Generation of high-frequency current by the products of a photochemical reaction

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It has been observed that the products of a photochemical reaction in a magnetic field generate a high-frequency current in a tank-circuit coil surrounding the ampul with the reacting mixture.

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It is known that in diamagnetic products of many radical reactions carried out in a constant external magnetic field H_0 the populations of the nuclear Zeeman energy levels deviate greatly from the Boltzmann equilibrium.[1] This phenomenon, called chemical polarization of nuclei (CPN) is due to Zeeman and hyperfine interactions (HFI), which lead to mixing of the singlet and triplet states in the radical pair. Diamagnetic products come only from those radicals which are in the singlet state at the instant of encounter. In strong magnetic fields, the character of the polarization is determined by the type of the radical pair, by the difference between the g-factors, and by the sign of the HFI constant. At definite ratios of these parameters, the upper Zeeman levels turn out to have excess population, and the nuclear-magnetization vector **M** of the reaction product is directed counter to the external field H_0. The presence of inverted population of the nuclear spin states of the reaction products at the instant of production allows us to regard them as an active medium capable in principle of amplifying or generating radio waves with a frequency close to the frequency of the transitions between the Zeeman levels of the polarized nuclei, as well as of inducing a high-frequency current in a resonant tank-circuit coil surrounding the ampul with the reaction products.[2] In classical electrodynamics this process is described as self-excitation of the precession of the nuclear-magnetization vector at the Larmor frequency $\omega = \gamma H_0$, due to the interaction of the tank circuit with the reaction field, while in quantum mechanics it is treated as a manifestation of coherence in the nuclear-spin system.

The most suitable type of chemical reaction in which this effect can be observed turns out to be the reversible phototransport of an electron from porphyrin to quinone. Such reactions proceed via intermediate radical stages and are accompanied by unusually strong negative polarization of the quinone protons.[3] Figure 1 shows the ^{1}H-NMR spectrum of a reaction mixture containing 10^{-3} mol/liter porphyrin and quinone; the solvent is chloroform and the proton donor is trichloracetic acid. The reaction mixture was exposed to light from a DRSh-1000 lamp ($\lambda = 546$ nm) in the pickup of the PS-100 NMR spectrometer at $H_0 = 23.5$ kOe. The line of the polarized quinone protons has an emission character, and the ratio of the nonequilibrium and equilibrium nuclear magnetizations is $\sim 2 \times 10^3$. However, owing to the low concentration of the quinone, self-excitation of the precession called for an increase of the effective Q of

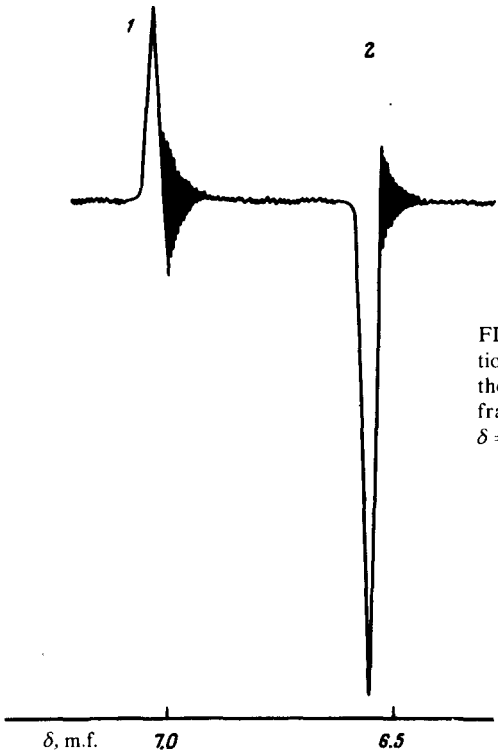

FIG. 1. ^{1}H-NMR Spectrum (100 MHz) of the reaction mixture exposed to light: 1—absorption line of the protons of chloroform (solvent), $\sigma = 7.25$ mol. frac., 2—line of polarized protons of quinone, $\delta = 6.55$ m.f.

the receiving tank circuit via a regenerative scheme analogous to those used in masers with dynamic nuclear polarization.[4]

The voltage induced in the receiving circuit when the precession was self-excited and the high-frequency current appeared was registered by the receiving section of the spectrometer. Figure 2 shows a record of the low-frequency beats between the generation frequency and the frequency of the reference oscillator of the recording system. The beat frequency depends on H_0. The beat amplitude is proportional to the amplitude of the high-frequency voltage on the receiving circuit and, as shown in[2], is proportional to the transverse component of the nuclear magnetization $M_\perp = (M_x^2 + M_y^2)^{1/2}$. After turning the light on, the CPN produces a longitudinal negative magnetization M_z of the quinone protons, which reaches the generation threshold after 5–10 sec. At that instant, a transverse component $M_\perp$ appears and reaches a stationary state after a transient process ("spike structure"), while the high-frequency amplitude becomes stationary. The envelope of the beats, i.e., the amplitude of the high-frequency oscillations, agrees qualitatively with the theoretical curve given in[2]. When the light is turned off, the precession attenuates and the generation ceases. The reaction is reversible in practice, so that the generation can continue for a sufficiently long time. When the light is turned on again, the process repeats. In principle, both the precessing vector of the nuclear magnetic moment of the sample and the

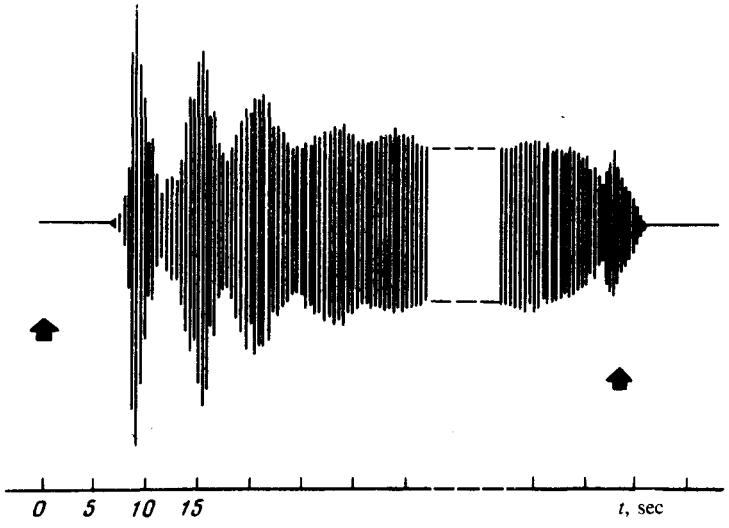

FIG. 2. Variation of the amplitude of the high-frequency current in the receiving resonant tank circuit. The arrows mark the instants when the light is turned on and off.

high-frequency current generated in the tank-circuit coil are potential sources of radio emission that accompanies the chemical or photochemical reaction.

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