

LÜHIUURIMUSI КРАТКИЕ СООБЩЕНИЯ

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INTERMOLECULAR DOUBLE RESONANCE AND OVERHAUSER EFFECT IN LIQUIDS

Intramolecular Overhauser effect is well known and can be used to construct energy level diagrams in high-resolution NMR spectra [1-5] as well as for the determination of relaxation parameters [6-11]. In most cases it has been assumed that local population changes are produced, involving first of all such spectral lines that have energy levels in common with the perturbed line and that the lattice retains thermal equilibrium. Yet this is clearly not the case if intermolecular processes make a significant contribution to spin-lattice or spin-spin relaxation. Such processes are very important even in large molecules [12] and since they depend upon two-quantum transitions with probabilities W_0 and W_2 in which the magnetic quantum number m of some coupled pair of nuclei belonging to two interacting molecules changes by 0 or ± 2 , depending on whether the relaxation is predominantly scalar or dipolar, one can expect population and line intensity changes for one kind of nuclei if the signal of the other kind of nuclei, possibly in another molecule, is saturated. As can be seen from Eq. (1-3), a predominantly dipolar coupling gives a positive and scalar coupling a negative Overhauser effect, if the interacting nuclei have magnetogyric ratios of the same sign. If the other interacting spin belongs to a free electron, then these effects are much stronger and with reversed signs [13-15]. Regardless of the particular kind of spin, such phenomena are well described by the theory of Solomon [14, 16, 17], and although it is strictly applicable to AX systems (like HF) only, it remains qualitatively true even in much more complicated cases. The equation of motion for the mean value of the z-component of magnetization $\langle I_z \rangle$ of one kind of the nuclei can be written as follows:

$$\frac{d\langle I_z \rangle}{dt} = -\rho\{\langle I_z \rangle - I_0\} - \sigma\{\langle S_z \rangle - S_0\} \quad (1)$$

where S designates the nucleus whose NMR signal is being saturated by a strong rf field H_2 . I_0 and S_0 are equilibrium magnetisations, while ρ and σ depend upon relaxation transition probabilities W . Using the notation of Abragam [14], one obtains

$$\rho = (W_0 + 2W_1 + W_2) = \frac{1}{T_1^I} = S(S+1) \left\{ \frac{4\delta}{3} + \frac{2A^2}{3} \cdot \frac{\tau_e}{1 + (\omega_I - \omega_S)^2 \tau_e^2} \right\} \quad (2)$$

$$\sigma = (W_2 - W_0) = \frac{1}{T_1^S} = I(I+1) \left\{ \frac{2\delta}{3} - \frac{2A^2}{3} \cdot \frac{\tau_e}{1 + (\omega_I - \omega_S)^2 \tau_e^2} \right\} \quad (3)$$

$$\frac{1}{T_2^I} = S(S+1) \left\{ \frac{4\delta}{3} + \frac{A^2}{3} \tau_e \left[1 + \frac{1}{1 + (\omega_I - \omega_S)^2 \tau_e^2} \right] \right\} \quad (4)$$

where $\delta = \gamma_I^2 \gamma_S^2 \hbar^2 b^{-6} \tau_c$ and $A = 2\pi J$; b is the distance between interacting spins, τ_c and τ_e are correlation times for dipolar relaxation and scalar relaxation respectively, while ω_I and ω_S are resonance frequencies of the interacting pair of nuclei.

Intermolecular transient Overhauser effects were first observed by Nagumo and Kakiuchi [18] in solutions of substituted aromatic hydrocarbons in proton-containing solvents. Similar effects, where line intensities depended upon sweep direction if a fairly strong measuring field H_1 was used, were noted by Wertz [19]. Intermolecular Overhauser effects were also investigated under stationary conditions [20] and using a flowing solution of sodium hypophosphite [21].

Our experiments were carried out at 40 Mc and room temperature (30°C) with a universal NMR spectrometer [22], stabilized by a spin generator and using frequency synthesis to generate the necessary r_f fields H_1 and H_2 , whose frequencies ω_1 and ω_2 could be swept independently. All samples were purified by repeated freeze-pump-thaw cycles under vacuum and sealed in 4 mm o.d. glass tubes. No internal TMS-standard was used. The strength of the saturating field H_2 was 2.4 cps. Overhauser effects were measured as changes of peak values of spectral lines and are given in the following table.

It appears that intermolecular Overhauser effect is quite widespread, provided that intramolecular relaxation is not too prevalent (as in pyridine). Largest effects are observed in systems with high mobility of components (mixtures with cyclohexane) while molecular association tends to diminish the effect (acetone + 2,4 xyleneol). In the last case the correlation time τ_c increases and this may increase the contribution of intramolecular dipolar relaxation or even diminish the intermolecular dipolar relaxation, depending on the magnitude of increase in τ_c . No Overhauser effect could be observed between aromatic and methylene protons in tetraline and cyclohexylbenzene (but a small effect was observed in toluene and acetic acid). Either the intramolecular relaxation in tetraline and cyclohexylbenzene must be much stronger than in benzene and cyclohexane or these liquids must have a quite orderly structure. Orderly structures may exist, as can be seen from the fact that the protons of dimethylformamide do not relax hypophosphite protons, but the water protons do in a three-component solution. The negative Overhauser effects in alcohols are not strictly intermolecular, but the scalar relaxation depends upon proton exchange between molecules. Large effects are observed, and it is clear that scalar relaxation in acidified alcohols is much stronger than dipolar relaxation. The exchange time τ_e was computed from the linewidths by the use of Eq. (4). τ_e appears to be very sensitive to small admixtures of aprotic solvents and can be sharply increased by a single drop of CCl_4 or CS_2 into the sample tube. In sodium hypophosphite dipolar relaxation dominates, contrary to the suggestion of [21] and the magnitude of the effect is not abnormal, in a strong field H_0 at least. The dynamic polarization is quickly achieved in alcohols since in the presence of a strong r_f field H_2 the time constant T_0 for the change of $\langle S_z \rangle$ is $1/T_0 = 1/2(1/T_1 + 1/T_2)$ [23] that may be very short if the lines are broad. The time

Systems studied	Molar ratio of components	Investigated group of spins	Saturated group of spins	Overhauser effect $\frac{\langle I_z \rangle - I_0}{I_0}$	$(\omega_I - \omega_S) \tau_e$
Chloroform + cyclohexane	1 : 4	CHCl ₃	CH ₂	0.40	
Chloroform + cyclohexane	1 : 1	CHCl ₃	CH ₂	0.20	
Chloroform + benzene	1 : 4	CHCl ₃	CH	0.20	
Chloroform + cyclohexylbenzene	1 : 4	CHCl ₃	CH ₂	0.22	
Chloroform + cyclohexylbenzene	1 : 4	CHCl ₃	CH	0.10	
Chloroform + cyclohexylbenzene + CS ₂	1 : 1 : 3	CHCl ₃	CH ₂	0.13	
Chloroform + dioxane	1 : 5	CHCl ₃	CH ₂	0.27	
Chloroform + acetone	1 : 4	CHCl ₃	CH ₃	0.21	
Chloroform + acetone + D ₂ O ¹	1 : 4 : —	CHCl ₃	CH ₃	0.21	
Chloroform + acetone + H ₂ O ¹	1 : 4 : —	CHCl ₃	CH ₃	0.18	
Chloroform + acetone + H ₂ O ¹	1 : 4 : —	H ₂ O	CH ₃	0.0	
Chloroform + acetone + H ₂ O ¹	1 : 4 : —	CHCl ₃	H ₂ O	0.0	
Benzene + cyclohexane	1 : 4	CH	CH ₂	0.31	
Methyl alcohol + cyclohexane (HCl) ²	1 : 12	CH ₃	CH ₂	0.20	
Methyl alcohol + cyclohexane (HCl) ²	1 : 12	OH	CH ₂	0.20	
Pyridine + cyclohexane	1 : 4	CH	CH ₂	0.0	
Nitrobenzene + cyclohexane	1 : 4	CH	CH ₂	0.23	
Toluene + cyclohexane	1 : 4	CH	CH ₂	0.22	
Toluene + cyclohexane	1 : 4	CH ₃	CH ₂	0.20	
Cyclohexane + benzene	1 : 4	CH ₂	CH	0.14	
Ethyl acetate + benzene	1 : 4	CH ₃	CH	< 0.05	
Ethyl acetate + benzene	1 : 4	CH ₂	CH	< 0.05	
Ethyl acetate + benzene	1 : 4	COCH ₃	CH	< 0.05	
Dimethylformamide + benzene	1 : 4	CH ₃ ³	CH	0.13	
Dimethylformamide + benzene	1 : 4	CH ₃ ⁴	CH	0.10	
Benzene + acetic acid	1 : 4	CH	CH ₃	0.15	
Benzene + acetic acid	1 : 4	COOH	CH ₃	0.13	
Pyridine + acetic acid	1 : 10	CH	CH ₃	0.0	
Acetone + cyclohexane + dioxane	1 : 1 : 5	CH ₃	dioxane	0.17	
Acetone + cyclohexane + dioxane	1 : 1 : 5	CH ₂	dioxane	0.18	
Acetone + dioxane	1 : 4	CH ₃	dioxane	0.24	
Acetone + 2,4 xylenol	1 : 1	acetone	CH	0.03	
Acetone + 2,4 xylenol	1 : 1	CH	acetone	0.03	
Cyclohexylbenzene	neat	CH	CH ₂	0.0	
Tetraline	neat	CH	CH ₂	0.0	
Tetraline	neat	CH ₂	CH	0.0	
Toluene	neat	CH	CH ₃	0.10 ⁵	
NaH ₂ PO ₂ · H ₂ O 51% solution in H ₂ O ⁶	1 : 5.6	PH	H ₂ O	0.22	
NaH ₂ PO ₂ · H ₂ O 51% sol. in H ₂ O + + dimethylformamide ⁶	1 : 1 by volume	PH PH	H ₂ O CH ₃	0.10 0.0	
Methyl alcohol + HCl ⁷	neat	CH ₃	OH	—0.82	1.2
Methyl alcohol + HCl ⁷	neat	OH	CH ₃	—0.93	1.2
Methyl alcohol + HCl + benzene ^{6,7}	1 : 2	OH	CH ₃	—0.85	1
Methyl alcohol + CS ₂ + HCl ²	1 : 1	OH	CH ₃	0.0	1
Methyl alcohol + CS ₂ + HCl ⁸	20 : 1	OH	CH ₃	0.0	1
Ethyl alcohol + HCl ^{6,7}	neat	OH	CH ₂	—0.50	1
Ethyl alcohol + HCl ^{6,7}	neat	OH	CH ₃	0.0	1
Deuterated CH ₃ CHDOH + HCl ^{6,7}	neat	OH	CH	—0.40	1
alcohol CH ₃ CHDOH + HCl ^{6,7}	neat	OH	CH ₃	0.0	1

¹ Saturated with water (D₂O and H₂O).² Acidified to collapse alcohol multiplets.³ High-field line.⁴ Low-field line.⁵ Measured with an electronic integrator.⁶ Sample contains oxygen.⁷ Acidified with HCl for largest Overhauser effect.⁸ Prior to the addition of CS₂ the sample was acidified for largest Overhauser effect.

constants of the apparently exponential recovery of the investigated spectral lines are much larger, since they depend upon T_1^{II} and T_1^{IS} only, with no contribution from T_2 . As in the experiment of Kaiser [20] and in the case of dipolar relaxation in our experiments the relaxation time T_1 of proton I did not change measurably when the signal from protons S was saturated. This is consistent with the very small absolute changes of populations of the spins S and the corresponding two-quantum transition probabilities W_0 and W_2 for the spin I .

The intermolecular Overhauser effect has considerable promise for the study of the structure of solutions and molecular interactions in solutions. In this respect, too, it has something in common with electron-nuclear double resonance [15]. Also, it can cause complications if Overhauser effects are being used to assign transitions to energy levels or for the determination of relaxation parameters.

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Межмолекулярный двойной резонанс и эффект Оверхаузера в жидкостях

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Molekulidevaheline topeltresonants ja Overhauseri efekt vedelikes.