

Acoustic paramagnetic resonance in an aqueous solution of Fremy's salt

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Acoustic paramagnetic resonance in a dielectric liquid (APRL) has been observed for the first time.

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Until recently, no one has succeeded in observing APRL and it was assumed that this agrees with the estimates of^[1], according to which the APRL lines

should have a width $\delta_\alpha \sim \tau^{-1} \sim 10^{10} - 10^{12}$ Hz, corresponding approximately to the rate of the rotational relaxation of the molecules. It was shown theoretically in^[2,3] that despite the smallness of τ there should exist in liquids narrow albeit weak APRL lines of approximately the same width as the width δ of the corresponding NMR or ESR lines.

The Doppler broadening and shift, which impede the search for very narrow lines of nuclear APRL,^[4] exert practically no effect on the broader electronic APRL lines. We have investigated this resonance at low frequencies in weak magnetic fields, $H \sim 10$ Oe, inasmuch as at the ordinary ESR frequencies $\sim 10^9$ Hz it is difficult to produce the necessary acoustic energy density in the sample. The APRL was registered by the saturation method, that is, an ESR spectrometer^[5] was used to measure the sound-induced change in the populations of the spin-system levels. The investigated liquid was an aqueous solution of Fremy's salt with concentration 0.01 mol. % and was placed in a cylindrical cell, in which longitudinal sound was admitted through a X-cut quartz plate.^[6] The cell was placed in the coil of the ESR spectrometer in such a way that its axis was perpendicular to H . The end of the cell not in contact with the quartz radiator was closed with a tapered stopper. The acoustic field in the sample was therefore practically isotropic. The spin Hamiltonian of the free radical of Fremy's salt is^[7]

$$\hat{\mathcal{H}} = g\beta HS + aIS + g_1\beta \phi_{\gamma\delta}^g H_\gamma S_\delta + a_1 \phi_{\gamma\delta}^a I_\gamma S_\delta \quad (1)$$

where g , a , g_1 , a_1 , $\phi_{\gamma\delta}^g$, and $\phi_{\gamma\delta}^a$ are the constants and the tensors of the anisotropic and isotropic g -factor and of the hyper-fine interaction of the spin of the nitrogen nucleus ($I=1$) and the electron spin ($S=1/2$). $\phi_{\gamma\delta}^g$ and $\phi_{\gamma\delta}^a$ are connected with the tensor $\phi_{\gamma\delta}$ describing the orientation of the free radical, and relax at a rate $\sim \tau^{-1}$. The ESR levels are formed by the isotropic part of $\hat{\mathcal{H}}$.

The sound frequency ν was chosen such that we could excite the transitions $3 \leftrightarrow 4$ as well as $1 \leftrightarrow 3$ (Fig. 1). Owing to the spin-lattice relaxation, the sound-induced change of the populations $n_{1,3,4}$ of levels 1, 3, and 4 should influence $n_6 - n_1$. The intensity I of the ESR signal registered by a stationary method at the frequency $\nu_{16} \sim 77$ MHz is proportional to $n_6 - n_1$ ($1 \leftrightarrow 6$ transition). It is seen from Fig. 2 that at resonance, ~ 1 W/cm² of sound power decreases I by 10–15%. With increasing voltage U_e on the piezoelectric converter, I decreases (Fig. 3) and levels off at $U_e \sim 150$ V. This is natural, since the sound saturates not the $1 \leftrightarrow 6$ transition but $3 \leftrightarrow 4$, and possibly $1 \leftrightarrow 3$. A detailed measurement of the APRL line shape is a complex task, for even in the case of strong saturation of the transitions $3 \leftrightarrow 4$ and $1 \leftrightarrow 3$ by sound, I decreases only by 25–30%. In the case of deviation (due to variation of H) of the sound absorption from resonance, the influence of this absorption on I decreases. The APRL line width estimated by this method is $\delta_a < 2$ MHz. These results, which certainly exceed the error of the ESR spectrometer, were reproduced many times, and such factors as electric noise, the influence of the ultrasound generator on the ESR spectrometer, and the heating of the sample by sound were eliminated. Recognizing that $\nu \ll \nu_{16}$, it must be admitted that on the whole the effect is large (Figs. 2 and 3).

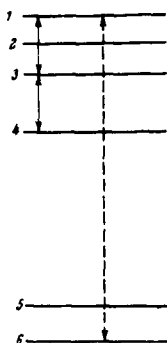


Fig. 1. Level scheme of free radical of Fremy's salt ($H \sim 10$ Oe).

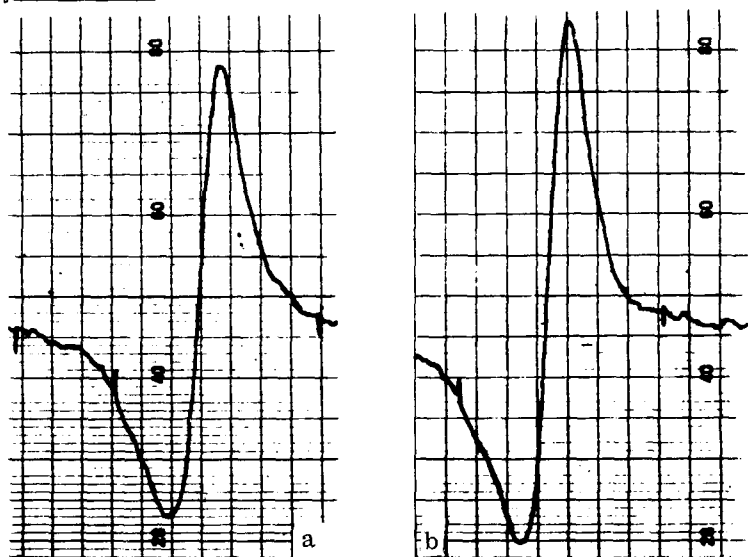


Fig. 2. Influence of resonant sound absorption on I : a) sound turned on; b) sound turned off; $\nu = 13.75$; $\nu_{34} = 13.3$; $\nu_{13} = 15.4$; $\nu_{16} = 77$ (MHz).

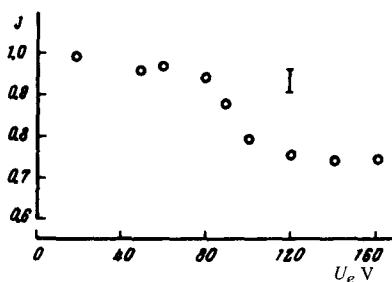


Fig. 3. Dependence of I on U_e (volts). $I = 1$ at $U_e = 0$. $\nu = 13.8$; $\nu_{16} = 77.3$ (MHz).

The wave functions of the states ψ_1 and ψ_4 of levels 1 and 4 are $\psi_1 = |\frac{1}{2}, 1\rangle$ and $\psi_4 = |-\frac{1}{2}, 1\rangle$ (the indices in $|\gamma\delta\rangle$ are the projections of S and I on the direction of H). Therefore modulation of the isotropic^[2,3] Zeeman and hyperfine interaction (1) by sound therefore does not produce the transitions $3 \leftrightarrow 4$ and $1 \leftrightarrow 3$. These transitions are due to the anisotropic^[1] part of the Zeeman interaction, and especially the hyperfine interaction.^[2,3] Their probability is large by vir-

tue of the following: The energy of the molecule depends^[1] on its orientation $\phi_{\gamma\delta}$ relative to the spins. Therefore fast fluctuations of $\phi_{\gamma\delta}$ occur near the *non-isotropic* distribution determined by the spin orientation. Since the latter precess with a frequency ω_s , the molecule takes part as a result in two motions: fast relaxation motion with frequencies $\omega_m \lesssim \tau^{-1}$ and slow motion with $\omega_m \approx \omega_s$. It is known^[8-10] that when $\omega = 2\pi\nu \sim \omega_m$ then, owing to the interaction of the shear deformations and $\phi_{\gamma\delta}$, additional dispersion and sound absorption take place. This occurs also in our case, but not at $\omega \sim \tau^{-1} \sim 10^{10} - 10^{12}$ Hz, as was established long ago, but at the frequency $\omega \approx \omega_s$ of the slow reorientation of the molecules following the spins.

For the simplest model, wherein the liquid consists of uniaxial molecules^[8] each with spin $S = 1/2$ and with anisotropic g factor (1), the calculation by the method of^[9] using the Bloch-Blombergen equation leads to the following dispersion relation for the longitudinal sound:

$$\omega^2 \approx \frac{K^\infty}{\rho_0} q^2 \left[1 - \frac{4}{3} \frac{\mu^\infty}{K^\infty} \frac{i\omega r}{1 - i\omega r} - \frac{\mu^\infty}{K^\infty} \frac{f^2 \sin^2 2\theta}{4T} \beta^3 g g_1^2 H^3 \frac{1}{\omega_s - \omega - i\delta} \right], \quad (2)$$

$$\omega \approx \omega_s = g\beta H.$$

q is the momentum; ρ_0 is the density; K^∞ and μ^∞ are the hydrostatic compression and shear moduli at $\omega = \infty$; T is the temperature; θ is the angle between \mathbf{q} and \mathbf{H} ; f is a certain constant; $f^2 \sim T^{-1}$. The APRL line (2) is narrow,^[2,3] but the matrix element of the resonant transition does not contain the parameter $\omega\tau \ll 1$, so that the probability of the resonant sound at $\nu = 10^7$ Hz and $\tau \sim 10^{-11}$ sec is increased, roughly speaking, by $(\omega\tau)^{-2} \sim 10^6$ times in comparison with^[2,3]. More detailed results will be published separately.

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