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Spectral spin diffusion in the presence of an extraneous dipolar reservoir

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An explanation is presented for the observed inverse quadratic dependence of the spectral spin-diffusion rate constant on the frequency difference of the two involved spin species in the presence of a large extraneous dipolar reservoir. The result applies to spin diffusion in the laboratory frame and to cross polarization in a rotating frame.

Since the pioneering work on spin diffusion in solids by Bloembergen,[1,2] numerous papers on this subject have appeared.[3–11] Spin diffusion, i.e., the propagation of spin energy in a rigid crystal frame, is of importance for the understanding of numerous phenomena in solid-state magnetic resonance, including nuclear relaxation by paramagnetic impurities,[1,12] dynamic nuclear polarization by Overhauser and solid-state effects,[12,13] distant electron-nuclear double resonance[14] (ENDOR), and cross polarization in the rotating frame using Hartmann-Hahn matching or adiabatic demagnetization and remagnetization.[15–18]

We have to distinguish between spatial spin diffusion, proceeding among equivalent spins separated in space, and spectral spin diffusion among nonequivalent spins where diffusion may be considered to take place in frequency space. The present Communication is concerned with spectral spin diffusion between two nuclear species in the presence of a large extraneous dipolar reservoir. It is attempted to explain features of the frequency dependence of the spin-diffusion rate which have previously not been fully understood.

The same basic principles that apply to spectral spin diffusion among spins in the laboratory frame[3–11] are also applicable to cross-polarization dynamics in the presence of radio frequency fields in the rotating frame.[15–18] In both cases, spin order is transmitted by flip-flop processes which drive the involved spins towards thermal equilibrium. Laboratory-frame spin diffusion depends on the separation $\Delta\Omega = \Omega_1 - \Omega_2$ of the involved resonance frequencies while, in analogy, Hartmann-Hahn cross polarization depends on the mismatch $\Delta\omega = \gamma_I B_I - \gamma_S B_S$ of the two rf fields applied to the two nuclear species I and S.

Experimental[16,19,20] and theoretical[16,18] studies have found an exponential dependence of the cross-polarization rate on $\Delta\Omega$ in calcium fluoride,[16] silver trifluoroacetate,[19] and in adamantane.[20] A more detailed theoretical study by Demco *et al.*[18] has demonstrated that the dependence, although roughly exponential in many cases, is often more complicated.

In contrast to these well accepted findings, Lang and Moran[17] have measured for cross polarization between ^{6}Li and ^{7}Li in LiF an inverse quadratic dependence of the cross-polarization rate on $\Delta\omega$. Neither Lang and Moran[17] nor Demco *et al.*[18] give a quantitative explanation of these experimental facts. We have made related measurements on laboratory-frame spin diffusion, and found the same inverse quadratic frequency dependence. We will provide a theoretical explanation of these observations.

We measured ^{14}N spectral spin diffusion in the laboratory frame among the four nonequivalent $^{14}NH_4^+$ ions in ammonium sulfate, $(NH_4)_2SO_4$, single crystal.[21] The spectrum consists of four quadrupolar doublets whose splittings can be varied by controlled rotation of the single crystal for measuring the dependence of spin diffusion on the frequency separation $\Delta\Omega$. The proton spins provide a large extraneous dipolar reservoir which will prove to be important in the spectral spin-diffusion process.

Two-dimensional (2D) spectroscopy, an ideal method for the investigation of exchange processes,[22,23] was used to measure the spin-diffusion rates in the laboratory frame.[24] The pulse scheme employed is indicated in Fig. 1. In a 2D experiment,[22,23] the spin-diffusion pathways are traced out by "frequency labeling" before diffusion the various magnetization components by their precession frequencies such that after diffusion their origin can be determined uniquely. A two-dimensional ^{14}N spin-diffusion map is shown in Fig. 2. Four of the eight ^{14}N resonance lines of $(NH_4)_2SO_4$ are visible along the diagonal (numbered 1–4). The occurrence of off-diagonal cross peaks indicates magnetization ex-

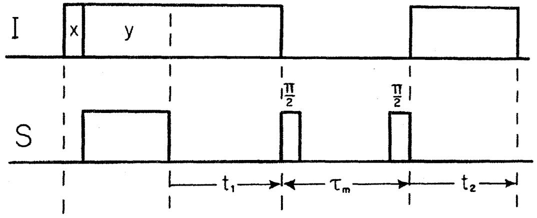

FIG. 1. Pulse scheme for the measurement of S spin diffusion.

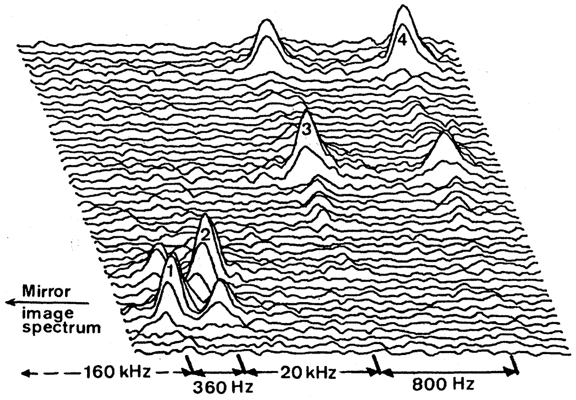

FIG. 2. 2D ^{14}N spin-diffusion spectrum of single crystal $(NH_4)_2SO_4$ recorded at 5.2 T (Ref. 25). The four lines shown are the high-field lines of the four quadrupolar doublets. Note the data compression by frequency folding.

change by spin diffusion between the signal pairs (1,2) and (3.4). The spin-diffusion rate constants are obtained by variation of the mixing time τ_m.

The spin-diffusion rate constants T_{ik}^{-1}, measured for five crystal orientations, are plotted in Fig. 3 as functions of the frequency separation $\Delta\Omega$ of the resonance lines. The exponential dependence, $T_{ik}^{-1} = a\exp(-b\Delta\Omega)$ predicted and measured previously for different systems,[16,18–20] cannot explain the present results. On the other hand, a quadratic fit, $T_{ik}^{-1} = a(\Delta\Omega)^{-2}$ leads to good agreement within experimental accuracy. It is tempting to attribute these findings to the same (yet undetermined) origin as those observed in LiF by Lang and Moran.[17]

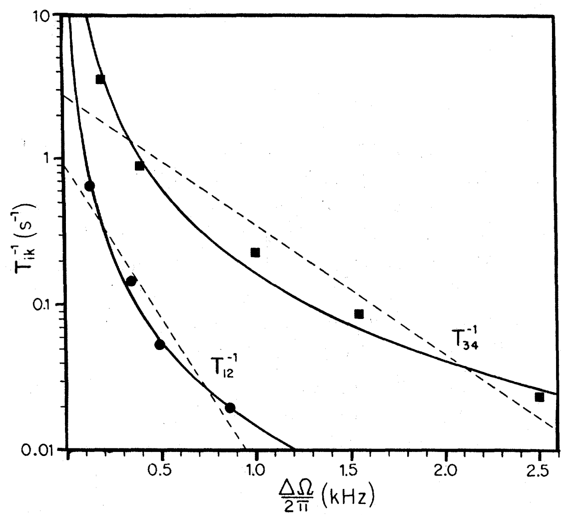

FIG. 3. Spin-diffusion rate constants T_{12}^{-1} and T_{34}^{-1} as functions of the frequency difference $\Delta\Omega$ of the two resonance lines. The experimental data are fitted by a quadratic (——) and an exponential function (– – –).

The common feature of cross polarization in LiF and spin diffusion in $(NH_4)_2SO_4$ is the involvement of three spin species. S_1 and S_2 participate actively in the transfer of spin order (^{6}Li, ^{7}Li, or $^{14}N_1$, $^{14}N_2$, respectively), while the third species I (^{19}F or ^{1}H, respectively) presents a large dipolar reservoir which may act as a heat sink.

The Hamiltonian of such a system consists of Zeeman plus quadrupolar (one index) and dipolar terms (two indices):

$$\mathcal{H} = \mathcal{H}_{S_1} + \mathcal{H}_{S_2} + \mathcal{H}_I + \mathcal{H}_{S_1S_1} + \mathcal{H}_{S_2S_2} + \mathcal{H}_{S_1S_2} + \mathcal{H}_{S_1I} + \mathcal{H}_{S_2I} + \mathcal{H}_{II} \quad . \tag{1}$$

For spin diffusion between well-resolved quadrupolar transitions belonging to different sites, it is possible to replace the quadrupolar spins by fictitions spins $\frac{1}{2}$, absorbing the quadrupolar splitting in Ω_p, e.g.:

$$\mathcal{H}_{S_1} = \Omega_1 \sum_i S_{1iz} \quad ,$$

$$\mathcal{H}_{S_1S_2} = -\sum_i \sum_k b_{ik}^{S_1S_2}(2S_{1iz}S_{2kz} - \tfrac{1}{2}S_{1i}^+S_{2k}^- - \tfrac{1}{2}S_{1i}^-S_{2k}^+) \quad ,$$

$$\mathcal{H}_{S_1I} = -\sum_i \sum_l b_{il}^{S_1I} 2S_{1iz}I_{lz} \quad ,$$

$$b_{il}^{S_1I} = (\mu_0/4\pi)\gamma_{S_1}\gamma_I\hbar r_{il}^{-3}P_2(\cos\theta_{il}) \quad .$$

We now combine the two S spin Zeeman terms,

$$\mathcal{H}_{S_1} + \mathcal{H}_{S_2} = \mathcal{H}_\Sigma + \mathcal{H}_\Delta \quad , \tag{2}$$

introducing the *mean frequency Zeeman Hamiltonian*

$$\mathcal{H}_\Sigma = \tfrac{1}{2}(\Omega_1 + \Omega_2)\left[\sum_i S_{1iz} + \sum_k S_{2kz}\right] \tag{3}$$

and the *difference frequency Zeeman Hamiltonian*

$$\mathcal{H}_\Delta = \tfrac{1}{2}(\Omega_1 - \Omega_2)\left[\sum_i S_{1iz} - \sum_k S_{2kz}\right] \quad . \tag{4}$$

We arrive then at the commutation diagram shown in Fig. 4. $\mathcal{H}_\Sigma$ and $\mathcal{H}_I$ commute with the remaining Hamiltonian. They represent constants of the motion and hence have not to be considered further. Creation of nonequilibrium polarization, say of spins S_1, generates difference frequency Zeeman polarization, $\langle\mathcal{H}_\Delta\rangle \neq 0$. Spin diffusion from S_1 to S_2 amounts then to dissipation of $\langle\mathcal{H}_\Delta\rangle$ polarization and, therefore, to a change of the total Zeeman energy of the system. Energy conservation is accomplished by a corresponding change of the dipolar interaction energy $\langle\mathcal{H}_{S_1S_2}\rangle$ of the two spin species. The heat capacity of this dipolar reservoir is, however, very small, and, for completion of the process, the energy must be transfered further to the $\langle\mathcal{H}_{II}\rangle$ reservoir which has a virtually infinite heat capacity.

This prompted us to make the following identification of commuting reservoirs $\mathcal{H}_1$ and $\mathcal{H}_2$ and coupling Hamiltonian $\mathcal{H}_p$ responsible for transfer of spin order:

$$\begin{aligned} \mathcal{H}_1 &= \mathcal{H}_\Delta + \mathcal{H}_{S_1S_2} + (\mathcal{H}_{S_1S_1} + \mathcal{H}_{S_2S_2}) \ , \\ \mathcal{H}_p &= \mathcal{H}_{S_1I} + \mathcal{H}_{S_2I} \ , \\ \mathcal{H}_2 &= \mathcal{H}_{II} \ . \end{aligned} \tag{5}$$

With the identification of Eq. (5), it is possible to directly apply the results of the projection operator treatment of cross polarization by Demco *et al.*[18] In particular, we can compute the spin-diffusion rate constant T_{12}^{-1}:

$$\begin{aligned} T_{12}^{-1} = & \frac{-1}{\mathrm{Tr}\{\mathcal{H}_1{}^2\}} \\ & \times \int_0^\infty d\tau \, \mathrm{Tr}\{[\mathcal{H}_p,\mathcal{H}_1] \exp[-i(\hat{\hat{\mathcal{H}}}_1 + \hat{\hat{\mathcal{H}}}_2)\tau] \\ & \times [\mathcal{H}_p,\mathcal{H}_1]\} \ . \end{aligned} \tag{6}$$

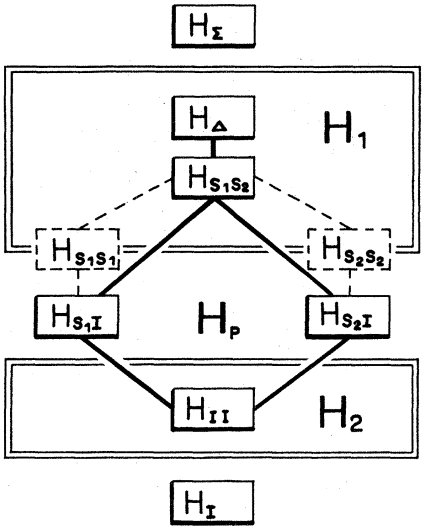

FIG. 4. Commutation diagram of the Hamiltonian, Eqs. (1) and (2). A connecting line indicates noncommutation.

An evaluation of this general equation leads to the result

$$T_{12}^{-1} = [\Delta\Omega^2 + (b^{S_1S_2})^2]^{-1} (b^{S_1S_2})^2 4 \int_0^\infty d\tau \cos(\omega_{\mathrm{eff}}\tau) \, \mathrm{Tr}_I \left(\sum_k (b_k^{S_1I} - b_k^{S_2I}) I_{kz} \exp(-i\hat{\hat{\mathcal{H}}}_{II}\tau) \sum_l (b_l^{S_1I} - b_l^{S_2I}) I_{lz} \right| \ , \tag{7}$$

$$\omega_{\mathrm{eff}} = [\Delta\Omega^2 + (b^{S_1S_2})^2]^{1/2} \ . \tag{8}$$

Equation (7) is in agreement with the experimentally observed offset dependence of the spin-diffusion rate T_{12}^{-1}. For $(b^{S_1S_2})^2 << \Delta\Omega^2 << M_{2II}$ (M_{2II} is the second moment of II interaction), we obtain an inverse quadratic dependence of T_{12}^{-1} on the frequency difference $\Delta\Omega = \Omega_1 - \Omega_2$. For small offsets, a Lorentzian deviation from the quadratic dependence is found, while for very large offsets, the spectral density expressed by the integral in Eq. (7) becomes dependent on ω_{eff} and thus on $\Delta\Omega$.

The assumptions inherent in Eq. (6) are discussed in the paper of Demco *et al.*[18] To derive Eq. (7), we made the additional assumption that a single S_1S_2 pair interaction is dominating, neglecting further S spin interactions, $\mathcal{H}_{S_1S_1} = \mathcal{H}_{S_2S_2} = 0$. For the calculation of the heat capacity of $\mathcal{H}_1$, a truncated dipolar interaction $\mathcal{H}'_{S_1S_2} = b^{S_1S_2}\frac{1}{2}\cdot(S_1^+S_2^- + S_1^-S_2^+)$ is used. The neglected part of $\mathcal{H}_{S_1S_2}$ commutes with the rest of the Hamiltonian.

Phenomenologically, spin diffusion can be considered as a thermodynamic process between the three heat reservoirs $\langle\mathcal{H}_\Delta\rangle$, $\langle\mathcal{H}_{S_1S_2}\rangle$, and $\langle\mathcal{H}_{II}\rangle$ with the heat capacities $C_\Delta, C_{S_1S_2}, C_{II}$ and the spin temperatures $\beta_\Delta, \beta_{S_1S_2}, \beta_{II}$, respectively. It is governed by a master equation of the form

$$\frac{d}{dt}\begin{pmatrix} \beta_\Delta C_\Delta \\ \beta_{S_1S_2} C_{S_1S_2} \\ \beta_{II} C_{II} \end{pmatrix} = \begin{pmatrix} -R & R & 0 \\ R & -R-k & k \\ 0 & k & -k \end{pmatrix} \begin{pmatrix} \beta_\Delta \\ \beta_{S_1S_2} \\ \beta_{II} \end{pmatrix} \tag{9}$$

with the two rate constants R and k. Assuming that equilibrium between $\langle\mathcal{H}_\Delta\rangle$ and $\langle\mathcal{H}_{S_1S_2}\rangle$ is rapidly established by a fast process R, we find for their common spin temperature $\beta_\Delta = \beta_{S_1S_2}$ the rate equation

$$\dot{\beta}_\Delta = 2k[\Delta\Omega^2 + (b^{S_1S_2})^2]^{-1}(\beta_{II} - \beta_\Delta) \ , \tag{10}$$

where we have used the heat capacities

$$\begin{aligned} C_\Delta &= \mathrm{Tr}\{\mathcal{H}_\Delta^2\} = \tfrac{1}{2}\Delta\Omega^2 \ , \\ C_{S_1S_2} &= \mathrm{Tr}\{\mathcal{H}'^2_{S_1S_2}\} = \tfrac{1}{2}(b^{S_1S_2})^2 \ . \end{aligned} \tag{11}$$

The frequency dependence of the rate constant in Eq. (10) is the same as in Eq. (7). It is obvious that it is a direct consequence of the heat capacity of $\mathcal{H}_\Delta$ being proportional to $\Delta\Omega^2$. The larger C_Δ is, the slower will be the emptying of the $\mathcal{H}_1$ heat reservoir through the bottleneck presented by the SI interaction.

It should be noted that the process $\langle\mathcal{H}_\Delta\rangle \overset{R}{\rightleftarrows} \langle\mathcal{H}_{S_1S_2}\rangle$ is not purely thermodynamic since the two terms do not commute. The result is a precessional motion in a three-dimensional operator subspace formed by the operators $X = \frac{1}{2}(S_1^+S_2^- + S_1^-S_2^+)$, $Y = -\frac{1}{2}i(S_1^+S_2^- - S_1^-S_2^+)$, and $Z = \frac{1}{2}(S_{1Z} - S_{2Z})$ which fulfill the standard commutation relations of angular momentum operators. The Hamiltonian $\mathcal{H}_1 = b^{S_1S_2}X + \Delta\Omega Z$ leads to a rotation with angular velocity ω_{eff} [Eq. (8)] about an inclined axis in the XZ plane and causes an oscillatory exchange of spin order between $\langle \mathcal{H}_\Delta \rangle$ and $\langle \mathcal{H}_{S_1S_2} \rangle$ which is damped by further interactions.[26] This allows one to set $\beta_\Delta = \beta_{S_1S_2}$ and enables a thermodynamic treatment of spin diffusion.

In conclusion, we have found that the proportionality to $(\Omega_1 - \Omega_2)^{-2}$ of the rate constant for spectral spin diffusion between frequencies Ω_1 and Ω_2 can be explained as a heat-capacity effect in systems containing three or more spin species. The difference frequency Zeeman reservoir, with a heat capacity proportional to $(\Omega_1 - \Omega_2)^2$, has to be emptied through the connecting dipolar reservoir to the dipolar reservoir of an extraneous third spin species.

The model presented applies directly to spectral spin diffusion in $(NH_4)_2SO_4$ with a regular network of ^{14}N-^{14}N interactions. However, in LiF, investigated by Lang and Moran,[17] the random distribution of the low abundance ^6Li causes additional complications. The required averaging over the distribution function of ^6Li-^7Li pairs leads to a slightly modified frequency dependence of the spin-diffusion rate constant. The pecularities of dilute spin systems, exemplified by ^{13}C spin diffusion will be discussed elsewhere.

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