

Efficient Spectral Simulations in NMR of Rotating Solids. The γ -COMPUTE Algorithm

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We explore the time-translational relation between one of the powder angles (γ) and the sample rotation angle ($\omega_r t$) in NMR spectroscopy of rotating solids. Averaging over the γ powder angle is shown to be generally equivalent to a cross correlation of two periodic functions. This leads to a fundamental relation concerning the phases of NMR spectra of rotating solids as well as improved strategies for efficient simulation of experimental spectra. Using these results in combination with the frequency-domain simulation procedure COMPUTE (M. Edén *et al.*, *J. Magn. Reson.* **A 120, 56 (1996)), it proves possible to reduce the computation time for spectral simulations by typically a factor 10–30 relative to the state-of-the-art calculations using the original COMPUTE algorithm. The advantage and the general applicability of the new simulation procedure, referred to as γ -COMPUTE, are demonstrated by simulation of single- and multiple-pulse MAS NMR spectra of ^{31}P - ^{31}P and ^1H - ^1H spin pairs influenced by anisotropic chemical shielding and homonuclear dipolar interactions.** © 1999

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INTRODUCTION

Extraction of detailed information about molecular structure and dynamics from solid-state NMR powder spectra often relies on numerical simulations. To obtain molecular parameters with the highest possible accuracy, the spectral simulations are typically combined with iterative fitting procedures. For spectra of rotating polycrystalline powders this data analysis can be extremely time consuming, not only because the Hamiltonian describing the spin system is time dependent, but also because a spectrum averaged over three powder angles needs to be calculated for each iteration. The ability to conduct reliable computer simulations and iterative fitting within a reasonable period of time therefore highly depends on the development of efficient simulation methods.

The typical procedure for simulating NMR spectra of rotating solids can be divided into two major steps: (i) integration of the equation of motion to obtain propagators for the time evolution and (ii) calculation of the free-induction decay (FID) based on these propagators. For a polycrystalline powder these steps are repeated for each crystallite orientation and the results coadded to obtain the final FID. The two steps are typically

associated with widely different requirements for the computation time as demonstrated in Table 1. In the most common approach, step (i) concerns a time-ordered product of propagators, corresponding to infinitesimal rotations induced by approximately time-independent Hamiltonians. For periodic Hamiltonians this step only involves one period and is often relatively inexpensive with respect to computation time. In its simplest form (henceforth referred to as the direct method), step (ii) may involve formation of thousands of FID points by successive multiplication of propagators from step (i), propagation of the density operator, and evaluation of the signal as the scalar product between the density operator and the hermitian adjoint of the observable. For typical spectral simulations this step may account for up to 99% of the computation time. This observation is of fundamental importance for the design of efficient simulation procedures.

Previous methods to reduce the computational effort associated with γ averaging have included the method of “time translation,” in which step (i) may be performed with significantly increased efficiency using the fact that one of the powder angles (γ) and the sample revolution ($\omega_r t$) both correspond to a rotation about the rotor axis (I). This implies that the propagators formed under step (i) for one γ powder angle may be reused to form the propagators for all other γ angles. In a more advanced approach based on Floquet theory Levante *et al.* (2) and Kubo *et al.* (3) recently demonstrated that the γ averaging may be described analytically, and the latter group showed that in case of ideal pulse excitation this averaging may be conducted implicitly in the Fourier transformation of the free-induction decay. For spectral simulations, which may involve a huge number of matrix multiplications under step (ii), such frequency-domain techniques are often very efficient as also demonstrated recently by Edén *et al.* (4) by the introduction of the COMPUTE (computation over one modulation period using time evolution) algorithm. Exploiting the periodicity of the Hamiltonian and performing the calculations in the frequency domain, the COMPUTE algorithm leads to a substantial reduction (typically a factor of about 5 in our implementation relative to the direct method) in the computation time required for calculation of spectra associated with periodic Hamiltonians.

TABLE 1

Computational Effort Distributed over Initialization, Integration of the Equation of Motion, and Spectrum Generation for Calculation of Typical Magic-Angle Spinning Solid-State NMR Spectra Using a Direct Method, COMPUTE, and γ -COMPUTE (See Text)^a

Method\stage	Initialization ^b	Integration ^c	Spectrum generation ^d
Direct	0.3	0.1	99.6
COMPUTE	21.8	2.4	78.2
γ -COMPUTE	45.8	4.3	50.0

^a As a percentage of the total CPU time. The calculations used the ³¹P-³¹P spin-pair parameters given in the legend to Fig. 2.

^b Typically involves parameter input, tensor transformations, and output of results.

^c Step (i): Solution of the equation of motion by a time-ordered product of propagators.

^d Step (ii): Calculation of the spectrum or FID from the propagators.

In this paper we demonstrate that the symmetry relation between the angle γ and the periodic time dependence of the Hamiltonian for rotating solids can be used directly in the frequency domain, thereby providing new analytical insight and significantly faster simulation procedures. It is shown that the fundamental explanation of Levitt (5), concerning the uniform phase of spinning sidebands in magic-angle-spinning (MAS) powder spectra arising from inhomogeneous interactions (*vide infra*), may be generalized to homogeneous interactions in the sense of Maricq and Waugh (6). This result may be exploited to virtually remove the cost of γ averaging in numerical simulations of NMR spectra for rotating powders. The time-translational symmetry property is most efficiently exploited in the frequency domain by an improved version of the COMPUTE algorithm, dubbed γ -COMPUTE, which performs the γ -averaging by a *cross correlation* (7) of two periodic functions. In typical cases this leads to a reduction by a factor of 10–30 in computation time for the simulations as compared to the state-of-the-art combination of the original COMPUTE algorithm with “ γ averaging by time translation.”

THEORY

Consider the high-field truncated time-dependent Hamiltonian governing a NMR interaction λ

$$H^\lambda(t) = C^\lambda \sum_j (R_{j,0}^\lambda)^L T_{j,0}^\lambda, \quad [1]$$

where C^λ is constant and $T_{j,0}^\lambda$ and $(R_{j,0}^\lambda)^L$ are components of the j -rank tensors describing spin and spatial dependencies, respectively. The spatial tensor in the laboratory frame (L) is related to a rotor-fixed frame (R) and a crystallite-fixed frame (C) through

$$(R_{j,0}^\lambda)^L = \sum_{k,l=-j}^j (R_{j,k}^\lambda)^C \exp\{-ik\alpha_{CR}\} d_{k,l}^{(j)}(\beta_{CR}) \times \exp\{-il(\gamma_{CR} + \omega_r t)\} d_{l,0}^{(j)}(\beta_{RL}), \quad [2]$$

where $d^{(j)}$ is a reduced Wigner matrix of rank j , $\{\alpha_{CR}, \beta_{CR}, \gamma_{CR}\}$ the set of Euler angles connecting C to R , and $\{\alpha_{RL} = \omega_r t, \beta_{RL}, 0\}$ the set of Euler angles relating R to L . ω_r is the angular spinning frequency and β_{RL} the angle between the rotor axis and the static field direction.

Time-Translational Symmetry

From Eq. [2] it is evident that γ_{CR} may equivalently be regarded a translation in time by γ_{CR}/ω_r . This leads to the following relations for the Hamiltonians and propagators for the two angles $\gamma_{CR} = \gamma_0$ and $\gamma_{CR} = 0$

$$H(t; \gamma_0) = H\left(t + \frac{\gamma_0}{\omega_r}; 0\right), \quad [3]$$

$$U(t_2, t_1; \gamma_0) = U\left(t_2 + \frac{\gamma_0}{\omega_r}, t_1 + \frac{\gamma_0}{\omega_r}; 0\right), \quad [4]$$

where the propagator U is evaluated from time t_1 to t_2 . Equations [3] and [4] can be recast in a discrete form to additionally include the case of general periodic RF irradiation, rotor synchronized with n periods in one rotor period $\tau_r = 2\pi/\omega_r$. For $\gamma_{CR} = p(2\pi/n)$ the relations are

$$H\left(t; p \frac{2\pi}{n}\right) = H(t + p\tau; 0), \quad [5]$$

$$U\left(j\tau, (j-1)\tau; p \frac{2\pi}{n}\right) = S_j^p = S_{(p+j-1 \bmod n)+1}^0, \quad [6]$$

with $\tau = \tau_r/n$ and S_j^p being the propagator for the j th period ($j = 1, 2, \dots, n$) of the general timing scheme in Fig. 1 corresponding to the γ_{CR} angle $p(2\pi/n)$. It is noted that we use a notation similar to that used by Edén *et al.* (4) to facilitate a direct comparison between COMPUTE and the new algorithm γ -COMPUTE.

It is evident that Eq. [6] may be used directly in numerical simulations to generate all propagators S_j^p from the set of propagators S_j^0 corresponding to $\gamma_{CR} = 0$. Hence, the explicit integration of the equation of motion need only be performed for $p = 0$ and a factor close to n can be saved in step (i) of the simulation. This corresponds to “ γ -averaging by time translation” (1). However, physical insight and much higher benefit in terms of saved computation time may be gained by considering the consequences of the time-translational symmetry in the frequency domain.

γ -COMPUTE: γ -Angle Averaging as a Cross Correlation

Consider the timing of a rotor period $\tau_r = n\tau$, as sketched in Fig. 1, accommodating n blocks of identical, arbitrary pulse sequence elements (obviously including the important case of no RF irradiation) of duration τ . For the crystallite angle $\gamma_{CR} = p(2\pi/n)$, the accumulated propagators A_j^p are recursively defined as

$$A_j^p = \begin{cases} S_j^p A_{j-1}^p, & \text{for } j > 0 \\ 1, & \text{for } j = 0 \end{cases} \quad [7]$$

Using the time-translational property in Eq. [6], A_j^p may be related to the propagator A_j^0 corresponding to $\gamma_{CR} = 0$ by

$$A_j^p = A_{j+p \bmod n}^0 (A_n^0)^m (A_p^0 \bmod n)^{\dagger} \quad [8]$$

with

$$m = \text{int}\left(\frac{j+p}{n}\right) - \text{int}\left(\frac{p}{n}\right) \quad [9]$$

where $\text{int}(a/b)$ denotes the integer part of the fraction a/b .

For a N -level spin system, the propagator A_n^p accumulated over the rotor period τ_r is represented by a unitary $N \times N$ matrix. For $p = 0$, this matrix may be unitarily diagonalized according to

$$A_n^0 = X \exp\{-iD\tau_r\} X^{\dagger}, \quad [10]$$

where D is a real, diagonal matrix. A_n^0 has N complex eigenvalues λ_r ($r = 1, 2, \dots, N$). Using the complex logarithm function, the real transition frequencies can be calculated as

$$\bar{\omega}_{rs} = D_{rr} - D_{ss} = \frac{\ln \lambda_r - \ln \lambda_s}{-i\tau_r}. \quad [11]$$

Likewise, for $\gamma_{CR} = p(2\pi/n)$ with $0 < p < n$ the propagator $A_n^p = A_p^0 A_n^0 (A_p^0)^{\dagger}$ over a full modulation period τ_r may be diagonalized according to

$$A_n^p = X_p \exp\{-iD\tau_r\} X_p^{\dagger}, \quad X_p = A_p^0 X. \quad [12]$$

Clearly, for all of the n different γ_{CR} angles the propagators over a full modulation period have the same eigenvalues and therefore identical transition frequencies (line positions). This fundamental property suggests that a simple relation exists between single-crystal spectra differing only in γ_{CR} and motivates a search for improved spectral simulation procedures.

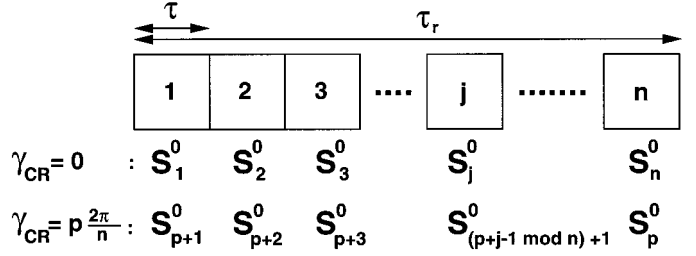


FIG. 1. Schematic illustration of the periodic time-translational symmetry between γ_{CR} and $\omega_r t$. For $\gamma_{CR} = p(2\pi/N)$ the propagator for the j th period S_j^p is related to the propagator S_k^0 for $\gamma_{CR} = 0$. Each propagator may represent a period of free precession (delay) or a pulse sequence element.

For $\gamma_{CR} = p(2\pi/n)$, the NMR signal at the j th point is given by

$${}^p s(j\tau) = \text{Tr}[A_j^p \rho_0 (A_j^p)^{\dagger} Q], \quad [13]$$

where the matrices ρ_0 and Q represent the initial density and observable operator, respectively. By use of Eq. [8] in combination with the invariance of the trace to similarity transformations, Eq. [13] may be rewritten

$${}^p s(j\tau) = \text{Tr}[\exp\{-im\tau_r D\} {}^p \rho_0^{\text{mod } n} \exp\{im\tau_r D\} {}^p Q_j^T] \quad [14]$$

with m defined in Eq. [9] and using the definitions

$${}^p \rho_0^T = X^{\dagger} (A_p^0)^{\dagger} \rho_0 A_p^0 X, \quad [15]$$

$${}^p Q_j^T = X^{\dagger} (A_{p+j \bmod n}^0)^{\dagger} Q A_{p+j \bmod n}^0 X = {}^0 Q_{p+j \bmod n}^T. \quad [16]$$

Equation [14] may conveniently be recast in the form

$${}^p s(j\tau) = \sum_{r,s=1}^N {}^p f_{rs}^{(j)} \exp\{i\bar{\omega}_{rs} j\tau\}, \quad [17]$$

with ${}^p f_{rs}^{(j)}$ defined as

$${}^p f_{rs}^{(j)} = \exp\{i\bar{\omega}_{rs} m\tau_r\} [{}^p \rho_0^{\text{mod } n}]_{sr} [{}^0 Q_{j+p \bmod n}^T]_{rs} \exp\{-i\bar{\omega}_{rs} j\tau\}. \quad [18]$$

We note that only Q matrices for $p = 0$ are needed to obtain ${}^p f^{(j)}$ for all n different γ_{CR} angles and that ${}^p f^{(j)}$ is periodic in p and j with period n . Furthermore, since only the amplitudes (and not the positions) of the lines depend on the γ_{CR} -angle index p , the signal can be averaged over the n different γ_{CR} angles by averaging the $f^{(j)}$ matrices leading to

$$\bar{s}(j\tau) = \sum_{r,s=1}^N \bar{f}_{rs}^{(j)} \exp\{i\bar{\omega}_{rs} j\tau\}, \quad [19]$$

with

$$\begin{aligned}\bar{f}_{rs}^{(j)} &= n^{-1} \sum_{p=0}^{n-1} p f_{rs}^{(j)} \\ &= n^{-1} \sum_{p=0}^{n-1} [p \bmod n \rho_0^T]_{sr} \exp\left\{i \left[p - \text{int}\left(\frac{p}{n}\right)n \right] \bar{\omega}_{rs} \tau\right\} \\ &\quad \times [{}^0 Q_{j+p \bmod n}^T]_{rs} \exp\left\{-i \left[j + p - \text{int}\left(\frac{j+p}{n}\right)n \right] \bar{\omega}_{rs} \tau\right\},\end{aligned}\quad [20]$$

being identified as a discrete cross correlation of two periodic functions (7).

By introducing the Fourier transform relations

$$\mathcal{F}\{\bar{f}_{rs}^{(j)}\}(\omega) = \sum_k \bar{a}_{rs}^{(k)} \delta(\omega - k\omega_r), \quad [21]$$

$$\bar{a}_{rs}^{(k)} = n^{-1} \sum_{j=0}^{n-1} \bar{f}_{rs}^{(j)} \exp\{-i2\pi jk/n\}, \quad [22]$$

where $k = -n/2 + 1, \dots, n/2$ (n even) or $k = -(n-1)/2, \dots, (n-1)/2$ (n odd), and δ is a standard delta function ($\delta(x) = 1$ for $x = 0$ and otherwise zero), the γ_{CR} -averaged spectrum may be expressed as

$$\begin{aligned}\mathcal{F}\{\bar{s}(j\tau)\}(\omega) &= \sum_{r,s=1}^N \mathcal{F}\{\bar{f}_{rs}^{(j)}\}(\omega) \otimes \delta(\omega - \bar{\omega}_{rs}), \\ &= \sum_{r,s=1}^N \sum_k \bar{a}_{rs}^{(k)} \delta(\omega - \omega_{rs}^{(k)}),\end{aligned}\quad [23]$$

with

$$\omega_{rs}^{(k)} = \bar{\omega}_{rs} + k\omega_r. \quad [24]$$

Equations [23] and [24] show that the frequency-domain spectrum consists of n spinning sidebands of complex amplitude $\bar{a}_{rs}^{(k)}$ separated by ω_r . Using the Fourier transform properties of the cross correlation of periodic functions (7), the sideband amplitudes can be expressed as

$$\bar{a}_{rs}^{(k)} = (r_{sr}^{(k)})^* q_{rs}^{(k)}, \quad [25]$$

where

$$r_{sr}^{(k)} = n^{-1} \sum_{j=0}^{n-1} ([j\rho_0^T]_{sr})^* \exp\{-i\bar{\omega}_{rs} j\tau\} \exp\{-i2\pi jk/n\} \quad [26]$$

$$q_{rs}^{(k)} = n^{-1} \sum_{j=0}^{n-1} ([{}^0 Q_j^T]_{rs}) \exp\{-i\bar{\omega}_{rs} j\tau\} \exp\{-i2\pi jk/n\}. \quad [27]$$

Equation [25] represents a generalization of expressions valid for inhomogeneous (6) interactions given earlier by Levitt (5) and in a more general form by Skibsted *et al.* (8) taking nonideal RF excitation into account.

The general formulas in Eqs. [25]–[27] have several important implications for numerical simulations. First, they enable efficient γ_{CR} averaging for simulation of all NMR spectra of rotating solids independently on the spin system and interactions. Second, they exploit all the attractive features of COMPUTE (4) while performing the γ_{CR} averaging as an implicit part of the Fourier transformation. For this reason the new method may be referred to as γ -COMPUTE. Third, they allow straightforward exploitation of additional constraints on the initial and observable operators. The latter aspect is addressed in the following section.

Ideal Excitation

In phase-sensitive NMR the initial density operator is often related to the observable operator according to

$$\rho_0 = \frac{1}{2} (Q + Q^\dagger). \quad [28]$$

This is the case when the pseudo observable Q takes the form $Q = I_\alpha + iI_\beta$, where I_α and I_β are operators corresponding to observation along two orthogonal axes (typically, $\alpha = x$ and $\beta = y$) and the initial density operator is along the real axis ($\rho_0 = I_\alpha$). A typical example would be $\rho_0 = I_x$ after ideal preparation and $Q = I^+$ being the pseudo observable corresponding to quadrature detection. According to Eqs. [15] and [16] this relation implies that

$${}^p \rho_0^T = \frac{1}{2} ({}^0 Q_p^T + ({}^0 Q_p^T)^\dagger) \quad [29]$$

and that the sideband amplitudes can be written

$$\bar{a}_{rs}^{(k)} = \frac{1}{2} (|q_{rs}^{(k)}|^2 + q_{sr}^{(-k)} q_{rs}^{(k)}). \quad [30]$$

This expression shows that the sideband amplitudes of any ideally excited NMR spectrum of a rotating solid consist of a real and a complex contribution, of which the latter is symmetric with respect to the RF carrier frequency ($q_{rs}^{(-k)}$ and $q_{sr}^{(k)}$ correspond to mirror frequencies). Furthermore, we note that Eq. [30] only requires Fourier transformation of the Q^T matrices in Eq. [27]. As a digression, we mention that for non-phase-sensitive detection, the symmetry $\rho_0 = Q$ leads to the corresponding relations

$$\bar{a}_{rs}^{(k)} = |q_{sr}^{(k)}|^2 = |q_{rs}^{(-k)}|^2 = q_{sr}^{(-k)} q_{rs}^{(k)} \quad [31]$$

derived using the fact that the density operator is always hermitian (9) and so are the ${}^j\rho_0^T$ matrices. Equation [31] shows that the symmetry $\bar{a}_{rs}^{(k)} = \bar{a}_{sr}^{(-k)*}$ inherent to a pure real signal is restricted further by the γ_{CR} averaging.

In the special case of an *inhomogeneous* interaction (6), the matrices A_j and X are diagonal (the latter being the unity matrix) and the sparsity of the Q_j^T matrices is identical to that of the observable Q . This implies that only the last term in Eq. [29] and consequently the first term in Eq. [30] contributes to the spectrum. This conforms well with the finding of Levitt (5) who analyzed MAS spectra influenced by anisotropic chemical shielding and found that the amplitude of each spinning sideband upon γ_{CR} averaging is given by the sum of the square modulus of the complex sideband amplitude corresponding to the individual γ_{CR} angles. The general applicability of Eq. [30] opens the possibility to treat evolution under *homogeneous* interactions in the same manner. It turns out that the sparsity of the Q_j^T matrices also in this case prevents contributions from the last term in Eq. [30]. This can be proven using the fact that the Q_j^T matrices have the same rotational symmetry with respect to the z axis as Q when the propagators A_j correspond to free precession. Decomposition of the Q matrix into components which constitute irreducible representations of the one-dimensional rotation group will therefore reveal the sparsity of the Q_j^T matrices. Typically $Q = I^+$ which means that only first-rank components of the Q_j^T matrices will be nonzero. Besides proving that any single-pulse MAS NMR spectrum has spinning sidebands of uniform phase (within the high-field approximation), this fact can be used to preselect relevant transitions for optimum simulation efficiency. For homonuclear spin pairs, for example, only 4 entries out of 16 need to be Fourier transformed. Accordingly, γ_{CR} averaging may be performed with the same efficiency as for the inhomogeneous case. In comparison earlier approaches to γ_{CR} averaging in such cases (1) are rather complicated and inefficient (*vide infra*).

Turning to the special case where the n sequence elements within the rotor period (cf. Fig. 1) involves identical RF irradiation, the last term in Eq. [30] cannot be neglected. For example, this is the case for MAS nutation (10–12) and CRAMPS (15, 16) spectra which may have imaginary contributions arising from the second term in Eq. [30].

EFFICIENT NUMERICAL SIMULATION

The results obtained in the previous sections can be used to significantly enhance the efficiency of numerical simulations. At the same time the procedure for spectral simulation is simplified. Instead of averaging the spectrum over all three Euler angles, the γ_{CR} averaging is conducted implicitly in the generation of the spectrum. Calculating the Q^T (and ρ^T matri-

TABLE 2
Relative Operation Count for Different Steps in the COMPUTE and γ -COMPUTE Algorithms^a

Step\method	COMPUTE ^b	γ -COMPUTE ^b
Q_j^T	$n^2 4N^3$	$n4N^3$
$f_{rs}^{(j)}$	$n^2 2N^2$	0
$\mathcal{F}(f^{(j)})$ or $\mathcal{F}(Q)^{c,d}$	$\sigma n^2 \log_2(n) N^2 / \sigma n^3 N^2$	$2\sigma n \log_2(n) N^2 / 2\sigma n^2 N^2$
ρ^T or ${}^p\rho^T$	$n4N^3$	0

^a Operation counts correspond to averaging over n γ_{CR} angles and using the symmetry of ideal excitation ($\rho = \frac{1}{2}(Q + Q^T)$) in the γ -COMPUTE algorithm.

^b σ expresses the sparsity of the $\tilde{f}^{(j)}$ matrices, as can be exploited through preselection based on its rotational symmetry, and is given as the number of nonzero entries divided by N^2 .

^c $\mathcal{F}(Q)$ signifies the Fourier transformation given in Eq. [25].

^d The operation counts are given for the FFT/nonfast FT case.

ces in the case of nonideal excitation) according to Eqs. [15] and [16] leads, via the Fourier transformations being an intrinsic part of Eq. [30] for ideal excitation or Eq. [25] in the more general case, to the γ -averaged amplitudes $\bar{a}_{rs}^{(k)}$. By running through the detectable transitions $r, s = 1, \dots, N$, and $k = -n/2 + 1, \dots, n/2$ (n even) or $k = -(n-1)/2, \dots, (n-1)/2$ (n odd) and storing the amplitude $\bar{a}_{rs}^{(k)}$ at the position $\omega_{rs}^{(k)}$ in the spectrum, the γ_{CR} -averaged spectrum for a single (α_{CR}, β_{CR}) crystallite-angle pair is obtained. Averaging over these two powder angles results in the spectrum in the form of a histogram. To obtain proper lineshapes, the full powder averaged spectrum is Fourier transformed to the time domain, apodized, and finally Fourier transformed back to the frequency domain.

γ -COMPUTE versus COMPUTE

The γ -COMPUTE algorithm possesses several advantages relative to the original COMPUTE algorithm with explicit γ_{CR} averaging. In γ -COMPUTE (i) the accumulated propagator over a full modulation period, A_n , needs to be diagonalized and the transition frequencies calculated only for $\gamma_{CR} = 0$, (ii) the ${}^jQ^T$ matrices need only be calculated once, and (iii) the Fourier transform to obtain the sideband amplitudes $\bar{a}^{(k)}$ is performed for all n γ_{CR} angles at the same time. To give a more detailed picture of these advantages, Table 2 gives the relative operation count or number of complex multiplications for the most demanding steps of the two algorithms. The two most demanding steps in COMPUTE are the formation of the ${}^jQ^T$ matrices and the Fourier transformation of the N^2 data sets $f_{rs}^{(j)}$, which both must be performed for each of the n γ_{CR} angles. Both of these steps are significantly reduced using γ -COMPUTE, in which Fourier transformation is conducted only twice (Eq. [25]) or once (Eq. [30]), reducing this effort by a factor n relative to COMPUTE as specified in Table 2. Thus, the overall saving factor is approximately equal to the number of γ_{CR} angles, which is typically in the range of 10–50.

RESULTS AND DISCUSSION

In general, spectral analysis of MAS spectra influenced by homonuclear dipolar coupling as well as anisotropic chemical shielding represents a challenge to numerical simulation procedures. The extraction of parameters for the various interactions responsible for the complex spectral features associated with such homogeneously (6) evolving systems typically requires combination with iterative fitting procedures calling for a large number of simulated spectra. Time-consuming spectral analysis of this kind represents a typical application for which γ -COMPUTE may lead to very large absolute time savings relative to current methods. As an example, Fig. 2a shows a simulated zero-order rotational resonance spectrum for a ^{31}P - ^{31}P spin pair in a transition-metal phosphine complex (13). The spectrum was averaged over 256 α_{CR} , β_{CR} crystallite orientations distributed according to the REPULSION scheme (14) and the equivalent of 16 γ_{CR} angles, corresponding to a total number of 4096 crystallites. Simulations based on Fortran-77 implementations of the direct method as well as the COMPUTE and γ -COMPUTE algorithms on a Digital Alpha 100 4/200 work station and using the same input parameters resulted in identical spectra but required computation times of 40.9, 6.6, and 1.2 CPU s, respectively. The calculations were performed under the assumption of ideal excitation, i.e., $\rho_0 = I_x$ and $Q = I^+$, which allowed the use of Eq. [30] for γ -COMPUTE and preselection of the four relevant (r , s) transitions using the rotational properties of the Q_j^T matrices for COMPUTE as well as γ -COMPUTE.

The total computation time for simulation of ^{31}P - ^{31}P spin-pair spectra (Fig. 2a) using the three different methods is shown graphically in Fig. 2b as a function of the number n of γ_{CR} angles and rotor divisions. It is evident that the computation time for the direct method using a large number of FID points (1024 in the present case) is linear in n . This is ascribed to the fact that the vast number of matrix multiplications associated with generation of the FID in this method is repeated n times upon γ_{CR} averaging. We note that the computation time for this method is also linear in the number of FID points. Figures 2b and 2c indicate that the total computation time for the COMPUTE algorithm is proportional to n^2 for n being an integer power of 2, in which case fast Fourier transformation (FFT) (17) may be used, or n^3 for all other values of n .¹ For γ -COMPUTE this dependence is somewhat changed because the cost of the Fourier transformation is reduced relative to other stages in the algorithm. Finally, it is seen from Figs. 2b and 2c that for the γ -COMPUTE algorithm, the CPU time is close to linear in n .

¹ Efficient Fourier transform routines specialized for certain (small) values of the number of points n , which are noninteger powers of 2, exist, e.g., those devised by Winograd (18). Because of the lack of generality, we found the implementation of such routines impractical, and we focus instead mainly on comparing the performance of γ -COMPUTE to that of COMPUTE for Fourier numbers.

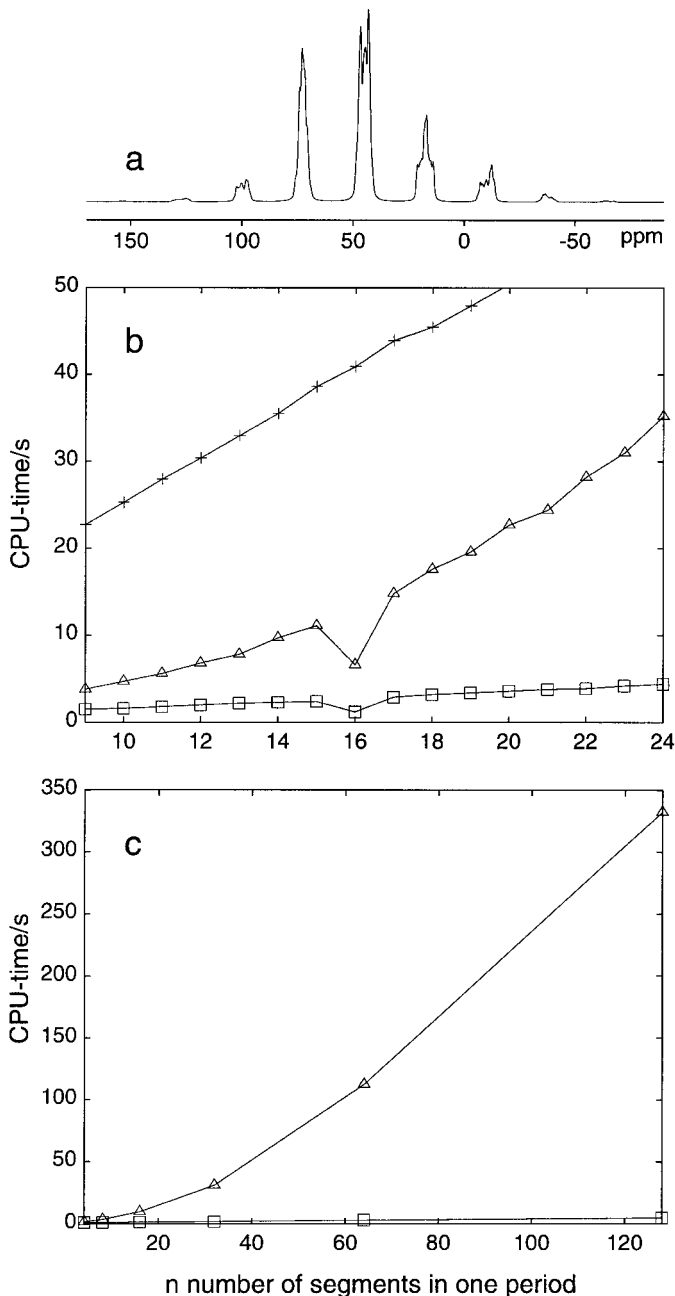


FIG. 2. (a) Simulation of a ^{31}P MAS NMR spectrum of $\text{NiP}_2\text{C}_{32}\text{H}_{36}\text{O}_2$ corresponding to a static field of 7.1 T and a spinning frequency of $\omega_r/2\pi = 1111$ Hz. The simulation used the ^{31}P - ^{31}P spin-pair tensor parameters given in Ref. (13), $n = 16$ γ_{CR} angles and rotor divisions, and 256 pairs of (α_{CR} , β_{CR}) crystallite angles. The simulation required only 1.2 CPU s using the γ -COMPUTE algorithm while 9.7 and 47.3 CPU s were required for COMPUTE and the direct method, respectively. (b) The total number of CPU seconds used for calculating the spectrum in (a) as a function of the number n for the direct method (crosses), COMPUTE (triangles), and γ -COMPUTE (squares). (c) The same as in (b) but using only Fourier numbers.

It is apparent from Fig. 2 that the advantage of using γ -COMPUTE becomes particularly pronounced for spectra with many spinning sidebands (i.e., for large values of n). This

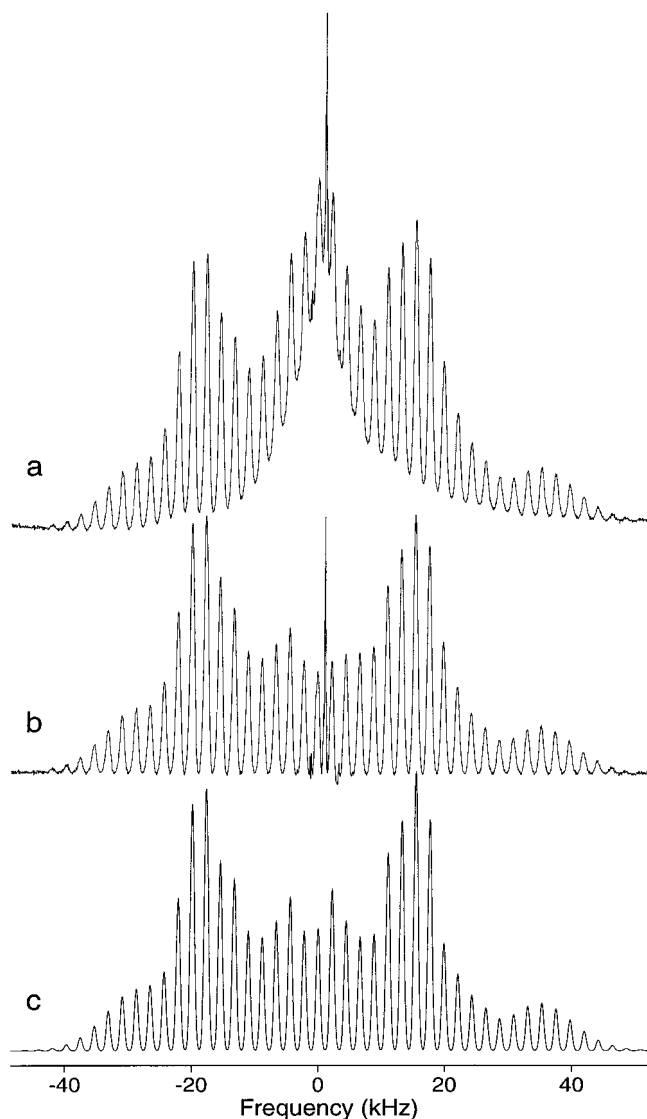


FIG. 3. (a) Experimental ^1H single-pulse MAS spectrum (9.4 T) of $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ recorded using $\omega_r/2\pi = 2300$ Hz. The spinning sidebands are superimposed on a broad hump. (b) The same spectrum as in (a) but using a simple baseline correction to remove the broad hump (ascribed to dynamics (19)). (c) Simulation using γ -COMPUTE with $n = 44$, which required 5.0 s of CPU time. The large n value leads to correspondingly large computation times of 696.8 and 208.1 CPU s for COMPUTE and the direct method, respectively.

aspect becomes evident in Fig. 3 from simulation of the experimental single-pulse ^1H MAS spectrum (Fig. 3a) of the ^1H - ^1H spin pair in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ recorded at 9.4 T using a sample spinning frequency of 2300 Hz. Recently, Tekely *et al.* (19) analyzed similar spectra and determined the chemical shielding anisotropy to be $\sigma^{\text{aniso}} = 10.5 \pm 0.5$ ppm for both protons and a dipolar coupling constant to be $b_{IS}/2\pi = 43,750$ Hz. In order to facilitate comparison between experimental and simulated spectra, Fig. 3b shows the same spectrum

as in Fig. 3a but using baseline correction to remove the broad hump (also observed by Tekely *et al.* (19) and ascribed to dynamics) on which the sidebands are superimposed. The best agreement between simulated and experimental spectra is obtained using the chemical shielding anisotropy and dipolar coupling parameters from Ref. (19) along with the optimum fitted Euler angles $\alpha_{PC} = 0$, $\beta_{PC} = 18.5^\circ$, $\gamma_{PC} = 0$, leading to the spectrum in Fig. 3c. We note that the spectrum is quite insensitive to the asymmetry parameter which has been set to $\eta = 1.0$ for the simulation in Fig. 3c. For this specific example, the computation time for calculations using the γ -COMPUTE, COMPUTE, and direct method is 2.6, 76.0, and 165.3 s, respectively. This corresponds to a gain in efficiency of almost a factor 30 for γ -COMPUTE relative to COMPUTE and a factor of 64 relative to the direct method.

To demonstrate the capability of γ -COMPUTE to cover cases with identical RF irradiation between the n sampling points, Fig. 4 shows a series of simulated ^1H MSHOT-3 CRAMPS (20–22) spectra. We have recently demonstrated that ^1H shielding anisotropies can be extracted from the spinning sidebands of MSHOT-3 CRAMPS spectra by iterative fitting using simple single-spin simulations with scaled shielding parameters (22). However, to search the limits of such approximations, it is important to be able to perform simulations with the RF irradiation taken into account. An investigation of the stability of this method for obtaining ^1H chemical shielding anisotropies toward strong homonuclear dipolar couplings is given in Fig. 4. Specifically, Figs. 4a–4f show MSHOT-3 CRAMPS spectra for a ^1H - ^1H spin-pair system (only one resonance shown) with the homonuclear dipolar coupling set to 0, 5, 10, 15, 20, and 25 kHz. The calculations used a RF field strength of 300 kHz corresponding to the best commercially available equipment. It is seen that only minor variations in the spinning sideband amplitudes are induced by dipolar couplings below 20 kHz. For larger homonuclear couplings, the accuracy of the method may be influenced by residual dipolar terms and care should be taken in the data analysis. The computation time required for calculating one of the spectra in Fig. 4 using γ -COMPUTE, COMPUTE, and direct method is 38.9, 63.4, and 71.7 s respectively. The relatively low gain values (compared to the earlier examples) indicate that step (i) in this case takes up a large fraction of the total computational effort because of the complicated multiple-pulse RF irradiation. Despite this observation, it is evident that even in cases with relatively few sampling points per rotor period (with or without RF irradiation) it is still advantageous to use γ -COMPUTE in comparison to COMPUTE.

CONCLUSION

In conclusion, we have analyzed the time-translational relationship between the γ_{CR} powder angle and the periodic time modulation $\omega_r t$ induced by macroscopic sample rotation relevant for solid-state NMR of rotating powders. It has been

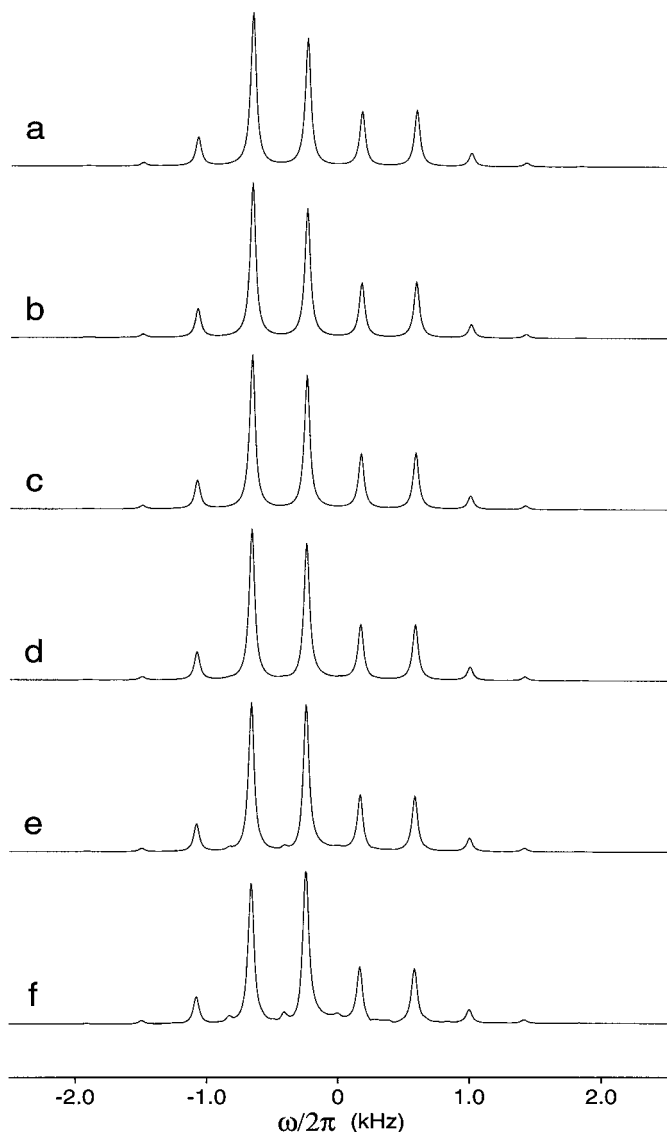


FIG. 4. Simulated ^1H CRAMPS spectra for a ^1H - ^1H spin pair (only one resonance shown) characterized by the interaction parameters $-\omega_0\sigma_A^{\text{iso}}/2\pi = 1$ kHz, $-\omega_0\sigma_A^{\text{iso}}/2\pi = 5$ kHz, $\eta_A = 0$, $-\omega_0\sigma_B^{\text{iso}}/2\pi = -1$ kHz, $-\omega_0\sigma_B^{\text{iso}}/2\pi = 0$ kHz, $\eta_B = 0$, and $b_{\text{IS}}/2\pi = 0$ (a), 5 (b), 10 (c), 15 (d), 20 (e), and 25 (f) kHz. The calculations were performed with two MSHOT-3 blocks between each sampling point using $n = 25 \gamma_{\text{CR}}$ and 25 sampling points per rotor period (corresponding to 593 Hz spinning). The RF field strength was 300 kHz, leading to a cycle time of 33.75 μs for the MSHOT-3 sequence.

shown that γ_{CR} averaging may always be expressed as a simple cross correlation of two periodic functions. This finding gives new insight concerning the relative phases of spinning sidebands for powder spectra induced by inhomogeneous as well as homogeneous interactions and essentially eliminates the need for γ_{CR} powder averaging in numerical simulations of solid-state NMR spectra. When combined with COMPUTE-type calculations in the frequency domain, γ_{CR} averaging by

cross correlation may speed up simulation of solid-state NMR spectra by a factor of 10–30 relative to state-of-the-art calculations using COMPUTE. In addition the so-called γ -COMPUTE method is conceptionally easier to incorporate into numerical simulation software. Due to its high efficiency we anticipate that γ -COMPUTE will find immediate application as a tool in numerical simulation and iterative fitting of solid-state NMR spectra.

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