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Study of nuclear-spin conversion with the use of the Haupt effect and NMR dispersion spectrometry

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A new, simple NMR dispersion method to study and disentangle mixed Zeeman and dipolar NMR lines is described and used for absolute dipolar polarization measurements. A beautiful confirmation of Provotorov's theory is provided. The Haupt effect in γ-picoline is investigated and a twofold detailed experimental study of nuclear-spin conversion in this substance is made. This leads to a thermodynamic three-reservoir model, in excellent agreement with experiments, which yields, among other things, precise values of the tunnel splitting, the conversion time, and the order of conversion kinetics in γ-picoline.

I. INTRODUCTION

NMR techniques, such as adiabatic demagnetization in the rotating frame[1] (ADRF), off-resonance saturation,[2] and the application of a pair of phase-shifted rf pulses,[3] are often used to produce dipolar polarization, dipolar order of nuclear spins, and hence dipolar spin cooling, in solids. In the ADRF method the (weak) Zeeman polarization of the nuclear spins with respect to the large external static magnetic field H_s is reduced to zero and "transformed" into (strong) spin polarization with respect to the small internal dipolar magnetic fields H_D, produced by the neighboring spins. An alternative and much faster method to transform Zeeman order into dipolar order is to apply a pair of phase-shifted rf pulses, as proposed by Jeener.[3] In the third method, off-resonance saturation, the absorption of each quantum from the radio frequency field is accompanied by a lowering of the dipolar energies by an amount equal to the off-resonance Zeeman energy $\hbar\omega_d$, defined as

$$\omega_d \equiv \omega - \omega_s ,$$

where $\omega \equiv \omega_{\text{oscillator}}$ which is the frequency of the rf field, $h_1 = 2H_1 \cos\omega t$, delivered by the spectrometer oscillator, and $\omega_s \equiv \gamma H_s$ the resonance value of ω. (Throughout this paper the subscript d stands for deviation from resonance, while the subscript D stands for dipolar.)

There is yet another possibility to produce dipolar order. In some (exceptional) cases a drastic lowering of the nuclear dipolar temperature T_D is obtained by a sudden cooling or heating of the sample.[4] This phenomenon called *Haupt effect,* occurs in samples containing rotating CH_3 groups which are very slightly hindered and undergo, consequently, UHF tunneling while librating. The tunneling motion involves a third energy reservoir (besides the Zeeman and dipolar reservoirs), the *tunnel reservoir,* which is coupled to the two other reservoirs and to the lattice; the much stronger coupling, however, is to the dipolar reservoir. After the sudden jump of the sample temperature, i.e., of the lattice temperature, the relaxation transitions (slow spin-conversion transitions) in the tunnel reservoir—bringing back this reservoir into thermal equilibrium with the lattice—induce "extra" and very efficient cooling transitions in the dipolar reservoir, resulting in a large dipolar polarization. This polarization gradually decreases in time as the number of the "driving" spin-conversion transitions, the conversion *rate,* decreases. As long as the large dipolar polarization persists, the observed NMR line is a sum of a Zeeman and a dipolar contribution, as explained by Provotorov's theory.[5] So, the evolution in time of dipolar polarization and its contribution to the NMR line shape are probes for studying librational tunneling of the CH_3 rotor and, in particular, of the transition probabilities (the spin-conversion rates) between the tunnel levels.

Thanks to specific characteristics of our NMR dispersion spectrometer,[6] we are able to disentangle both contributions from the experimental NMR line, to measure in an absolute way T_D, and to study its evolution in time. The nuclear-spin-conversion time τ_{con} of the CH_3 rotor in γ-picoline is deduced from our experimental data in a twofold way. Comparison leads to a precise value for the conversion time as well as for the order of the kinetics of the conversion process. The conversion process, the kinetics, the tunnel splitting, and other properties are discussed.

II. PHENOMENA AND THEORY

A. Haupt effect

At low temperatures rotating methyl groups in solids exist in three different proton-spin isomers, i.e., proton-symmetry species: A, E_a, and E_b, with molecular nuclear-spin quantum numbers of, respectively, $\frac{3}{2}$, $\frac{1}{2}$, and $\frac{1}{2}$. The difference ϵ between the rotational energy of the A species (e.g., in the ground level) and the two degenerate E species (e.g., in the first excited level) is equal to $\hbar\omega_t$, where ω_t is the tunnel frequency. A lot of research work has already been done—and is still being done—to determine experimentally these frequencies and their temperature dependence in the

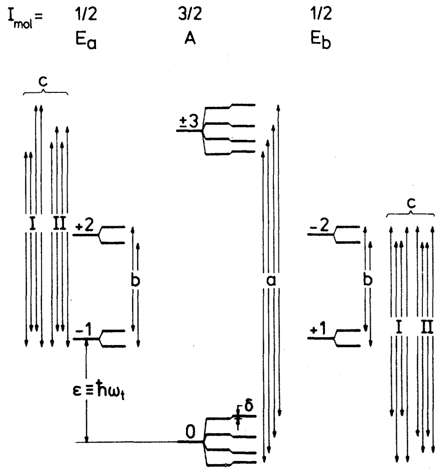

FIG. 1. Energy-level scheme (not on scale) of the three species of a CH_3 rotor without and with a magnetic field. The rotational quantum numbers $0, \pm 1, \pm 2, \pm 3$ are indicated on the zero-field rotational levels. ϵ is the tunnel splitting. The dipolar shift is due to intrarotor dipolar interaction. Transitions a and b are very fast, while transitions c ($A \leftrightarrow E$ transitions) are very slow. They lead to nuclear-spin conversion. They also produce dipolar polarization in the CH_3 rotor's proton spin system (Haupt effect).

innumerable existing CH_3 configurations, as well as the conversion times between the species.

After a temperature jump of the sample, placed in a magnetic field H_s, (for example, from 77 to 4.2 K), very fast nonmagnetic phonon-assisted transitions (such as a and b in Fig. 1) restore almost instantaneously a thermal-equilibrium distribution *within* each of the three subsets of rotational levels, each subset consisting of all the rotational levels of one species. The difference *between* the A and E species populations, however, is tending to its own thermal-equilibrium value very slowly, because such transitions (such as c) cannot be produced by phonons only and require also magnetic, hence very weak, dipolar interactions.

The latter transitions, giving rise to (quite slow) nuclear-spin conversion, also generate dipolar polarization. In Fig. 1 all such $A \leftrightarrow E$ conversion transitions are shown. They are subdivided into two groups, *I* and *II*: *I*, to and from upwards-shifted levels, and *II*, to and from downwards-shifted levels. The shift δ is due to intrarotor dipolar interaction.

Each transition generates a change in dipolar energy of magnitude δ, but opposite in sign. However, as shown by Haupt,[4] the sum of all these changes of dipolar energy weighted by the transition probabilities *is not zero.* Hence there is a net negative change of dipolar energy, which results in dipolar cooling and polarization.

B. Provotorov's theory

The Provotorov theory of saturation,[5] which takes full advantage of the spin-temperature concept, yields, besides steady-state expressions, time-dependent expressions for resonance dispersion and absorption during relaxation, i.e., while the Zeeman and dipolar temperatures T_Z and T_D vary:

$$\chi'(\omega_d) = C\beta + \pi C(\omega_s \alpha - \omega_d \beta) g'(\omega_d) , \qquad (1)$$

$$\chi''(\omega_d) = \pi C(\omega_s \alpha - \omega_d \beta) g''(\omega_d) , \qquad (2)$$

where $\chi' \equiv u/H_1$, which is the real rf susceptibility of the nuclear-spin system, $\chi'' \equiv v/H_1$, which is the imaginary rf susceptibility of the nuclear-spin system, C is the Curie constant of the nuclear-spin system, $g'(\omega_d)$ is the normalized dispersion line shape at low rf field, $g''(\omega_d)$ is the normalized absorption line shape at low rf field, $\alpha \equiv 1/T_Z$, and $\beta \equiv 1/T_D$.

Except for $C\beta$, both resonance lines (1) and (2) consist of two terms: one term from the Zeeman reservoir and the other one from the dipolar reservoir. Normally $\omega_d \ll \omega_s$, and so $\omega_d\beta$ is much *smaller* than $\omega_s\alpha$. If we neglect it, Eqs. (1) and (2) are reduced to the well-known expressions for NMR dispersion and absorption. In case, however, the Zeeman order is fully transformed into dipolar order, β becomes much larger than α and hence $\omega_d\beta$ much *larger* than $\omega_s\alpha$. In that case it is possible to observe pure dipolar χ' and χ'' signals, which are then proportional to $\omega_d g'(\omega_d)$ and $\omega_d g''(\omega_d)$, respectively. Because of the additional factor ω_d, their variation as a function of ω_d resembles the *derivatives* of the normalized line-shape functions. In the absorption mode, this means that we get "absorption" at one side and "emission" at the other side of resonance.[1]

Let us now consider the special case of the Haupt effect, i.e., temperature-induced dipolar polarization: The dipolar reservoir gets strongly polarized, while *also* the Zeeman reservoir remains normally polarized. Now, the observed line is a *mixture* of both contributions with intensities of the same order. A gradual decrease of dipolar polarization (β) as a function of time—due to the decrease in the spin-conversion *rate*—will bring about a gradual change in the mixture and the line shape, which will evolve finally to the normal shape.

III. EXPERIMENTAL METHODS AND RESULTS

Dipolar polarization is usually measured by means of NMR pulse spectrometry. A 90° rf pulse induces a transient magnetic moment in the plane perpendicular to the external magnetic field. By measuring the resulting signal with an inspection pulse, one can observe either Zeeman or dipolar polarization by choosing the right phase of this pulse. If the amplitude of the inspection pulse is small, the dipolar polarization can be measured without disturbing it significantly. Nevertheless, for different reasons, absolute measurements of dipolar order and of T_D are almost impossible.

So, we decided to use a new cw dispersion spectrometer, described in Ref. 6. Instead of looking at some signal proportional to the voltage induced across the sample coil by the resonant rf magnetization—as one does in all cw and pulse methods—we measure the frequency shift $\Delta\omega$ of a simple but very stable oscillator, due to the change of the coil inductance while H_s is scanned through resonance:

$$\Delta\omega = -\tfrac{1}{2}\eta\omega\chi' . \tag{3}$$

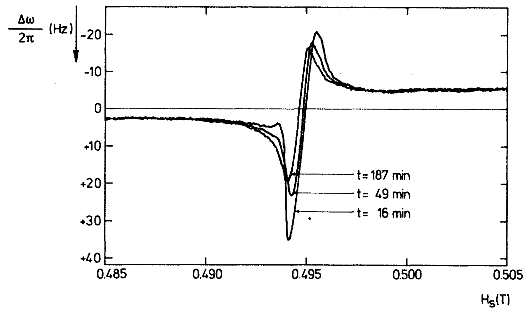

FIG. 2. Some proton NMR dispersion spectra of γ-picoline at 4.2 K, taken at different times t after a temperature jump from 77 K. $\omega/2\pi = 21.01$ MHz.

[One should not confuse the frequency *shift* $\Delta\omega \equiv \omega(\tilde{H}_s) - \omega(H_s = \omega/\gamma)$ at variable field and "constant" frequency with a frequency *scan* $\omega_d \equiv \tilde{\omega} - \omega_s$ at constant field and variable frequency.] Using Eq. (1) and remembering that in the experiments ω is "constant" and H_s is variable, the output of our spectrometer as a function of H_s or H_d is given by

$$\Delta\omega(H_d) = -\tfrac{1}{2}\eta\omega C[\beta + \pi(\gamma H_s\alpha - \gamma H_d\beta) \times g'(H_d)] , \tag{4}$$

where $H_d \equiv \omega_d/\gamma$. Since H_d ($\sim$2 mT) $\ll H_s$ ($\sim$0.5 T) and $\Delta\omega$ ($\sim$120 Hz) $\ll \omega_d$ ($\sim$500 kHz), we may put with good approximation:

$$\gamma H_s = \omega \text{ and } \omega = \text{const} .$$

Hence Eq. (4) becomes

$$\Delta\omega(H_d) = -\tfrac{1}{2}\eta\omega C[\beta + \pi(\omega\alpha - \gamma H_d\beta) \times g'(H_d)] . \tag{5}$$

The Zeeman and dipolar contributions to the oscillator-frequency shift are, respectively,

$$(\Delta\omega)_Z = -\tfrac{1}{2}\eta\pi C\omega^2\alpha g'(H_d) , \tag{6}$$

and

$$(\Delta\omega)_D = -\tfrac{1}{2}\eta\pi C_D[\omega\beta/\pi - \omega\beta\gamma H_d g'(H_d)] . \tag{7}$$

C_D is introduced to take into account the possibility that only part of the nuclear-spin system produces an observable dipolar contribution.

In Eq. (7) the term $\omega\beta/\pi$ is H_d independent and therefore unobservable while scanning H_d. The peak-to-peak value of $(\Delta\omega)_D$, the "intensity" of the

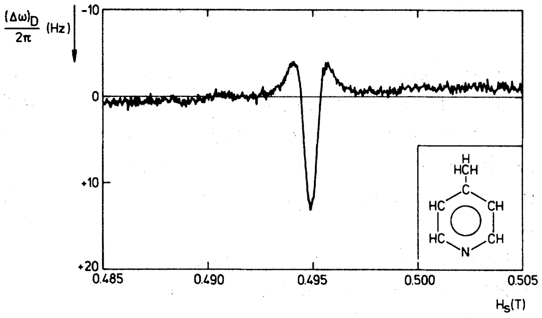

FIG. 3. Typical "pure" dipolar NMR dispersion spectrum of γ-picoline, as obtained 49 min after the temperature jump from 77 K. $\omega/2\pi=21.01$ MHz. In the inset the molecule γ-picoline is shown. It has three rotor protons and four nonrotor protons.

line $(\Delta\omega)_{Dm}$, all other parameters being constant, is proportional to β:

$$(\Delta\omega)_{Dm} \propto \beta \text{ and } \beta=K(\Delta\omega)_{Dm} \ . \qquad (8)$$

Measurements were carried out on a sample of commercially available γ-picoline (4-methylpyridine). The freeze-pump-thaw cycle technique was used for further purification, and in particular to eliminate oxygen because of its well-known influence (as a paramagnetic impurity) on relaxation times, on the spin-lattice relaxation times as well as on the spin-conversion time.

Figure 2 represents the dispersion spectra $\Delta\omega$ vs H_s of γ-picoline taken at, respectively, 16, 49, and 187 min after a temperature jump from 77 to 4.2 K. The jump itself takes about 3 min. The spectrometer frequency ω ($\equiv\omega_0$) is $2\pi(21.01)$ MHz and the field scan is 0.02 T wide. The spectrum at 187 min is already a pure Zeeman resonance line, free from any dipolar admixture. The others show an important dipolar contribution and indicate that a very strong dipolar polarization must be present.

If we want to study the dipolar polarization and its evolution in time, we have to disentangle both contributions. To do so, we have used a novel technique, based upon the unique feature of our spectrometer[6]: There is a direct, absolute proportionality, free from any unknown parameters whatsoever, between the frequency shift $\Delta\omega$ and χ'. From the mixed spectra $\Delta\omega(t)$ vs H_s, we subtract the pure Zeeman spectrum $(\Delta\omega)_Z$ vs H_s, which is $\Delta\omega(t=\infty)$ vs H_s, multiplied by a factor $f\equiv C/C_\infty \equiv C(t)/C(t=\infty)$, where C_∞ is the final Curie constant, when nuclear-spin conversion is completed. This factor compensates for the increase in time, due to conversion, of the Curie constant C, appearing in $(\Delta\omega)_Z$ [Eq. (6)]. An accurate determination of f is quite easy: One has to take such value as to produce the most symmetrical dipolar line shape; the choice is critical. Figure 3 gives an example of a "purified" dipolar spectrum, obtained at 49 min after the temperature jump. As Provotorov's theory predicts, its line shape resembles the derivative of the normal line shape.

In Fig. 4 the intensity $(\Delta\omega)_{Dm}$ of the successive pure dipolar lines is plotted as a function of time

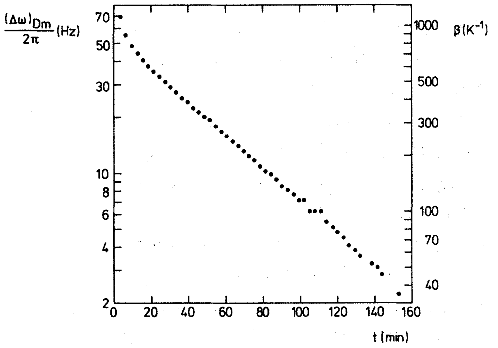

FIG. 4. Semilogarithmic plot of the "intensity" of the dipolar NMR dispersion line and of the reciprocal dipolar temperature β in γ-picoline at 4.2 K as a function of time after the temperature jump from 77 K. $\omega/2\pi=21.01$ MHz. The time constant of the exponential decay is 50 ± 1 min. There is quite a large deviation from exponential behavior in the very beginning. Besides an "after-cooling" effect via $(1-f)$ (see Fig. 5), other more genuine transient effects, related to the sudden strong dipolar cooling immediately after the temperature jump, could provide a possible explanation.

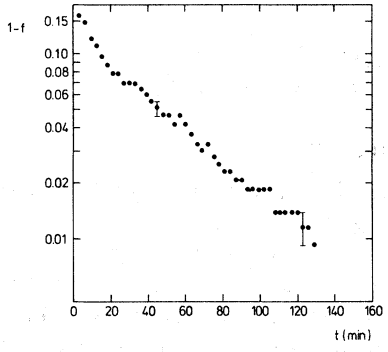

FIG. 5. Semilogarithmic plot of $1-f\equiv C^+/C_\infty$ in γ-picoline at 4.2 K as a function of time after the temperature jump from 77 K. The time constant of the exponential decay is 52 ± 3 minutes. There is some nonexponential evolution in the beginning, which is most probably due to a slight "after-cooling" of the sample over some tenths of a degree K during the first 10 or 20 min after the temperature jump.

after the temperature jump. The curve shows a nearly exponential decay, for which a time constant of 50 ± 1 min can be deduced, which we call $\tau_{\text{con}}^{(\beta)}$.

The factor f, defined above, increases with time according to the concentration of converted species. In Fig. 5 we plot $(1-f)\equiv(C_\infty-C)/C_\infty$ as a function of time. We notice that the evolution is also quite exponential with a time constant of 52 ± 3 min, which we call $\tau_{\text{con}}^{(C)}$.

We are able to determine the dipolar temperature T_D, or its reciprocal β, not only in a relative way, using Eq. (8), but in an absolute way as well. The ratio R of the Zeeman and dipolar frequency shifts for a given H_d can be deduced from Eqs. (6) and (7):

$$\begin{aligned} R &\equiv (\Delta\omega)_Z/(\Delta\omega)_D \\ &= (C/C_D)(\omega/\gamma H_d)(\alpha/\beta)\ , \end{aligned} \tag{9}$$

where C, which is the Zeeman Curie constant of all proton spins, equals fC_∞, and C_D is the dipolar Curie constant of the CH_3 rotor's proton spins, the only ones displaying dipolar polarization. Its value is $0.356C_\infty$, as, from a dipolar view point, $[I(I+1)]_{\text{rotor}}=\frac{9}{4}$.

Since the Zeeman spin-lattice relaxation time of γ-picoline is quite short (about 1 min), $\alpha=T^{-1}$. From the experimental and calculated or known values of R, f, ω, H_d, T, C_∞/C_D, and γ, we can determine β for some well-chosen values of t for which we know $(\Delta\omega)_{Dm}$. Comparison with Eq. (8) calibrates the constant K, expressed in units of $\text{Hz}^{-1}\text{K}^{-1}$:

$$\begin{aligned} K &= \frac{\omega}{\gamma H_d T}\,\frac{C_\infty}{C_D}\,\frac{f_t}{R_t(\Delta\omega)_{Dmt}} \\ &= 16.0\pm0.3\ . \end{aligned} \tag{10}$$

The values of β calculated from (8) and (10) are given in Fig. 4.

Provotorov's predictions in Eqs. (6) and (7) that $(\Delta\omega)_Z\propto\omega^2$ and $(\Delta\omega)_D\propto\omega$ are confirmed by our experiments. Indeed, besides the experiments at 21.0 MHz, we carried out experiments at 38.6 MHz. The results are, for $t=49$ min:

$$\frac{(\Delta\omega)_{Zm}^{38.6}}{(\Delta\omega)_{Zm}^{21.0}}=3.24 \quad \text{while} \quad \left[\frac{38.6}{21.0}\right]^2=3.38\ ,$$

$$\frac{(\Delta\omega)_{Dm}^{38.6}}{(\Delta\omega)_{Dm}^{21.0}}=1.83 \quad \text{while} \quad \left[\frac{38.6}{21.0}\right]=1.84\ .$$

IV. DISCUSSION AND CONCLUSIONS

The phenomenon of temperature-induced dipolar polarization in γ-picoline brings about a beautiful example for Provotorov's theory. The line shape of the dipolar spectrum as well as its frequency dependency confirms the predictions made in this theory.

Our cw dispersion method is very well suited to disentangle and measure, as a function of time, the pure dipolar and Zeeman contributions to the NMR spectrum in case one has a strongly polarized dipolar reservoir while also the Zeeman reservoir remains normally polarized. A simple three-reservoir model which we will introduce will allow us to relate the time dependency of *both* contributions independently to the nuclear-spin-conversion process. Comparison of both relations leads to confirmation of the experimental results, to higher precision in determining the conversion time, but also, and in particular, to an independent calculation of the order of the kinetics of the conversion process and of other characteristics of the conversion and of the Haupt effect.

At 4.2 K, our experimental temperature, the spacing between the lowest tunneling-split rotational levels of the CH_3 group in γ-picoline (about 6k eV) is comparable with the thermal energy. After the temperature jump, conversion between the nuclear-spin species takes place and permits the CH_3 rotors to take up, very slowly, their new Boltzmann distribution.

Consequently, the Zeeman NMR signal increases in time, due to the increase in time of the concentration $n(t)$ of A-species molecules, which have a higher $I(I+1)$ value than the E-species molecules.

On the other hand, the dipolar NMR signal decreases in time, due to the decrease in time of the rate $dn(t)/dt$ of the spin conversion, this rate being the "driving force" of the dipolar polarization. More precisely, in a thermodynamical three-reservoir model, including dipolar, tunnel, and lattice reservoirs, the rate of change of $-\beta^+$, the deviation of the reciprocal temperature of the cool dipolar reservoir from the reciprocal lattice temperature, is governed by the following differential equation, containing two terms, a heat leak from the lattice and a cold leak (by Haupt effect) from the tunnel reservoir:

$$\frac{d\beta^+}{dt}=\frac{-\beta^+}{\tau_{1D}}+\xi\frac{dn^+}{dt}\ , \tag{11}$$

where $\beta^+\equiv\beta_\infty-\beta$, with $\beta_\infty=T^{-1}$, the final reciprocal dipolar temperature, $n^+ \equiv n_\infty - n$, with n_∞ being the final concentration of A species, τ_{1D} the dipolar spin-lattice relaxation time, and ζ a constant, the "Haupt efficiency." For the three-reservoir model and Eq. (11) to be valid, the coupling between the Zeeman and dipolar reservoirs should be negligible with respect to couplings between the other reservoirs involved. This is, of course, the case when the Haupt effect occurs. If we assume, furthermore, that the rate dn^+/dt, which strongly influences the dipolar reservoir, is not influenced by this reservoir itself, this rate is given by

$$\frac{dn^+}{dt} = \frac{-n^{+\nu}}{\tau_{\text{con}}} , \tag{12}$$

where ν is the order of the kinetics of the conversion mechanism. Quite often in the literature on conversion processes—too often—ν is given the value 1, which means that one assumes a mechanism leading to a conversion process evolving exponentially in time. This assumption is acceptable whenever the conversion is not influenced by "external" factors and develops like a normal, spontaneous, noncatalyzed chemical reaction, where the reaction rate is just proportional to the concentration of the reagent. In many cases, however, the conversion does not evolve exponentially,[7,8] which brings about ν values different from 1. Therefore, we shall try to solve the above model for an arbitrary value of ν.

Substitution of Eq. (12) into Eq. (11) yields

$$\frac{d\beta^+}{dt} = -(\beta^+ + qn^{+\nu})/\tau_{1D} , \tag{13}$$

where $q \equiv \zeta\tau_{1D}/\tau_{\text{con}}$. This equation cannot be solved in a closed form, since β^+ and n^+ are both functions of time. Therefore we first solve Eq. (12), which yields:

$$n^+ = n_0^+ \exp(-t/\tau_{\text{con}}) \quad \text{for } \nu = 1 , \tag{14}$$

$$n^+ = [(\nu-1)t/\tau_{\text{con}} + n_0^{+(1-\nu)}]^{1/(1-\nu)} \quad \text{for } \nu \neq 1 , \tag{15}$$

where $n_0^+ \equiv n^+(t=0)$. Introducing Eqs. (14) and (15) into Eq. (13) leads to differential equations, whose solution yields the following expressions:

$$\beta^+(t) = q[\exp(-t/\tau_{1D}) - 1] \quad \text{for } \nu = 0 , \tag{16}$$

$$\beta^+(t) = q[n_0^+ \exp(-t/\tau_{1D}) - n_0^+ \exp(-t/\tau_{\text{con}})] \quad \text{for } \nu = 1 , \tag{17}$$

$$\begin{aligned}\beta^+(t) = {} & A \exp(-t/\tau_{1D}) \\ & + \exp(-t/\tau_{1D}) \\ & \times \int_0^t \exp(t'/\tau_{1D}) Q(t') dt' \quad \text{for } \nu \neq 0, 1 ,\end{aligned} \tag{18}$$

with

$$Q(t') = -(\zeta/\tau_{\text{con}})[(\nu-1)t'/\tau_{\text{con}} + n_0^{+(1-\nu)}]^{\nu/(1-\nu)} .$$

It is clear—and confirmed by numerical integration—that for $t' \gg \tau_{1D}$ and $\not\gg \tau_{\text{con}}$, by far the largest contribution to the integral in (18) comes from the interval near t. If, then, $Q(t')$ does not vary too much in that interval, which certainly is the case for all values of ν below 2, $Q(t')$ may be taken constant and equal to $Q(t)$. Hence,

$$\begin{aligned}\beta^+(t) = q\{ & n_0^{+\nu} \exp(-t/\tau_{1D}) \\ & - [n_0^{+(1-\nu)} - (1-\nu)t/\tau_{\text{con}}]^{\nu/(1-\nu)}\} \\ & \text{for } 0 \leq \nu \leq 2 ,\end{aligned} \tag{19}$$

At 4.2 K the dipolar spin-lattice relaxation time of γ-picoline is about 20 s.[9] All our experiments are performed at times after cooling down, which are much longer: $t \gg \tau_{1D}$. On the other hand, in our experiments $\beta_\infty \ll \beta$. Therefore expressions (16), (17), and (19) can be reduced to the following:

$$\beta(t) = q \quad \text{for } \nu = 0 , \tag{20}$$

$$\beta(t) = qn_0^+ \exp(-t/\tau_{\text{con}}) \quad \text{for } \nu = 1 , \tag{21}$$

$$\beta(t) = q[n_0^{+(1-\nu)} - (1-\nu)t/\tau_{\text{con}}]^{\nu/(1-\nu)} \quad \text{for } 0 \leq \nu \leq 2 , \tag{22}$$

The results of the dipolar signal measurements in Fig. 4 must be compared with Eqs. (20), (21), and (22), while the results of the Zeeman signal measurements, or $(1-f)$ measurements, in Fig. 5 must be compared with expressions for $C^+/C_\infty [\equiv (C_\infty - C)/C_\infty]$. A general expression for C^+/C_∞ can easily be calculated from the $I(I+1)$ values of, respectively, $\frac{27}{4}$ for the A-species and $\frac{15}{4}$ for the E-species molecules:

$$\frac{C^+}{C_\infty} = \frac{4n^+}{4n_\infty + 5} .$$

With the use of Eqs. (14) and (15) we obtain the following:

$$\frac{C^+}{C_\infty} = \frac{4(n_0^+ - t/\tau_{\text{con}})}{4n_\infty + 5} \quad \text{for } \nu = 0 , \tag{23}$$

$$C^{+}/C_{\infty}=\frac{4n_{0}^{+}\exp(-t/\tau_{\text{con}})}{4n_{\infty}+5}\quad \text{for } \nu=1\ , \tag{24}$$

$$C^{+}/C_{\infty}=\frac{4[n_{0}^{+(1-\nu)}-(1-\nu)t/\tau_{\text{con}}]^{1/(1-\nu)}}{4n_{\infty}+5}\quad \text{for } 0\leq\nu\leq 2\ . \tag{25}$$

It is interesting to compare in a qualitative way the expressions for $\beta(t)$ [(20), (21), and (22)] with those for C^{+}/C_{∞} [(23), (24), and (25)]. For $\nu=0$, $\beta(t)$ is time independent, while C^{+}/C_{∞} is time dependent; for $\nu=1$ both are time dependent in exactly the same way; for other values of ν both are time dependent, but in a different way as one sees from the exponents.

When the evolution in time of β and C^{+}/C_{∞} is nearly exponential—as in our case—we have to compare the time constants of both. Their ratio V is

$$V=\frac{d\ln\beta}{dt}\Big/\frac{d\ln(C^{+}/C_{\infty})}{dt}\ . \tag{26}$$

Its experimental value is given with excellent approximation by the ratio of the measured values of τ_{con}, $\tau_{\text{con}}^{(C)}/\tau_{\text{con}}^{(\beta)}$. Introducing expressions (20) to (25) into (26) we find *for all values of* ν that

$$V=\nu\ .$$

The theoretical conclusions of the three-reservoir model for arbitrary values of the order of the kinetics ν allow thus to determine ν, not only, in the usual (somewhat qualitative) way, from the degree of linearity of the $\ln(1-f)$ vs t and $\ln\beta$ vs t curves, but also in a quantitative way:

$$\nu=V=\tau_{\text{con}}^{(C)}/\tau_{\text{con}}^{(\beta)}\ .$$

From our experimental values of $\tau_{\text{con}}^{(C)}$ and $\tau_{\text{con}}^{(\beta)}$, we conclude that the nuclear-spin-conversion process in γ-picoline has an order of kinetics $\nu=1.04\pm0.06$, which confirms that the conversion is purely exponential. Its time constant τ_{con} is 50 ± 1 min. This value is in not too bad agreement with the value of 63 min, given in Ref. 9. The difference could be ascribed to differences in sample origin and preparation. It is known that oxygen can have an important influence.[7]

The Haupt efficiency ζ can be calculated from Eq. (21), which gives, for $t\rightarrow0$,

$$\beta(0)=qn_{0}^{+}=\zeta\tau_{1D}n_{0}^{+}/\tau_{\text{con}}\ .$$

Hence,

$$\zeta=\beta(0)\tau_{\text{con}}/\tau_{1D}n_{0}^{+}\ .$$

$\beta(0)$ is determined experimentally by extrapolating the results obtained from Eqs. (8) and (10): $\beta(0)=880\pm80\ \text{K}^{-1}$. n_{0}^{+}, calculated from the Boltzmann distributions over the tunnel levels at 77 and 4.2 K, is 0.288. For τ_{1D} we take 20 s. So we get a value for ζ of $(4.3\pm0.5)\times10^{5}\ \text{K}^{-1}$.

The tunnel splitting ϵ of γ-picoline is known with reasonable accuracy from inelastic neutron scattering experiments (INS) to be $6k$ eV.[10] Our spin-conversion measurements, providing absolute $(1-f)$ values, i.e., level population values, allow us to estimate the tunnel splitting, with less accuracy, however. We assume that at $t=0$ the A and E levels are populated according to the very small high-temperature value of the Boltzmann ratio, $\epsilon/77k$; hence $n_{0}=0.519$. At $t=\infty$ the Boltzmann ratio is $\epsilon/4.2k$; hence

$$n_{\infty}=[1+\exp(-\epsilon/4.2k)]^{-1}\ .$$

$(1-f)$ at $t=0$ is given by

$$C_{0}^{+}/C_{\infty}=4(n_{\infty}-n_{0})/(4n_{\infty}+5)$$

(see above). Thus, ϵ can be calculated from our extrapolated $(1-f)$ value at $t=0$ and 4.2 K, which is 0.14 ± 0.02. The poor accuracy is largely due to the derivation from exponentiality at low values of t, as can be seen in Figs. 4 and 5. The result is a tunnel-splitting value $\epsilon=(6.0\pm1)k$ eV, in good agreement with the INS data.

The case of a seemingly zeroth-order nuclear-spin-conversion process is reported in the literature for methane.[7] Standard pulse NMR measurements of relative FID signal amplitudes $f\ (\equiv C/C_{\infty})$ versus time yield an almost linear evolution between 0 and a time τ_{c}, after which f keeps its equilibrium value 1. As mentioned above [Eqs. (23)–(25)], linearity in $f(t)$ indicates $\nu=0$, a zeroth order and nonpurely intermolecular conversion mechanism, in full contrast to the first-order mechanism in γ-picoline. In pure methane τ_{c} (which is different from τ_{con}: $\tau_{\text{con}}\cong5\tau_{c}$) is 140 ± 10 min. Strikingly enough, the purer the methane, the neater is the linearity. It would be worthwhile to investigate, on the one hand, the conversion process in methane by means of NMR dispersion spectrometry, and to study, on the other hand, the influence of paramagnetic impurities on the conversion process in γ-picoline.

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