

Cross-singular dips in the NMR absorption line of polycrystals with isolated spin pairs

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Cross-singular dips at the center of the spectra of polycrystals of Pake systems, i.e., systems containing well-isolated pair groupings, are obtained by numerical calculations of the NMR absorption line for a 10-spin ($I=1/2$) model. The physical reason for such dips is the behavior of the flip-flop component of the interpair dipole–dipole interactions (“6/5 factor”). Cases of experimental manifestation of cross-singular dips are noted. © 1998 American Institute of Physics. [S0021-3640(98)01713-7]

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Cross-singular dips are the most intriguing of the so-called cross-singular effects observed under certain conditions in well-resolved NMR spectra of polycrystalline samples.^{1,2} These dips are due to the presence of a singularity in the distribution of frequencies corresponding to crossing spectral lines of individual crystallites over the spectrum of a polycrystal.

Thus far only cross-singular dips in the ¹⁹F NMR spectra of octahedral molecules and ions with quite high anisotropy of the chemical shift of the fluorine nuclei have been studied conclusively both theoretically and experimentally.^{3–5} Recently, cross-singular dips have been observed experimentally in the spectra of fluorine systems of a more general type, specifically, systems that do not contain isolated groupings.⁶ Unfortunately, there are still no experimental data on cross-singular dips predicted theoretically for isolated two-spin systems with an anisotropic chemical shift of the resonating nuclei.^{7,8}

The existence of a similar cross-singular dip can be easily verified by an analytical calculation of the NMR line shape for a polycrystal containing isolated pairs of quadrupolar nuclei with $I=1$. As in the case of nuclei with an anisotropic chemical shift, the flip-flop component of the dipole–dipole interaction between the spins is responsible for the dip. The difference lies only in the fact that instead of the “9/4 factor,” describing the increase in the second moment of the crossing spectral components, in the second case a “6/5 factor” appears.⁹ For this reason, it is quite obvious that there is a possibility of observing cross-singular dips in polycrystalline spectra of quadrupolar nuclei, despite the absence of experimental data (with the apparent exception of the ²D NMR spectrum of polytetramethylene oxide¹⁰).

It is much more difficult to substantiate the cross-singular nature of the dips that are

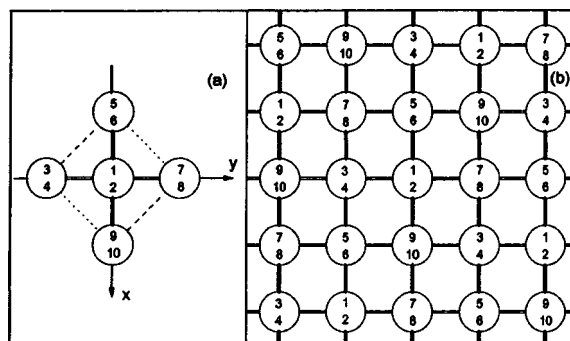


FIG. 1. Model of a 10-spin grouping (a) used for the calculations, including a variant with "quasicyclic" boundary conditions (b).

sometimes recorded in purely dipole–dipole systems. For example, for several years now it has been impossible to arrive at a consensus concerning the origin of the unusual dip positively recorded in the ^1H NMR spectrum of dellaitite ($\text{Ca}_6(\text{OH})_2(\text{Si}_2\text{O}_7)$), which contains well-isolated proton pairs.^{1,2} The main reason is that in contrast to the cases considered above, where the fine structure of the spectrum of a polycrystal can be described by chemical shifts or quadrupole effects, while the dipole–dipole interaction between spins of an isolated pair participates in the formation of the cross-singular dip, in the purely dipole–dipole case¹¹ with a Pake structure of the spectrum¹² one must deal with interpair dipole–dipole interactions, encompassing all the surrounding spins and taken into account in the Gaussian broadening model, which, as is well known, cannot give any anomalies.¹³ Another important circumstance is that the "6/5 factor," long drawing attention in connection with Pake systems,^{14–16} has still not been convincingly demonstrated experimentally even for H_2O molecules undergoing 180° flipping (proton exchange),¹⁷ where the analogy with quadrupolar ($I=1$) nuclei is most obvious. Unfortunately, our attempt¹⁸ to obtain a cross-singular dip on the basis of the four-spin ($I=1/2$) model, which is conventionally employed to analyze the interpair dipole–dipole interaction, was also unconvincing.

Nonetheless, active searches for alternative reasons explaining the anomaly under discussion have inevitably returned to the cross-singular mechanism as the only possible one. For this reason, we decided to perform numerical calculations of the NMR line shape using a sufficiently large number of spins so that it was possible to form quasicontinuous components of the Pake doublet. Using the standard procedure of Ref. 19 and the computer resources available to us, we decided on a 10-spin system. The present work is essentially a computer simulation with five identical, rigid (i.e., no 180° flipping) spin pairs. Despite the fact that such a system has no direct relation to any particular compound, it does make it possible to obtain a general idea about the character of the collective manifestation of interpair dipole–dipole interactions in Pake objects.

The first results justified our expectations. They were obtained for an equidistant arrangement of spin pairs of unit length, oriented along the z axis, in the xy plane. As is shown in Fig. 1a, where the numbers in the circles enumerate the spins, the central pair at the origin $(0, 0, \pm 0.5)$ is surrounded on four sides $(\pm r, \pm r, \pm 0.5)$ by equivalent pairs. The distance r makes it possible to vary the degree of isolation of the Pake pairs,

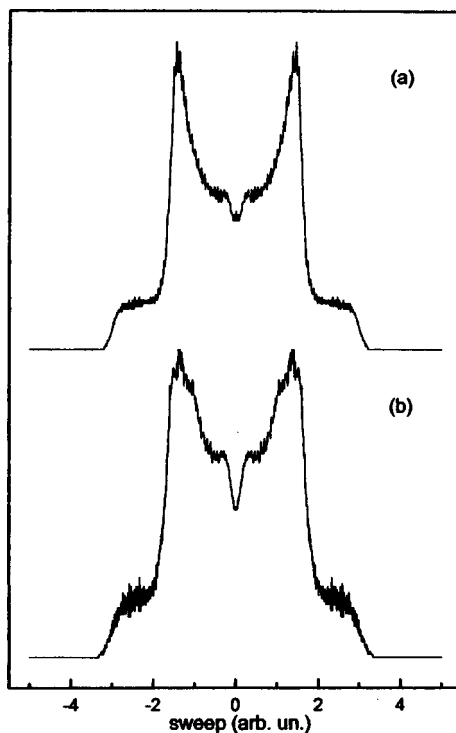


FIG. 2. Computed spectra of a polycrystal for variants (a) and (b), respectively.

i.e., the degree to which the Pake spectrum, determined by intrapair interactions, can be resolved. It is convenient to divide the set of 40 dipole–dipole constants between spins belonging to different pairs, of which in the general case only 18 are different, into groups in accordance with the interpair distances: r (shown by the double and heavy lines in Fig. 1a), $r\sqrt{2}$ (dashed and dotted lines), and $2r$ (not shown). As a rule, the interactions in the first group are strongest, though on account of anisotropy they often fade into the background.

Figure 2a shows the NMR spectrum obtained for a “polycrystal” with the optimum value $r=2.5$. As one can see, a central dip, whose depth concedes essentially nothing to the depth observed experimentally in dellaite, comes through here distinctly. As r increases, the dip vanishes; as r decreases, the dip broadens and the structure of the entire spectrum becomes more complicated (pairs become nonisolated). Such behavior is characteristic for cross-singular dipoles.^{1,4} Besides r , the depth of a dip depends on the orientation of the spin pairs and on the geometry of their relative arrangement, which often causes the dip to vanish.

As noted above, in real crystals (even, for example, in zeolites) it is difficult to find isolated clusters which in turn have several well-isolated pairs of nuclei. Ordinarily, the environments of all pairs are approximately the same, whereas in the model employed (Fig. 1a) for each central pair there are four peripheral pairs; this fundamentally differs from the typical experimental situation. The way out of the situation could be the use of

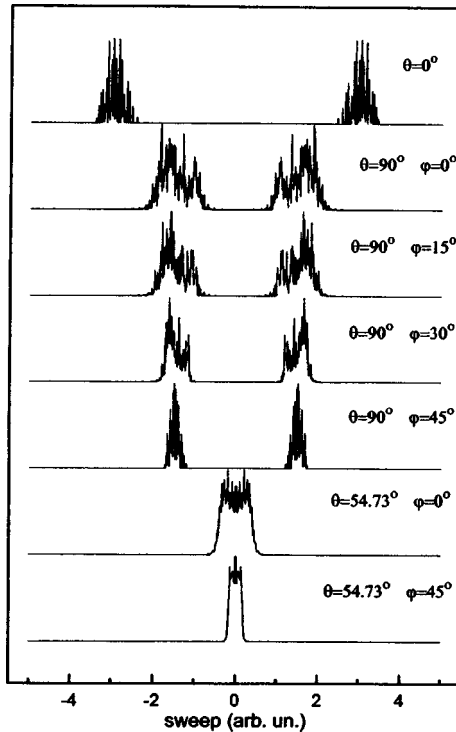


FIG. 3. Typical examples of spectra of a single crystal (variant (b)) for certain orientations of the magnetic field vector.

cyclic boundary conditions,²⁰ but the limited number of spins makes it possible to use them more or less rigorously only for a one-dimensional arrangement of pairs, which we propose to study in detail.

Nonetheless, sacrificing the possibility of taking into account all of the interactions, except those marked by the double and thick lines, we used unique “quasicyclic” boundary conditions that made it possible to place each of five spin pairs into an identical environment. Topologically, such a model can be represented by any five-vertex object (star, triangular bipyramid, and so on), but we prefer the two-dimensional representation shown in Fig. 1b. Of course, because of the small number of pairs, even such a model cannot claim to analyze real situations, but nonetheless it does expand the possibilities of studying the spectral manifestations of interpair dipole–dipole interactions. Compared with the previous model, here the contribution of interpair interactions is artificially increased. The number of different dipole–dipole constants decreases from 18 to 6, but for the components of Pake doublets quasicontinuity can be preserved in a “single crystal,” as one can see in Fig. 3. Only the first spectrum (for $H_0 \parallel z$) is an exception. Here, because of the high symmetry, only two interpair interaction constants are different. (When only one interpair constant remains, the components become line-like.)

The central dip for such a model with $r=2.5$ came through much more distinctly in the spectrum presented in Fig. 2b for a “polycrystal.” It is interesting that despite the

inherent broadening of the Pake structure of the spectrum, the width of the dip remained constant (which is why its depth increased). On the whole, the “quasicyclized” model gives a cross-singular dip that is more stable against a change in orientation and relative arrangement of the spin pairs.

We note here that all of the spectra in Figs. 2 and 3 are represented by histograms with a step size of 0.01 arbitrary units on the horizontal sweep scale (sweep of the frequency, magnetic field, and so on). No measures were taken to smooth the computed curves. The spectra of the polycrystals were obtained by the usual summation of the single-crystal spectra with the spherical angles changing by steps $\Delta\theta = \Delta\varphi = 1^\circ$ and with weighting factors $\sin\theta$. The obvious noisiness of the computed spectra is due not to computational errors (say, because of diagonalization of large matrices) but rather to the actual discrete nature of the spectra because of the small number of spins. The doublet structure sometimes seen on the components is also due to the small number of pairs.

The cross-singular nature of the dips, obtained computationally, in the Pake spectra follows from the fact that the values of the second moments of the individual components in the resolved doublets actually equal 5/6 of the Van Vleck values, and they strictly equal the Van Vleck values only for $\theta \approx 55^\circ$. For this reason, at the central point of the spectrum, which is the only location where the spectral lines cross, the width of the lines suddenly increases by a small amount, which results in a “shortfall” of the integrated intensity when averaging over θ and φ .

The most surprising circumstance, making it difficult to perceive the cross-singular mechanism, is that the much stronger change in the width of the components as a result of the anisotropy of the interpair Van Vleck second moment (clearly illustrated in Fig. 3) is essentially not manifested in the spectrum of a polycrystal, since it is “smeared” over the entire spectrum.

It follows from the results presented above that the cross-singular dip is an integral property of the Pake NMR spectra. However, it is very sensitive to the relative arrangement of Pake pairs, which often causes the dip to vanish. The experimental observation of a cross-singular dip apparently requires spectra which are better resolved than the spectra ordinarily observed in rigid crystal hydrates. Thus, besides the aforementioned dellaite, we call attention to the distinct cross-singular dip in the ^1H NMR spectrum of trichloroacetic acid,²¹ although the authors did not point it out. More demonstrative cases exist also. See, for example, Ref. 22, where a strongly expressed dip in the ^1H NMR spectrum of partially dehydrated magnesium perchlorate hexahydrate, which was recorded on the derivative as the “line of reverse phase,” was interpreted as an additional narrow peak with the corresponding physical conclusions.

To accumulate statistics on the dependence of the depth of a cross-singular dip on the characteristic features of the relative arrangement of pairs it will be necessary to improve the computational method employed, a task for which adequate resources are available. Specifically, the deep analogy with quadrupole systems makes it possible to increase substantially the number of Pake pairs in numerical models, where a nucleus with $I=1/2$ will play the role of a pair and the Pake splitting will be replaced by quadrupole splitting.

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