nance excitation and subsequent ionization using two linearly polarized light beams with different frequencies. The quantum-defect results obtained by Peach<sup>13</sup> have been used for photoelectron energies less than 0.15 Ry. (Similar quantum-defect results have been recently obtained by Lane and Hartquist.<sup>14</sup>)

The agreement between the quantum-defect results and the present close-coupling calculations (in the region of overlap) is an indication that the quantum-defect method should provide reliable photoionization cross sections for higher excited states of helium in the near-threshold region. Finally, Figs. 1 and 2 indicate good agreement with the experimental values determined by Dunning and Stebbings<sup>7</sup> at the wavelengths used in excitation from the metastable state.

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## Transient Oscillations in NMR Cross-Polarization Experiments in Solids\*

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Strong transient oscillations have been observed in proton-carbon-13 cross-polarization experiments in a ferrocene single crystal. These oscillations are in contrast with the usually observed exponential behavior of cross polarization. They are manifestations of coherence effects caused by the dipolar coupling of the carbon-13 to the directly bound proton. A simple model is described which explains the observations.

Cross-polarization experiments between rare and abundant spins have become recently of great interest for high-sensitivity detection of lowabundant nuclei, like <sup>13</sup>C, <sup>15</sup>N, and <sup>29</sup>Si, in solids. High-sensitivity and high-resolution spectra of rare nuclei have been obtained by direct observation of the polarized nuclei.<sup>1,2</sup> Related experiments for indirect detection of low-abundance nuclei have also become of practical importance.<sup>3,4</sup> The cross polarization is achieved in these experiments by matching the precession frequencies of the two spins in their respective rotating frames-the well-known Hartmann-Hahn condition.<sup>5</sup> A simple thermodynamic picture based on the spin-temperature hypothesis has led one to expect an exponential time dependence for cross polarization.<sup>2,5,6</sup> In many instances, such expo-

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nential behavior has indeed been observed,<sup>7</sup> and has been confirmed in our laboratory for <sup>13</sup>C resonance in adamantane. While for short cross-polarization times a Gaussian distortion of the exponential time dependence has been predicted and observed,<sup>6,7</sup> no major deviation from this behavior has been published, to the best of our knowledge.

In the course of our study of the cross-polarization dynamics between protons and carbon-13 spins in a ferrocene  $[(C_5H_5)_2Fe]$  single crystal at room temperature, we have observed, for mixing times up to 1 msec, strong transient oscillations in the <sup>13</sup>C magnetization as a function of the cross-polarization time  $\tau$ . The experiment performed is shown schematically in Fig. 1. It is quite conventional<sup>2</sup> except for the initial applica-



FIG. 1. Schematic representations of the pulse sequence for the cross-polarization experiments: I = abundant spin, S = rare spin.

tion of a long ( $\approx$  500  $\mu$ sec) rf pulse to the S system  $(^{13}C)$  followed by a waiting period of the order of  $T_{2S}$  to completely destroy its magnetization before the experiment. The observed magnetization is then entirely caused by the crosspolarization process during time  $\tau$ . Figure 2 gives representative plots of the <sup>13</sup>C magnetization  $M_{sx}(\tau)$  as a function of the contact time  $\tau$  for two orientations of the ferrocene crystal. The space group of ferrocene is  $P2_1/a$  and the unit cell contains two nonequivalent molecular sites. At room temperature, the molecules rotate freely about their fivefold axis and the carbon spins within each molecule are equivalent. The protondecoupled <sup>13</sup>C spectrum, therefore, generally consists of two separate lines of equal intensity. Figure 2 shows that the oscillations for the two lines have different frequencies and that the frequency also depends on the crystal orientation. These experiments have been performed on a Bruker SXP 4-100 high-power pulse spectrometer at 14 kG using a home-made probe with orthogonal proton and  $^{13}C$  coils and a Varian 620/Lcomputer for signal processing.

In a similar but different experiment, McArthur, Hahn, and Walstedt<sup>6</sup> observed an oscillatory behavior of the dipolar energy after adiabatic demagnetization of abundant *1* spins and a contact with rare *S* spins. The observed frequency was equal to the amplitude of the rotating rf field,  $-\gamma_{s}H_{1s}$ . Since the observed frequency in ferrocene is much lower, the observed effect must have a different origin.

Hartmann and Hahn<sup>5</sup> have shown that for crosspolarization experiments in liquids a coherent and oscillatory polarization transfer can be observed. It is caused by coherent off-diagonal elements of the density operator which are produced



FIG. 2. Normalized S-spin magnetization  $M_{Sr}(\tau)$  as a function of the cross-polarization time  $\tau$  for two orientations of the ferrocene crystal. The dots represent experimental data and the solid lines are based on Eq. (7). The experimental values for the rf fields were  $\gamma_I H_{1I}/2\pi = \gamma_S H_{1S}/2\pi = 16$  kHz. (a) Crystal orientation A. In this orientation, all molecules are magnetically equivalent and a single line results in the proton-decoupled spectrum. The computed curve uses  $R^{-1}=350$  $\mu$ sec and  $b/2\pi = 5.2$  kHz. The theoretical value is  $b/2\pi$ =5.48 kHz with  $r_{C-H}$ =1.05 Å and  $\theta$ =64° (from an analysis of the chemical-shift tensor). The undecoupled  $^{13}C$ spectrum, Fig. 3(a), gives  $b/2\pi = 5.3$  kHz. (b) Crystal orientation B, line 1. The computed curve uses  $R^{-1}$ = 350  $\mu$  sec and  $b/2\pi$  = 9.8 kHz. The theoretical value is  $b/2\pi = 9.98$  kHz with  $\theta = 74^{\circ}$ . The undecoupled spectrum, Fig. 3(b), gives  $b/2\pi = 9.8$  kHz. (c) Crystal orientation B, line 2. The computed curve uses  $R^{-1} = 350 \ \mu sec$  and  $b/2\pi = 2.9$  kHz. The theoretical value is  $b/2\pi = 3.0$  kHz with  $\theta = 50^{\circ}$ .

by the scalar spin-spin interaction between the I and S spins. On the other hand, in solids with a Gaussian line shape merely an initial Gaussian distortion of the exponential time dependence of cross polarization can be observed, in general. However, if there is a dominant dipolar interaction which causes a non-Gaussian line or even a line with fine structure, an oscillatory polariza-



FIG. 3. Undecoupled, proton-enhanced <sup>13</sup>C spectra of ferrocene for three crystal orientations: (a) Crystal orientation A from Fig. 2; (b) crystal orientation B from Fig. 2; (c) crystal orientation C with magic-angle position for one molecular site,  $\theta = 54^{\circ}$ .

tion transfer could also be observed in solids. Weak signal distortions of this kind have already been described by Lowe and Norberg.<sup>8</sup> These distortions are also responsible for the free-induction-decay beats which they have observed.

It can be seen from Fig. 3 that the undecoupled <sup>13</sup>C line shapes for ferrocene are far from being Gaussian. The dipolar coupling between the carbon-13 and the adjacent proton causes the two lines to split into well-resolved but overlapping doublets. The couplings to the more remote protons produce merely a broadening of the multiplet lines. These line shapes may qualitatively explain the observed oscillatory cross polariza-tion.

A simple theory will now be given. It is based on the following assumptions: (1) The dipolar interactions of the isolated S spin with the I spins are neglected except for the coupling to the directly bound I spin. All scalar interactions are disregarded. (2) The interaction of this particular I spin with the remaining I spins is taken into account in a phenomenological manner and described by an isotropic spin-diffusion process with the rate R. (3) Spin-lattice relaxation is neglected. (4) The concentration of the rare Sspins is sufficiently low to consider the *l*-spin system as an infinite energy reservoir. The system may be represented schematically as shown in Fig. 4.

The corresponding density operator equation in a double-rotating frame, rotating with the frequencies of the applied rf fields  $H_{1I}$  and  $H_{1S}$ , is given by

$$\dot{\sigma} = -(i/\hbar)[\mathcal{K},\sigma] - \Gamma(\sigma - \sigma_0) \tag{1}$$



FIG. 4. Schematic representation of the theoretical model used in the computations.

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with the Hamiltonian

$$\mathcal{K}/\hbar = \Delta\omega_I I_z - \gamma_I H_{1I} I_x + \Delta\omega_S S_z - \gamma_S H_{1S} S_x + b I_z S_z, \qquad (2)$$

where  $\Delta \omega_I = \omega_{0I} - \omega_I$  and  $\Delta \omega_S = \omega_{0S} - \omega_S$  are the resonance offsets of the rf fields,  $b = \frac{1}{2}(\gamma_I \gamma_S \hbar / \gamma_{C-H^3}) \times (3\cos^2\theta - 1)$  is the dipolar coupling, and  $\theta$  is the angle between the axis of free molecular rotation and the static magnetic field. The isotropic spin-diffusion operator may be represented by

$$\Gamma(\sigma) = R\left\{ \begin{bmatrix} I_{\star}, & J \end{bmatrix} + \begin{bmatrix} I_{\star}, & \sigma \end{bmatrix} \right\} + \begin{bmatrix} I_{\star}, & \sigma \end{bmatrix} + \begin{bmatrix} I_{\star}, & \sigma \end{bmatrix} \right\}.$$
(3)

 $\Gamma$  has the effect of bringing the particular *I* spin into internal equilibrium with the rest of the *I*-spin reservoir.

The general solution of Eq. (1) will be discussed at another occasion. Here, the following simplifying assumptions will be made:

$$\Delta \omega_I = \Delta \omega_S = 0, \quad |\gamma_I H_{1I} + \gamma_S H_{1S}| \gg |b| \gg R.$$
<sup>(4)</sup>

Then, it is possible to neglect nonsecular elements of the dipolar interaction in the Hamiltonian and one obtains  $^{5}$ 

$$\mathcal{H}/\hbar = \frac{1}{2} [s(I_x + S_x) + d(I_x - S_x) + b(I_z S_z + I_y S_y)],$$
(5)

with  $s = (-\gamma_I H_{1I} - \gamma_S H_{1S})$  and  $d = (-\gamma_I H_{1I} + \gamma_S H_{1S})$ .

The initial density operator  $\sigma(0)$  after spin locking the *l* magnetization at the beginning of the crosspolarization period is given by

$$\sigma(0) = (1 - \beta \hbar \omega_{0,I} I_{\chi}) / \mathrm{Tr}(1).$$
(6)

It does not commute with the Hamiltonian, Eq. (5), because of the dipolar coupling b. The time evolution of the density operator must contain oscillatory terms which can explain the observed oscillations.

When the Hartmann-Hahn condition is exactly fulfilled, d=0, it is particularly easy to determine the observed magnetization  $M_{Sx}(\tau)$ . One finds

$$M_{S_{x}}(\tau) = \operatorname{Tr}\left[\sigma(\tau)S_{x}\right] = \frac{1}{4}\beta\hbar \,\omega_{0\,I}\left(1 - \frac{1}{2}e^{-R\tau} - \frac{1}{2}e^{-3R\tau/2}\cos\frac{1}{2}b\,\tau\right). \tag{7}$$

The oscillation frequency of the magnetization is given by  $\omega_{\rm osc} = b/2$  and amounts to  $\frac{1}{2}$  of the multiplet splitting of the undecoupled S-spin resonance in good agreement with the observations on ferrocene, Figs. 2 and 3. The decay of the oscillatory term is by the factor  $\frac{3}{2}$  faster than the approach to the equilibrium magnetization.

When the Hartmann-Hahn condition is violated,  $d \neq 0$ , one obtains for the oscillation frequency  $\omega_{\rm osc} = (d^2 + b^2/4)^{1/2}$ . It also depends on a possible resonance offset of the rf fields but not on the rf field strengths  $H_{1S}$  and  $H_{1I}$  as long as they are large compared with the widths of the I-spin and S-spin resonance lines. For a spin-diffusion rate R of the same order of magnitude as the dipolar coupling b, the cross-polarization rate depends not only on R but also on b. Particularly the rate constant of the nonoscillatory part is strongly dependent on the ratio R/b, whereas the decay constant of the oscillatory part is to a large extent independent of b. This explains the rather poor fit of Fig. 2(c). A further damping mechanism is provided by the dipolar interaction of the S spin with the more remote I spins. These extensions will be treated in more detail at another occasion.

This transient oscillation makes it possible to transfer, in suitable cases, the complete equilibrium magnetization to the S spin in a very short time of the order of  $\tau = 2\pi/b$  when the contact is terminated exactly on the peak of the first oscillation. In the case of Fig. 2(b), we have obtained 95% polarization in 100  $\mu$ sec. The oscillation frequency  $\omega_{\rm osc}$  is a measure of the dipolar coupling and can be utilized as a diagnostic tool to assign lines and molecular orientations. It is sometimes difficult to obtain the same information from undecoupled spectra as the sensitivity is low and because overlapping multiplets may conceal the detailed features of the spectrum. Transitory oscillations of this kind should be observable in a large class of organic single crystals whenever there is a dominant dipolar interaction.

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## Volumetric Study of the Nematic-Smectic-A Transition of N-p-Cyanobenzylidene-p-Octyloxyaniline

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We have measured a change in specific volume of  $(0.5 \pm 0.2) \times 10^{-4}$  cm<sup>3</sup>/g at the nematicsmectic-A transition of N-p-cyanobenzylidene-p-octyloxyaniline. The order of this transition has recently been subject to dispute. On the basis of our data, we conclude unambiguously that it is of first order as is expected from theoretical analysis.

We report here conclusive evidence that the nematic-smectic-A transition of N-p-cyanoben-zylidene-p-octyloxyaniline (CBOOA) is first or-der. We have deduced this by measuring the temperature dependence of the density of CBOOA. The measurements were performed on a variety of amounts (35 g to a few hundred micrograms) and a variety of purities (the nematic-smectic-A transition temperature  $T_{SN}$  ranging from 81 to 83.4°C). We have found that the transition is always of first order, even in the case of rather impure samples.

This transition has been believed to be of second order <sup>1-3</sup> since early differential-scanningcalorimeter (DSC) measurements<sup>1</sup> did not show the transition. Subsequent DSC measurements<sup>4</sup> in purified samples did show a small "bump" at the nematic-smectic-*A* transition. This "bump" appeared to be a latent heat; its magnitude (0.06 cal/g) did not contradict theoretical estimates expected for this compound<sup>5</sup> and it became broader and ill-defined with increasing sample impurity. Unfortunately, DSC measurements cannot distinguish unambiguously between a latent heat and a specific-heat anomaly, so that further experimental evidence was required to define the order of this transition for CBOOA.

The unambiguous determination of the order of the nematic-smectic-A transition for this compound is currently of great theoretical and experimental interest. Stimulated by de Gennes's<sup>6</sup> analogy between the smectic-A-nematic transition and the superconductor-normal-metal transition and the theoretical result predicting the possibility of a second-order transition,<sup>5,7,8</sup> a great deal of experimental effort has been expended<sup>2,4</sup> studying pretransitional effects near the smectic-A transition of this reputedly second-order compound. Briefly, these experiments show that in the case of *pure* CBOOA the transition behaves "classically"<sup>4</sup> (in the sense of the Ginzburg criterion) whereas in the case of "dirty" CBOOA, "nonclassical" behavior has been observed.<sup>1,2,4</sup> The nonclassical behavior of CBOOA was analyzed<sup>1,2</sup> by assuming a priori that the smectic-A-nematic transition was second order, and on this basis it has been argued<sup>2</sup> that this nonclassical behavior is similar to that which occurs at the superfluid-helium transition. However, the observed "classical" behavior for pure CBOOA does not exclude the possibility that this transition is second order, because, as Alben<sup>9</sup> has pointed out, classical behavior is expected for helium-like systems when the transition is only barely second order, i.e., in the vicinity of a tricritical point.<sup>10</sup> More recently, Halperin and Lubensky<sup>11</sup> have predicted that the smectic -A – nematic as well as the superconductor-normalmetal transition must always be at least weakly first order, and that for type-I materials<sup>12</sup> the transition must occur outside the critical region.

Samples of CBOOA (Kodak No. 11963) were introduced in glass test tubes of about 1 to 3 cm i.d. and 5 to 10 cm length. These tubes were pre-