SUPER-REGENERATIVE DETECTION OF N.Q.R. A STEADY-STATE METHOD

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In a recent communication[1] the detection of nuclear quadrupole resonance (n.q.r.) using a super-regenerative oscillator was analysed in terms of a "transient nutation" approach (see for example ref.[2]). One prerequisite for the theoretical development of the nuclear induction equations is that of a large r.f. field. As this condition does not generally apply to super-regenerative spectrometers, an alternative approach (namely, a steady-state analysis) will be considered where, providing there is negligible saturation of the spin system, there is no requirement on the absolute magnitude of the r.f. field.

A steady-state analysis of the analogous n.q.r. Bloch equations[3,4] indicates that the resultant signal, $[\overline{V_s^2}]^{1/2}$, at exact resonance is given by

$$[\overline{V_s^2}]^{1/2} \propto H_1 T_2^*/(1+\xi\gamma^2 H_1^2 T_1 T_2^*) \tag{1}$$

where H_1 is the effective r.f. field in the direction of the coil axis; T_2^* is the apparent spin–spin relaxation time; T_1 is the spin–lattice relaxation time; γ is the magnetogyric ratio; and $\xi = (I \pm m)(I \mp m+1)$ where the signs indicate the $+m \rightarrow +m-1$ or $-m-1 \rightarrow -m$ transition respectively. The terms I and m are the nuclear spin and magnetic quantum numbers respectively. This result is applicable to a continuous r.f. field, $2H_1 \cos \omega t$, propagated in the direction of the coil axis. Super-regenerative operation involves irradiation by an amplitude modulated r.f. source of average on time, t_{on}, and off time, t_{off}. A steady-state analysis of the n.q.r. Bloch equations for such an r.f. source[5] indicates that the signal is given by

$$[\overline{V_s^2}]^{1/2} \propto \frac{H_1[t_{on}/(t_{on}+t_{off})]T_2^*}{1+\xi\gamma^2 H_1^2[t_{on}/(t_{on}+t_{off})]^2 T_1 T_2^*} \tag{2}$$

providing the quench frequency, $f_q(= 1(t_{on}+t_{off})) \gg 1/T_2^*$. Assuming negligible saturation of the resonance line, i.e.

$$\xi\gamma^2 H_1^2[t_{on}/(t_{on}+t_{off})]^2 T_1 T_2^* \ll 1$$

the result will be equivalent to that of Smith and Tong.[6] Although it is not possible

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[1] Caldwell, R. A., and Hacobian, S., *Aust. J. Chem.*, 1970, **23**, 1321.
[2] Torrey, H. C., *Phys. Rev.*, 1949, **76**, 1059.
[3] Bloom, M., Hahn, E. L., and Herzog, B., *Phys. Rev.*, 1956, **103**, 148.
[4] Bloom, M., Robinson, L. B., and Volkoff, G. M., *Can. J. Phys.*, 1958, **36**, 1286.
[5] Caldwell, R. A., Ph.D. Thesis, University of Sydney, 1970.
[6] Smith, J. A. S., and Tong, D. A., *J. scient. Instrum.*, 1968, No. 1, 8.

to write down an equation in analytic form for a Gaussian line shape it is generally agreed[7,8] that the result would be in the form

$$[\overline{V_s}^2]^{1/2} \propto \frac{H_1[t_{on}/(t_{on}+t_{off})]\pi f(\omega_0)}{1+\xi\gamma^2 H_1^2[t_{on}/(t_{on}+t_{off})]^2 T_1 \pi f(\omega_0)} \tag{3}$$

where $f(\omega_0)$ is the magnitude of the normalized line shape function at the central frequency ω_0.

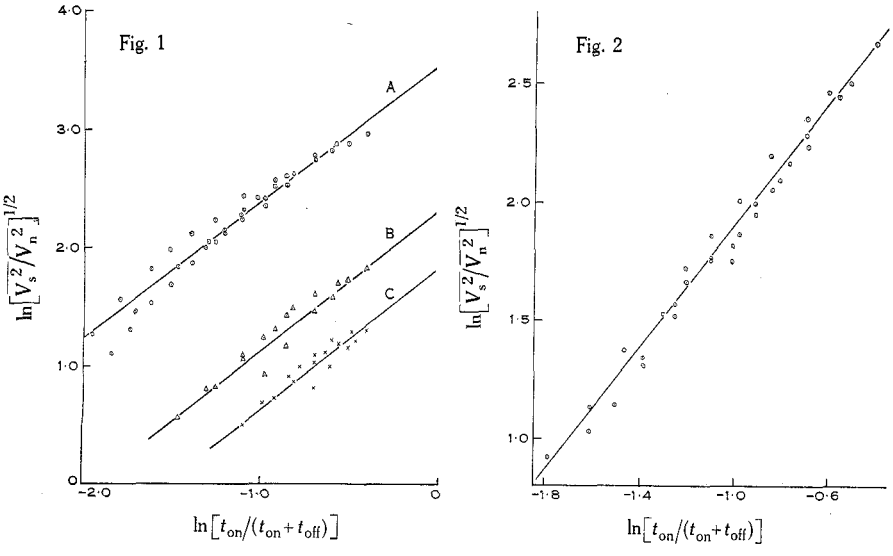

Fig. 1.—^{35}Cl nuclear quadrupole resonance measurements on *para*-dichlorobenzene containing A, 0·0; B, 0·5; C, 1·0 mol % *para*-dibromobenzene at room temperature (22°C). The values of t_{on} range between 20 and 60 μs; t_{off} varies between 30 and 160 μs.

Fig. 2.—^{35}Cl nuclear quadrupole resonance measurements on sodium chlorate at room temperature (22°C). t_{on} 20–60 μs, t_{off} 30–160 μs.

Most of the experimental details can be found in refs.[1,5] The detection equation used is

$$V_{out}(\text{WA}) \doteq [kaV_0/(t_{on}+t_{off})]\ln[\overline{V_s}^2/\overline{V_n}^2]^{1/2} \tag{4}$$

for $[\overline{V_s}^2/\overline{V_n}^2]^{1/2} \geqslant 4$; $V_{out}(\text{WA})$ is the output voltage at the operating modulation frequency measured with a Rohde & Schwarz wave analyser; V_0 is the r.f. pulse amplitude monitored by the detector; a is the rise time constant of oscillation build-up in the sample coil of the oscillator and k is a proportionality constant. From equation (2), assuming negligible saturation:

$$\ln[\overline{V_s}^2/\overline{V_n}^2]^{1/2} = V_{out}(t_{on}+t_{off})/kaV_0$$
$$= \ln\left[\frac{H_1\{t_{on}/(t_{on}+t_{off})\}T_2^*}{[\overline{V_n}^2]^{1/2}}\right] + \text{constant}$$

[7] Abragam, A., "Principles of Nuclear Magnetism." (Clarendon: Oxford 1961.)
[8] Redfield, A. G., *Phys. Rev.*, 1955, **98**, 1787.

The constant includes such parameters as the coil dimensions, the sample filling factor and the static nuclear susceptibility.[7,9]

Experimental data are presented in Figure 1 and providing equation (5) is applicable a slope of 1·0 is expected (observed 1·2). Also included are the results obtained for solid solutions of *para*-dibromobenzene. Figure 2 is the corresponding plot obtained for sodium chlorate. In Figure 1 the vertical disposition of points will be logarithmically proportional to the inverse line width parameter (or the apparent spin–spin relaxation time) T_2^*, providing all other terms in the right-hand side of equation (5) are constant for the three samples. This ratio is found to be 1 : 0·30 : 0·18 in reasonable agreement with the results of Woessner and Gutowsky[10] (1 : 0·39 : 0·27).

[9] Das, T. P., and Hahn, E. L., *Solid St. Phys.*, 1958, Suppl. 1.
[10] Woessner, D. E., and Gutowsky, H. S., *J. chem. Phys.*, 1963, **39**, 440.