what was termed "rattling," where a small set of nearly colinear particles had for short time periods many more collisions among themselves than the other particles in the system. What is, in any case, clear from the present study is that this phenomena must be quantitatively accounted for in the short time behavior of the force autocorrelation function since this effect counteracts the anticorrelations expected on geometric grounds.

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^{31}P Chemical Shielding Anisotropy in Solids. Single Crystal and Powder Studies at 99.4 MHz*

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Free induction decays of a single crystal of P_4S_3 and powders of Zn_3P_2, Mg_3P_2, and P_4S_{10} are studied at 99.4 MHz. The P_4S_3 molecule is found to have two ^{31}P chemical shielding tensors, one for the single apical phosphorus and one for the three phosphorus atoms of the basal triangle in the molecule. The tensors are more or less symmetric and the eigenvectors for the unique elements are found to be colinear within experimental error, thus suggesting that there is rapid motion about the C_3 axis of the molecule. A comparison with theoretical spectra bears this out. The general character of the spectra agrees with the crystal structure of the compound found by x-ray analysis and the isotropic shielding values agree with a previous spinning-sample study. ^{31}P powder patterns for Zn_3P_2 and Mg_3P_2 yield chemical shielding parameters and the spectra appear to disagree with previous pulsed and spinning-sample experiments on these compounds. The spectrum of P_4S_{10} indicates rapid molecular motion at room temperature. The possibility of low-temperature and liquid experiments is discussed.

INTRODUCTION

The anistropy of the chemical shift in NMR is an interesting quantity both from the point of view of molecular theory and for the structural information it can give when used empirically. In a mobile isotropic liquid one sees only the rotationally averaged scalar chemical shift in the spectrum, the anisotropy entering only through spin–lattice relaxation effects. An anisotropy is seen in liquid-crystal experiments,[1] but even here some information is lost through partial averaging. In solids the static dipolar broadening of the resonance, which may obscure the structure from which one would obtain the desired information, can sometimes be removed by fast sample rotation[2] or by various narrowing schemes using strong rf fields.[3] It is useful to keep in mind that such elaborate methods are not always needed if the dipolar broadening is not too great and if the chemical shifts are large.[4–6] In the present paper we report results on ^{31}P shielding anisotropies from powder samples of Zn_3P_2, Mg_3P_2, and P_4S_{10} and from single crystals of P_4S_3. Advantage is taken of the large size of ^{13}P anisotropies, the relatively small dipolar broadening, and the amplification of chemical shifts obtainable in large magnetic fields ($\sim 6T$ in these experiments). Figure 1 provides a graphic illustration of the dominance of ^{31}P chemical shifts over dipolar broadening in this situation, which may be compared with the inferior situation for powders in low fields.[7,8]

EXPERIMENTAL

Spectrometer

Data for these experiments were obtained at 99.4 MHz with a broad-band (20–250 MHz), pulsed spectrometer described in detail elsewhere.[9] Designed to perform multiple-pulse experiments, the instrument is equipped with a high-power transmitter, a fast-recovery receiver, and a pulse-programmer (PP) to produce the logic required by the particular experiment. The acquisition of data is automated by computer control (PDP-12A) of the PP. In addition to general servicing of the PP, the PDP-12A processes the raw data through signal averaging and Fourier transformation of the free induction decay signals. The resonance field was provided by an Oxford Instrument Co. superconductive solenoid.
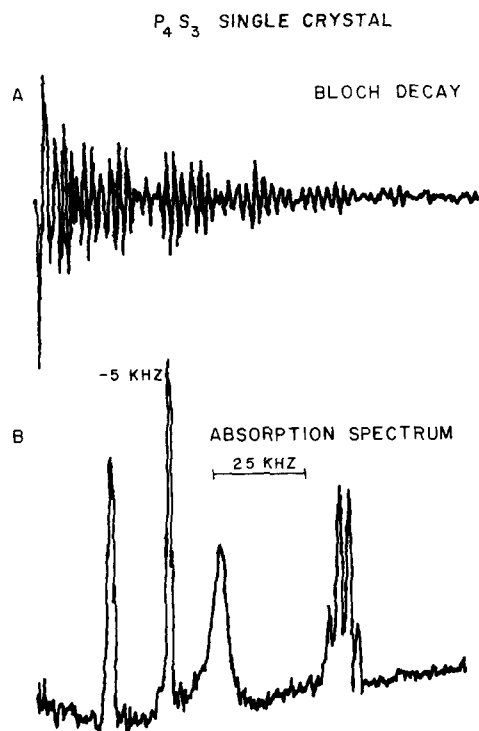
P₄S₃ SINGLE CRYSTAL

FIG. 1. (a) Free induction decay of ^{31}P spins in a single crystal of P_4S_3. The plot is from a 256-point digitized signal with a sampling period of 2 μsec. As explained in the text, there are four different P_4S_3 molecules with respect to chemical shielding (b) Fourier transform of (a). The two low-field sharp peaks are assigned to apical phosphorus atoms and the broad high-field peak and multiplet to the basal phosphorus atoms. The spectrum corresponds to an orientation angle of 10° in Fig. 4 where some collapse occurs, explaining why only two sharp peaks are seen. The spectrum is analyzed in the text in terms of rapid motion about the C_3 axis of the molecule. The frequency indicated refers to an external reference of 85% orthophosphoric acid.

The large chemical shifts in phosphorus compounds (in P_4S_3, total spread $\sim$700 ppm) place stringent requirements upon the signal sampling rate of the spectrometer. In order to satisfy the sampling theorem and thus prevent "folding over" of the signal, a Fabritek 952 fast digitizer was interfaced to the spectrometer. The Fabritek 952, triggered externally by the PP, samples the signal at a maximum rate of 1 MHz until its 1024 channel 5-bit memory is filled. The data are then transferred by the PP to the computer where they undergo processing.

Probe and Goniometer

To obtain full information relating to the chemical shielding tensor, a single crystal of P_4S_3 was rotated about three independent crystalline axes perpendicular to the Zeeman field, obtaining in each case the frequency shifts of the various lines as a function of the angle of rotation. For computational simplicity, the three crystalline axes were chosen as an orthogonal set. The crystal was first mounted by gluing a promi-

nent face to a precisely machined lucite plug, a matched fit to the Teflon inner disk of the goniometer shown in Fig. 2. The successive mountings were accomplished by gluing similar plugs to the crystal along orthogonal axes. The probe and goniometer are illustrated in Fig. 2. The calibrated, outer Teflon disk of the goniometer is secured to the glass inner jacket of the probe. By twisting the outer copper jacket, thus moving it relative to the fixed copper cylinder located inside the glass dielectric, the probe is tuned. Windows in the outer jacket permit orientation of the sample without removal of the jacket.

Materials

Single crystals of P_4S_3 were grown by evaporation from solution in a $\sim$1:1 mixture of acetone and carbon disulfide. The crystals were large with well-defined faces and easily cleaved. All compounds were obtained from commercial sources: P_4S_3, Zn_3P_2, and Mg_3P_2 (K&K Laboratories), P_4S_{10} (Matheson, Coleman, and Bell). Almost all samples had relatively long T_1's ($>$1 min).

DATA ANALYSIS

The general transformation relation

$$t_{ij}' = \Sigma_k \Sigma_l a_{ik} a_{jl} t_{kl} \qquad (1)$$

defines a Cartesian tensor in terms of an orthogonal transformation A. The chemical shift, due to the nature of the magnetic resonance experiment in which
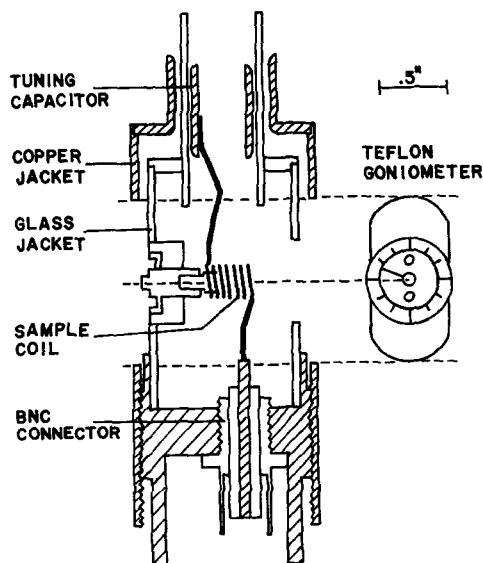

FIG. 2. Probe and goniometer. The probe is tuned by rotating the outer jacket, thus moving it relative to the inner fixed copper cylinder. Windows in the jacket permit an adjustment of the crystal orientation with the necessity of removing it. The crystal is mounted on precision-machined lucite plug which snaps onto the end of the inner goniometer piece projecting into the rf coil.

only the zz component is measured, assumes the form:

$$\sigma_{zz} = \Sigma_k \Sigma_l R_{zk} R_{zl} \sigma_{kl}, \qquad (2)$$

where R represents a general rotation of the crystalline axes (XYZ) relative to the laboratory frame (xyz) whose z axis is along the Zeeman field.

For the rotation of a single crystal about its X axis, for example, the chemical shift, as a function of the angle of rotation is thus given by:

$$\sigma_{zz}(\theta) = \tfrac{1}{2}(\sigma_{YY} + \sigma_{ZZ}) - \tfrac{1}{2}(\sigma_{YZ} + \sigma_{ZY}) \sin 2\theta$$
$$+ \tfrac{1}{2}(\sigma_{ZZ} - \sigma_{YY}) \cos 2\theta$$
$$= A + B \sin 2\theta + C \cos 2\theta. \qquad (3)$$

While the chemical shift tensor may in principle have an antisymmetric part, (3) makes it clear that only the symmetric part manifests its presence in the NMR spectrum. Measuring $\sigma_{zz}(\theta)$ for rotations about three mutually perpendicular directions more than specifies the six independent elements of σ in the XYZ frame. For example, σ_{XX} may be obtained separately from rotations about the Y or Z axes. For the purpose of treating the data of these experiments, an average of the two quantities was used. The resulting tensor is then diagonalized, the eigenvalues being the principal elements (σ_{11}, σ_{22}, σ_{33}) of the shielding tensor and the eigenvectors giving the directions of the principal axes with respect to the XYZ frame. Least-squares fitting of the raw measurements to (3) and diagonalization of σ were programmed for the PDP-12 in $FOCAL$.

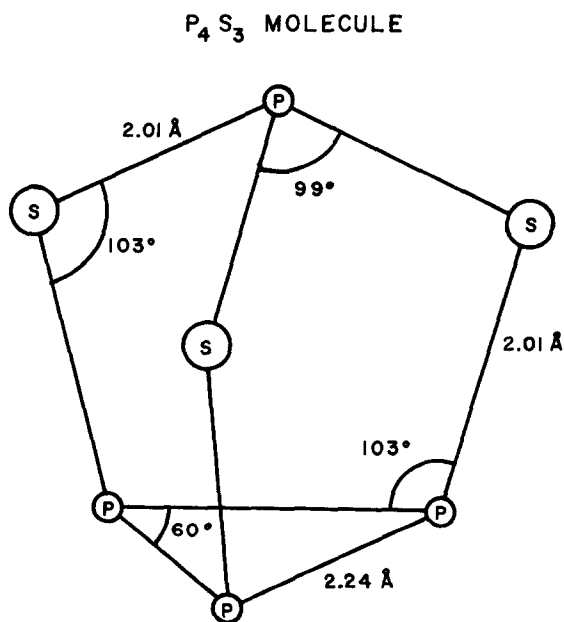In the case of powder samples the above procedure
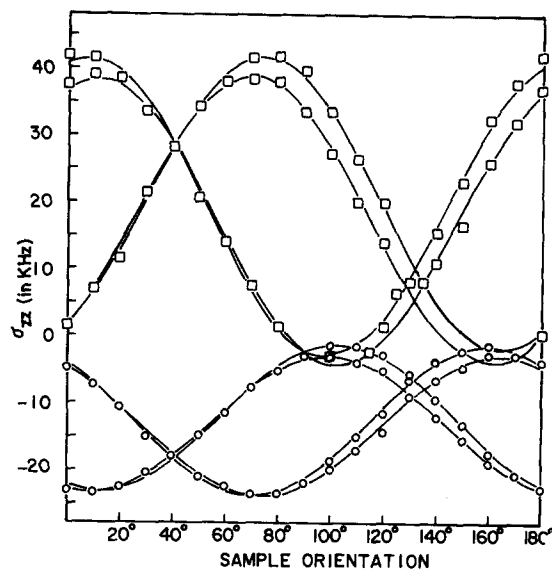
FIG. 4. A plot of the ^{31}P chemical shifts for the four P_4S_3 molecules as the crystal is rotated about one axis. The eight lines come from the apical (circles) and basal (squares) phosphorus atoms, each with a different shielding tensor. The solid lines are from least-squares fits.

cannot be used: The singularities in the powder spectrum give σ_{11}, σ_{22}, and σ_{33} directly, but all knowledge of the orientation is, of course, lost.

RESULTS AND DISCUSSION

Single Crystal Study of P_4S_3

The x-ray data[10] on crystalline P_4S_3 indicate a space group of P_{mnb} and eight molecules per unit cell. Consequently, the asymmetric unit consists of one molecule of P_4S_3. The presence of a center of symmetry results in four chemical shifts for every type of molecular phosphorus in the crystal. As indicated in Fig. 3, along with bond lengths and angles, the molecule possesses a close approximation to a C_3 axis.

The NMR results bear out the conclusions based on the x-ray data. A general spectrum consists of two sets of four equally intense lines. One set consists of narrow, structureless lines and the other of much broader lines exhibiting a dipolar or pseudodipolar structure. Figure 1 displays the free induction decay of the nuclear signal and its Fourier transform for an orientation at which the sets of four lines have collapsed to a set of two. Relying on the structural information, it is obvious that the set of two narrow singlet lines belong to the apical phosphorus atoms, and the remaining lines to the basal phosphorus atoms.

A plot of resonance frequency vs angle of rotation about a particular crystalline axis used in the experiment is provided in Fig. 4 where the four lines for each phosphorus are apparent. The results of a complete set of rotations are given in Table I as the princi-

$P_4 S_3$ MOLECULE

FIG. 3. Structure of the P_4S_3 molecule as determined by x-ray studies.[10] The molecule possesses a C_3 symmetry axis passing through the apical phosphorus and the center of the phosphorus triangle.

TABLE I. Principal values of ^{31}P chemical shielding tensors in P_4S_3.[a]

	Apical	Basal
σ_{11}	-25 ± 9	-101 ± 15
σ_{22}	-3 ± 4	-44 ± 14
σ_{33} [b]	-238 ± 11	$+406\pm20$
$\frac{1}{3}\,\mathrm{Tr}\sigma$	-89 ± 8	$+87\pm16$
$\frac{1}{3}\,\mathrm{Tr}\sigma$ [c]	-72	$+103$

[a] In ppm relative to 85% aqueous orthophosphoric acid. The main sources of error in this experiment were in crystal mounting and measuring the line positions.

[b] This element is the one referred to as belonging to the more or less unique axis of the shielding tensor.

[c] Andrew and Wynn, Ref. 2.

pal values of the shielding tensor. The difference in the two isotropic parts agrees well with that determined by Andrew and Wynn[2b] by sample spinning. The principal axes extracted by diagonalization of the tensor indicate that the more or less unique axes of the chemical shielding tensors for the apical and triangular phosphorus atoms in the same molecule are colinear within experimental error. Calculating the angles between the principal axes of different molecules, we get 63° (117°) and 5° (175°) in excellent agreement with those determined by x-ray between the molecular axes.[10]

Molecular Motion in P_4S_3

The result that the unique principal axes of the apical and basal phosphorus of the same molecule coincide is a strong indication that there is fast rotational motion about that axis (*vide infra*). This is
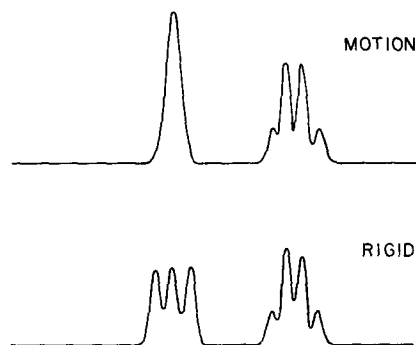
FIG. 5. Computer simulation of spectra for four phosphorus triangles with bond lengths of Fig. 3 and with the normals to their planes making angles of 97°, 101°, 157°, and 161° with the z axis. These angles were calculated for the orientation (Fig. 4, 10°) at which Fig. 1 was obtained by using the best-fit chemical shielding parameters, and the eigenvectors calculated as explained in the experimental section. It is clear that the low-field portion of the spectrum serves to distinguish between the rigid and rotating cases. Convolution with a Gaussian was used to facilitate comparison with the experimental spectrum.

supported by the observation that only one tensor is found for the three basal phosphorus atoms in the molecule. To test this notion, the dipolar structure of the triangular phosphorus was calculated at each orientation of the crystal for two cases: (1) rigid lattice and (2) rapid motion about the C_3 axis of the molecule. The formulas derived by Andrew and Bersohn[11,12] were utilized with the result that for some particular orientations the difference between the two structures was dramatic enough to enable us to make a judgment. An example is the orientation at which the spectrum of Fig. 1 was obtained. Using the angles calculated for this orientation between the molecular symmetry axis and the z axis, together with the bond lengths in Fig. 3, the spectra in Fig. 5 were calculated by the equations of Refs. 11 and 12 for the basal phosphorus atoms. The only assumption made is the colinearity of the more or less unique axes of the chemical shielding tensors and the molecular symmetry axes. Comparing these spectra with the
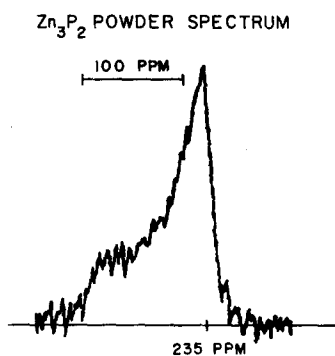
FIG. 6. ^{31}P powder pattern of Zn_3P_2 referred to 85% orthophosphoric acid.

high field peaks (basal P's) of Fig. 1, we see that our conjecture of motion about the C_3 axis is borne out.

Since there is molecular motion in this crystal, the chemical shielding parameters in Table I are not the real rigid lattice values but combinations thereof.[3b] This should certainly be the case for the basal phosphorus atoms where we would expect three different shielding tensors for the rigid triangle in the general case. However, in the case of the apical phosphorus where we expect a symmetric shielding tensor even in the rigid molecule due to the C_3 symmetry at the nucleus, the motion should have no appreciable effect. A check of this could be provided by low-temperature studies.

Powder Studies

Powder patterns of several phosphorus compounds were obtained. Zn_3P_2, the object of some earlier NMR studies[2b,13,14] possesses two magnetically inequivalent phosphorus atoms whose average shifts differ by 33 ppm. In Fig. 6 we see the spectrum obtained from the free induction decay in our experiment. The isotropic

splitting is not resolved and a large chemical shielding anisotropy ($\sim$120 ppm) is evident. The latter was of course averaged out in the sample-spinning experiments.[2b,12] Mansfield and Richards[14] associate a value of 88 ppm with something they call the "mean anisotropic part of the chemical shift tensor." Unfortunately, their analysis is based on faulty premises and their method has no utility for resolving chemical shifts, isotropic or anisotropic.

The powder pattern of Mg_3P_2 (Fig. 7) reveals two very different phosphorus sites, one with a peak broadened by what seems to be a chemical shielding anisotropy and the other with a considerably sharper doublet. This compound was previously studied in a sample-spinning experiment by Kessemeier and Norberg[13] who found two peaks separated by 24 ppm. Our dipolar broadening is too large to permit more than an estimate, but it does appear that what Kessemeier and Norberg observed was the high field doublet, the broad low field line being insufficiently narrowed at their spinning rates to be clearly seen. The narrow line probably reflects the nearly cubic site symmetry of the various corner atoms of the unit cell,[15] while the lower symmetry of the face sites result in the large anisotropy of the low field peak ($\sim$225 ppm). The 3:1 intensity ratio of the two main lines agrees with this assignment.

The NMR spectrum of P_4S_{10} consists of one sharp line, the width of which is determined by the field inhomogeneity. It is thus evident that there is a substantial amo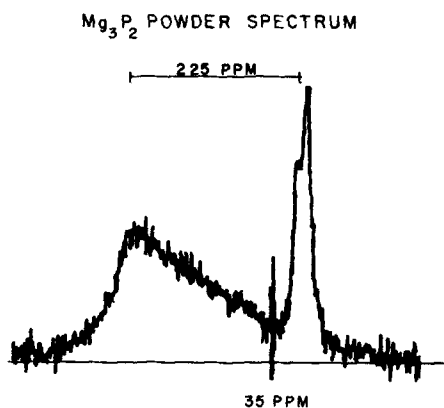unt of molecular motion and no line-narrowing techniques were needed to obtain the isotropic chemical shift.[2b] Again, low-temperature work would provide more information about these systems.

Some lines along which this research could be continued are relaxation studies in the solid and in solution. These should yield valuable information about motion in these systems and the nature of the interactions contributing to the relaxation. P_4S_3 should be ideally suited for such a study, since knowledge of the shielding parameters for the apical and basal phosphorus atoms should enable us to investigate anisotropic motion of the molecule from a field and temperature dependence of the relaxation times.

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Mg_3P_2 POWDER SPECTRUM

FIG. 7. Powder pattern of Mg_3P_2 showing two quite different phosphorus sites, referred to 85% orthophosphoric acid.