Survival of Dipolar Splittings between Equivalent Nuclei in High-Speed MAS-NMR—Interpretation of the ^{31}P Coupling Patterns for Tetraphosphorus Decaoxide

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Abstract: It has been demonstrated experimentally that homonuclear dipolar couplings may influence the line shapes in solid-state NMR spectra even at magic-angle sample spinning (MAS) speeds that are much larger than the dipolar couplings themselves. The effect occurs for chemically equivalent or nearly equivalent nuclei if the MAS speeds are smaller than, or of the same order of magnitude as, the chemical shift anisotropy, and is sensitive to even very small chemical shift differences. For tetraphosphorus decaoxide with dipolar couplings of about 900 Hz between phosphorus nuclei and a chemical shift anisotropy of about 60 kHz at 11.74 T, calculations show that even a hypothetical spinning speed of 100 kHz is not sufficient to remove dipolar line broadening completely. At technically feasible spinning speeds of 8–14 kHz, line splittings are observed that can be traced back to a spin system of three crystallographically equivalent nuclei and one nonequivalent nucleus. These coupling patterns are analysed quantitatively with the help of spectrum simulations. Information is obtained on the symmetry of the molecule and of its environment in the crystalline state. The findings imply that multipulse decoupling techniques may be needed in addition to high-speed MAS to obtain utmost resolution in ^{31}P solid-state NMR spectroscopy for a sizeable number of phosphorus compounds.

Keywords: NMR spectroscopy · solid-state structures · structure elucidation

Introduction

Highly symmetric, small molecules like tetraphosphorus decaoxide are of considerable interest for our understanding of chemical bonding as well as of crystal packing.[1] For the precise determination of solid-state structures of such systems, NMR spectroscopy employing the magic-angle sample spinning (MAS) method[2] is a valuable tool that complements X-ray crystallography. As compared to the latter method, MAS-NMR can detect different aspects of crystal structure since it features a different averaging over space and time. Furthermore MAS-NMR benefits from the high sensitivity of the chemical shift to even minor changes in the electron distribution. At the same time such molecules can serve as well-defined, relatively simple test cases for assessing the potential of solid-state NMR for structure determination on more complex systems.

In the case of P_4O_{10}, an initial crystal structure determination by X-ray diffraction[3] and a later refinement based on the same experimental data[4] revealed the space group $R3c$ with two different phosphorus sites. Furthermore, different lengths of 1.41 and 1.51 Å were obtained for the terminal phosphorus–oxygen bonds of the unique and the three symmetrically equivalent phosphorus atoms, respectively. However, in spite of the expected high sensitivity of ^{31}P chemical shifts to differences in the chemical environment of different kinds of phosphorus atoms, all phosphorus nuclei were found to be equivalent within experimental error in a first high-resolution MAS-NMR investigation of solid P_4O_{10}.[5] Indeed, a recent reinvestigation of the crystal structure employing diffractometer and Guinier powder data resulted in a geometry of the P_4O_{10} molecule with the same length for all terminal bonds and in accordance with T_d symmetry.[6] However, the space group $R3c$ was confirmed, and given the resolution usually obtained in ^{31}P MAS-NMR spectra, it was still suspect that the two different phosphorus sites could not be distinguished. The present work was undertaken with the aim of finding the reason for this lack of resolution and to check whether the NMR results are in agreement with the crystal structure derived from the X-ray data.

We found that the homonuclear dipolar couplings between phosphorus couplings lead to line splittings and/or broadenings at MAS speeds that exceed these couplings by more

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than an order of magnitude. The resulting coupling patterns were shown to be a source of structural information in cases where they are sufficiently resolved. It was demonstrated that undesired line broadenings due to this effect cannot be completely removed by technically feasible sample spinning speeds.

Results and Discussion

Symmetry of the spin system: In contrast to X-ray diffraction, which determines symmetry by averaging over the whole crystal and over times much longer than a second, NMR spectroscopy probes a local symmetry on a time scale well below a second. Furthermore, X-ray diffraction may have difficulty detecting small deviations from a high symmetry, since these lead only to very weak additional reflections that may be buried in the noise. In NMR spectroscopy, however, such deviations lead to an additional splitting of strong signals that is a very sensitive indicator of a different chemical environment of individual atoms in a structure. This is particularly useful for nuclei like phosphorus where the chemical shift range is large. The symmetry of the spin system as seen by NMR may therefore differ from the one expected from X-ray data, providing additional information on the structure. In the case at hand, the most recent X-ray data[6] suggest an A_3B spin system owing to the combined C_{3v} symmetry of the molecule and its environment. At first sight, the line shapes of the centerband and sidebands in the ^{31}P MAS-NMR spectrum acquired at a phosphorus Larmor frequency of $\omega_0 = 161.44$ MHz and $\omega_r = 8$ kHz (Figure 1) seem to contradict this expectation. Notably, the P–P distances in P_4O_{10} correspond to homonuclear dipolar couplings of about 900 Hz, so that one might expect at first sight that they are averaged out by the much faster sample rotation. Therefore only two lines corresponding to the two sites are anticipated; these lines should not exhibit any fine structure. An increase of only 25% in the phosphorus Larmor frequency leads to a visible improvement in resolution, as can be seen by comparing Figure 1 and Figure 2. This improvement cannot be explained solely by the scaling of the chemical shift difference with the external field. As a first approximation, the lineshapes can now be interpreted as a triplet and a singlet that overlap each other partially. The intensity ratio between the two multiplets is very close to 3:1, while the intensity distribution within the triplets deviates strongly from the ratio 1:1:1 which would be expected if the splitting was due to chemical inequivalence. J couplings between ^{31}P nuclei separated by two bonds are too small to account for the splittings. Furthermore, the splitting depends on the side band order and on ω_r. We are thus forced to reconsider the effect of the dipolar couplings.

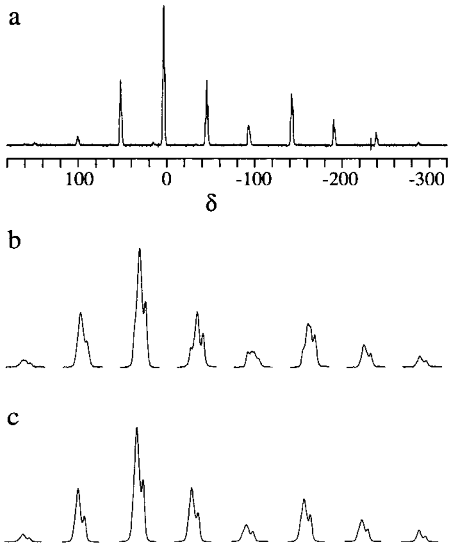

Figure 1. MAS-NMR spectrum of P_4O_{10} at a ^{31}P Larmor frequency of 161.44 MHz and a sample rotation frequency of 8 kHz. a) Experimental spectrum; b) detail plots of the sidebands with significant intensity; c) simulated lineshapes of the sidebands with significant intensity assuming the parameter set given in Table 1.

Abstract in German: *Anhand von Experimenten wird gezeigt, daß homonucleare dipolare Kopplungen die Linienform in Festkörper-NMR-Spektren selbst dann beeinflussen können, wenn sie viel kleiner sind als die Probenrotationsfrequenz bei einer MAS-Messung. Der Effekt tritt für chemisch äquivalente oder nahezu äquivalente Kerne auf, falls die Probenrotationsfrequenz von der gleichen Größenordnung oder kleiner ist als die Anisotropie der chemischen Verschiebung. Mit ihm lassen sich auch kleine Differenzen der isotropen chemischen Verschiebung messen. Für Tetraphosphordecaoxid mit dipolaren Kopplungen zwischen den Phosphorkernen von etwa 900 Hz und einer Anisotropie der chemischen Verschiebung von etwa 60 kHz (bei 11.74 T) zeigen Rechnungen, daß selbst eine hypothetische Rotationsfrequenz von 100 kHz nicht ausreichen würde, um die dipolare Verbreiterung völlig zu beseitigen. Bei den erreichbaren Rotationsfrequenzen von 8–14 kHz beobachtet man Aufspaltungen, die sich auf ein Spinsystem zurückführen lassen, das aus drei kristallographisch äquivalenten und einem nichtäquivalenten Kern besteht. Mit Spektrensimulationen gelingt es, die Kopplungsmuster quantitativ auszuwerten. Man erhält dabei Informationen über die Symmetrie sowohl des Moleküls selbst als auch seiner Umgebung im Kristall. Die Resultate zeigen, daß für eine Reihe von Phosphorverbindungen zusätzlich zur MAS-Technik die Anwendung von Multi-Puls-Entkopplungstechniken erforderlich wäre, um die größtmögliche Auflösung von ^{31}P-Festkörper-NMR-Spektren zu erreichen.*

The existence of a splitting for *chemically equivalent nuclei at the same crystal site* in solid-state NMR spectra is well understood. It results from the symmetry breaking introduced by the magnetic field if the principle axes of the chemical shift anisotropy (CSA) tensors do not coincide. It was also established early on by Maricq and Waugh[7] that this splitting is not averaged out by MAS in the same way as a heteronuclear dipolar coupling, since the Hamiltonians at different times do not commute. Following this seminal work the corresponding effects have been studied quite extensively[8] and it has been shown that they are inversely proportional to the MAS sample rotation frequency ν_r.[8a,d] It has also been

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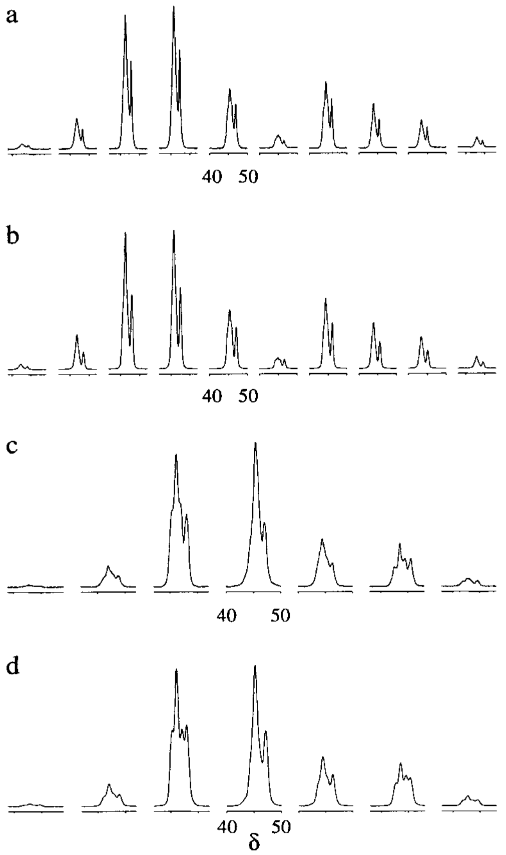

Figure 2. Sideband lineshapes in MAS-NMR spectra of P_4O_{10} at a ^{31}P Larmor frequency of 202.45 MHz and different sample rotation frequencies ν_r. For the centerband (isotropic line) a chemical shift scale is given. The parameters for the simulation are listed in Table 1. a) $\nu_r = 8$ kHz, experimental spectrum; b) $\nu_r = 8$ kHz, simulated spectrum; c) $\nu_r = 14$ kHz, experimental spectrum; d) $\nu_r = 14$ kHz, simulated spectrum.

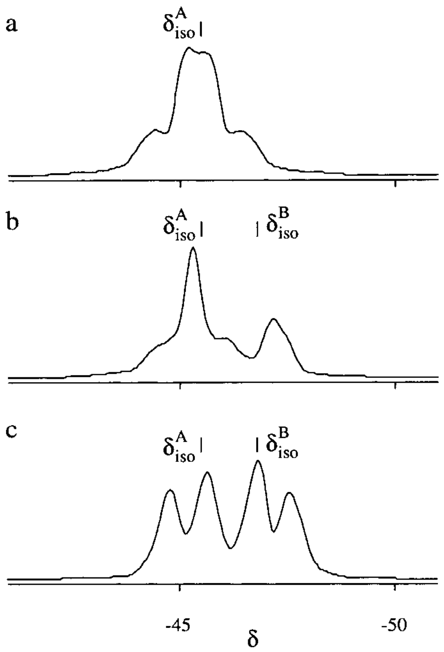

Figure 3. Simulated lineshapes of MAS-NMR side bands for different four-spin systems under conditions where the main features are resolved. The labels designate the isotropic chemical shifts. a) A_4 system; b) A_3B system; c) A_2B_2 system.

demonstrated that the corresponding mechanisms may introduce J coupling effects from couplings between chemically equivalent spins into MAS spectra.[9] The theoretical results suggest that homonuclear dipolar splittings might still be present at sample rotation frequencies that are much larger than the couplings themselves, but to the best of our knowledge this has never been demonstrated experimentally or by simulations.

To check if the lineshapes in the MAS spectra of P_4O_{10} are actually due to these effects, we have performed simulations for $\nu_r = 14$ kHz and $\nu_0 = 202.45$ MHz considering both chemical shift anisotropy and dipolar coupling for four-spin systems of the types A_4, A_3B, and A_2B_2[10] with a difference in the chemical shifts of 1.5 ppm between the P_A and P_B nuclei; the shapes of the isotropic lines are displayed in Figure 3a, b, and c, respectively. All simulations in this work were performed using the magnetic resonance software library GAMMA[11] with its implementation of Floquet operators.[12] This approach is related to the theoretical description for two-spin systems by Kubo and McDowell.[8a, b] Computational details are described in the Experimental Section. The dipolar coupling of $d = 890$ Hz used in the simulations corresponds to the P–P bond length of 2.810 Å that was calculated from the X-ray data.[6] T_d symmetry of the molecule was assumed to determine the mutual orientation of the tensors. From the shapes of the P_A line in Figure 3 we may conclude that the signal of *equivalent* nuclei shows a splitting with a multiplicity that equals the number of these nuclei, while the shape of the P_B line in Figure 3b does not feature a splitting due to the coupling to the P_A nuclei. We checked by further simulations that these general features of the multiplet pattern do not change in going to A_3X and A_2X_2 systems; the multiplet centers coincide with the isotropic chemical shift in these cases. Note that the splitting pattern is thus completely different from that expected in the liquid state, where an isotropic coupling in an A_3X system of $I = 1/2$ spins would lead to doublet and quadruplet splittings of the P_A and P_X line, respectively. A comparison of the lineshapes of the isotropic line and the sidebands (data not shown) in the simulated spectrum of the A_3B system with the experimental spectrum reveals that solid P_4O_{10} is characterized by an A_3B spin system and that our initial model already resembles the actual situation quite closely. To obtain the exact coupling and shift parameters, the simulations have to be fitted to the experimental data.

Symmetry of the P_4O_{10} molecule and its environment: The simulated pattern for an A_3B system with T_d symmetry of the molecule is in general agreement with the experimental observations (compare Figure 2c and Figure 3b). One may then conclude that deviations from the crystal structure obtained by X-ray diffraction must be small if they exist at all. This notion is supported by the fact that the CSA tensors of P_A and P_B are found to feature axial symmetry within experimental error. Note, however, that MAS sideband patterns are not sensitive to small deviations of the tensor from axial symmetry.[13] For T_d symmetry, the geometry of the coupling network of the four phosphorus atoms can be described by a single parameter, namely the distance r_{PP} between any two phosphorus nuclei. The direction of the unique axes of the four chemical shift anisotropy tensors is along the four C_3 axes of the molecule. A deviation of the molecular symmetry from T_d (to C_{3v}) leads to a trigonal pyramid. Its geometry can be described by introducing a second parameter $q = r'_{\mathrm{PP}}/r_{\mathrm{PP}}$, where r_{PP} is now the distance between two basal P_A nuclei and r'_{PP} is the distance between a basal P_A and the apical P_B nucleus. The unique axis of the CSA tensor of P_B is along the remaining C_3 axis. To a good approximation, the unique axis of the CSA tensors of the P_A nuclei points towards the center of gravity of the triangle formed by the three other P nuclei. We have fitted the two parameters q and r_{PP}, using the values calculated from the X-ray crystal structure ($q = 1$, $r_{\mathrm{PP}} = 2.810$ Å) as starting values. Indeed, any change in these parameters leads to a deterioration of the fit between experimental and simulated spectra. The maximum error of the two parameters can be estimated as $\delta q = 0.01$ and $\delta r_{\mathrm{PP}} = 0.04$ Å. For the difference in the isotropic chemical shifts of P_A and P_B we find $\Delta\delta_{\mathrm{iso}} = 1.3$ ppm. This value compares to solvent effects of up to 5 ppm on ^{31}P in similar chemical environments in liquid-state NMR, while the chemical shift range for P^V coordinated by four oxygen atoms extends from -5 to 60 ppm.[15] Hence the chemical shift difference can be accounted for satisfactorily by intermolecular effects, that is, by the different distances of P_A respectively P_B nuclei to atoms in neighboring molecules.

With the complete parameter set given in Table 1, a good agreement between the simulated and experimental spectra is obtained for different ^{31}P Larmor frequencies and sample spinning speeds (see Figures 1 and 2). Moreover, a simulation for the experimental conditions used by Grimmer and Wolf ($\nu_r = 3.5$ kHz and $\nu_0 = 109.3$ MHz) shows that the lack of resolution between the P_A and P_B sites in their investigation was predominantly due to residual effects of the dipolar couplings (Figure 4a). In fact, resolution at $\nu_r = 3.5$ kHz and $\nu_0 = 109.3$ MHz may be even worse than suggested by this figure. In our simulations we have assumed that Gaussian line broadening is the same at lower field and sample rotation speed as in our own experiments. Since part of this broadening is caused by the dipolar couplings to phosphorus atoms in neighboring molecules, it is actually expected to increase if field and sample rotation frequency are decreased.

Table 1. Best-fit NMR parameter set for P_4O_{10} consisting of the isotropic shifts δ_{iso}, the anisotropy $\Delta\sigma$ and asymmetry η of the CSA tensor, and the dipolar coupling d_A to P_A nuclei for both sites. The mutual orientation of the interaction tensors is determined by the T_d symmetry of the molecule.

Site	δ_{iso}	$\Delta\sigma$ [ppm]	η	d_A [Hz]
A	-45.5 ± 0.1	296 ± 5	0.0 ± 0.2	890 ± 25
B	-46.8 ± 0.1	291 ± 5	0.0 ± 0.2	890 ± 25

A detailed comparison of Figures 2a and 2c with Figures 2b and 2d shows that there are still minor lineshape deviations that cannot be explained by experimental inadequacies and that cannot be removed within the model of the spin system used up to now. As a source, we have excluded deviations of the chemical shift tensors from axial symmetry by simulations. We have also considered J coupling as a possible source of the lineshape deviations, since the second-order effects in the solid state may reintroduce it even for chemically equivalent nuclei.[9, 14] The introduction of a small isotropic J coupling improves the fits slightly, with the optimum at $J_{\mathrm{iso}} = 15$ Hz. Though this is within the expected range for a phosphorus–phosphorus J coupling through two bonds,[15] it is hardly significant in view of the remaining lineshape deviations. The most probable source for these deviations is dipolar coupling to equivalent phosphorus nuclei of the P_A type in neighboring molecules. From the known distances, such couplings can be estimated to be of the order of 100 Hz. An inclusion of neighboring molecules into the simulated spin system as would be necessary to obtain an even better fit is not feasible. Nevertheless we may conclude from the results displayed in Figures 1 and 2 that the NMR results are in full agreement with the most recent crystal structure.[6]

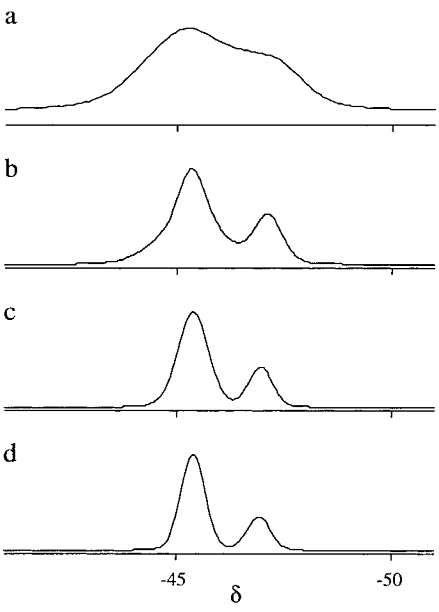

Figure 4. Simulated lineshapes of MAS-NMR centerbands for the best-fit parameter set for P_4O_{10} (cf. Table 1) at different ^{31}P Larmor frequencies ν_0 and sample rotation frequencies ν_r. a) $\nu_r = 3.5$ kHz, $\nu_0 = 109.3$ MHz; b) $\nu_r = 35$ kHz, $\nu_0 = 202.45$ MHz; c) $\nu_r = 100$ kHz, $\nu_0 = 202.45$ MHz; d) $\nu_r = 500$ kHz, $\nu_0 = 202.45$ Mhz.

Strictly speaking, NMR evidence derived from dipolar couplings confirms the T_d symmetry of only the phosphorus coupling network; it does not exclude differences in the length of the terminal P–O bonds as found in the older crystal structure.[4] In view of the large chemical shift range of P^V coordinated by four oxygen atoms, one would expect, however, that any variance of these bond lengths above 0.01 Å would lead to chemical shift differences that are resolved. The only observed shift difference is the one between the P_A and P_B nuclei of $\Delta_{\mathrm{iso}} = 1.3$ ppm, which is satisfactorily accounted for by the different intermolecular environments of the two nuclei. A difference in the bond length as large as 0.1 Å as in the older crystal structure[4] is expected to have much more dramatic effects. By means of simulations, we can also estimate that any unresolved chemical inequivalence between the three P_A must be smaller than 0.2 ppm, since larger values

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lead to a significant deterioration of the fit that cannot be removed by adjusting other parameters. This resolution for chemical inequivalence compares to a line width of about 0.5 ppm (full width at half height 100 Hz) for the singlet and the components of the triplet. The strong dependence of the homonuclear coupling pattern on chemical shift differences makes it an even more sensitive tool for the detection of symmetry deviations than a well-resolved isotropic MAS-NMR spectrum.

As a result of these investigations, we conclude that the NMR spectra are in best agreement with P_4O_{10} molecules of T_d symmetry in an environment of only C_{3v} symmetry. In this case, the dipole moment of the molecule vanishes and the stabilization of the crystal can be considered as exclusively due to van-der-Waals interactions. The crystal packing that leads to the space group $R3c$ can then be considered as driven by an optimization of the van der Waals interactions. It has been shown before by Cruickshank that the crystal packing found experimentally is more dense than in a hypothetical crystal of cubic symmetry.[4] On the other hand, a lower symmetry of the P_4O_{10} molecule would lead to a nonvanishing dipole moment and electric dipole interactions would have to be considered in the discussion of crystal packing. Neither the X-ray nor the NMR data indicate that this is the case.

General remarks on the effect of homonuclear dipolar couplings on MAS-NMR spectra: Theoretical results on the combined effects of homonuclear dipolar couplings and CSA on MAS spectra in the absence of significant J couplings are not yet reflected in textbooks and reviews and are widely disregarded in the interpretation of ^{31}P MAS-NMR spectra. Our experimental results and numerical simulations show clearly that even for MAS speeds much larger than the couplings themselves such effects can lead to resolved splittings or substantial line broadening if the coupled spins are nearly equivalent and if the CSA is not completely averaged out by MAS. Though numerical simulations based on the theory of Kubo and McDowell[8] account quantitatively for the effect, its significance is not easily recognized in analytical formulae, mainly since an analytical computation of the powder average is hardly possible. Nevertheless, a qualitative explanation can be given. The comparatively small homonuclear dipolar couplings survive high-speed MAS since they add to and are protected by the much larger anisotropy of the chemical shift. With this explanation, one expects that the removal of dipolar broadening or splitting by MAS requires $\nu_r \gg \nu_{CSA}$ instead of $\nu_r \gg \nu_d$ in the case of chemically equivalent or nearly equivalent nuclei. Indeed, this is found in simulations with the parameters for P_4O_{10} ($\nu_{CSA} = 60$ kHz). The broadening is still comparatively strong at $\nu_r = 35$ kHz (Figure 4b) and still visible at $\nu_r = 100$ kHz (Figure 4c). To obtain linewidths in the MAS spectra as they are observed for rare nuclei under otherwise similar experimental conditions, an MAS speed of $\nu_r = 500$ kHz would be needed (Figure 4d). Note that $\nu_r = 100$ kHz is already sufficient to suppress all sidebands, that is, this MAS speed would yield an isotropic spectrum if the CSA *only* was present. This is due to the fact that the CSA is an inhomogeneous interaction in the sense of Maricq and Waugh, where $\nu_r > \nu_{CSA}$ leads to complete removal.[7] Interestingly enough, the presence of *both* homonuclear dipolar coupling and CSA requires higher MAS speeds for complete averaging than the presence of any of the two interactions alone. Even state-of-the-art MAS systems are not expected to achieve the necessary MAS speeds in the near future.

Our simulations show that the effect diminishes strongly even for chemical shift differences that are still smaller than the dipolar couplings themselves: The interaction between the P_A and P_B nuclei leads to only a broadening but not to further splitting. Because of the T_d symmetry of the molecule, this weakening of the effect can be only be due to the chemical shift difference. Such a high sensitivity of the effect to deviations from chemical equivalence is also suggested by Equation (66) in Kundla and Lippmaa's work.[8d] The splittings are thus potentially a useful tool for proving *high* symmetry in a crystal structure, since they can be easily distinguished from chemical shift differences by their different response to changes in the static field and MAS speed.

These results are of considerable importance for MAS-NMR experiments on abundant nuclei with moderate gyromagnetic ratio and large CSA, as for instance ^{31}P and ^{205}Tl. As an example consider dipolar couplings between the nearly equivalent phosphorus nuclei in nucleotide di- and triphosphates that are of a similar order of magnitude to the ones in P_4O_{10}. Utmost resolution may not be obtained in such cases even with the highest technically feasible MAS speeds without resorting to homonuclear decoupling techniques like CRAMPS.[16] The feasibility of multipulse decoupling in ^{31}P MAS-NMR has been demonstrated before, albeit with the aim of improving resolution at artificially lowered MAS rotation speeds.[17] It may be suspected that intermolecular dipolar couplings between equivalent nuclei determine the line widths in a sizeable part of the ^{31}P MAS-NMR spectra measured to date. Even more significantly, splittings or strong broadenings due to intramolecular couplings may have been misinterpreted in the past as symmetry deviations in a number of cases. For instance, because of such an unexpected broadening in the spectrum of $P_4O_6S_4$ we postulated a small deviation from the crystal symmetry as determined by X-ray diffraction.[1] The broadening can now be traced back to the homonuclear couplings in an A_4 spin system and is in complete agreement with the X-ray data. Furthermore, one may expect that the resolution of MAS-NMR spectra for phosphate glasses with dense, infinite networks of chemically nearly equivalent phosphorus nuclei can be improved by homonuclear decoupling techniques.

Conclusion

MAS at sample rotation frequencies much larger than the homonuclear dipolar couplings in tetraphosphorus decaoxide was found to fail in averaging out these couplings. The effect is quantitatively accounted for by the spectrum simulations presented here, can be rationalized as a protection of the smaller anisotropy of the dipolar couplings by the larger anisotropy of the chemical shifts, and is in agreement with earlier theoretical results.[8] It has been demonstrated that completely isotropic spectra for typical ^{31}P NMR parameters cannot be obtained with technically feasible sample rotation speeds if equivalent or nearly equivalent nuclei couple with each other. Therefore, we suggest the investigation of combined multipulse homonuclear decoupling and MAS as a means for line narrowing in ^{31}P solid-state NMR spectra of both ordered and disordered systems.

The coupling patterns in the MAS-NMR spectra of P_4O_{10} have been interpreted within a model that assumes an isolated system of the four ^{31}P nuclear spins of one molecule and considers CSA and homonuclear dipolar couplings. For the first time, MAS spectra of such complexity were analysed quantitatively. This was achieved by identifying characteristics of the spectrum that depend only on a subset of the unknown parameters and by using Floquet formalism for the simulation of the sideband lineshapes. The symmetry of the spin system and the NMR parameters are in agreement with the space group $R3c$, the T_d symmetry of the molecule, and the intramolecular phosphorus–phosphorus distance of 2.81 Å found in the most recent X-ray diffraction study. The crystal packing can thus be discussed purely in terms of van der Waals interactions.

Experimental Section

Experimental details: NMR measurements were performed with a Varian Unity 400 and a Bruker ASX-500 spectrometer at phosphorus Larmor frequencies of 161.44 and 202.45 MHz, respectively. The MAS probe heads were purchased from Doty Scientific and Bruker. Tetraphosphorus decaoxide (Optipur, Merck, Darmstadt) was purified by sublimation and filled into standard zirconia MAS rotors (Bruker and Doty) in a glove box. Tight-fitting rotor caps were found to provide sufficient protection against moisture if the rotor was driven by dry nitrogen.

Data analysis: The parameter fit is based on a model of an isolated spin system consisting of the four phosphorus nuclei (spin 1/2) of one P_4O_{10} molecule. The Hamiltonian of this spin system includes four chemical shift tensors and six dipolar coupling tensors. Because of the size of the problem, it is important to restrict the size of the Floquet matrix to the minimum permissible number of Floquet states. If we use the convention of Levante et al. for the choice of the initial density matrix, the evolution of the system can be considered as a point-spread process in Floquet space.[18] From the appearance of the spectra it is then immediately obvious that during the whole experiment there are no significant coherences (and hence populations) that involve Floquet states much farther apart than the width of the static spectrum. More precisely, the Floquet matrix can be truncated to a dimension N_F [Expression (1)], where $\Delta\nu$ is the width of the static

$$N_F \geq 2\left(\frac{\Delta\nu}{\nu_r}+1\right) \qquad (1)$$

spectrum. To check this reasoning, we have numerically simulated our final spectra with values of N_F smaller and larger than the limit defined by this expression. The results show that the spectra obtained with a larger dimension of the Floquet matrix are for all practical purposes indistinguishable from the ones obtained with dimension N_F while a smaller dimension leads to visible distortions. With this truncation and for sufficiently high sample rotation frequencies, numerical simulations based on Floquet formalism are computationally much more efficient than simulations based on the technique of a piecewise constant Hamiltonian.

To further reduce the computational effort, spiral sampling[19] with the minimum permissible number of orientations N_O (89 orientations on the unit sphere for a spectrum with eight sidebands of significant intensity) was used in the powder average. For one parameter set at the largest sample spinning frequency of $\nu_r = 14$ kHz, it was found that even significant increases in N_O do not lead to visible changes in the simulated spectra. In simulations for other ν_r, both numbers were increased in proportion to the number of sidebands. One simulation for the four-spin system with $N_F = 10$ and $N_O = 89$ takes about six hours of CPU time on a Sun SparcUltra workstation. It is therefore of utmost importance to define characteristics of the spectra that depend strongly only on a subset of the free parameters. Such characteristics are the intensity distribution among the sidebands of each group of equivalent spins that depends only on the purely anisotropic part of the CSA tensor (see below), and the frequencies of the isotropic lines that depend only on the isotropic shifts and on a small correction for the dipolar splitting. The correction does not change significantly when the phosphorus–phosphorus distances and the bond angles are varied within a chemically reasonable range. As a third characteristic, the lineshapes of the isotropic lines and its sidebands depend only on the dipolar couplings and on the mutual orientation of the tensors if the parameters discussed above are already fixed. A first approximation for the purely anisotropic part of the chemical shift tensors was obtained with the program WIN-MAS (Bruker) that is based on a numerical implementation of the method of Herzfeld and Berger.[20] Though this method is, in principle, only valid for an isolated spin 1/2, we found that in our case the parameters for the CSA used in a simulation of a spectrum with couplings are recovered from a WIN-MAS analysis within experimentally feasible precision. We obtained dipolar coupling corrections of the isotropic shifts of 0.07 and 0.21 ppm for the P_A and P_B sites, respectively, from a simulation for the parameter set corresponding to the most recent crystal structure.[6] The latter correction is slightly larger than the experimental precision. The dipolar couplings and mutual orientations of the tensors can be calculated for a given geometry of the molecule by symmetry considerations as discussed above. The lineshapes of the isotropic line and its sidebands were fitted by varying the parameters that define this geometry. An additional Gaussian line broadening was introduced to account for relaxation and for effects of dipolar couplings to neighboring molecules; this broadening can be fitted separately after the quantum mechanical simulation.

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