from water protons to hypophosphate protons. The expected change of the amplitude for water was about 5%, but this could not be recorded reliably.

We must consider two possible cases of the observed polarization: 1) as a result of some process occurring in the space between the detectors L_1 and L_2 , and 2) polarization occurring within L_1 . Some proof can be advanced that the first case does not occur.

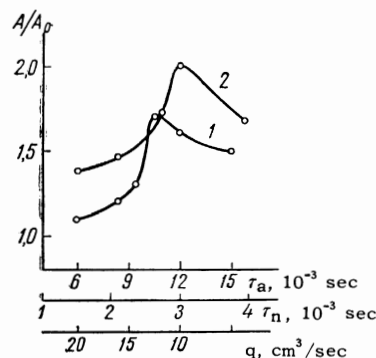


FIG. 3. Experimental relative growth of signal intensity, A/A_0 , for constant rotational angle $\theta = \pi/2$ of water proton magnetization direction vs. time of action τ_n by rf field in L_1 and versus observation time τ_a , for $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (10 moles in 1000 g H_2O) at 17°C (curve 2) and 27°C (curve 1).

¹⁾The rate of chemical exchange between water and sodium hypophosphate showed^[5] that the lifetime of hypophosphate protons for exchange with water exceeds 100 hours. Therefore the chemical exchange of protons does not affect the sign or magnitude of σ .

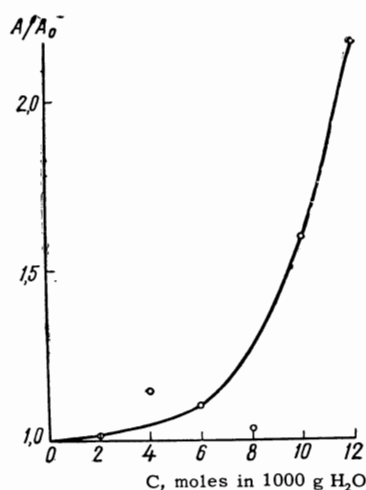


FIG. 4. Experimental relative growth of signal from sodium hypophosphate protons, with the water proton magnetization direction rotated through the angle $\theta = \pi$, versus hypophosphate concentration at 22°C.

1. Assuming that the pseudo-exchange interaction is dominant between water protons and hypophosphate protons, we arrive at the conclusion that the sign of the polarization occurring in the indicated region due to a transient polarization effect should be the opposite of the observed sign. The dominance of the pseudo-exchange interaction between hypophosphate and solvent protons is indicated not only by the sign of σ , but also by the temperature dependence of the polarization in the case of the observed transient polarization^[2] and in the case of polarization induced by saturating the solvent line.

2. From measurements of the hypophosphate proton line intensification for different volumes of the pipe between L_1 and L_2 while maintaining a constant total volume of the pipe between the polarizer and L_2 , it follows that the relative intensification is identical in all cases.

3. The direct measurement of the longitudinal relaxation time of hypophosphate protons with both equilibrium magnetization and inverse magnetization of the solvent protons in the given region between L_1 and L_2 shows that in the case of inverse magnetization of the water protons the salt proton relaxation time is somewhat shorter (by $\sim 3-5\%$) than in the case of equilibrium polarization.

We shall now consider the possible causes of polarization in L_1 . The flow time through this detector (i.e., the duration of the rf pulse) is of the order 3×10^{-3} sec; the volume of the detector is 0.03 cm³. Polarization associated with spin calorimetry^[6,7] is characterized by a change in the spin temperature of one spin system at the

expense of the other spin system in a time much longer than the transverse relaxation times of both spin systems. The transverse relaxation times for water protons and hypophosphate protons both equal approximately ~ 0.3 sec. The time of action of the rf field was about 3×10^{-3} sec, which is shorter by two orders of magnitude. Therefore polarization associated with the equalization of spin temperatures in a rotating coordinate system cannot account for the observed effect.

We might conclude that the observed polarization results from an interaction between the protons of the salt and of water during rf-field induced transitions between the Zeeman levels of the water protons, i.e., by simultaneous reorientations of two interacting spins. However, the simultaneous reorientation of two nuclear spins in forbidden transitions would require that the applied rf field frequency equal the difference between the Larmor frequencies of the nuclei in which simultaneous spin reorientations occur, i.e., $\nu = 257.5$ cps. It has already been mentioned that in the described experiments the field in L_1 has the Larmor frequency of water protons. We believe that the observed polarization of hypophosphate protons accompanying a resonant action on the solvent protons cannot be accounted for within the frameworks of existing nuclear polarization theories.

Some comments on aqueous hypophosphate solutions are in order. In^[8] it is noted that a hydrogen bond can possibly be formed between water and hypophosphate protons combined with phosphorus. For the hypophosphate and water molecules associated by the hydrogen bond we can expect that on the basis of a donor-acceptor interaction a pseudo-exchange spin-spin interaction takes place between nuclei with non-zero spins belonging to different molecules (a hypophosphate and water) of the association. This interaction will not produce a multiplet structure in the NMR spectrum if the mean lifetime of the hydrogen bond is much smaller than the reciprocal of the spin-spin interaction constant. However, in this case the given interaction furnishes an additional relaxation mechanism for the interacting nuclei. These ideas are fully supported by the transient polarization experiments that we have described ($\sigma < 0$).

In connection with any polarization mechanism in the hypophosphate-water system, the magnitude of the polarization should probably depend on the degree of association between the phosphate and water molecules and on the lifetime of the associ-

ation. This is supported by the temperature and concentration dependences of the polarization (Figs. 3 and 4). The dependence of hypophosphate proton polarization on the time of flow through L_1 and L_2 (Fig. 3) also probably depends on the lifetime of the associated state.

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Translated by I. Emin

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