A line shape analysis of the effects introduced by motions in the nuclear magnetic resonance spectra of decoupled solids

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An analysis of the effects of a two-site exchange process on the solid-state nuclear magnetic resonance (NMR) spectrum of an S spin coupled to an unlike I spin under rf irradiation is presented. It is shown that the line broadening that under certain conditions is shown by the S resonance can be calculated using a density matrix treatment. Although this approach has been used in order to evaluate the signal that arises from single crystallites, a simplification of the problem was introduced in order to evaluate the signal that arises from a powdered sample. With this approximation it was possible to evaluate the effects of exchange for a broad range of kinetic and decoupling conditions. The calculations were extended to include the effects of the chemical shift anisotropy of the S spins, and simulations obtained in this way agreed well with the experimental spectra of an exchanging solid recorded at different temperatures and decoupling fields. The relation between incoherent and coherent interference with decoupling in solids and in liquids is also briefly discussed.

I. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy has become one of the main tools available for the study of the structure and the dynamics of solids. In part, this is due to the relative simplicity with which the sequence of cross polarization (CP),[1] coupled to the averaging techniques of magic-angle spinning[2] (MAS), and of high-power decoupling allow to obtain for the dilute nuclei of a solid sample a solution-like NMR spectrum.[3] Nevertheless, the high resolution that is characterized by narrow resonances centered at the frequencies of the isotropic chemical shifts can be spoiled by the effects of molecular motions or of chemical exchange. One of the factors behind this decrease in resolution was first explained by Maricq and Waugh,[4] who showed that dynamic processes introduce a random modulation in the chemical shift of inhomogeneously broadened spin 1/2 nuclei that precludes the formation of rotor echoes by MAS. Indeed, subsequent studies have taken advantage of this effect in order to characterize the nature of molecular motions in several organic crystals.[5–7] An additional mechanism through which motions can affect the resolution of a solid-state NMR spectrum was discussed by VanderHart and coworkers,[8] who noted that motional modulation of the I–S dipolar coupling (where I and S are the abundant and the dilute nuclei, respectively) will interfere with the high-power decoupling process of the I spins. This effect was theoretically as well as experimentally analyzed by Rothwell and Waugh,[9] who used the master equation of motion for the spin density matrix in order to evaluate the relaxation of an S spin coupled to the an I spin under rf irradiation. In this study the modulation of the I–S coupling was assumed to orginate in an isotropic rotational motion, and the analysis yielded an expression of the line width of the S resonance as a function of the I–S dipolar coupling, the rate of the motion and the strength of the decoupling field. The behavior predicted by this theory was compared with the experimental NMR spectra of model organic compounds with well known molecular dynamics, and the overall agreement that was found was good. Since then, the Rothwell–Waugh analysis has been used as the basis of a number of studies on rotational motions in solids.[7,10]

Although isotropic rotational diffusion is relatively common in plastic crystals and in amorphous solid-like polymers,[11] NMR and x-ray studies have shown that in crystalline solids this motion is exceptional. The long range order that characterizes these systems usually confines the motions to well defined jumps of a group in the molecule or of the molecule as a whole about n-fold symmetry axes. With this picture in mind, a number of studies have appeared in which the effects of discrete molecular jumps on the NMR spectra of rotating solids were analyzed for different exchange and spinning regimes.[5,12,13] These studies have shown that, in addition to the parametric dependence on the shielding anisotropy, the spinning speed, and the rate of exchange that is predicted by a diffusion model,[5] the amount of line broadening introduced is also highly dependent on the specific kind of motion that is involved. Since these line shape analyses have not been extended to include the effects of molecular jumps on the decoupling process it is the purpose of the present work to complement the above mentioned studies by evaluating the effects of a two-site exchange process on the NMR spectrum of an I-decoupled S nucleus.

As was noted by Rothwell and Waugh, there is a similarity between the mechanism through which motions interfere with the MAS process and the mechanism through which they interfere with decoupling. In order to stress this similarity we shall introduce a physical picture which, albeit crude, may be helpful to understand the mechanism of the line broadening process. The NMR system under consideration will consist of isolated pairs of I–S unlike spins (e.g., a ^{1}H–^{13}C pair). For this case, the Hamiltonian H is given by

$$H = H_S + H_I + H_{IS}, \tag{1}$$

where H_S represent the Zeeman interaction of S, H_I is composed of the Zeeman and the rf interactions of I, and H_{IS} is

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the dipolar spin–spin coupling between I and S. This Hamiltonian can be transformed into the I and S rotating frames to yield, after suitable truncation, the well-known Hamiltonian

$$H = -\omega_1 I_x + B_{IS} I_z S_z\,, \tag{2}$$

where ω_1 is the angular frequency associated with the decoupling field and $B_{IS} = (\mu_0/4\pi)\gamma_I\gamma_S\hbar(1\text{–}3\cos^2\beta)\,r_{IS}^{-3}$ is the dipolar coupling constant between I and S. If relaxation is not taken into account, the time-domain signal (FID) of the S spin after a $\pi/2$ pulse or a CP sequence can be obtained by diagonalizing the Hamiltonian of Eq. (2) as[14]:

$$S(t) = \mathrm{Tr}(e^{-iHt}S_x e^{iHt}S_+) \tag{3a}$$

$$= \left(\frac{4\omega_1^2}{B_{IS}^2 + 4\omega_1^2}\right) + \left(\frac{B_{IS}^2}{B_{IS}^2 + 4\omega_1^2}\right)\cos\left(\frac{\sqrt{B_{IS}^2 + 4\omega_1^2}}{2}\,t\right). \tag{3b}$$

This FID is purely real and consists of a time-independent term and a term that oscillates with a frequency $a = \sqrt{B_{IS}^2 + 4\omega_1^2}/2$. This frequency defines a "decoupling cycle," at the end of which the S signal has regained its starting magnitude [Figs. 1(a) and 1(b)]. If at a certain moment the I–S vector undergoes a reorientation, the change in the coupling constant will prevent the complete refocusing of the S signal [Fig. 1(c)]; and therefore the frequency domain signal of S will become broadened. However, if the I–S vector undergoes many reorientations during each decoupling cycle the S spin will evolve under a motionally averaged dipolar coupling that will allow a complete refocusing of the signal [Fig. 1(d)] and, therefore, the obtention of an exchange-narrowed S resonance in the frequency domain.

A more detailed analysis of this problem is given below. In Sec. II, a full density matrix treatment is used in order to obtain the NMR spectrum of an I–S pair that is exchanging between two sites under decoupling conditions. In Sec. III, an approximation is introduced that allows a significant simplification of the calculations, which are therefore extended to the evaluation of powder NMR spectra for a broad range of jump angles, jump rates and decoupling fields. The effects of the chemical shift anisotropy of the S spins were also included in the analysis, and the theoretical spectra calculated in this way agreed well with the experimental spectra of an exchanging solid recorded at different temperatures and decoupling fields. Finally, some of the implications that the present study may have for future work on the nature of decoupled spectra of dilute spins are briefly discussed.

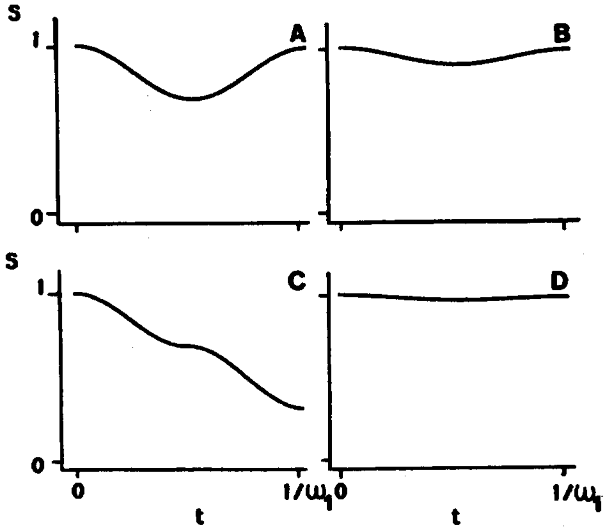

FIG. 1. Signal arising from a ^{13}C bonded to a ^{1}H under rf irradiation. (a) The C–H bond is parallel to the external field. (b) The C–H bond is perpendicular to the external field. (c) The C–H bond is originally parallel to the external field and undergoes a 90° reorientation at a time $t = 1/2\omega_1$. (d) The C–H bond is undergoing a fast exchange between the two perpendicular orientations. In all the cases the parameters are $r_{\mathrm{CH}} = 1.05$ Å; $\omega_1 = 30$ kHz.

II. EXACT THEORY OF EXCHANGE WITH DECOUPLING

In order to evaluate the changes that are introduced in the NMR spectrum of the S spins, we shall consider two pairs of spins I_1–S_1, I_2–S_2 which upon a molecular reorientation exchange their orientations with respect to the external magnetic field B_0. If we disregard the anisotropy of the I and S chemical shifts and assume on-resonance decoupling, the Hamiltonian of the system can be expressed in the rotating frame as

$$H = -\omega_S(S_{1z} + S_{2z}) - \omega_1(I_{1x} + I_{2x}) + B_1 I_{1z} S_{2z} + B_2 I_{2z} S_{2z}\,, \tag{4}$$

where ω_S is the off-resonance shift of S; and B_1, B_2 are the constants that characterize the dipolar interaction for each orientation. If the effects of relaxation are neglected, the evolution of the density matrix is given by the Alexander–Kaplan equation[15,16]

$$\frac{d\rho}{dt} = i[\rho, H] + k(R\rho R - \rho)\,, \tag{5}$$

where k is the rate of the molecular reorientation and R is the exchange operator which in the present case fulfills the condition $R = R^{-1}$. The presence of this operator precludes the analytical calculation of an evolution operator; and it is therefore convenient to rewrite Eq. (5) in Liouville space as[17]

$$\frac{d\rho}{dt} = \Gamma\rho\,, \tag{6}$$

where the superoperator Γ is given by

$$\Gamma = i(H \otimes E - E \otimes H) + k(R \otimes R - E \otimes E)\,. \tag{7}$$

The elements of Γ can be calculated from the elements of H and of R in Hilbert space, which are readily evaluated in the composite product base $\{|I_1S_1I_2S_2\rangle\}$. Therefore, ρ consists of $16^2 = 256$ elements and Eq. (6) can be expressed as

$$\frac{d\rho}{dt}_{ij} = \sum_{kl} \Gamma_{ijkl}\,\rho_{kl}\,, \tag{8}$$

where Γ_{ijkl} is a supermatrix of $256^2 = 65\,536$ elements. In order to calculate the evolution of the density matrix after the CP sequence, we assume an initial condition $\rho_0 = \rho(t=0) = S_{1x} + S_{2x}$ and evaluate the density matrix at a time t as

$$\rho(t) = e^{\Gamma t}\rho_0\,. \tag{9}$$

From a practical point of view, it is more convenient to calculate first the matrix D which diagonalizes Γ and then to evaluate the density matrix $\rho(t+\Delta t)$ from $\rho(t)$ as

$$\rho(t+\Delta t) = De^{\Lambda\Delta t}D^{-1}\rho(t)\,. \tag{10}$$

Finally, the signal at each time t becomes available from $\rho(t)$ as:

$$S(t) = \mathrm{Tr}[\rho(t)(S_{1+}+S_{2+})]\,. \tag{11}$$

Since in this signal only 16 elements of the density matrix are selected, it is possible to simplify the 256 coupled differential equations in Eq. (8) to only 64 differential equations before performing the numerical evaluation of the time domain signal.

Figure 2 shows the spectra calculated with Eqs. (4)–(11) for different values of ω_1 and of k. For the exchange model two *C–H* pairs related by a 90° rotation were used, and the effects of the motion were evaluated for two different initial orientations of the pairs. As can be seen, these simulations present many of the features that were discussed by Rothwell and Waugh. For each set of coupling constants and decoupling fields, an increase in the rate of the motion shifts the slow-exchange spectrum into the intermediate and then into the fast exchange regime. In addition, the simulations illustrate how an increase in the decoupling power reduces the amount of line broadening that is introduced by the motion. Finally, it should be noted that since the simulations reveal that the line broadenings depend on the difference B_1–B_2; the numerical predictions for the effects of a two-site exchange process on a powdered sample may deviate considerably from those that can be deduced form the simple isotropic-motion model.

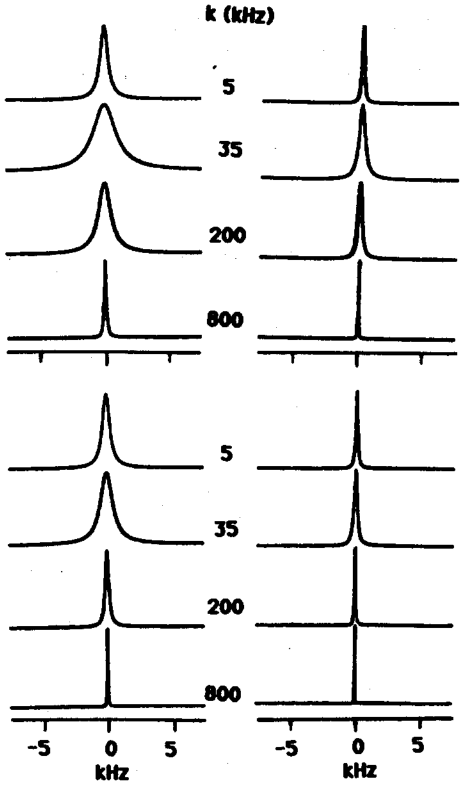

FIG. 2. Calculated ^{13}C NMR spectra for the case of single ^{13}C–^{1}H systems ($r_{\rm CH} = 1.05$ Å) undergoing a two-site exchange process with different rates k. The two upper sets of spectra were simulated assuming a decoupling field $\omega_1 = 40$ kHz; whereas in the two lower sets a decoupling field of 80 kHz was used. In the two left-hand sets of spectra the angles between the exchanging C–H bonds and the external field are 0° and 90°; whereas in the right-hand sets these angles are 30° and 120°.

III. MAGNETIZATION-VECTORS APPROACH

A. Theoretical considerations

The next step in the present analysis should be the extension of the results introduced in the preceeding section to the case of powdered samples. However, such a procedure would suffer from two major drawbacks. In the first place, the need to diagonalize 64×64 matrixes a large number of times (at least $30^2 = 900$ times for a not-too-fine subdivision of the solid sphere) can become very time consuming even with the aid of a fast digital computer. On the other hand, the theory introduced in the preceeding section does not provide a suitable physical picture for a further analysis of the problem. Therefore we shall introduce an approximation which, in addition of being still able to produce good numerical results in a relatively small amount of computer time, is closely akin to the image of decoupling as a "stirring" with rf fields.[18]

Using the transformation $W = e^{-i\omega_1 I_x t}e^{-i(\omega_I^0 I_z + \omega_S^0 S_z)t}$ (where ω_I^0, ω_S^0 are the Larmor frequencies of the I and S spins), the Hamiltonian of Eq. (1) can be rewritten as

$$H_W(t) = -\omega_S S_z + B_{IS}\,[I_z\cos(\omega_1 t) + I_y\sin(\omega_1 t)]\,S_z\,. \tag{12}$$

The time evolution operator $U(t)$ of this Hamiltonian is given by

$$U(t) = T\exp\left\{iS_z\int_0^t [\omega_S - B_{IS}(I_z\cos\omega_1 t' + I_y\sin\omega_1 t')]\,dt'\right\}, \tag{13}$$

where T is the Dyson time ordering operator. Since H_W is not self-commuting at different times, $U(t)$ has to be calculated by dividing t into a large number of intervals $\Delta t'$ during which H_W is almost constant, and then carrying out a time-ordered product of the evolution operators during each interval. In the present case, we shall take each subinterval $\Delta t'$ as π/ω_1, so that the piecewise constant Hamiltonian is given by

$$H_W(t) = \begin{cases} -\omega_S S_z + B_{IS}I_z S_z: & 2\pi(n-1)/\omega_1 < t' < 2\pi(n-1)/\omega_1 + \pi/\omega_1\,, \\ -\omega_S S_z - B_{IS}I_z S_z: & 2\pi(n-1)/\omega_1 + \pi/\omega_1 < t' < 2\pi n/\omega_1\,. \end{cases} \quad n = 1,2,\ldots\,. \tag{14}$$

According to this approximation, the signal of each spin S arises from two magnetization vectors which are initially precessing with frequencies $\omega_S + B_{IS}/2$ and $\omega_S - B_{IS}/2$. After a time π/ω_1 these magnetizations exchange their precession frequencies, and therefore they refocus at the end of the "decoupling cycle" $2\pi/\omega_1$.

Within this context, it is relatively simple to appreciate the effects of molecular reorientations on the spectrum of the S spins. If at a certain moment before the end of a decoupling cycle there is a change in the orientation of the I–S bond, the B_{IS} will change its value and the refocusing of the magnetization vectors at the end of the cycle will be incomplete. If as in the previous section the case of molecular reorientations between equally populated sites is considered, the evolution of the magnetization vectors can be obtained from the classical McConnell equations[19]

$$\frac{d}{dt}M_A = i\omega_A M_A - kM_A + kM_B\,,$$

$$\frac{d}{dt}M_B = i\omega_B M_B + kM_A - kM_B\,, \qquad (15)$$

where A and B are the two exchanging sites and k is the rate of the process. The evolution matrix for M_A and M_B can be easily found by diagonalization of the 2×2 system in Eq. (15), and its elements are found to be dependent on k, on $\delta = \omega_A - \omega_B$ and on $\Omega = (\omega_A + \omega_B)/2$. In order to test the usefulness of this approach, spectra derived from Eqs. (14) and (15) were calculated for the same set of parameters as those used in Fig. 2. These results are shown in Fig. 3 and, as can be seen, the overall agreement between the two methods of analysis is very good.

In order to extend the calculations to a powdered sample, spectra like those shown in Fig. 3 have to be calculated for different orientations of the I–S vectors and then added with their appropriate weighting factors. In cases of mutual two-site exchange like those under consideration, it is convenient to define a molecular reference system (MRS) to which the principal axes systems (PAS) of the dipolar interactions of the exchanging sites are related through $\pm\theta$ rotations about the $Y_{\rm MRS}$ axis. In this frame, δ and Ω can be expressed as

$$\delta_{\rm MRS} = R_y(\theta)B_{\rm PAS}R_y^{-1}(\theta) - R_y^{-1}(\theta)B_{\rm PAS}R_y(\theta)$$

$$\Omega_{\rm MRS} = \omega_S E + [R_y(\theta)B_{\rm PAS}R_y^{-1}(\theta) + R_y^{-1}(\theta)B_{\rm PAS}R_y(\theta)]/2\,, \qquad (16a)$$

where $R_y(\theta)$ is the Euler rotation matrix, E is the identity matrix and

$$B_{\rm PAS} = b_{IS}\begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}; \qquad (16b)$$

with $b_{IS} = (\mu_0/4\pi)\gamma_I\gamma_S\hbar r_{IS}^{-3}$. The final frequencies in the Zeeman frame can be obtained using the transformation $R(\alpha,\beta)$ that relates the MRS with the external field B_0. This operation yields

$$\delta = \mp 6b_{IS}\sin\theta\cos\theta\cos\alpha\cos\beta\sin\beta\,, \qquad (17a)$$

and

$$\Omega = \omega_S \pm b_{IS}[\cos^2\theta(1 - 3\cos^2\beta) + \sin^2\theta(1 - 3\cos^2\alpha\sin^2\beta)]/2\,, \qquad (17b)$$

as the relevant evolution frequencies during each subinterval of time. Using Eq. (15), the total FID of the sample becomes available as

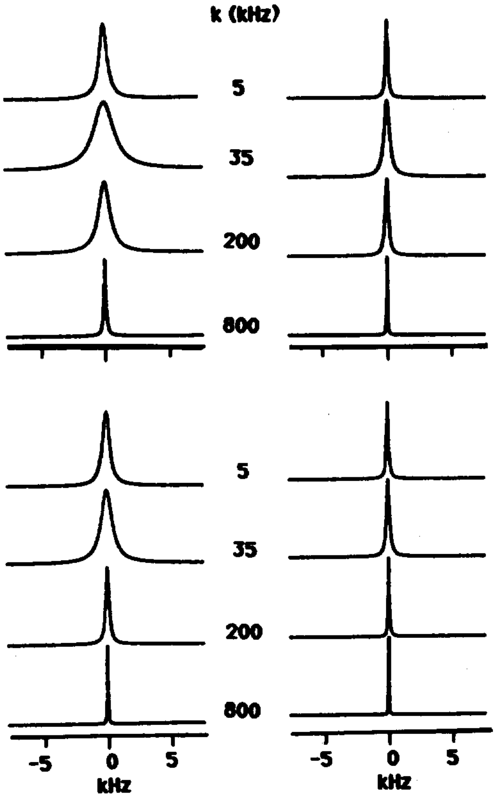

FIG. 3. Sets of NMR spectra for single spin packets undergoing two-site exchange calculated using the magnetization-vectors approach. The exchange and decoupling parameters are the same as those used in Fig. 2.

$$S(t) = \int_0^\pi \int_0^\pi [M_A(\alpha,\beta;t) + M_B(\alpha,\beta;t)]\sin\beta\, d\beta\, d\alpha\,. \qquad (18)$$

In order to investigate the dependence of the powder spectra on the different parameters that are involved, simulations were performed for the case of ^{13}C–^{1}H pair undergoing different kinds of reorientational jumps. Figure 4 shows the results of these calculations for various rates of exchange and for two models of reorientations about $Y_{\rm MRS}$: (a) 90° rotations similar to those observed in the case of porphine[10]; and (b) 120° rotations like those that take place in the case of a phenyl ring undergoing 180° flips around its para axis.[7] As can be seen in the figure, the changes introduced by the motion are only slightly dependent on the particular geometry of the molecular jump. The maximum line width that is observed in all the cases is smaller than the one predicted for the same decoupling power and coupling constants by the isotropic diffusion model. In the intermediate exchange regime the line shapes of the powder signals are no longer Lorentzians, but rather a complex superposition of many Lorentzians with widely different line widths. Due to this reason, the effect of the motion on the S signal that is observed will not only be the introduction of an additional broadening but also a significant decrease in the overall signal intensity. This is illustrated in Fig. 5, that shows the effects of motion on the absolute intensity of a ^{13}C bonded to a ^{1}H for different decoupling fields and rate constants of exchange. As can be seen the log plot exhibits the character-

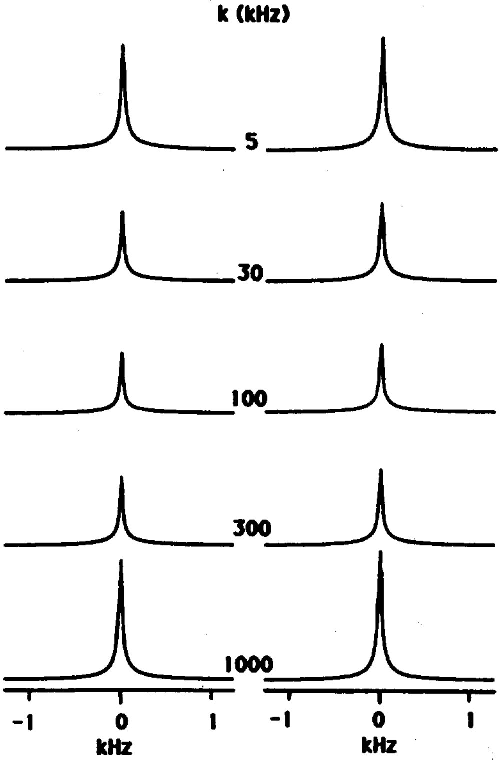

FIG. 4. Calculated powder NMR spectra for the case of a ^{13}C–^{1}H pair undergoing a two-site exchange process with different rates k. The angles between the sites are 90° (left-hand column) and 120° (right-hand column). All spectra were calculated assuming a decoupling field $\omega_1 = 30$ kHz and an $r_{CH} = 1.05$ Å. The same scaling factor was used in all the simulations.

istic "V"-shaped behavior predicted by the diffusion model, as well as a decrease in the effects of the motion as higher decoupling fields are used.

B. Experimental results

One of the main differences between the predictions of the two-site exchange model and the isotropic diffusion model is the amount of line broadening that they predict for the S spin signal. Although both approaches predict a similar decrease in the absolute intensity of the signals the two-site model also predicts, for the intermediate exchange regime, a signal composed of Lorentzians whose line widths may range from a few Hz to several hundreds of Hz. In order to verify this prediction it would be necessary to label separately the signals that arise from each crystallite in a powdered sample. This can be partially accomplished by recording the NMR spectrum of a static sample, where the anisotropy in the chemical shift of the S spins provides a dispersion in the resonance frequencies of the spin packets. In the present study we have chosen dimethylsufone (DMS) as the model compound for carrying out this analysis. DMS presents a number of advantages, e.g.; (a) it gives a single well-resolved ^{13}C powder pattern; (b) the methyl groups of DMS are a good approximation for the case of isolated I–S spin systems; and (c) Solum *et al.*[20] have already characterized the 180° flip motion of DMS ($k_{\text{jump}} = 5.44\ 10^{13}\, e^{-7601/T}$ Hz, jump angle about $Y_{\text{MRS}} = 108°$, chemical shift anisotropy $\Delta\omega = 56$ ppm) and therefore no attempt to fit the spectral parameters is necessary. On the other hand, a study on this compound suffers from two disadvantages; namely, that the ^{13}C are already partially decoupled from the protons by the fast $-CH_3$ rotation, and that the melting point of the compound is not high enough to allow a departure from the slow-exchange regime.

In order to evaluate the dipolar coupling between the carbon and the protons it is convenient to define an axes system coincident with the PAS of the chemical shielding tensor; i.e., with its Z axis parallel to the S–C bond and its X axis lying in the plane defined by one of the S–C–H bonds. Since the methyl is rotating fast about its C_3 axis and the S–C–H angle is 109.4°; the average dipolar interaction of each proton is diagonal in the PAS introduced above and its strength is equal to 1/3 of the strength that characterizes a static ^{13}C–^{1}H interaction. Although the total dipolar coupling of the three protons will be the sum of two dipolar interactions of different magnitudes, we shall simplify the problem by taking the average of these interactions. This yields a coupling equivalent to the one introduced by a single proton placed along the C–S bond at a distance $d = 1.26 d_{CH}$ from the ^{13}C nucleus. Finally, in order to evaluate the time domain signal of each spin packet, it is necessary to evaluate the quantities δ and Ω that determine the behavior of the exchanging magnetizations during each of the evolution intervals defined above. This can be done as described in Eq. (16), to yield

$$\delta = (4\Delta\omega \mp 6 b_{CH}) \sin\theta \cos\theta \cos\alpha \cos\beta \sin\beta \quad (19a)$$

$$\Omega = \omega_S + \left(\frac{\Delta\omega}{3} \pm \frac{b_{CH}}{2}\right)[\cos^2\theta(1-3\cos^2\beta) + \sin^2\theta(1-3\cos^2\alpha\sin^2\beta)]\,. \quad (19b)$$

The left-hand side of Fig. 6 shows the ^{13}C powder NMR spectra of DMS recorded at different temperatures using a decoupling field $\omega_1 = 24.7$ kHz. At room temperature the signal consists of an almost completely symmetric powder pattern, which becomes almost completely asymmetric due

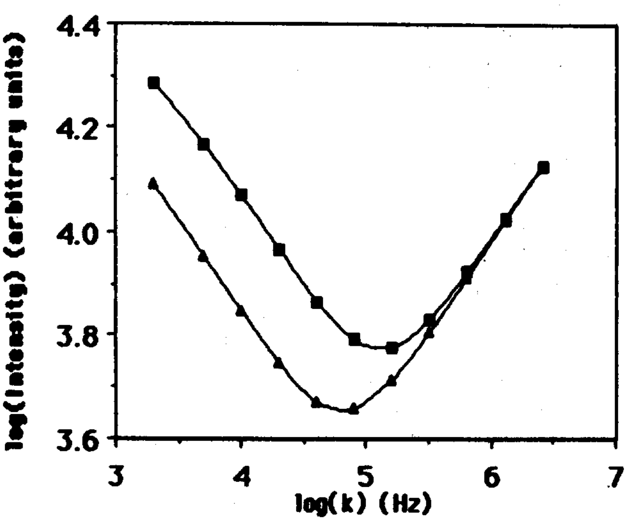

FIG. 5. Log plot of the intensity measured for the ^{13}C powder resonance (1296 orientations) of ^{13}C–^{1}H pairs ($r_{CH} = 1.05$ Å) undergoing 90° jumps as a function of the rate of exchange for $\omega_1 = 20$ kHz (▲) and 40 kHz (■). The solid lines are drawn for visual comparison.

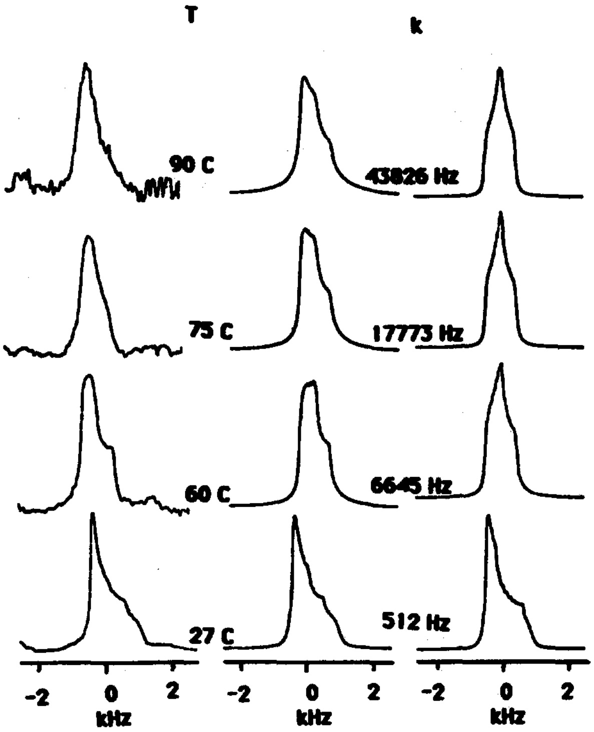

FIG. 6. Experimental (left-hand column) and calculated (center column) powder NMR spectra of DMS recorded at different temperatures using a decoupling field $\omega_1 = 24.7$ kHz. The right-hand column shows the spectra that can be expected if the effects of motion on the decoupling process were disregarded. The exchange rates k for each temperature were obtained from the Eyring equation given in Ref. 20. The isotropic frequency of the powders was placed at the origin of frequencies. A line broadening of 60 Hz was used in the simulations, which were obtained as powder averages over 1296 different orientations.

to the presence of the molecular motions at ~60 °C. However, as was noted in the original study of DMS,[20] the exchange narrowing ceases at this temperature and, upon further heating, the powder pattern departs from its expected line shape (spectra at 75 and 90 °C). Although sample decomposition was suggested as a possible origin of this distortion, the theory described above is also able to fit the observed changes (center column of Fig. 6). The effects of the dipolar coupling are very small for the range of exchange rates that affect the chemical shift tensor, but become more relevant as the temperature is increased and give the powder patterns a symmetric-like line shape. For the purpose of comparison, the right-hand column of Fig. 6 shows the spectra that can be expected for DMS in case that the effects of the motion on the ^{1}H decoupling process could be disregarded.

Further evidence for the interpretation given to the high-temperature spectra of DMS is shown in the left-hand side of Fig. 7, which illustrates the effects of using different decoupling powers on the ^{13}C CP NMR spectra of DMS recorded at 80 °C. To the right of each spectrum is the theoretical prediction that can be obtained using the same parameters as those used in the simulations shown in Fig. 6. As can be seen, the ideal asymmetric powder pattern begins to emerge in the spectra as the decoupling field increases; a fact that implies that the sample has not been affected by temperature.

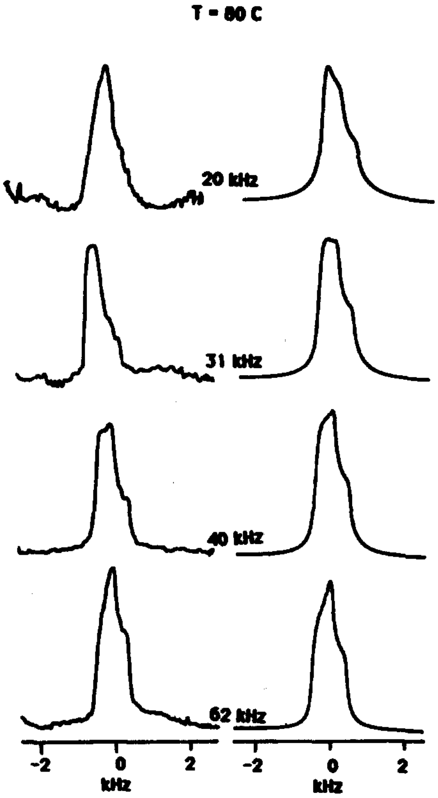

FIG. 7. Experimental (left-hand column) and calculated powder NMR spectra of DMS recorded at 80 °C using the different decoupling fields indicated in the figure. The exchange rate k used in the simulations is 24 217 Hz. Other spectral parameters are as in Fig. 6.

IV. EXPERIMENTAL

DMS was obtained by oxidation of methylsulfide with $KMnO_4$, followed by extraction of the reaction mixture with CCl_2H_2 and finally by recrystallization of the reaction product from hot water. The ^{13}C NMR spectra were recorded at 25.16 MHz on a Varian XL-100 NMR Spectrometer modified for performing the CP sequence. The spectrometer is equipped with a home-built variable-temperature probe capable of achieving Hartmann–Hahn matching[21] at 63 kHz with a transmitter power of 86 W in the ^{13}C channel and a decoupling power of 24 W in the ^{1}H channel. The variable-temperature operation was implemented by heating air with a resistor placed inside the probe. Temperatures were controlled by means of a 100 Ω resistance placed at ~1 cm from the sample coil, and are considered accurate to ± 1 °C. In order to avoid the introduction of spurious noise from the heating resistor, a computer-controlled NAND gate was used to turn off the heating during the acquisition time of the signal. The ω_1 values for each decoupling power were measured using the method described by Rothwell and Waugh. Although the spectra shown in Figs. 6 and 7 were obtained using a contact time of 2 ms and a repetition time of 3 s, similar spectra could also be recorded using different mixing times or pulse delays.

V. DISCUSSION AND CONCLUSIONS

In the present study we have described a line shape method of analysis to calculate the NMR spectra of an I-

decoupled S spin undergoing a two-site exchange motion. An extension of the analysis to the case of an n-site exchange process using the exact density matrix theory appears considerably cumbersome for $n \geqslant 3$. Although the use of the magnetization-vectors approach seems more viable since it confines the problem to diagonalization of $n \times n$ matrices, it can be expected that in many of these cases the model of a rotational diffusion about the axis of symmetry of the motion will yield good numerical predictions of the spectra. On the other hand, the magnetization-vectors approximation presents a suitable framework in order to analyze the effects of motion on more complex $I_n S$ systems.

The description employed in Sec. III appears useful in order to further analyze the different effects that could interfere with the decoupling process. According to this treatment, the determining factor in the line broadening of the S resonance is the change that dynamic processes introduce in the coupling constant B_{IS} during the decoupling cycle. Following the idea of Rothwell and Waugh we have assumed that these changes arise from the presence of molecular reorientations in solids. Nevertheless, similar considerations could be applied to, for example, $^{15}\mathrm{N}$–$^{1}\mathrm{H}$ systems in solution in which changes in the isotropic J coupling constant originate in intermolecular $^{1}\mathrm{H}$ exchange or in $>\mathrm{N{-}H} \rightleftarrows\, >\mathrm{N}$ tautomerization processes. Although in the cases of exchange the fluctuations of the I–S coupling constant are stochastic, problems in the refocusing of the S magnetizations may also arise if these changes are of a coherent nature. It can therefore be expected that in the cases of fast-rotating samples in MAS,[22] where the sample spinning introduces appreciable changes in B_{IS} during each decoupling cycle, there will be a reduction in the efficiency of the decoupling. An extreme example of this has been recently presented by Oas *et al.*,[23] who showed that when the decoupling field and the speed of sample rotation in MAS are equal, there is a considerable recoupling of the I–S pairs.

Finally, it should be mentioned that although in the present study we have regarded the effects of motions on decoupling as a tool for the characterization of molecular motions; these effects may become a considerable nuisance for recording a high-resolution spectrum with a reasonable signal to noise ratio. A possible solution for this problem is to use a high-enough decoupling field (as illustrated in Fig. 7), although this may not always be possible due to technical reasons. A second method that might deserve further consideration is the use of random noise decoupling.[24] Since in this case decoupling is achieved by a procedure that is equivalent to a chemical exchange process between two sites separated by a frequency B_{IS}, the introduciton of a second dynamic process (the molecular motion) may be unable to produce the considerable dephasing of the spin-packets that it produces when coherent decoupling is employed.

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