coupling between the C-H (C-D) molecular modes along the chain direction. This again is consistent with the particular importance of the TCNQ chains, and it appears that this observation may contain the microscopic reason for much of the behavior of TTF-TCNQ.

The author is indebted to his former colleagues at Brookhaven National Laboratory for initiating his interest in one-dimensional conductors. The communication of unpublished results from H. Mook and G. Shirane, and useful conversations with K. Bechgaard and O. Faurshov Nielsen are gratefully acknowledged.

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# New Coherent Averaging Effect in Magnetic Resonance: Modulation-Induced Reduction of Dipolar Coupling

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(Received 19 July 1976)

Modulation was used in a transient nutation experiment to remove dipolar splitting. We calculate this new effect and demonstrate it for an isolated two-spin system. The relatively simple technique works efficiently for line narrowing in polycrystalline solids and preliminary results indicate that it should be useful for uncovering chemical-shift and heternuclear-coupling information obscured by homonuclear broadening.

Modulation has been used extensively in NMR spectroscopy, especially for detection in solid-state experiments and for both detection and decoupling in liquid-state studies. Recently, there has been considerable interest in the effect of strong modulating fields on the Larmor frequency of spins in both optical and NMR experiments. The phenomenon of "photon dressing," in which the modulation frequency is much greater than the Larmor frequency, has been of particular interest.[1] In this communication, we report a new coherent averaging process in magnetic resonance which is effected by the use of modulation. By adjusting the modulation frequency and index, it is possible to reduce the homonuclear dipolar coupling among spins, suggesting a relatively simple new technique for obtaining high-resolution NMR spectra in ordered media.

Consider a coupled two-spin system subjected to modulation of the static field $H_0$ as well as continuous rf irradiation at the center of the spectrum. The Hamiltonian viewed from a reference frame rotating with the frequency $\omega_0$ of the resonant field is[2]

$$\mathcal{H} = -\omega_1(I_{X1}+I_{X2}) - \kappa\omega_M\cos\omega_M t(I_{Z1}+I_{Z2}) - A(3I_{Z1}I_{Z2} - \vec{I}_1\cdot\vec{I}_2), \quad (1)$$

where $\omega_1 = \gamma H_1$, and $2H_1$ is the peak amplitude of the linearly polarized rf field. The first term represents the Zeeman interaction in the rotating frame and the last term is the truncated dipolar interaction. The second term, which is the one of most interest, couples the spins to a linearly polarized modulation field parallel to $H_0$. No constraints are placed on the frequency, $\omega_M$, or on the peak amplitude, $H_M$; $\kappa = \gamma H_M/\omega_M$ is the modulation index. We have solved this problem numerically using a data-simulation language (DSL/360)[3] and the results of the calculation agreed so well with our data that it was possible to use them to optimize experimental conditions. However, in order to arrive at a more physical picture of the spin dynamics, we sought an approximate analytical solution as follows: If $\omega_1 \gg A$, then the dipolar interaction may be treated as a perturbation. The remaining rotating-frame Hamiltonian has the same form as an off-resonance laboratory-frame Hamiltonian with the substitutions $Z \to X$, $\omega_0 \to \omega_1$, $\omega \to \omega_M$, and $2H_1 \to H_M$. In the laboratory-frame experiment, where $\gamma H_1 = \omega_1 \ll \omega_0$, the rotating-wave approximation permits solution of the equation of motion[4]; however, in our experiment, where $\gamma H_M = \kappa\omega_M \sim \omega_1$, this approximation fails, since the counterrotating component of $\omega_M$ has a strong influence on the spin motion. Therefore, a theory which calculates these effects to a much higher order of approximation was used.[5] Briefly, the method permits calculation of the best approximate time-evolution operator for the rotating-frame spin Hamiltonian comprised of the first two terms in Eq. (1). The operator is generated by a series of coordinate transformations consisting of alternate rotations and tilts about the $X$ and $Y$ axes, respectively, of the rotating frame. The same transformations must be applied to the dipolar coupling term when added as a perturbation, and the result is

$$\tilde{\mathcal{H}}_{dip} = \tfrac{1}{4}A(3\cos^2\beta - 1)(3I_{z1}I_{z2} - \vec{I}_1\cdot\vec{I}_2),$$

where $\beta$ is one of the tilt angles and is given by

$$\tan\beta = \kappa(1-x)/[(\omega_1/\omega_M)J_0(\kappa x) - 1],$$

and $x$ is a solution of the equation

$$\kappa(1-x) = 2J_1(\kappa x)\omega_1/\omega_M .$$

$J_0(\kappa x)$ and $J_1(\kappa x)$ are Bessel functions. For $\omega_M > \omega_1$ and $\omega_M/\omega_1 \lesssim 1.4$, $\kappa$ can be adjusted so that $3\cos^2\beta = 1$. Thus, the dipolar splitting can be reduced to zero by appropriate adjustment of the modulation parameters. The theory gives results which agree to within 5% of the numerical calculation for $\kappa \lesssim 1$. Several spectra simulated using the numerical method are shown in Fig. 1(a). The calculation of the frequency shift of the center of the doublet also reproduced the numerical calculation quite well.

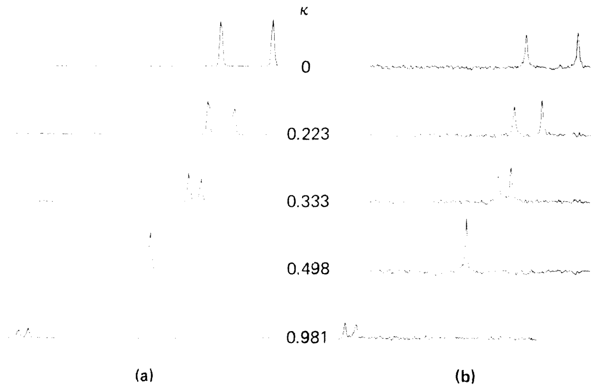

FIG. 1. (a) Theory: Fourier-transform spectra of modulated transient nutations calculated for a coupled two-spin system. The rf is centered on the doublet with $\omega_1 = 17.58A$ and $\omega_M/\omega_1 = 1.168$. (b) Experiment: Fourier-transform spectra of modulated transient nutations of the two coupled $^{19}$F nuclei in 1,1-difluorotetrachloroethane oriented in a nematic liquid crystal solvent. To match theory, the rf (23 MHz) is centered on the laboratory-frame doublet (splitting = 710 Hz, $A = 237$ Hz) with $\omega_1 = 3982$ Hz and $\omega_M = 4661$ Hz. The value of the modulation index, $\kappa$, is shown with each pair of plots.

In order to demonstrate the effect clearly, experiments were actually performed on an isolated two-spin system by orienting a molecule with two fluorine atoms (1,1-difluorotetrachloroethane) in a nematic liquid crystal solvent (Eastman nematic mixture, No. 11900). The chlorine nuclei are quadrupole relaxed too rapidly to couple to the fluorines, so that only a sharp doublet is obtained in the laboratory-frame $^{19}$F spectrum.[6] The rotating-frame experiment without modulation was performed as follows: rf irradiation was turned on suddenly at the center of the doublet spectrum, and the time evolution of the magnetization (transient nutation) was observed.[7] This was done quasicontinuously by using time sharing; a train of rf pulses was applied and the receiver was gated on between pulses.[8] With care in the choice of flip angle, the spins experience a continuous rf field of reduced amplitude. Several factors confirm that the pulses play no role except to facilitate observation: (1) Rotary saturation experiments,[2] where the rf is truly cw, were performed with similar results; and (2) all calculations were done with cw rf fields, and, as indicated previously, were in good agreement with experiment. The nutation is then Fourier transformed. The results of an on-resonance nutation without modulation is shown in Fig. 1(b). The splitting is half of the laboratory-frame value, as expected.[9] The results of a series of runs using different values of modulation index are also shown in Fig. 1(b). The agreement between theory and experiment is clear.

Other preliminary results have been obtained: (1) The experiment works efficiently in polycrystalline solids—we have succeeded in reducing the linewidth of the proton spectrum in adamantane by two orders of magnitude. Since the linewidth at this point is the same as that of a liquid sample, rf-field inhomogeneity appears to be the limiting factor. (2) Reduction of the dipolar coupling is just as dramatic when the rf is off resonance, and we have observed preservation of chemical-shift structure in liquids under these conditions. Thus, the potential exists for uncovering chemical-shift anisotropies and heteronuclear couplings obscured by homonuclear broadening. (3) The experiment works as well with frequency modulation of the rf field, and also for $\omega_M < \omega_1$. (4) A variety of multiple-quantum transitions are observed when modulation is used. (5) No reduction of the dipolar coupling is achieved when the requirements for photon dressing (i.e. $\omega_M \gg \omega_1$) are met.

These and other aspects of the experiment are under investigation and will be reported on in more complete form.

We thank R. D. Kendrick for technical assistance, F. F. Abraham for help with DSL/360, and D. E. Horne for help with the spectrometer.

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# Electronic Momentum Densities by Two-Dimensional Angular Correlation of Annihilation Radiation in Aluminum*

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(Received 2 July 1976)

Two-dimensional angular correlation of two $\gamma$'s from positrons annihilating in aluminum have been measured with a multidetector apparatus and compared with momentum densities based on orthogonal-plane-wave electron wave functions. Anisotropy in the momentum distributions and direct evidence for annihilation with the high-momentum components of the conduction band are found.

In this Letter we report the first two-dimensional (2D) angular correlation measurements of $2\gamma$ annihilation radiation from oriented single crystals of aluminum, and compare the results with theoretical predictions. The experiments were performed to test the sensitivity of the technique to the electron and positron wave functions and, in particular, to study the nature of the high-momentum components (HMC) of the correlations in a simple metal.

The applicability of the positron technique to the study of electronic band structure[1] and particularly of Fermi surfaces[2] (FS) is well known. In the independent-particle model (IPM) the momentum distribution $\rho(\vec{p})$ carried by the annihilation photons from a periodic lattice at zero temperature is given by[1]

$$\rho(\vec{p}) = \text{const} \sum_{\vec{k},n} \left| \int d^3r \exp(-i\vec{p}\cdot\vec{r}) u_0^+(\vec{r}) u_{\vec{k},n}^-(\vec{r}) \exp(i\vec{k}\cdot\vec{r}) \right|^2 = \text{const} \sum_{\vec{k},n} \sum_{\vec{G}} A_{\vec{G}}(\vec{k},n) |^2 \delta(\vec{p}-\vec{k}-\vec{G}), \tag{1}$$

where $u_0^+(\vec{r})$ is the ground-state ($\vec{k}=0$) positron Bloch wave function $u_{\vec{k},n}(\vec{r}) \exp(i\vec{k}\cdot\vec{r})$ is the electron wave function with crystal momentum $\vec{k}$ and band index $n$, $\vec{G}$ is a reciprocal lattice vector, and

$$u_0^+(\vec{r}) u_{\vec{k},n}^-(\vec{r}) = \sum_{\vec{G}} A_{\vec{G}}(\vec{k},n) \exp(i\vec{G}\cdot\vec{r});$$