

E. T. Lippmaa. *High-Resolution Magnetic Resonance of Rare Nuclei in Solids*. Recent years have seen rapid development of various high-resolution magnetic resonance methods in solids, for the most part on abundant ( $^1\text{H}$ ,  $^{19}\text{F}$ ) and rare ( $^{13}\text{C}$ ,  $^{29}\text{Si}$ ) nuclei. In the absence of fast molecular motion, the classical nuclear induction methods give only unresolved structures in which the natural line width is usually many times greater than the entire range of chemical shifts of the nucleus under study, while the very long spin-lattice relaxation times result in a sharp decrease in the signal/noise ratio.

By combining such characteristic methods of modern molecular spectroscopy as the use of the nonlinear effects that arise under the influence of strong coherent perturbing electromagnetic fields, parametric modula-

tion, and mini-computer storage and transformation of the entire information-carrying signal, it becomes possible to register high-resolution spectra from solid samples and even to separate lines that overlap practically completely. Figure 1 shows  $^{13}\text{C}$  spectra of a solid polycarbonate polymer (Lexan). The spectrum of Fig. 1a was recorded under monoresonance conditions by Fourier transformation of the signal of free nuclear magnetization precession in the  $x$ ,  $y$ -plane after its extraction by a resonant  $\text{H}_{1x}^{13\text{C}}$  radio-frequency pulse from the equilibrium state along the  $z$  axis. This spectrum consists of a superposition of seven lines of very low intensity, the intrinsic width of each of them exceeding the width of the entire spectrum, while the entire visible "structure" is due solely to spectrometer thermal noise. The spectrum of Fig. 1b was recorded by the same procedure, but with decoupling of the  $^{13}\text{C}$

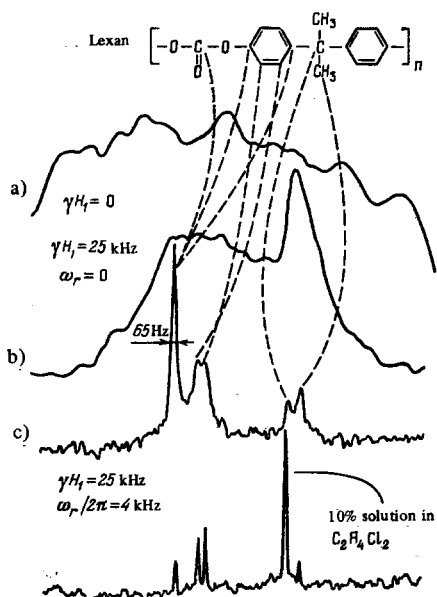


FIG. 1.

nuclei from the  $^1\text{H}$  nuclei by subjecting the latter to a resonant-high-frequency-high-amplitude field ( $\gamma H_{1x}^1 > 2/T_2, \Delta\delta_{1H}$ ) and transfer of the nuclear magnetization from the common  $^1\text{H}$  nuclei to the rare  $^{13}\text{C}$  nuclei under spin-lock conditions with satisfaction of the Hartman-Hahn<sup>[1]</sup> condition for cross relaxation in a rotating coordinate system ( $\gamma_H H_{1x}^1 = \gamma_C H_{1x}^{13C}$ ). This is accompanied by equalization of the spin temperatures of the  $^1\text{H}$  and  $^{13}\text{C}$  nuclei with a sharp increase in the magnetization (and useful signal) of the latter, and the tensor of the dipole-dipole coupling between the  $^1\text{H}$  and  $^{13}\text{C}$  nuclei ( $\overline{D}_{CH} = 0$ , as in liquids as in fast stochastic molecular motion<sup>[2]</sup>) and the tensor of the spin-spin coupling between the  $^1\text{H}$  and  $^{13}\text{C}$  nuclei ( $J_{CH} = 0$ ), as in heteronuclear double resonance experiments,<sup>[3]</sup> are averaged to zero.

As yet, decoupling of nucleus spins with total collapse of the corresponding spin multiplets can be brought about only in NMR, but many of the effects that arise at small amplitudes of the pulsed perturbing high-frequency field (appearance of new lines in the spectra, splitting and shape change of lines associated with the perturbed transition, spin echo) have their analogs in other types of molecular spectroscopy, including optics. Under conditions of heteronuclear decoupling and transfer of nuclear polarization from common to rare nuclei, the chemical-shift tensors  $\sigma_i$  of the latter are not averaged, and the strong anisotropic broadening of the corresponding lines due to the anisotropy of their chemical shifts persists. In simple compounds, this last circumstance is a source of useful additional information on electronic structure and the dynamics of molecular motion in solids, but in the case of complex molecules and polymers it results in the appearance of inhomogeneously broadened regions and regions that defy interpretation in the spectra (Fig. 1b).

The averaging of the chemical-shift tensor  $\overline{\sigma}_{i_{xx}} = 1/3 \text{Sp } \sigma_i$  that is characteristic for liquids, and averaging of the homonuclear dipole-dipole interaction, can be brought about by mechanical rotation of the entire

sample at an angle  $\beta = 54^\circ 44'$  toward the direction of the constant magnetic field. It follows from Andrew's theory<sup>[4]</sup> that when the sample is rotated very rapidly ( $\omega_r > 2/T_2, |\sigma_{11} - \sigma_{11}|$ ), the homo- and heteronuclear dipole-dipole interaction operator is multiplied by  $(3 \cos^2 \beta - 1)/2$  and the chemical shifts are averaged to  $(1/3) \text{Sp } \sigma_i$ .

Combining the necessary complex sequence of powerful high-frequency pulses with rapid (from 2 to 5 kHz) vibrationless rotation of a nonmetallic sample, not to mention measurement of the very weak free-precession signal from the  $^{13}\text{C}$  nuclei at the natural content of this isotope (1.1%), is a difficult task but not an impossible one. An analytically useful spectrum of the high-polymer polycarbonate Lexan with resolved signals from most of the magnetically nonequivalent carbon atoms appears in Fig. 1c. The spectrum was obtained from a solid sample of this plastic during 23 minutes at a frequency of 10 mHz, using an NIC-1085 computer to accumulate and Fourier-transform the measured signal and for automatic generation of the complex sequences of high-frequency pulses together with an NIC-293 input-output unit.

The spectra of Fig. 1 do not contain information on the shapes and relaxation of individual lines. It may seem almost paradoxical that even this information is accessible in spite of the practically complete overlapping of lines of unknown shape. Figure 2 shows the scheme of the corresponding experiment using the double Fourier transformation (first with respect to  $t_1$  with decoupling of the spins of the  $^{13}\text{C}$  nuclei from  $^1\text{H}$  and, accordingly, acquisition of a high-resolution  $^{13}\text{C}$  spectrum where the individual narrow lines take the role of markers, and then with respect to  $t_2$ , which corresponds to relaxation of the transverse magnetization of the  $^{13}\text{C}$  nuclear spins without strong perturbing fields, so that the shape of each of the lines is obtained separately in the monoresonance spectrum after Fourier transformation). The line shapes and the corresponding nuclear relaxation processes are of a nature intermediate between Lorentzian and Gaussian. The effect can be brought about by synchronized motion of molecules in solid norbornadiene at  $-75^\circ\text{C}$  and lower temperatures.

In all of the experiments described above, the NMR

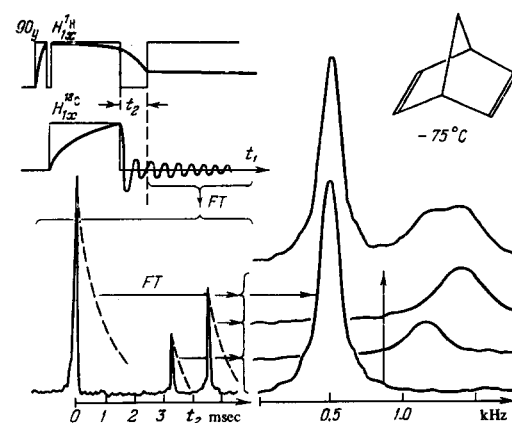


FIG. 2.

spectra were obtained by using the Fourier transform of the nuclear magnetization free precession signal after pulsed excitation of the entire investigated part of the spin system of the solid sample. This is not always possible (for example, in optics) or convenient, and in the case of weak, broad lines of quadrupolar nuclei ( $^{17}\text{O}$ ), the optimum signal-noise ratio is obtained by exciting the system under study with "white noise" in the form of a pseudorandom pulse sequence generated by a shift register with feedback and by applying the Hadamard transformation to the corresponding output signal. Here the cross correlation function of the input

and output noises is formed initially, and the desired spectrum is obtained by Fourier transformation of the latter.

<sup>1</sup>S. R. Hartmann and E. L. Hahn, *Phys. Rev.* **128**, 2042 (1962).

<sup>2</sup>A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.* **59**, 569 (1973).

<sup>3</sup>E. T. Lippmaa, *Zh. Strukt. Khim.* **8**, 717 (1967).

<sup>4</sup>E. R. Andrew and R. G. Eades, *Disc. Farad. Soc.* **34**, 38 (1962).

<sup>5</sup>M. Alla and E. Lippmaa, *Chem. Phys. Lett.* **37**, 260 (1976).

Translated by R. W. Bowers