INVESTIGATION OF INDIRECT SPIN-SPIN INTERACTIONS BY PULSED NQR METHODS

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The detection of slow beats in the envelope of quadrupole spin echo signals due to indirect spin-spin interaction between nuclei via the electron shell is reported. The effect was first observed experimentally in crystalline iodine and bromine. A theory of the effect is proposed. The hyperfine splitting constants J and K are determined on the basis of experimental data for I_2 and Br_2. The nature of the halogen-halogen bond in iodine and bromine is discussed.

1. INTRODUCTION

THE splitting of NQR (nuclear quadrupole resonance) lines due to indirect interactions between nuclei was first observed in crystalline iodine.[1,2] The NQR line of I^{127} for the transition $\frac{1}{2} \rightarrow \frac{3}{2}$ was split into five components. Soon after similar phenomena were discovered in solid bromine,[3] chlorine,[4] nitrogen,[5] and other substances.

Since in the solid state NQR lines are broadened on account of magnetic dipole-dipole interactions between nuclei, as well as various inhomogeneities of the crystal lattice, the agreement between theory and experiment in the case of stationary methods is unsatisfactory. For example, for I_2 and Br_2 agreement is obtained if one takes $J = K = 3$ kHz, where J and K are the spin-spin interaction constants. The case $J = K$ lacks physical significance, since in this case the theory predicts 100% s-hybridization of the halogen-halogen bond. In addition, in steady-state methods it is difficult to distinguish the splitting of NQR lines due to indirect spin-spin interactions from that due to crystal effects. If the resonating atoms are inequivalently arranged in the lattice, a multiplet structure of the NQR lines arises, which can mask the spin-spin splitting. Thus, in investigating indirect spin-spin interactions by the static NQR method, it is necessary to know the crystalline structure of the substance, which strongly limits the possibilities of the method.

The pulse method of spin echoes was first used in[6] for the investigation of spin-spin interactions in NQR. Unlike the static method, the pulse method affords a marked simplification of the process of obtaining useful information from the experimental data. In this paper we set forth a theory for the phenomenon of slow beats in the envelope of spin echo signals which has been discovered and discuss the experimental results for a number of compounds.

2. EXPERIMENTAL METHOD

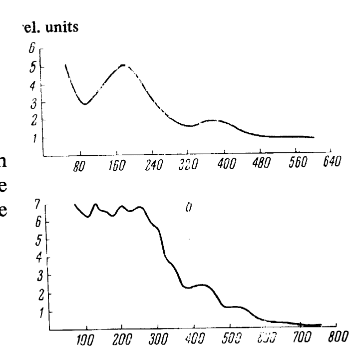
We first described a spin echo apparatus for the frequency region 130 to 300 MHz in[7]. The use of grid modulation was found, however, to be inconvenient in further application of the apparatus. With grid modulation the grid of the generator tube becomes contaminated with heavy ions, leading to the appearance of thermoelectric grid current and eventual destruction of the tube. Hence the grid modulator in our apparatus worked for less than 100 h before replacement of the 6S5D tube became necessary. It turned out to be more convenient to use anode modulation with an accumulator condenser charged from a high-voltage source through a diode. This kind of modulator was first used in radio direction finding stations for gun aiming in World War II (see, for example, the modulator of the English SCR-584 station). Through the use of this modulator in the spin echo apparatus in the frequency range 130–600 MHz, we succeeded in obtaining powerful rf pulses of length from 1 to 60 μs, which is adequate for quadrupole spin echo experiments in solids. We usually worked with a voltage of 2–2.5 kV on the accumulator condenser.

Since the amplitude of the spin echo signal from I^{127} is only a few microvolts, we used a highly sensitive receiver which had a cascade amplifier with grounded grid as the input stage. The use of this standard superheterodyne receiver afforded high sensitivity. In addition the sensitivity could be enhanced by storage of the envelopes of the spin echo signals in a 1024-channel accumulator with a ferrite cube memory. In this case "scanning" of the echo signals was synchronized with the switching of the accumulator channels.

Development of the apparatus for observation of quadrupole spin echoes over the frequency range 130–600 MHz opened the way the study of spin-spin interactions between nuclei in NQR.

3. EXPERIMENTAL RESULTS

The quadrupole spin echo signals from I^{127} in I_2 and Br^{79} in Br_2 at 77°K were observed at the frequencies



The results of tracing out 100 accumulations of the envelope of the spin echo signal of Br^{79} and I^{127} nuclei as a function of τ on an X-Y recorder: a – envelope of the signal of Br^{79} in Br_2; b – envelope of the signal of I^{127} in I_2. The 1024-channel accumulator was synchronized from the first pulse.

333.945 and 382.435 MHz, respectively. The figure shows the envelopes of the spin echo signals as a function of the time τ between the 90 and 180° pulses. It is seen that the envelope is not a monotonic function of the time—there are slow beats in the envelope. This has not been observed in NQR before.

Note that these slow beats are not the usual kind of beats that arise from the superposition of two echo signals. Such "fast" beats have been observed many times in NQR. To obtain them it is necessary to excite two nearby NQR lines that are not coupled in any way. But if the wave functions of the corresponding states are mixed, then slow beats can arise in the envelope.

Thus, use of the pulse NQR method permits isolation of the contributions to the multiplet structure of NQR lines. The multiplet structure due to crystal effects is not manifested in slow beats in the envelope, but leads only to the appearance of "fast" beats in the echo signal itself. On the other hand, indirect spin-spin interactions evoke slow beats in the envelope.

The spin-lattice relaxation time of I^{127} in I_2 was found equal to 480 ± 20 μs at 77 K; in Br_2 we found T_1 = 1200 μs (determined by the three-pulse method). Scanning of the accumulator in the figure was synchronized from the first pulse. By measuring the spacing between corresponding bumps from the beginning of the scan, it is possible to measure the frequency of the slow beats (to within ± 5%). For Br_2 we obtained two frequencies: 5 and 10 kHz; similarly, for I_2 we found four frequencies: 7, 11, 21, and 32 kHz.

Only one isotope contributes to the spin echo signal in I_2, whereas there are two isotopes in Br_2, Br^{79} and Br^{81}. Hence in Br_2 (Br^{79}) the observed spin echo signal is from heteromolecules ($Br^{79}Br^{81}$) and homomolecules ($Br^{79}Br^{79}$). Both these kinds of molecules give the same contribution to the signal intensity. Similar slow beats were found by us in the complex of iodine with benzene.

4. DISCUSSION OF RESULTS

To construct a theory of quadrupole spin echo with indirect spin-spin interactions between the nuclei taken into account we take the interaction Hamiltonian in the form[8]

$$\mathscr{H} = \mathscr{H}_Q + \mathscr{H}_{1,2} = A \sum_{n=1,2} [3\hat{I}_{zn}^2 - \hat{I}_n^2 + \eta(\hat{I}_{xn}^2 - \hat{I}_{yn}^2)] + J\hat{I}_{z1}\hat{I}_{z2} + K(\hat{I}_{x1}\hat{I}_{x2} + \hat{I}_{y1}\hat{I}_{y2}), \quad (1)$$

where $A = eQq_{zz}/4I(2I-1)$, eQq_{zz} is the quadrupole interaction constant, I is the nuclear spin, η is the asymmetry parameter, and $\hat{I}_x$, $\hat{I}_y$, $\hat{I}_z$ are the operators of the components of the nuclear spin moment; J and K are constants characterizing the indirect interaction of the nuclei via the electron cloud.

We carry out the calculation of the amplitudes of the spin echo signals by the density matrix method.[9] Here it is necessary to use a ψ_{m_1}, ψ_{m_2} representation of order $(2I_1 + 1)(2I_2 + 1)$, since it is a two-particle problem. It is possible to use the representation $\psi_M^{I_t}$, where I_t and M are the values of the total spin of the system of two nuclei and its projection on the z axis. For the transformation to the latter representation we used the tables of Wigner coefficients in[10].

The amplitude of the spin echo signal is determined by the average value of the operator $\hat{I}_x$:

$$\langle I_x \rangle = \mathrm{Sp}\,[\rho(t)\hat{I}_x], \quad (2)$$

where $\rho(t)$ is the density matrix. Values of $\langle I_x \rangle$ were calculated for $I_1 = I_2 = 5/2$, $I_1 = I_2 = 3/2$ (both nuclei resonating) and $I_1 = I_2 = 3/2$ (I_1 the resonating nucleus, I_2 nonresonating).

As the calculation showed, the amplitude of the spin echo signal was modulated by the frequencies of the hfs (hyperfine splitting). However, we were mainly interested in the frequencies of the slow beats in the envelopes of the spin echo signals with changing τ. These slow beats arise if the rf pulse excited two frequencies of the transition between one energy level and two others lying higher than the first in the energy scale. Then the amplitude of the spin echo signal (for $t = 2\tau$) can be represented in the form

$$E_i(\tau) \sim [1 - A' \sin^2(\pi\Delta_i\tau)], \quad (3)$$

where A′ is a constant of the order of 2, and Δ_i is the frequency of the slow beats. The values of Δ_i for different spins are given in the table.

The table shows that instead of 15 frequencies, which would be obtained in the steady-state method,[8] there are only six frequencies by the pulse method for the transition $\pm 1/2 \rightarrow \pm 3/2$ in the case of I_2. This simplification allows a more accurate determination of the constants J and K. Using the experimental values for the slow-beat frequencies and considering that the asymmetry parameter η is 0.17 for I_2 and 0.2 for Br_2, we obtain for Br_2: J = 7 kHz, K = 2 kHz; for I_2: J = 14 kHz, K = 3.5 kHz. It should be observed that because of the short transverse relaxation time T_2 slow-beat frequencies less than 5 kHz cannot be measured. Hence in I_2 we can observe only the four highest frequencies.

The value J = K = 3 kHz obtained by the steady-state experiments[8] for I_2 makes no sense physically, since the NQR line of I^{127} is asymmetrical, which is a consequence of $J \neq K$. In addition, as we have already mentioned, if J = K, then on the basis of Eq. (18) of[8] one finds that the degree of s-hybridization of the halogen-halogen bond is 100%. On the other hand, direct quantum-mechanical calculation gives s = 20% for I_2 and 15% for Br_2.[11] But from the data of the pulse experiments, one gets s < 30% for I_2 and Br_2 using this same formula. Considering the approximate nature of the relations connecting the constants J and K with the degree of s-hybridization of the bond, it may be concluded that the experimental values J/K = 4 for I_2 and J/K = 3.5 for Br_2 lead to good agreement of all the known facts about the nature of the halogen-halogen bond.

$I_1 = I_2 = 3/2$		$I_1 = I_2 = 3/2$	
$\pm 1/2 \rightarrow \pm 3/2$	$\pm 3/2 \rightarrow \pm 3/2$	homonuclear molecule	heteronuclear molecule
$\left\lvert J + \left(\frac{9}{2} \pm \frac{20}{9}\eta\right) K \right\rvert$	$\lvert -J + 5K \rvert$	$\lvert J - (3+2\eta) K \rvert$	$\lvert 3J \rvert$
$\left\lvert J - \left(\frac{9}{2} \pm \frac{196}{9}\eta\right) K \right\rvert$	$\left\lvert J + \frac{20}{9}\eta K \right\rvert$	$\lvert J - (2 \pm 4\eta) K \rvert$	$\lvert \sqrt{J^2 + 12K^2} \rvert$
$\lvert J - (8 \pm 12\eta) K \rvert$		$\lvert J + 2K \rvert$	

We also remark that in the I_2 crystal indirect spin-spin interaction is about twice as strong as in Br_2, which likewise is not in contradiction with quantum-mechanical calculations.[11]

Thus, the pulse NQR method affords more accurate data on the spin-spin interaction constants in the presence of line broadening due to crystal inhomogeneities. The resulting simplification in obtaining all the necessary information holds out the promise that the phenomenon of slow beats will find ready application in investigating the nature of chemical bonds in semiconductors.

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91