JOURNAL OF MAGNETIC RESONANCE **133,** 352–357 (1998)
ARTICLE NO. MN981478

Counting Spins with a New Spin Echo Double Resonance

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Received December 9, 1997

In traditional spin echo double resonance (SEDOR), the echo amplitude M is decreased when the observed spins S are flipped by π together with the π refocusing pulse on the observed spins I; the dependence on τ is then determined. In the new version of SEDOR, the echo amplitude is measured as a function of the S spin flip angle θ at a constant pulse spacing τ. The analysis is simple and powerful for long τ, where the strong collision limit applies. There, the variation of M with θ can be fit, yielding the number n of spins S to which each spin I is coupled. Data from amorphous silicon with ^{1}H and ^{2}D show the described effect. A MAS version of the new method is used on multiply labeled alanine and urea, with results in good agreement with the predictions for $n = 2$, as expected. By Fourier transforming M with respect to the flip angle θ, a stick spectrum results; the largest numbered non-vanishing stick yields the number n of spins S coupled to each spin I. Simulations are presented for an $n = 2$ system. The present technique is compared to the multiple-quantum spin-counting method.

Key Words: **double resonance; SEDOR; solid-state NMR; unlike spins; spin echo.**

INTRODUCTION

Conventional spin echo double resonance (SEDOR; see pulse sequence of Fig. 1a) is a robust technique for characterizing unobserved nuclear spins S that may be near the observed spins I (*1, 2*). The basic idea is that I–S spin–spin interactions (usually dipolar) are bilinear in I_z and S_z. Thus, when the S-spin π pulse is omitted (Fig. 1a), the I–S interaction is refocused and the echo has its full amplitude, $M_{(2\tau)}^{\text{without}}$. With the S-spin π pulse, the I–S interaction is unchanged by the simultaneous I and S π pulses, so the echo amplitude $M_{(2\tau)}^{\text{with}}$ is diminished by the I–S interaction.

At its simplest, SEDOR allows a yes/no determination of the presence of S spins near each I spin. Furthermore, the time evolution of the I–S interaction (*3–6*) can be measured from the SEDOR ratio $R_{(2\tau)} \equiv M_{(2\tau)}^{\text{with}}/M_{(2\tau)}^{\text{without}}$. The ratio $R_{(2\tau)}$ is, within certain limitations, the free induction decay (FID) signal that would obtain if the I–S interaction were the only source of linewidth. Because it is a ratio quantity, the I-spin T_2 damping is removed. A rapid S spin T_1 and/or rapid S spin flip-flops driven by S–S interactions may lead to a motional narrowing (like the AgF effect, ref. *7*) in $R_{(2\tau)}$, complicating the analysis. Nevertheless, $R_{(2\tau)}$ is nearly the I–S FID and can be fit in the time or frequency domains. In the case of a single S coupled to each I, the dipole interaction strength deduced from the Pake pattern (*7, 8*) allows the I–S distance to be calculated, assuming a purely dipolar interaction (as appropriate for low- and modest-Z nuclear spins).

One circumstance in which the 2τ dependence of the SEDOR ratio will be of little value is that in which each spin I (assumed to be relatively isolated from other I) is coupled to several (n) spins S. This circumstance is not rare in many kinds of solids. Provided none of the I–S couplings is overwhelmingly larger than the others, central limit theorem reasoning (*7*) leads one to expect $R_{(2\tau)}$ to be nearly Gaussian (likewise for its Fourier transform). Since the Gaussian is characterized by a single width parameter (i.e., the I–S second moment), there is little useful information content. Specifically, neither the separate values of the I–S distances nor even the number of spins S coupled to I can be separately determined. The weakness described here is of course present in dipolar lineshapes whenever there are many interacting spins (*7*).

The new version of SEDOR presented here is able to determine the number n of spins S coupled to each I. Thus, it will be most useful precisely when the traditional SEDOR is not.

CONCEPT

The pulse sequence for the new version of SEDOR is presented in Fig. 1a. This is the same as the traditional SEDOR (*1, 2*), except that the S spin pulse flip angle θ is varied from 0 to 2π with the pulse spacing τ held constant. The spin echo amplitude M is recorded as a function of θ. Any spin S which is flipped (change in m_s quantum number describing operator S_z) by the RF pulse causes a shift in the frequency of the spin I to which it is coupled. As a result, the echo amplitude M is decreased.

For $\theta = 0$ or 2π, no spins S change their m_s values and the amplitude M has its largest value. For $\theta = \pi$ and $S = \frac{1}{2}$, *every*

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1090-7807/98 $25.00

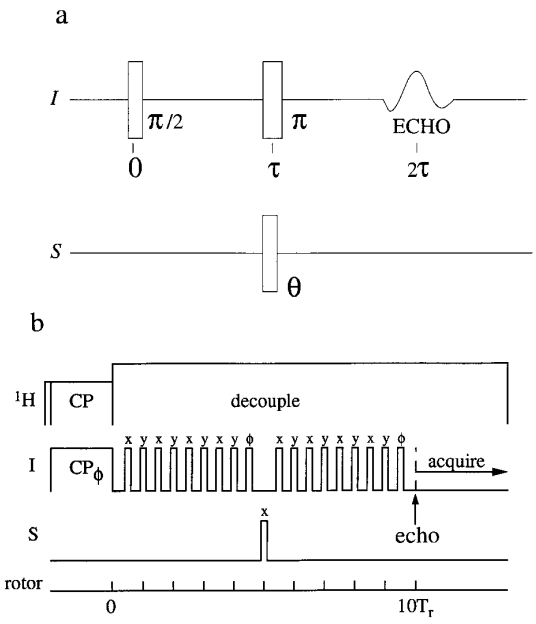

FIG. 1. (a) SEDOR pulse sequence. For the traditional SEDOR, the *I*-spin echo amplitude M is compared with and without a π pulse (i.e., $\theta = \pi$ or 0) on the *S* spins. The resulting ratio $R = M^{\text{with}}/M^{\text{without}}$ is measured as a function of 2τ. In the present version of SEDOR, M is measured as a function of the flip angle θ applied to the *S* spins. In the long τ limit, the interpretation of $M_{(\theta)}$ in terms of the number n of spins *S* coupled to each *I* is particularly simple. (b) REDOR pulse sequence from ref. (*14*), allowing MAS to be used with the version of SEDOR presented in (a). In this sequence, only a single pulse of angle θ is applied to the *S* spins. All of the short pulses applied to *I* are π pulses, with *xy*-8 phase cycling. The rotor period is T_r.

spin *S* is flipped and M will generally attain its smallest value. For intermediate pulses, a crucial conceptual element is that a fraction of the spins S are flipped; which of the spins *S* flip is random.

In greater detail, we assume that the spins *S* are $S = \frac{1}{2}$. Flipping a spin *S* causes the frequency of the neighboring *I* spin to change by $\Delta\omega$, where $\Delta\omega$ depends on *I*–*S* distance, orientation of the *I*–*S* vector relative to the static field, and whether $\Delta m_s = +1$ or -1. The net precessional phase error at 2τ is just $\Delta\omega\tau$. We now assume that, for a given spin *I*, the flip of any spin *S* causes either a negligible phase error (*S* is too distant from *I*) or a large error, $|\Delta\omega\tau| \gg 1$ (the strong collision limit). We assume there are n such spins *S* coupled non-negligibly to each *I*. (This is clearly an idealized situation—if nothing else, the angular factor $3\cos^2\alpha - 1$ in the *I*–*S* dipole interaction is small at certain orientations.) We further assume the n dipole interactions bear no special relation to each other (like equality); generally, the angular factor in the dipole coupling prevents such ''coincidences.'' This last assumption rules out certain geometries such as those in which the *I*–*S* dipole tensors are equal, like a linear S_1–*I*–S_2 arrangement. There, the flip ($\Delta m_s = +1$) of one *S* spin could exactly cancel the effect on *I* of the flop ($\Delta m_s = -1$) of the other *S* spin. In summary, the above assumptions mean that the magnitude of the phase error ϕ is much larger than one whenever one or more of the n spins *S* is flipped or flopped by the RF pulse.

In the strong collision limit (*2*), the spins *I* that suffer mid-pulse sequence frequency changes from one or more nearby *S* will be so strongly dephased ($\phi \gg 1$) that they do not contribute to the echo. Those *I* for which none of the n non-negligibly coupled spins *S* is flipped will contribute to the echo in full. The simple result is that the echo amplitude is proportional to the probability that none of the n spins *S* is flipped. For a single *S* spin $\frac{1}{2}$, an RF pulse of angle θ has probability amplitude $\cos(\theta/2)$ of remaining in its initial m_s state (*2*). Thus, the probability of not being flipped is $p(\theta) = \cos^2(\theta/2) = (1 + \cos\theta)/2$. Because the spins *S* act independently, the probability that the pulse flips *none* of the n spins *S* to which *I* is coupled is just $[p(\theta)]^n = [(1 + \cos\theta)/2]^n$; this expression is also the relative echo amplitude in the long τ/strong collision limit. The data $M_{(\theta)}$ may be compared to $[p(\theta)]^n$ for various n to determine the number of spins *S* near each spin *I*. We note that as n increases, the function $[p(\theta)]^n$ becomes more sharply peaked at $\theta = 0, 2\pi, 4\pi \ldots$ and becomes nearly zero for angles between these values.

RESULTS AND DISCUSSION

SEDOR experiments were performed on amorphous silicon (*9*) powdered samples containing approximately 8 at. % total hydrogen (H + D) by plasma deposition from SiH_4 and D_2 gas. The sample contained approximately 50:50 ^{1}H:^{2}D. Protons were the observed nuclei and deuterons the unobserved nuclei. The stimulated echo pulse sequence was employed, with the RF pulse to the deuterons applied between the second and third proton $\pi/2$ pulses (spacing of 2000 μs). The relatively long spacings between the RF pulses (100–400 μs between the first two $\pi/2$ proton pulses) produced a very strong filtering effect. Only a small fraction of the protons, presumably those most isolated from other protons, contributed to the stimulated echo.

Data from this system are presented in Fig. 2 (upper) for $\tau = 100$ μs. The variation in echo amplitude with the pulse angle θ applied to the deuterons is nearly cosinusoidal, as one might naïvely expect. The damping of the oscillation is a result of the inhomogeneous RF field H_1 acting upon the deuterons. Upon increasing τ to 400 μs, a remarkable sharpening of the echo amplitude variation occurs, as in Fig. 2 (lower). Here the echo amplitude decreases rapidly as θ increases from zero, with a large valley of nearly zero amplitude for angles between (and not too close to) 0 and 2π. Again, H_1 inhomogeneity (^{2}D) causes the echo at $\theta = 2\pi$ to be smaller than at $\theta = 0$. The sharpening of the echo amplitude variation with θ is exactly the behavior predicted above (concept section) for large n in the long τ, strong collision limit. However, the results obtained there are specific to spins $S = \frac{1}{2}$, while deuteron is $S = 1$. For this reason, and because amorphous silicon provides a wide distribution of environments (*10*) for the H and D, we do not quantitatively analyze the ^{1}H–^{2}D SEDOR data of Fig. 2. Nev-

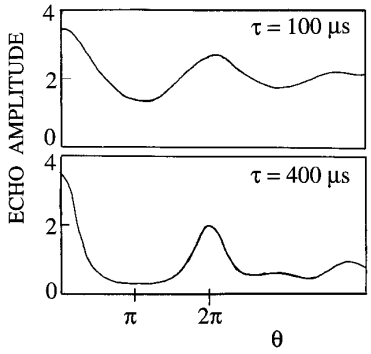

FIG. 2. SEDOR stimulated echo amplitude M in hydrogenated-deuterated amorphous silicon as a function of the deuteron pulse angle θ. For both τ values (spacing between pulses 1 and 2 on the observed proton spins), the deuteron pulse occurs between the second and third proton pulses (spacing of 2000 μs). The nearly consinusoidal variation of M with θ at short τ becomes more sharply peaked at long τ, showing that each proton interacts with more than one deuteron.

ertheless, the pronounced sharpening in Fig. 2 indicates that each proton interacts with more than one deuteron ($n > 1$).

The analysis of the SEDOR experiment with fixed τ and varied flip angle θ is simplest in the long τ limit, as described above. However, large values of τ invite new complications from *S–S* spin flip-flops driven by *S–S* spin interactions, making the simple analysis invalid. One way to suppress *S–S* flip-flops is to use magic-angle spinning (MAS), averaging the *S–S* dipolar interactions to zero (*2*). To reintroduce (''unaverage'') the desired *I–S* interactions, REDOR pulse sequences are used, applying π pulses to *I* and/or *S* synchronously with the sample rotation (*11–13*). We note that MAS conditions offer the further benefits of *I* spin chemical shift selectivity and improved *S/N* by virtue of the smaller bandwidth of the observed spins.

One version (*14*) of REDOR is suitable for the present experiment, since it uses only a single RF pulse applied to the *S* spins. As shown in Fig. 1b, the remainder of the π pulses are applied to the *I* spins with *xy*-8 phase cycling (*15*). Previously, this sequence has been applied with the *S* pulse angle $\theta = \pi$, with the echo amplitude measured as a function of time (i.e., the number of rotor cycles). Here, the number of rotor cycles is held constant and θ is varied.

A sample of (racemic) DL-alanine with 99% ^{15}N enrichment and ^{13}C enrichment of the methyl and carboxyl carbons was obtained from Cambridge Isotope Laboratories. It was diluted to 5% in natural abundance DL-alanine so that intermolecular spin interactions were less important. The REDOR pulse sequence of Fig. 1b was used with a 1s recycle time, 2 ms cross-polarization interval, fixed 22 rotor cycles, and rotor frequency of 1000 Hz. The ^{15}N spins were observed with the ^{13}C spins functioning as the unobserved nuclei and with the protons decoupled. Data are presented from 18,000 averages in Fig. 3a; the agreement of the ^{15}N echo amplitude for ^{13}C pulse angles $\theta = 0$ and 360° shows the excellent H_1 homogeneity with this sample, located in the middle two-thirds of the length of the RF coil. The proton frequency was 151.4 MHz.

The small echo amplitude at $\theta = 180°$ shows that the strong collision limit has been obtained, or nearly so. The curves in Fig. 3a are the function $p^n_{(\theta)} = [(1 + \cos\theta)/2]^n$, for $n = 1$, 2, and 3. As expected for this molecule, the $n = 2$ curve shows the best agreement with the data.

Multiply labeled urea has also been examined. Here ^{13}C is the observed nucleus with the two ^{15}N spins on each molecule serving as unobserved (dephasing) spins. The labeled urea (from Isotec, 99% ^{13}C and ^{15}N) was diluted to 10% in natural abundance urea. A 150 s recycle time, 1 ms cross-polarization, fixed 6 rotor cycles, and 3200 Hz rotation frequency were used. The data of Fig. 3b are the result of 48 scans (each value of θ); more values of θ are presented here than for the alanine measurements. Good agreement is found between the data and a function

$$a[(1 + \cos\theta)/2]^n + b,$$

with $n = 2$ and the baseline b representing the signal from natural abundance molecules (no dephasing from ^{15}N). Measurements at longer times (10 rotor cycles instead of 6) appear very similar, showing that the data of Fig. 3b are already in the strong collision limit for which the simple theory applies.

The echo amplitude M is predicted to vary as $[(1 + \cos\theta)/2]^n$ in the long τ limit. By expansion of the product of the n terms, one obtains the expression

$$M_{(\theta)} = \sum_{m=0}^{n} A_m \cos(m\theta).$$

That is, the highest frequency term in the Fourier series has frequency m equal to n, the number of spins *S* with which each *I* interacts. Hence, the data $M_{(\theta)}$ of Fig. 3b (urea) have been Fourier transformed with respect to θ, after extension of the data to the interval from π to 2π using reflection,

$$M_{(\pi+\theta)} = M_{(\pi-\theta)}.$$

The resulting stick spectrum appears in Fig. 3c. As predicted, nonvanishing amplitudes appear for frequencies 0, 1 and 2, but at higher frequencies only noise appears.

It is easy to show that the absence of frequency components with frequencies greater than n applies generally, not just in the strong collision limit. The behavior of any spin *I* will be determined by which of its n spins *S* was flipped by the RF pulse of angle θ. A spin *I* may be characterized by a n-bit binary number, representing whether each spin *S* was flipped or not. Clearly, there are 2^n such subsets of spins *I*, based on the 2^n possible fates of the n spins *S*. The echo amplitude contribution from each subset depends on two terms: the relative probability of the subset (which

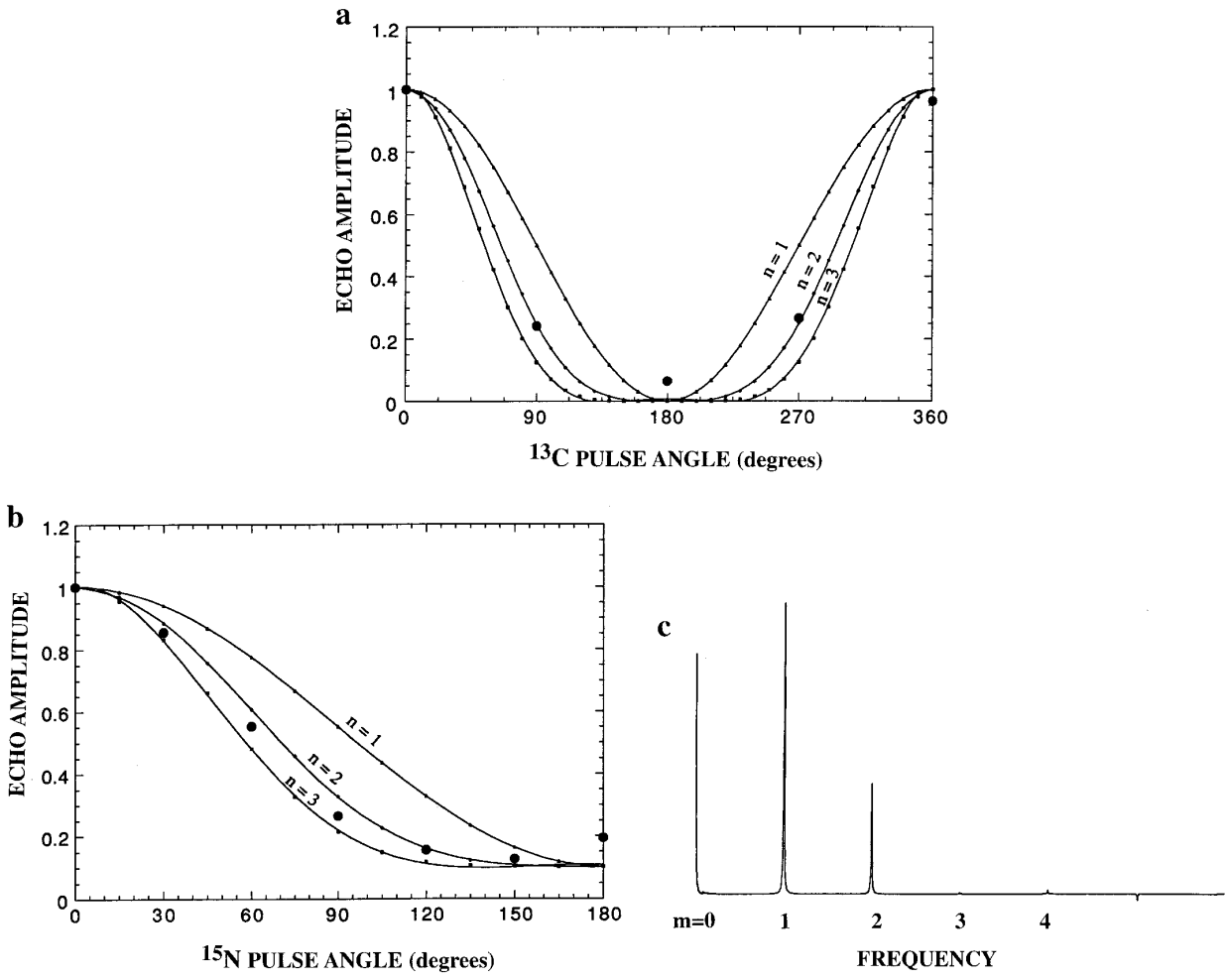

FIG. 3. *I* spin echo amplitude as a function of *S* spin pulse angle θ. (a) For multiply labeled alanine, with one $^{15}N(=I)$ and two $^{13}C(=S)$ on each molecule. The data are in good agreement with the predictions of the strong collision limit theory for $n = 2$. (b) For multiply labeled urea, with one $^{13}C(=I)$ and two $^{15}N(=S)$. The data are well described by a fit to $n = 2$ with a constant baseline representing the natural abundance urea (no dephasing). (c) Stick spectrum resulting from Fourier transform of urea data from (b). Note that the highest frequency stick with nontrivial amplitude is at frequency 2, corresponding to the number of spins *S* coupled to *I*.

depends in turn on the pulse angle θ) and precessional factors involving the dipolar distances and angles and the pulse spacing τ. This last factor is independent of θ for a given subset. Thus, the total echo amplitude, the sum over the subsets, has a dependence on θ at fixed τ which is simply a weighted sum of the relative probabilities of the various subsets (the weights are the above precessional factors). For a subset in which m specific spins S are not flipped and $n - m$ specific spins are flipped by the pulse, the probability is

$$\left(\frac{1 + \cos\theta}{2}\right)^m \left(\frac{1 - \cos\theta}{2}\right)^{n-m}.$$

The highest power term of $\cos\theta$ in the product is $\cos^n\theta$, demonstrating that the highest frequency (i.e., frequency conjugate to θ) in the probabilities and hence in $M(\theta)$ is equal to n. Thus, identification of the number of spins S with the frequency of the highest frequency nonvanishing spectral component is valid in general. However, the spectral amplitudes may differ widely from the strong collision case.

Numerical simulations were performed for the REDOR echo amplitude M, averaging over 4000 angular orientations of the molecule relative to the field. A single spin I was dipolar coupled to two spins S (I_zS_z coupling terms), with a linear S_1–I–S_2 geometry. The I–S distances were varied independently. The REDOR fraction $(M_{(0)} - M_{(\theta)})/M_{(0)}$ is plotted in Fig. 4 for $\theta = \pi/2$ and π. In the strong collision limit, the REDOR fractions are expected to be $\frac{3}{4}$ and 1 for $\theta = \pi/2$ and π, respectively. By definition, the REDOR fraction is 0 at $\theta = 0$. We note that these three values are sufficient to determine the amplitudes of all the frequency components (conjugate to θ; $m = 0$, 1 and 2) for the case at hand, $n = 2$.

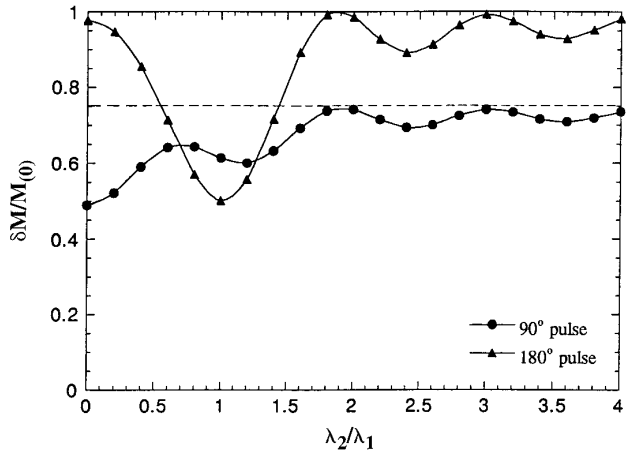

FIG. 4. Numerical simulation results for REDOR fractions $\delta M/M_{(0)}$ for $\theta = \pi/2$ and $\theta = \pi$ pulse applied to the *S* spins. The dimensionless dipole coupling strength is fixed at $\lambda_1 = 2$ while λ_2/λ_1 is varied. For most values of λ_2/λ_1, the REDOR fractions are nearly equal to $\frac{3}{4}$ and 1, the limiting values for $\lambda_1, \lambda_2 \gg 1$. The effect of a weak coupling ($\lambda_2 \sim 0$) is felt at $\lambda_2/\lambda_1 \ll 1$ and the effect of equal dipole tensors is important at $\lambda_2/\lambda_1 = 1$.

The dipolar coupling strengths are represented by the dimensionless parameters λ_1 and λ_2, with

$$\lambda_i = \frac{\gamma_I \gamma_s \hbar \tau}{2\pi R_i^3} .$$

Thus, the long τ limit becomes $\lambda_1, \lambda_2 \gg 1$. The value of λ_1 is fixed at 2 and the ratio λ_2/λ_1 is varied. As presented in Fig. 4, the REDOR fraction nearly attains the limiting values of $\frac{3}{4}$ and 1 for most values of λ_2/λ_1. However, for $\lambda_2 \ll \lambda_1 = 2$, λ_2 is too small to influence the echo amplitude. Thus, the REDOR fraction for $\lambda_2 = 0$ becomes nearly 0.5 and 1.0 for $\theta = \pi/2$ and π, respectively, the values expected for strong interaction with the sole remaining *S* spin. Also for $\lambda_2/\lambda_1 = 1$, an important interference between the two *I–S* interactions occurs. Because the two *I–S* dipole tensors are parallel (linear S_1–*I*–S_2 geometry), for $\lambda_1 = \lambda_2$ the flip of one *S* spin and flop of the other *S* spin will produce zero change in frequency of the *I* spin. Thus, for $\lambda_1 = \lambda_2$ the REDOR fractions deviate strongly from $\frac{3}{4}$ and 1. This shows a limitation of the technique for applications with simple or symmetric geometries (such as linear).

Numerical simulations were also performed for a S_1–*I*–S_2 molecule with nonlinear geometry but equal *I–S* distances, relevant to the case of urea. There the ratio of amplitudes of the $m = 2$ and $m = 1$ Fourier coefficients was examined as a function of the dimensionless (and equal) coupling parameters λ and the S_1–*I*–S_2 angle. The conclusion of those simulations is that the ratio is quite near the expected $\frac{1}{4}$ (from expansion of $(1 + \cos\theta)^2$) except for $\lambda \lesssim 1$ and near molecular angles 0 and π (where the two dipole tensors have the same orientations).

It is interesting to recall that multiple-quantum NMR (*16*) has been used for counting spins in solids (*17, 18*). There, one can use either the more or less Gaussian distribution of coherence amplitude vs quantum order or the fact that *n* spins *I* give rise to a highest order coherence with order *n*. In this way, the present SEDOR and REDOR methods seem similar to the multiple quantum approach. Conceptually, the present method is much simpler, involving only longitudinal changes in the *S* spins (i.e., no precessing coherences). Thus, in the present method the Fourier amplitudes can easily be computed for the long τ limit by expanding $[(1 + \cos\theta)/2]^n$, but the amplitudes of the multiple-quantum coherences appear to depend on the details of the dipolar Hamiltonian.

An interesting similarity appears for the Fourier amplitudes in the present SEDOR experiment and the multiple-quantum technique. The Fourier amplitudes of $[(1 + \cos\theta)/2]^n$ are essentially the binomial coefficients (specifically, the coefficients of $(a + b)^{2n}$, as can be demonstrated by direct comparison for several values of *n*). In the limit of large *n*, these values approach a Gaussian distribution. We note that the statistical approximation (binomial, becoming Gaussian at large *n*) has been used to describe the multiple-quantum Fourier amplitudes, in the long time limit (*16, 17*).

CONCLUSIONS

A new version of the spin echo double resonance (SEDOR) experiment has been described. Instead of measuring the echo amplitude *M* as a function of the pulse-spacing τ, the *S* spin pulse flip angle θ is the important variable. In general, a random fraction of the spins *S* will be flipped by the *S* spin pulse. At long values of τ the strong collision limit applies: if any of an *I*-spin's neighboring *S* spins is flipped by the pulse, its contribution to the echo will be completely dephased. Thus, the echo amplitude will be proportional to the probability that none of the *n* spins *S* coupled to *I* is flipped by the pulse. By fitting the echo amplitude $M_{(\theta)}$ to the simple predictions of the strong collision limit, the number *n* may be determined.

Proton–deuteron SEDOR data from amorphous silicon are presented that confirm the concept of the new version of SEDOR. A magic-angle spinning version, based on a REDOR pulse sequence, has been applied to multiply labeled alanine and urea. The results of both samples agree well with the predictions for $n = 2$. Fourier transformation of *M* with respect to θ yields a stick spectrum. The highest numbered stick with nonvanishing amplitude corresponds to the number *n* of spins *S* coupled to *I*. Comparison of the present technique and multiple quantum spin counting is presented.

ACKNOWLEDGMENTS

The authors thank Ken Sakaie for helpful conversations. The mathematical assistance of W. H. Dickhoff is appreciated. Financial assistance through NSF grant DMR-9705080 (MSC), NSF grant CHE-9796188 (TG and JMJ), and grant DMR-9305344 (REN and TSC) is gratefully acknowledged. The work was partially supported (TG and JMJ) through a grant of the Petroleum

Research Fund, administered by the American Chemical Society. TSC gratefully acknowledges partial support as a Sirovich Fellow.

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