9

ADVANCED DIPOLAR SOLID STATE NMR SPECTROSCOPY OF GLASSES

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9.1 INTRODUCTION

Compared to crystalline solids, glasses present a formidable challenge to structure elucidation. Owing to the lack of long-range periodicity in the glassy state, diffraction techniques are fairly powerless, and the structural concepts typically emerge from the joint interpretation of numerous complementary spectroscopic experiments. For a comprehensive view, glass structure must be discussed on different length scales: (i) short-range order involving only the first atomic coordination spheres (distance region 0.15–0.3 nm), (ii) second-nearest neighbor environments (0.3–0.5 nm), (iii) nanostructure (0.5–3 nm), (iv) mesostructure (3–500 nm), and finally, (v) microstructure (> 500 nm). Spectroscopic methods such as NMR, Raman scattering, photoelectron and extended X-ray absorption fine structure (EXAFS) provide primarily local information about the first few coordination spheres. While the utility of solid state NMR for characterizing the short-range order of glasses was discussed in the preceding chapter, the present contribution concerns the study of structural issues on the 0.3–3 nm length scale (domains (ii) and (iii), particularly in the sub-nanometer region commonly denoted as medium-range structure. The structural issues addressed include (i) the connectivity between different
network former species, (ii) the *distance correlations* involving network former and network modifier species, and (iii) the overall *spatial distribution* of the network modifier ions (see Figure 9.1).

As discussed in the preceding chapter, and also recently reviewed in Reference 1, important information about these questions can be obtained from chemical shift measurements using magic-angle-spinning NMR. However, a more direct and more powerful approach makes use of the *indirect and direct magnetic dipole–dipole interactions* between the nuclei. The magnetic nuclei not only feel the externally applied magnetic field, moderated by shielding effects caused by their surrounding electron clouds, but they also sense the magnetic moments of their neighbors. In most cases, these interactions are considerably weaker than those dominating the lineshape of the NMR spectra in the solid state. The research challenge then consists of (i) selectively extracting reliable dipolar coupling information from the complex internal NMR Hamiltonian, and (ii) translating this information into a structural description. For task (i) the NMR spectroscopist’s toolbox contains a considerable number of powerful selective averaging strategies to measure, in a site-selective fashion, both homo- and heteronuclear indirect and direct spin–spin interactions. Based on this highly specific and accurate information, it is then possible to address task (ii), which is putting structural models for glasses to a quantitative test. The present contribution is focused on this aspect of glass structure and reports important progress made in this direction made during the past few years, complementing recent summaries already available in the literature on this topic [1, 2].

Of course the information obtained by such experiments is combined with that gathered on the short-range order from standard solid state NMR spectra. As detailed below, such studies have given important insights into the local environments and the spatial distribution of the network former and the network modifier species in numerous glass-forming systems.
9.2 THEORETICAL ASPECTS

The total spin Hamiltonian determining the spectroscopic energy levels in solid-state NMR can be written as [3–7],

$$\mathcal{H}_{\text{total}} = \mathcal{H}_z + \mathcal{H}_{\text{ms}} + \mathcal{H}_D + \mathcal{H}_J + \mathcal{H}_Q$$ (9.1)

where $\mathcal{H}_{\text{ms}} + \mathcal{H}_D + \mathcal{H}_J + \mathcal{H}_Q$ define the relevant Hamiltonians of distinct types of internal interactions, namely, (a) the magnetic interactions of the nuclei with the surrounding electrons (magnetic shielding), $\mathcal{H}_{\text{ms}}$, (b) the internuclear direct and indirect magnetic dipole–dipole interactions, $\mathcal{H}_D$ and $\mathcal{H}_J$, respectively, and (c) interactions between the electric quadrupole moments of spin > 1/2 nuclei and the electrostatic field gradients sensed by these nuclei (quadrupolar interaction), $\mathcal{H}_Q$. In the solid state, all of these interactions are anisotropic, that is, their influence on the precession frequency depends on molecular orientation in the magnetic field. As a result, extensive line-broadening is produced in powdered samples.

Magnetic shielding ($\mathcal{H}_{\text{ms}}$) and nuclear electric quadrupolar interactions ($\mathcal{H}_Q$) have been discussed in detail in the preceding chapter. In general, the anisotropies of these interactions are described by second-rank tensors in the limit of first-order perturbation theory. Using the technique of magic-angle-spinning, the anisotropy of the magnetic shielding can be removed, resulting in high resolution spectra, where different local environments can be generally differentiated by resolved resonances characterized by distinct isotropic chemical shift ranges. For example, in silicate and phosphate glasses, the various types of $Q(n)$ environments ($4 \geq n \geq 0$, $n$ being the number of bridging oxygen atoms on a particular unit) can be differentiated by distinct isotropic chemical shift ranges. This is also true for the central transition of quadrupolar nuclei in the limit of first-order perturbation theory. In the case of stronger quadrupolar interactions ($\mathcal{H}_Q > 0.05 \mathcal{H}_Z$), however, second-order perturbation theory must be used, resulting in more complicated lineshapes, for which the averaging by MAS is incomplete. In favorable cases (e.g., $^{11}$B MAS-NMR in glasses) distinct lineshapes can be observed from which the electric field gradient size and asymmetry can be deduced by lineshape simulation methods. In most cases, however, the variation of local environments and topologies results in distributions of both isotropic chemical shifts and nuclear electric quadrupole coupling constants, which dominate the MAS-NMR lineshape [1]. By comparison, the magnetic dipole–dipole interactions are considerably weaker and have normally a negligible influence on the MAS-NMR lineshape. To extract this information from the spectra, special selective averaging and two-dimensional techniques are required. It is the purpose of this chapter to review the most important ones of these techniques and highlight some recent applications of them for the quantitative structural analysis of glasses.

There are two distinct mechanisms, through which magnetic dipole–dipole interactions are being transmitted: first, there are the direct magnetic dipole–dipole couplings which act merely through space and hence depend only on distance and relative orientation with respect to the NMR quantization axis (the direction of the externally applied magnetic field). Second, there are the indirect spin–spin couplings, which are
transmitted via the polarization of bonding electrons. These indirect couplings do not depend straightforwardly on internuclear distances as their magnitudes are greatly influenced by the extent of orbital overlap and covalency. For each mechanism, one has to differentiate between homonuclear and heteronuclear spin–spin interactions. As discussed in more detail below, the various types of interactions can be discerned from each other and addressed selectively using suitable selective NMR averaging methods.

9.2.1 Direct Magnetic Dipole–Dipole Coupling

The Hamiltonian of the direct dipole–dipole interaction (“through-space”) is proportional to the inverse cube of the internuclear distance, providing a straightforward connection to geometric structure. In the limit of first-order perturbation theory, it is given by the expressions [3]

\[
H_{D-homo} = -\left(\frac{\mu_0}{4\pi}\right) \frac{\gamma^2 \hbar^2}{r_{ij}^3} \left(3\cos^2\theta - \frac{1}{2}\right) \left(3\hat{I}_z \hat{J}_z - \hat{J}_z^2\right) \tag{9.2}
\]

\[
H_{D-hetero} = -\left(\frac{\mu_0}{4\pi}\right) \frac{\gamma\gamma_s\hbar^2}{r_{is}^3} \left(3\cos^2\theta - \frac{1}{2}\right) \left(\hat{I}_z \hat{S}_z\right) \tag{9.3}
\]

The orientational dependence is described by the \(3\cos^2\theta - 1\) term where \(\theta\) is the angle between the internuclear distance vector and the magnetic field direction. Dipolar interactions in two-spin systems can be treated straightforwardly by considering the eigenstates whose energies are modified according to a treatment on the basis of first-order perturbation theory. In systems characterized by multiple-spin interactions, this approach is not practical and one specifies an average mean square of the local field (called second moment). The relation to internuclear distance distributions is given by the van Vleck formulae [8], which predict

\[
M_{2homo} = \frac{3}{5} \left(\frac{\mu_0}{4\pi}\right)^2 I(I+1)\gamma^4 \hbar^2 \sum_{i\neq j} r_{ij}^{-6} \tag{9.4}
\]

\[
M_{2hetero} = \frac{4}{15} \left(\frac{\mu_0}{4\pi}\right)^2 S(S+1)\gamma_I^2 \gamma_S^2 \hbar^2 \sum_{S} r_{is}^{-6} \tag{9.5}
\]

for homo- and heteronuclear interactions, respectively.

As described below, both homo- and heteronuclear dipole–dipole couplings can be measured selectively under static conditions using different versions of spin echo decay spectroscopy. It is frequently desirable, however, to measure the strength of magnetic dipole–dipole interactions under high resolution (i.e., under MAS) conditions, in order to obtain the dipolar coupling information in a site-resolved fashion. Magic-angle spinning, however, by its very experimental design, averages the direct homo- and heteronuclear magnetic dipolar interactions to zero. To overcome this dilemma, special dipolar recoupling techniques are available. In the following sections, the most important techniques used for measuring and quantifying direct and indirect magnetic
HETERONUCLEAR EXPERIMENTS

349

dipole–dipole interactions are being reviewed. Thus, methods are available to selectively
measure $M_{2\text{homo}}$ as well as $M_{2\text{hetero}}$ contributions. These values can then be compared
with average values of second moments calculated via (9.4) and (9.5), respectively,
from the distance distributions of any structural scenario or computer-simulated model.
By means of this quantitative comparison, the model can be either corroborated or
discounted.

9.2.2 Indirect Spin–Spin Coupling

Indirect spin–spin coupling proceeds via polarization of bonding electrons linking the
nuclei involved; typically via one, two, or three linkages ($^1J$-, $^2J$-, or $^3J$-coupling, respec-
tively). The relevant Hamiltonian is given by the tensor product

$$\mathcal{H}_J = \hat{I} \vec{J} \hat{S}$$

(9.6)

where $\vec{J}$ is the indirect spin–spin coupling tensor. Its magnitude and anisotropy depend
to a great extent on the symmetry of the electron distribution in the chemical bond,
but also on the sizes of the magnetic moments involved. For a two-spin interaction, the
tensor is generally axially symmetric, and can be split into an isotropic component $J_{\text{iso}}$
and an anisotropic component $\Delta J$. While the anisotropic part is averaged out by magic
angle spinning, the isotropic part produces peak splittings that are frequently observable
in the spectra of crystalline solids. In glasses, such splittings are generally not observable
because they are obscured by line-broadening effects resulting from distribution effects
affecting $\delta_{\text{iso}}$; thus two-dimensional measurements are generally needed to identify
them. Both homo- and heteronuclear spin–spin interactions of the observed nuclei to $n$
nuclei having spin quantum number $I$ yield a peak multiplicity of $\Pi(2nI + 1)$, where
the product comprises all contributions from magnetic nuclei in the sample. In the solid
state, the spectra are influenced both by isotropic and anisotropic $J$-couplings, however,
the anisotropy can be eliminated by MAS.

The magnitudes of the $\vec{J}$ tensor components depend not directly on distance, but
are greatly influenced by the electronic properties and bonding characteristics. DFT
calculations of $J_{\text{iso}}$ values with GAUSSIAN or TURBOMOLE are possible in principle
[9, 10], even though the accuracy is lower than that of magnetic shielding calculations.
Nevertheless, the experimental detection of isotropic indirect spin–spin coupling in
MAS-NMR spectra provides direct evidence of bond connectivity and the observed
peak multiplicity gives information about the number of spins to which the observe-
nuclei are coupled.

9.3 HETERONUCLEAR EXPERIMENTS

9.3.1 Spin Echo Double Resonance

Spin echo double resonance (SEDOR) measures the strength of the heteronuclear dipole–
dipole interactions between two different spin species $I$ and $S$ in an incremented Hahn
spin echo experiment ($90^\circ-t_1-180^\circ-t_1$) conducted on the observed $S$ nuclei [11]. While
this interaction is being refocused by the $\pi$ pulses applied to the observed spins I, this refocusing can be un-done by a $\pi$ pulse applied to the non-resonant S spins at some time during the dipolar evolution period $2t_1$. One then compares the spin echo intensity of the observed nuclei as a function of dipolar evolution time (a) in the absence and (b) in the presence of these recoupling pulses. Experiment (a) produces a decay $F(2t_1)/F_0$, which is largely governed by homonuclear dipole–dipole interactions (see below), while experiment (b) results in an accelerated decay reflecting the contribution from the heteronuclear dipole–dipole interaction. For multi-spin systems, a Gaussian decay is expected, the rate of which is given by the heteronuclear second moment $M_{\text{hetero}}^2$.

$$I(2t_1) = \frac{F(2t_1)}{F_0} \cdot \exp\left(-\frac{2t_1^2 M_{\text{hetero}}^2}{9.7}\right)$$

The first applications of SEDOR to amorphous systems involved spatial proximity studies of boron and phosphorus in compensated semiconductors based on amorphous silicon [12] and the speciation of selenium atoms in P-Se glasses [13]. Later on, $^{23}\text{Na}\{^7\text{Li}\}$ and $^{23}\text{Na}\{^6\text{Li}\}$ SEDOR were applied to investigate the relative spatial distribution of Na$^+$ and Li$^+$ ions in mixed-alkali lithium silicate [14–16], borate [17], and chalcogenide glasses [18]. Recently, this approach has been extended to study Li–F interactions in Li ion conducting oxyfluoride glasses [19]. Figure 9.2 illustrates an application to measure heteronuclear $\{^6\text{Li}\}^7\text{Li}$ dipole–dipole interaction strengths in a sample of $^6\text{Li}$-enriched lithium carbonate. The Hahn spin echo amplitude of the residual $^7\text{Li}$ nuclei is measured as a function of dipolar evolution time $2t_1$ in the absence and the presence of the $^6\text{Li}$ recoupling pulses. An important limitation of the SEDOR sequence is its sensitivity to imperfections of the $\pi$ pulse lengths and resonance offset effects affecting the dephaser nuclei S. The latter issue is particularly serious if S is a quadrupolar nucleus interacting with a local electric field gradient. As pointed out in the preceding chapter, the anisotropy of the nuclear electric quadrupolar interaction produces strong line broadening effects for the non-central Zeeman transitions, resulting in incomplete population inversion for the nuclei contributing to those transitions and hence a weakening of the SEDOR effect. While it is sometimes possible to account for such deviations by calibrating the technique with crystalline model compounds having similar spin dynamics as the system under study, the accuracy of the SEDOR method may be limited to those applications where experimental data are compared to distinct structural scenarios making vastly different predictions.

### 9.3.2 Rotational Echo Double Resonance

The *Rotational echo double resonance* (REDOR) experiment introduces the SEDOR concept into MAS-NMR experiments, affording site-selective heteronuclear dipole–dipole coupling information in high resolution spectra [20]. Figure 9.3 shows a typical pulse sequence used for such purposes [21]. Recoupling is accomplished by 180° pulse trains applied to the I-spins, while the S-spin signal is detected by a rotor-synchronized Hahn spin echo sequence. One measures the normalized difference signal $\Delta S/S_0 =$
Figure 9.2. Measurement of the $^7\text{Li}(^6\text{Li})$ dipolar second moment in isotopically enriched lithium carbonate (95% $^6\text{Li}$), using the SEDOR sequence. Filled squares, F(2$t_1$)/F(0); open triangles, I(2$t_1$)/I(0). The dashed curve is a fit to Eq. 9.7, while the solid curve was calculated with this expression using the $M_2$ value calculated with Eq. 9.5 from the known internuclear distances in lithium carbonate.

(S$_0$ – S)/S$_0$ in the absence (intensity S$_0$) and the presence (intensity S) of the recoupling pulses. A REDOR curve is then generated by plotting $\Delta S/S_0$ as a function of dipolar evolution time NT$_r$, the duration of one rotor period multiplied by the number of rotor cycles.

For isolated two-spin-1/2 pairs, the REDOR curve has universal character and can be directly used to extract the internuclear distance. In contrast, for larger spin-clusters, the REDOR curve depends on the detailed shape and distance geometry of the spin system [22,23]. In glasses, one generally expects a distribution of spin geometries and magnetic dipole coupling strengths, which is a priori unknown. As previously shown, this problem can be circumvented by limiting the REDOR data analysis to the initial curvature, where $\Delta S/S_0 < 0.2$ [2, 23–25]. In this limit of short dipolar evolution times, the REDOR curve is found to be geometry-independent and (for spin-1/2 non-observe nuclei) can be approximated by

$$\Delta S/S_0 = \frac{S_0 - S}{S_0} = \frac{4}{3\pi^2} (NT_r)^2 M_2$$

(9.8)

where the average van-Vleck second moment defined by Eq. 9.5 can be extracted from a simple parabolic fit of the experimental data. Figure 9.3, bottom shows an application to BPO$_4$, a crystalline model compound for borophosphate glasses. In this compound,
Figure 9.3. Top: Timing of a REDOR pulse sequence, showing the evolution of the dipolar coupling Hamiltonian during the rotor cycle [21]. Bottom: Experimental and calculated $^{11}\text{B}^{[31}\text{P}]$ REDOR curve of crystalline BPO$_4$. The dotted curve shows the parabolic approximation.

Each of the boron atoms forms four B–O–P linkages to phosphate units. Equation 9.8 turns out to be an excellent approximation to the theoretically simulated REDOR curve, yielding a dipolar second moment of $14.5 \times 10^6$ rad$^2$/s$^2$ in reasonable agreement with the value ($18.7 \times 10^6$ rad$^2$/s$^2$) calculated from the crystal structure. Other ternary crystalline borophosphates yield a similar level of agreement [26,27]; there appears to be a trend that
slightly underestimates $M_2$ by 10–20%, owing to experimental imperfections (resonance offset effects, non-perfect 180° flip angles. The performance of the sequence can be improved by applying a compensation scheme, that corrects for pulse imperfection and resonance offset effects. In this compensation scheme, a second reference signal $S_D$ is obtained, with an additional $\pi$ pulse applied to the non-observed spins in the middle of the dipolar evolution period [24]). Under perfect conditions, the difference signal $S_0 - S_D$ should be zero, as the extra $\pi$ pulse serves to cancel the recoupling effect. In reality, however, a non-zero difference signal is invariably observed. Simulations show that the magnitude of this extra difference signal produced by deviations of the recoupling pulses from the exact 180° flip angle is approximately equal to the extent to which the REDOR effect is weakened by this imperfection [24]. Hence a compensated REDOR curve can be constructed by taking the sum $(S_0 - S)/S_0 + a(S_0 - S_D)/S_0$, where the scaling factor $a$ has a value near unity, depending on the duty cycle. The $\pi$ pulse lengths for both I and S nuclear species should be as close as possible, as the compensation method only works if both pulses are applied at exactly the same time and for the same duration.

The initial curvature analysis of REDOR data discussed above has the disadvantage that owing to spinning speed limitations, only a few data points may be available for parabolic fitting. This drawback can be overcome by a variation of REDOR, in which the number of rotor cycles is held constant, but the timing of the recoupling $\pi$ pulse is changed systematically during the rotor cycle ("constant time, CT-REDOR", see Figure 9.4) [28,29]. This method is advantageous for systems with very strong magnetic dipole couplings, short spin–spin relaxation times and/or experiments done with low spinning speeds.

### 9.3.3 Rotational Echo Adiabatic Passage Double Resonance

Compared to the S\{I = 1/2\} case, REDOR curves of S-spins coupled to I > 1/2 spins are affected by two additional aspects [30, 31]. First of all, the extent of dephasing of the S nuclei depends on the Zeeman state of the particular I nuclei they are coupled to, reflecting the dependence of the $z$-component of the I magnetic moment on the orientational quantum number. In the presence of nuclear electric quadrupolar interactions, first-order perturbation theory results in a wide spectral dispersion of the non-central Zeeman transitions, rendering coherent $\pi$ recoupling pulse trains ineffective due to resonance offset problems. Then, in the case of large quadrupole splitting of the I spins, only those S nuclei that are coupled to I spins in the central Zeeman levels will give a REDOR response. Both effects can be accounted for with the help of simulations if the quadrupole tensor components are known, and a dipolar analysis is still possible [32]. Alternatively, the rotational echo adiabatic passage double resonance (REAPDOR) method can be used, which recouples the dipolar interaction to the non-observed spins in all of the Zeeman states [33], see Figure 9.5. Here, a long continuous-wave pulse, lasting at least 1/3 of the MAS rotor period, leads to a mixing of I-spin Zeeman states, thereby resulting in more effective dipolar recoupling of the S-spins. In this case, the extent of the dipolar recoupling depends—besides on the magnitude of the dipole–dipole coupling—on the I-spin quadrupolar frequency, the MAS rotor frequency and the amplitude of the applied radio frequency field (expressed as the I-spin nutation frequency).
Based on reliable input data, the effect can be taken into account by simulation, yielding quantitative dipolar coupling information to be compared with experimental data.

### 9.3.4 Cross-polarization

Another common approach for recoupling heteronuclear magnetic dipole–dipole interactions into the MAS Hamiltonian is the cross-polarization experiment [34]. This experiment utilizes the heteronuclear dipole–dipole coupling as a mechanism for transferring magnetization from a spin reservoir of source nuclei (labeled I) to recipient nuclei S, whose signal is then detected. Figure 9.6 shows the pulse sequence involved. In general,
transverse spin magnetization of the source nuclei is created by a $90^\circ$ pulse and spin-locked by applying a strong radiofrequency field along the direction of the magnetization in the rotating frame. During the application of this radiofrequency field, the spin states are now quantized in a direction orthogonal to $B_0$ and the transverse magnetization is forced to precess around this direction with the I-spin nutation frequency $\omega_{1I} = \gamma_1 B_{1I}$. As the spin-locked magnetization is much higher than the value corresponding to the value
of $B_{1I}$, this situation reflects a non-equilibrium state, from which the system seeks to escape via relaxation. This can be accomplished via magnetization transfer to the recipient $S$ nuclei, utilizing magnetic dipole–dipole interactions. For transfer to be possible, the I and S nuclei must have identical precession frequencies in the rotating frame. The S nuclei are irradiated on resonance for a duration (contact time) of several milliseconds, with their radio frequency amplitude $B_{1S}$ chosen according to the Hartmann–Hahn matching condition [35].

$$\gamma_I B_{1I} = \gamma_S B_{1S} \tag{9.9}$$

During the contact time, I-spin polarization is then transferred to the S-spins, whose signal is subsequently detected. The rate of this process is characterized by the cross-relaxation time $T_{IS}$ (see Figure 9.6), which depends on the strength of the heteronuclear magnetic dipole–dipole interactions. Competing relaxation mechanisms involve energy interchange with the lattice (spin lattice relaxation in the rotating frame, characterized by the time constant $T_1\rho$ (see Figure 9.6).

As the dipole–dipole couplings utilized by cross-polarization experiments on inorganic glasses are usually relatively weak, fast MAS modulates the Hartmann–Hahn matching condition, leading to $\gamma_I B_{1I} = \gamma_S B_{1S} \pm n\omega_r$, where $n$ is an integer and $\omega_r$ is the angular rotor frequency. To account for this modulation, one now frequently uses a ramped cross-polarization variant, where the nutation frequency of the I or S nuclear species is systematically stepped up linearly during the contact time period. This important modification has led to significant signal-to-noise gains, particularly in cross-polarization experiments involving source nuclei other than $^1$H.

As the rate of the magnetization transfer depends on the strength of the magnetic dipole–dipole interactions (and hence on spatial proximity), qualitative information about relative internuclear distances can be extracted from systematic cross-polarization experiments as a function of contact time. In a useful two-dimensional version of CPMAS, an incremented evolution period $t_1$ is inserted between the I-spin preparation pulses and the subsequent spin-locking field. In this way, resolved resonances of the source nuclei can be correlated with resolved resonances of the recipient nuclei [36]. To illustrate the utility of such heteronuclear correlation experiments, in connection with variable contact time studies, Figure 9.7 shows a $^{19}$F/$^{11}$B NMR result obtained on a lead fluoroborate glass. The $^{19}$F NMR signal comprises two distinct contributions, at $-108$ and $-50$ ppm versus CFCl$_3$. The minority signal at $-108$ ppm, which is preferentially detected at short contact time, is assigned to F species directly bonded to tetrahedral boron (BO$_{3/2}$F species), whereas the signal near $-50$ ppm comes from F species that are more remote from boron and thus require longer contact times for magnetization transfer [37]. Other applications of cross-polarization and heteronuclear correlation experiments to structural studies of glasses have been recently reviewed by Edén [1].

In many applications, the “source” I nuclei are highly abundant quadrupolar nuclei such as $^7$Li, $^{11}$B, $^{23}$Na, and $^{27}$Al. The fact that such quadrupolar nuclei have usually relatively short $T_1$ values makes them attractive source nuclei for CPMAS experiments. It is important, however, to be aware of some potential complications when using them. As discussed in the literature [38], spin-locking such quadrupolar nuclei under MAS
Figure 9.7. $^{19}\text{F}{}^{11}\text{B}$ heteronuclear correlation experiment of a lead fluoroborate glass. Top: Contact time 200 $\mu$s; preferential detection of the B-bonded F species. Bottom: Contact time 5 minutes, proportional detection of both B-bonded and non-B-bonded F species.
conditions leads to level crossings and mixing of spin states causing very rapid loss of transverse magnetization. The rotating-frame spin-lattice relaxation time $T_1\rho$, which characterizes how long spin-lock can be maintained, depends critically on the strength of the quadrupolar coupling, the nutation frequency, and the rotor speed. With the latter two parameters under the experimenter’s control, it is at first necessary to find those radiofrequency amplitudes with which good I-spin-locking can be accomplished, before the Hartmann–Hahn matching conditions can be adjusted. Finally, the recycle delay to be used for signal accumulation must be adjusted in accordance with the spin-lattice relaxation time $T_1$ of the source nuclei.

### 9.3.5 Connectivity Studies Based on the Detection of Indirect Spin–Spin Interactions

Even though their detection constitutes direct proof of interatomic connectivity, heteronuclear indirect spin–spin interactions have thus far been little utilized for structural studies of glasses. Potentially useful two-dimensional experiments include the heteronuclear J-resolved experiment [39] and correlation spectroscopy based on the detection of heteronuclear double quantum coherences [40,41]. If the isotope with which J-coupling is to be detected has a low natural abundance, the indirect detection of the abundant spin species is often preferable and can be used for HETCOR experiments [42]. Furthermore, this method can be used for spectral editing purposes. Figure 9.8 shows the pulse sequence stimulating heteronuclear double quantum (DQ) coherences [40–42] and an application of this sequence as a heteronuclear double quantum filter for the $^{31}\text{P}$ resonance of a crystalline chalcopyrite alloy of composition $\text{Zn}_{0.875}\text{Cd}_{0.125}\text{GeP}_2$. In these alloys, the P atoms are coordinated to two Ge and two Group-12 atoms. At the composition chosen, two $^{31}\text{P}$ signal contributions are dominant, corresponding to the $\text{PGe}_2\text{Zn}_2$ and the $\text{PGe}_2\text{ZnCd}$ local environments. As illustrated by this figure, the latter resonance can be detected selectively by exciting (and detecting) the $^{31}\text{P}-^{113}\text{Cd}$ heteronuclear double quantum coherence, thereby offering a useful lineshape constraint for the deconvolution of the full spectrum [42]. In recent years, it was shown that this sequence, improved with refined DQ excitation schemes, may have potential for counting Si–O–Al connectivities in aluminosilicate glasses [43–46].

### 9.3.6 Instrumental Considerations and Caveats.

All of the above experiments can be conducted on standard NMR instrumentation constructed during the past two decades. Obviously, the spectrometer must have at least two distinct heteronuclear radio frequency channels that can be separately addressed by the pulse programmer. As commercial spectrometers are usually furnished with a separate $^1\text{H}/^{19}\text{F}$ channel, a three-channel instrument is needed. In addition, probes are necessary, which can be tuned simultaneously at the resonance frequencies of the two heteronuclei involved. The minimum frequency separation amounts to about 30 MHz; at lower values it becomes difficult to accomplish rejection of the frequency of nucleus X in the Y-channel of the probe and vice versa. “Crosstalk” problems of this kind generating a lot of noise are even more serious if both nuclei are pulsed simultaneously (like in
CP) or if the signal of nucleus X must be acquired with high-power Y-decoupling. In our experience, passing the high power rf amplifier output through narrow band pass filters on both sides prior to entering the probe goes a long way toward beating noise problems. If the two frequencies are very close (such as is the case for the combinations $^{31}\text{P}/^{7}\text{Li}$, $^{27}\text{Al}/^{13}\text{C}$ or $^{23}\text{Na}/^{51}\text{V}$, it is possible to conduct the experiment using a modified single-tuned probe that is sufficiently broad-banded to accept both frequencies [47–51].

One important caveat, which applies to the interpretation of heteronuclear second moments $M_{z}^{\text{SI}}$ extracted from either S{I} REDOR or REAPDOR data has to be
pointed out here: in glasses these quantitative dipole coupling data are frequently used to infer the number of “connectivities”, that is, S··I linkages, based on reasonable assumptions (or experimental results from EXAFS, diffraction, or MD simulations) of S··I internuclear distances in either the first or the second coordination spheres. Several examples of such an application are discussed in the “Case studies” below. Because of the through-space mechanism of dipolar coupling, however, bond connectivity is not a pre-requisite for measuring a REDOR effect. The translation of $M_2$ values into bond connectivity values is based on the inherent assumption that the dipolar coupling strength associated with such first or second coordination sphere S··I linkages is much higher than that from through-space interactions at longer distance ranges. We have found this inherent assumption to be generally justified, also in view of the $r^{-6}$ dependence of second moment values. More rigorous information about bond connectivities comes from heteronuclear J-based spectroscopic methods such as those discussed in Section 3.5.

### 9.4 HOMONUCLEAR EXPERIMENTS

#### 9.4.1 Static Spin Echo Decay Spectroscopy

Homonuclear magnetic dipole–dipole interactions can be measured selectively by Hahn spin echo decay spectroscopy, using the pulse sequence shown in Figure 9.9 [52]. For a spin-1/2 system the normalized echo intensity $I/I_0$ is only influenced by homonuclear dipole–dipole interactions, while all of the other abovementioned types of interactions

![Figure 9.9](image-url)  
**Figure 9.9.** Timing diagram of the spin echo decay method. The spin echo amplitude is measured as a function of total dipolar evolution time $2t_1$. 
plus the heteronuclear dipole–dipole couplings are being refocused. For a multi-spin system, one observes a Gaussian decay as a function of evolution time $2t_1$,

$$\frac{I(2t_1)}{I_0} = \exp \left[ -\frac{M_{2\text{homo}}}{2}(2t_1)^2 \right]$$

(9.10)

affording a reliable measurement of the homonuclear van Vleck second moment $M_{2\text{homo}}$.

The method has been validated by measurements on crystalline model compounds [53] and widely applied for examining the spatial distribution of $^{31}$P spins ($I = 1/2$) in a variety of non-oxide glasses [54–58]. Of course it is necessary that dynamic motional narrowing effects are absent. Any change in resonance frequency for a given nucleus during the dipolar evolution time $2t_1$ because of nuclear motion or reorientation will accelerate the spin echo decay and thus not provide valid information upon the structure of the material. As pointed out in Reference 53, the method is quantitatively reliable only if the magnitude of the dipole–dipole interaction (in Hz) is smaller than the difference in resonance frequency of the participant nuclei. This situation is usually the case in glasses because a wide chemical shift distribution exists. As a result, the resonance frequencies of neighboring nuclei are rather different, and the spin-exchange term that is usually part of the homonuclear dipolar Hamiltonian can be neglected. The homonuclear dipolar Hamiltonian then takes form $\mathbf{H}_D \sim \mathbf{I}_1 \cdot \mathbf{I}_2$, which is analogous to that present in heteronuclear dipole couplings. As a consequence, the pre-factor $3/5$ in Eq. 9.4 needs to be replaced by the pre-factor $4/15$.

It was also possible to extend this method to the study of certain quadrupolar nuclei such as $^{23}$Na, where the first-order quadrupolar splitting is sufficiently large such that the Hahn spin echo pulse sequence selectively acts on the central $1/2 <-> -1/2$ Zeeman transition [59,60]. For the case of spin-3/2 nuclei, $M_2$ is given by [60]

$$M_2 = 0.9562 \left( \frac{\mu_0}{4\pi} \right)^2 \gamma^4 \hbar^2 \sum_j r_{ij}^{-6}. \tag{9.11}$$

The validity of Eq. 9.11 was confirmed experimentally for homonuclear $^{23}$Na–$^{23}$Na dipole–dipole interactions in crystalline solids, for which the $M_2$ values are readily calculable from the known crystal structures [60]. Comprehensive studies of $^{23}$Na spin echo decays as a function of ion concentration have been published for a wide range of binary oxide glasses (see Reference 61 and Section 9.5). Unfortunately, significant deviations from Gaussian decays (Eq. 9.10) are often observed, particularly if the observed nuclei are quadrupolar. These deviations reflect the influence of higher moments contributing to the description of the echo decay. To minimize such additional interferences, the data range for quantitative analysis is frequently curtailed to just the initial decay in the limit of short evolution times, where the second moment dominates. There are a number of other caveats. The $180^\circ$ pulse length has to be well-defined, that is, $\mathbf{H}_Q \gg \mathbf{H}_Z$ (selective excitation of the central transition, Eq. 9.11) or $\mathbf{H}_Q \gg \mathbf{H}_Z$ (non-selective excitation of all the Zeeman transitions) must hold; in the second case, an equation different from (Eq. 9.11) has to be used [59]. To test whether the regime of validity for this sequence is
realized in a given situation, a nutation experiment yielding clear sinusoidal behavior of signal amplitude on pulse length is expected. In addition, erroneous results are obtained, if the observed nuclei I are coupled to another spin species S, which are strongly coupled among themselves and hence undergo rapid spin state fluctuations compromising the formation of an echo. Finally, for nuclei with spin quantum number \( > \frac{3}{2} \), the method is less well-tested and presumably also less reliable.

9.4.2 Homonuclear Dipolar Recoupling Experiments

To re-introduce homonuclear dipole–dipole couplings into the MAS Hamiltonian, many different approaches exist [62–68], using the build-up of zero-quantum (ZQ) or double-quantum (DQ) coherences via direct or indirect dipole–dipole interactions. To date, the large majority of applications to glasses have been of a qualitative nature, using a variety of two-dimensional NMR approaches for correlating resonances on the basis of the spatial proximity of the nuclei associated with them. Most recently, second-moment information at the same level of quantitative detail has become available by either DQ excitation spectroscopy [68] or the DQ-DRENAR experiment (Double-Quantum-based Dipolar Recoupling Effects Nuclear Alignment Reduction; see Section 9.4.2.1).

9.4.2.1 Two-Dimensional Correlation Methods Based on ZQ or DQ Coherences

A large number of dipolar recoupling methods utilize zero-quantum (ZQ) or double quantum (DQ) coherences for spectroscopically correlating resonances of dipolar-coupled spins. Zero-quantum coherences are the result of spin diffusion (coupled “up and down” transitions) which can occur even under MAS conditions. The simplest probe of this effect is the radio frequency driven recoupling (RFDR) experiment shown in Figure 9.10a [65]. Following excitation by a 90° pulse, the spins are frequency-labeled during the evolution time \( t_1 \). The subsequent 90° pulse terminates the evolution and stores the magnetization along the magnetic field direction. During the mixing time \( t_m \), spin diffusion among spatially close nuclei occurs, and the corresponding frequency exchange picked up during the detection period \( t_2 \) (following the final 90° pulse) manifests itself as a cross-peak in the corresponding two-dimensional correlation plot. The spin diffusion during \( t_m \) is enhanced by coherently applying trains of 180° pulses. Figure 9.10b shows a simple application to the ion conductor Ag\(_7\)P\(_3\)S\(_{11}\). This compound has three crystallographically distinct sites, giving rise to the resolved resonances A, B, and C. A represents an isolated PS\(_4^{3-}\) ion, while B and C are the signals of a P\(_2\)S\(_7^{4+}\) group. In the RFDR spectrum, the homonuclear magnetic dipole–dipole coupling between the two P atoms of this pyrothiophosphate group results in cross peaks between resonances B and C. As discussed in Reference 1, applications of this technique to glasses have concentrated on \(^{31}\)P connectivities in various phosphate glass systems.

Alternatively, the excitation of homonuclear double-quantum (DQ) coherences can be used [66]. If the individual nuclei have resonance frequencies \( \omega_{L1} \) and \( \omega_{L2} \), the double quantum coherence oscillates with the sum frequency of the spins \( \omega_{L1} + \omega_{L2} \) during an evolution period \( t_1 \). Subsequently, it is reconverted to observable single-quantum coherence by applying an analogous de-excitation scheme. For detection, a 90° pulse
Figure 9.10. Top: The RFDR sequence with two $\pi/2$-pulses sandwiching the $t_1$ evolution period. The mixing period is comprised of rotor-synchronized $\pi$-pulses. The third $\pi/2$-pulse produces transverse magnetization. Bottom: $^{31}$P RFDR spectrum of the ion conductor Ag$_7$P$_3$S$_{11}$. The two crystallographically distinct phosphorus sites B and C belonging to the P$_2$S$_{7}^{4-}$ group give rise to a cross-peak indicating the presence of homonuclear magnetic dipole–dipole coupling between them. The weaker dipolar couplings between more distant P atoms are not observed under the experimental conditions used.
Figure 9.11. $^{31}$P Homonuclear single quantum (SQ)/ double quantum (DQ) NMR correlation spectrum of the ion conductor $\text{Ag}_7\text{P}_3\text{S}_{11}$. The two crystallographically distinct phosphorus sites B and C belonging to the $\text{P}_2\text{S}_7^{4-}$ group give rise to the strongest cross-peak owing to the strongest homonuclear magnetic dipole–dipole coupling between them. Weaker couplings are also observed and give rise to the correlation peaks A–A, A–B, A–C, B–B, and C–C.

Figure 9.11 illustrates an application to $\text{Ag}_7\text{P}_3\text{S}_{11}$. The strongest magnetic dipole–dipole coupling occurring within the pyrothiophosphate group results in the strongest cross-peak intensity. In addition, the weaker dipolar couplings (A–A, A–B, A–C, B–B, and C–C) are also being observed.

9.4.2.2 Second Moment Measurements

The goal of quantifying homonuclear second moments in REDOR-analog experiments has been realized only recently. A viable strategy is to measure the rate with which DQ coherences are excited by suitable schemes. Indeed, experiments on a number of crystalline thiophosphates revealed that the rate of such build-up curves is correlated with the homonuclear dipole–dipole coupling strengths. However, accurate second moment information is not available by this technique, because the build-up is superimposed by a decay caused by the creation of higher order coherences. In addition, the intensities are often limited by low DQ excitation efficiencies, which are greatly affected by resonance offset effects. Nevertheless, a rough distinction between different kinds of thiophosphate binding was possible. In addition, the conversion of lithium pyrothiophosphate glass with P–S–P linkages to $\text{Li}_4\text{P}_2\text{S}_6$ (containing a phosphorus–phosphorus bond) upon crystallization could be demonstrated by this method [71]. Recently, the DQ-spin counting approach has been greatly improved by including a constant-time approach [72], introducing super cycles and normalizing the DQ intensities, taking advantage of the fact that the DQ Hamiltonian changes sign upon
90° phase shifting [68]. Using this improved method, Saalwächter et. al. were able to measure accurate site-resolved second moments from initial build-up rates in MgP₄O₁₁ [68]. Based on the successes of this method, applications to glasses can be envisioned in the future. Recently, a different variant of this principle has been implemented, where no DQ coherence intensities are measured, but rather a diminution of z-magnetization based on the excitation of DQ coherences [73, 74]. In this method, recoupling is accomplished in the form of an effective DQ Hamiltonian created by a symmetry-based POST-C⁷ sequence consisting of two excitation blocks [70], attenuating the signal (intensity S'). For comparison, a reference signal S₀ with the dipolar recoupling absent is generated by shifting the phase of the second block by 90° relative to the first block. As in REDOR, the homonuclear dipole–dipole coupling constant can then be extracted from a plot of the normalized difference signal (S₀ − S')/S₀ versus dipolar evolution time. Figure 9.12 illustrates this method, which has been dubbed DQ-DRENAR (Double-Quantum-based Dipolar Recoupling Effects Nuclear Alignment Reduction) [74]. For short dipolar evolution times (usually ΔS/S₀ < 0.5), a parabolic approximation analogous to Eq. 9.8 in the heteronuclear case is applicable.

\[
\frac{S_0 - S'}{S_0} = \frac{0.86\pi^2}{15} \sum_{j<k} b_{jk}^2 (NT_r)^2 \tag{9.12a}
\]

where the term \(\sum_{j<k} b_{jk}^2\) is directly proportional to the van Vleck dipolar second moment. In the case of an effectively heteronuclear interaction (with the exchange term I⁻I⁺ quenched by large differences in resonance frequencies) one obtains

\[
\frac{S_0 - S'}{S_0}_{(t=NT_r)} = 0.0717M_2(NT_r)^2 \tag{9.12b}
\]
Figure 9.13. Top left: DQ-DRENAR results on Ag$_7$P$_3$S$_{11}$ [74]. Top right: Results on some phosphate glasses: squares and circles, data for Q$^2$ and Q$^1$ units in (Na$_2$O)$_{0.6}$(P$_2$O$_5$)$_{0.4}$ glass (inset, spectra for measurement of $S_0$ and $S'$ at $NT_r = 0.89$ ms). Up-triangles, Q$^0$ units in gel-prepared AlPO$_4$; down-triangles, Q$^0$ units in 0.5AlPO$_4$-0.5SiO$_2$ glass [73]. Solid curves represent parabolic fits to the initial data range. Bottom left: Experimental results on (Ag$_3$PO$_4$)$_x$(AgI)$_{1-x}$ glasses (0 $\leq$ $x$ $\leq$ 1) and crystalline Ag$_3$PO$_4$. Right: Linear dependence of the average mean squared dipolar coupling constant on phosphate concentration as expected from a random spatial distribution of the phosphate ions [77].

Figure 9.13 shows an application of this technique to Ag$_7$P$_3$S$_{11}$. The dipolar dephasing curves of the PS$_4^{3-}$ and P$_2$S$_7^{4-}$ groups are well-differentiated in this experiment, yielding dipolar second moment values in close agreement with those calculated from Eq. 9.4. Also this Figure illustrates the applicability of this method to phosphate-based glasses. The data obtained for a binary sodium phosphate glass of composition 60Na$_2$O-40P$_2$O$_5$ clearly reveal the ability of homonuclear REDOR of differentiating between the different types of Q$^{(n)}$ species on the basis of their different numbers of P–O–P linkages. In addition, data are shown for a mesoporous sol-gel glass of composition 0.5AlPO$_4$-0.5SiO$_2$. This material had been previously conjectured, but never proven, to be phase separated on the nanoscale [75]. The identical second moments, measured for this material and for pure glassy AlPO$_4$ provides strong evidence for this assertion. Quantitative $^{31}$P dipolar coupling measurements via DRENAR or DQ-build-up curves have been also reported for various bioactive silicate glasses containing phosphate species [76],
HOMONUCLEAR EXPERIMENTS

Figure 9.14. Top: Two-dimensional homonuclear J-resolved spectroscopy. Following the preparation by a $\pi/2$ pulse, evolution takes place under the influence of homonuclear J-coupling during the evolution time $t_1$. Chemical shift and heteronuclear J-coupling evolution are refocused by the central $\pi$ pulse, and direct dipolar couplings are averaged out by MAS. The evolution is stopped by the second $\pi/2$ pulse, while the third $\pi/2$ pulse is used for detection. During the acquisition period $t_2$ the regular MAS Hamiltonian is effective. Bottom: Two-dimensional-J-resolved spectroscopy of Ag$_7$P$_3$S$_{11}$.

as well as ion-conducting Ag$_3$PO$_4$-AgI glasses [77] (see Figure 9.13, bottom), and the dipole–dipole coupling strengths have been related to the spatial distribution of the phosphate species. Overall, these results indicate the suitability of DQ-based methods for characterizing the spatial spin distribution and for detecting and quantifying the extent of nanoscale segregation and phase separation processes in glasses, glass-ceramics, and nanocomposite materials.

9.4.2.3 Recovery of Homonuclear Indirect Spin–Spin Interactions

The detection of indirect spin–spin interactions is valuable as it usually constitutes direct proof of bond connectivity, rather than mere spatial proximity. Two pulse sequences that have been quite useful for the structural analysis of glasses are homonuclear J-resolved spectroscopy (Figure 9.14) and refocused INADEQUATE (Figure 9.15). J-resolved
spectroscopy combines the two types of selective averaging afforded by MAS and the Hahn spin echo, in a two-dimensional experiment [78, 79]. In glassy solids, the MAS-NMR peak is generally inhomogeneously broadened by distributions of isotropic chemical shifts, which makes it impossible to resolve peak splitting produced by indirect spin–spin interactions in directly acquired spectra. This problem is solved by conducting a Hahn spin echo in the indirect \( t_1 \) dimension of a two-dimensional NMR experiment: at the end of each evolution period \( t_1 \), the inhomogeneous broadening is refocused so that the amplitude and phase of the signal are exclusively governed by the strength of the isotropic J-coupling. Thus, the corresponding signal observed after Fourier-transforming the data acquired along the time domain \( t_1 \) allows a selective measurement of the homonuclear indirect dipole–dipole coupling constant. Figure 9.14 shows the application to crystalline Ag\(_7\)P\(_3\)S\(_{11}\), which is an excellent compound for optimizing the experimental set-up. The two crystallographically distinct P atoms of the P\(_2\)S\(_7\)^{4-} group are unambiguously identified by doublets in the second dimension of the two-dimensional spectrum. From the individual cross-sections, the indirect spin–spin coupling constant is available. Recently, two-dimensional homonuclear through-bond correlation and J-resolved spectroscopy results were successfully applied for the study
of P–P and P–Se–P connectivities in P–Se glasses [80], extending earlier work based on through-space dipolar spectroscopy [54, 55].

An alternative method of recovering indirect spin–spin interactions is the INADEQUATE experiment (Figure 9.15) [81]. The $90^\circ - \tau - 180^\circ - \tau - 90^\circ$ pulse block utilizes the homonuclear indirect magnetic dipole–dipole interactions (“J-couplings”) for creating double quantum coherences between the nuclei involved. For maximum DQ intensity, the preparation time $2\tau$ should be equal to $1/2J$, where $J$ is the isotropic spin–spin coupling constant. In practice, frequently smaller values are used as a good compromise between maximum DQ yield and irreversible signal decay during $\tau$ due to spin–spin relaxation. Following a short evolution time $t_1$, during which they evolve under their combined resonance offsets, the DQ coherences are transferred to observable magnetization, which is then detected via a rotor-synchronized Hahn spin echo, while all single quantum coherences are completely eliminated by phase cycling. Figure 9.15 illustrates the application to Ag$_7$P$_3$S$_{11}$, leading to the selective detection of the P$_2$S$_7^{4-}$ units, while the PS$_4^{3-}$ resonance is removed by the double quantum filter. Note the absence of all the other cross peaks that were observable in Figure 9.11 (peaks A–A, B–B, A–B, A–C, and C–C) as a result of DQ coherence build-up effected by direct dipole–dipole couplings. In the INADEQUATE spectrum, only the B–C peak is visible as DQ coherence build-up occurs selectively through the indirect spin–spin interactions, making this method a very powerful tool for proving through-bond connectivity in glasses. Indeed, INADEQUATE has been widely applied to phosphate glasses, for creating two-dimensional P–O–P connectivity maps between the various phosphate units linked to each other; this has been reviewed in Reference 1. If a singular short value of $t_1$ is used (typically $\sim 10 \mu s$), the experiment can also be used in a one-dimensional mode and used for double quantum filtering.

In recent years, dipolar and J-based homonuclear recoupling methods utilizing the stimulation of DQ coherences have been extended successfully to quadrupolar nuclei [82]. Successful applications to glasses have been comprehensively reviewed by Edén [1]. Particularly noteworthy is recent progress leading to the detection of Al–O–Al connectivities in various aluminosilicate and aluminate glasses [83–86], giving insights about the structural role of alumina as an intermediate oxide, which can act both as a network former and a network modifier species.

### 9.4.3 Instrumental Considerations and Caveats

From the experimental viewpoint, an important limitation regarding the feasibility of these two-dimensional experiments is the spin–spin relaxation time $T_2$. In many cases, $T_2$ values are shortened by strong homonuclear dipole–dipole interactions and/or dynamical processes. In addition, pulse sequences based on windowless pulsed excitation of DQ coherences (such as the DQ-DRENAR technique) require spectrometer hardware with short switching times ($\sim 50$ ns) to function properly. Quite generally, chemical shift anisotropy and resonance offset effects tend to interfere with the efficiency of two-dimensional NMR pulse sequences and seriously affect the quantification of dipole–dipole interactions. For these reasons, fast spinning ($\sim 30$ kHz), hard pulses (nutation frequencies near 100 kHz), and moderately weak external magnetic field strengths (4.65
or 7.05 T) present ideal conditions for such measurements, at least when spin-1/2 nuclei are involved.

Finally, it must be stated, that the two-dimensional NMR methods reviewed here are only a small group within a plethora of techniques available for homonuclear recoupling. This field is still under active development and new pulse sequences appear regularly. The design of these methods and the analysis of experimental results obtained with them are greatly aided by the availability of program packages that calculate the behavior of the spins under the influence of the external and internal interaction Hamiltonians using standard time-dependent perturbation theory. Especially noteworthy is the “SIMPSON” program, which enables the simulation of complex NMR experiments under the precise conditions used in the spectrometer [87]. This freeware has proven invaluable in the analysis of complex experiments and profoundly influenced NMR research in many laboratories.

9.5 CASE STUDIES

9.5.1 Spatial Distributions of Mobile Ions in Alkali Silicate and Borate Glasses

Application of $^{23}$Na spin echo decay spectroscopy to a wide range of oxide glasses provided detailed quantitative information about the spatial distribution of sodium ions in various binary oxide glass systems [61]. Figure 9.16 compares the results obtained

![Figure 9.16](image_url)
for sodium silicate and sodium borate glasses. In the silicates, a more or less constant value of $M_2 = 4.5 \times 10^6$ rad²/s², observed at Na concentrations below $1.5 \times 10^{28}$ m⁻³ (20 mole% Na₂O), indicates significant clustering of the sodium ions. In contrast, much smaller $M_2$ values are observed in the sodium borate glass system, where $M_2$ ($^{23}$Na–$^{23}$Na) is found to be proportional to the sodium number density, consistent with a random ion distribution in space. The inhomogeneous distributions of alkaline ions in silicate glasses are consistent with the proposal of ion-conducting channels, maintaining the possibility of long-range ion transport even at relatively low cation contents [88]. In contrast, a statistical mobile ion distribution results in very large average jump distances at low cation contents, making ion transport improbable. On this basis it is now possible to understand why at a given number density the ionic conductivities of alkali silicate glasses are significantly larger than those of the corresponding alkali borate glasses, as reported in Reference 89.

In principle, the same approach could be used to measure $^7$Li–$^7$Li dipolar second moments in the analogous lithium oxide-based glass systems. Owing to the much weaker $^7$Li nuclear electric quadrupolar interactions, very soft $^7$Li $\pi$ pulses have to be used in this case, to avoid excitation of the outer Zeeman transitions. While progress in this direction has been recently reported [90], a suitable alternative is to conduct a heteronuclear experiment, using $^7$Li{${^6}$Li} SEDOR on $^6$Li-enriched glasses [91]. Figure 9.17 compares experimental results for a lithium silicate and a lithium borate glass with comparable lithium oxide contents (10 mol%) and a $^6$Li enrichment level of 95%. Clearly, the $^7$Li spins in the silicate glass dephase much more rapidly in the dipolar field of the surrounding $^6$Li spins, indicating much stronger dipolar interactions that in the borate glass. Systematic studies of the dependence of $M_2$ on the lithium content in these glasses show completely analogous results to the situation in Figure 9.16, consistent with lithium clustering in the silicate, but not in the borate glass systems.

It is important to realize that any kind of clustering affecting the spatial distribution of cations must be accompanied by analogous clustering of the charge-compensating anions. In alkali silicate glasses with relatively low alkali oxide contents (< 33 mole %) these anions are the non-bridging oxygen atoms associated with the Q(3) units. Cation clustering thus implies also preferred associations among the Q(3) species as proposed by the “modified random network model” (MRN) based on molecular dynamics simulations [88]. The scheme of Figure 9.18, bottom, suggests that the modifier cations are concentrated in cluster regions and coordinated primarily by non-bridging oxygen atoms [92], resulting in the formation of “ion-conducting channels” at higher concentrations [93]. Such an arrangement implies that the $^{29}$Si–$^7$Li dipolar interactions are significantly stronger for the anionic Q(3) sites than for the neutral Q(4) sites.

This hypothesis can be probed by measuring the magnetic dipole–dipole interactions between the nuclei associated with the network formers and those of the network modifiers. Thus, Figure 9.18 shows $^{29}$Si{${^7}$Li}REDOR data of lithium silicate glasses containing less than 20 mole% Li₂O [92]. While the Q(3) units show a substantial REDOR effect, the signal of the Q(4) units is essentially unaffected by $^7$Li irradiation, indicating that bridging oxygen atoms connecting between two Q(4) units make essentially no contribution to the local Li environment. Thus the Q(4) species reside in spatial regions that are largely cation-depleted, consistent with the known tendency of lithium
Figure 9.17. Top: $^7$Li-$^6$Li SEDOR measured on (Li$_2$O)$_{0.1}$-(SiO$_2$)$_{0.9}$ glass (top) and (Li$_2$O)$_{0.1}$-(B$_2$O$_3$)$_{0.9}$ glass (middle). Both glasses have a $^6$Li/$^7$Li isotope ratio of 9:1. The Hahn spin echo amplitude of the residual $^7$Li nuclei is measured as a function of dipolar evolution time $2t_1$ in the absence (solid symbols) and the presence (open symbols) of the $^6$Li recoupling pulses. The dotted curves are fits to the experimental data using Eq. 9.7. Bottom: Dipolar second moment $M_2(^6$Li-$^7$Li) measured via $^7$Li-$^6$Li SEDOR in lithium silicate and lithium borate glasses as a function of cation number density.
Figure 9.18. Top: Site-resolved $^{29}\text{Si}(^{7}\text{Li})$ REDOR data on a lithium silicate glass containing 15 mole% Li$_2$O. Middle: Dependence of $M_{2}(^{29}\text{Si}(^{7}\text{Li}))$ for the $Q(3)$ and $Q(4)$ units on lithium oxide content $x$ in the (Li$_2$O)$_x$(SiO$_2$)$_{1-x}$ glass system. Bottom: Schematic illustrating lithium clustering in lithium silicate glasses, bringing multiple Li ions into proximity of multiple $Q(3)$ units.
silicate glasses to phase-separate. By combining the $Q^{(3)}$–Li and $Q^{(4)}$–Li pair distribution functions $f_{\text{SiLi}}(r)$ extracted from complementary MD simulations with these NMR results new information is available about the structural organization of the lithium-rich nanophase. Based on the average $Q^{(3)}$–Li distances determined from the maxima in these curves ($\sim 318$ pm), we can estimate the number of Li nearest neighbors to a $Q^{(3)}$ silicon unit from the experimental $M_2$ values. Thus, taking $r_{\text{SiLi}} = 318$ pm as the relevant average $Q^{(3)}$–Li closest distance in the $x = 0.1$ glass, each closest lithium neighbor would—on average—produce a contribution of $3.3 \times 10^6$ s$^{-2}$ to $M_2^{(29\text{Si}\{^{7}\text{Li}\})}$. Based on the experimental $M_2$ values near $11 - 12 \times 10^6$ rad$^2$/s$^2$ and considering that these values also include minor contributions from more remote $^{7}\text{Li}$ spins, we can conclude that the $Q^{(3)}$ units are surrounded by three closest lithium ions. Independent confirmation for the model illustrated in Figure 9.18 comes from a study of the dipole–dipole interactions among the lithium spins, studied by $^{7}\text{Li}\{^{6}\text{Li}\}$ SEDOR [91]. The limiting $M_2^{(7\text{Li}\{^{6}\text{Li}\})}$ value near $10 \times 10^6$ rad$^2$/s$^2$ measured at low lithium contents (see Figure 9.17) is quantitatively consistent with the presence of four lithium ions in the second coordination sphere at an average Li-Li distance of 273 pm [61].

Analogous results have been obtained for sodium silicate glasses [94]. Again, the combined analysis of $^{23}\text{Na}$ spin echo decay spectroscopy and $^{29}\text{Si}\{^{23}\text{Na}\}$ REDOR experiments indicates that the sodium arrangement is highly non-statistical, with large and constant dipolar second moments at low Na concentrations. In contrast, REDOR results on sodium borate glasses reveal a strikingly different picture [94]. In this case, the neutral species are trigonal BO$_{3/2}$ units and the anionic species are four-coordinate BO$_{4/2}^-$ species. The $^{11}\text{B}$ resonances of both structural units are nicely resolved by MAS, thereby facilitating site-resolved $^{11}\text{B}\{^{23}\text{Na}\}$ REDOR measurements. Figure 9.19, top, shows a typical REDOR curve: Clearly, the extent of dephasing is rather similar for both types of boron structural units. In agreement with the conclusions from Figure 9.16, this result argues strongly against cation clustering in sodium borate glasses. With increasing sodium content, the $M_2$ values characterizing the $^{23}\text{Na}^{\text{11}}\text{B}$ dipole–dipole interactions for the BO$_{3/2}$ groups increase linearly (Figure 9.19, bottom), consistent with a random distribution. In contrast, the $M_2^{(23\text{Na}^{\text{11}}\text{BO}_{4/2}^-)}$ data approach a constant “baseline” value as expected for isolated Na$^+$–BO$_4^-$ charge compensation pairs. The second moment analysis indicates that the average Na–B distance is near 340 pm [95].

### 9.5.2 Connectivity Distribution in 70 SiO$_2$-30 [(Al$_2$O$_3$)$_x$(P$_2$O$_5$)$_{1-x}$] Glasses

Advanced dipolar NMR methods have been successfully applied to characterize the connectivity distribution in glasses with the composition 70 SiO$_2$-30 [(Al$_2$O$_3$)$_x$(P$_2$O$_5$)$_{1-x}$] [96]. The $^{31}\text{P}$ and $^{27}\text{Al}$ magic-angle spinning NMR data are highly sensitive to the P/Al ratio suggesting that there are clear Al–O–P connectivity preferences as might be expected based on bond valence considerations. At low phosphorus contents (e.g., in glasses with Al/P ratios > 1) the MAS-NMR spectra reveal a constant local phosphorus environment with parameters similar to those of amorphous AlPO$_4$ (prepared by sol-gel methods) [97]. The $^{31}\text{P}$ spin echo decay data (Figure 9.20) show, however,
Figure 9.19. $^{11}\text{B}^{(23}\text{Na})$ REDOR results on sodium borate glasses. Top: Site-resolved REDOR data on trigonal and tetrahedral boron species. Bottom: Site-selective $M_2^{\text{B-Na}}$ values extracted from these data as a function of sodium oxide content. (From Reference 95).
Figure 9.20. Static $^{31}$P NMR spectra (top) and spin echo decay (bottom) of glasses in the system 70 SiO$_2$-30 [(Al$_2$O$_3$)$_x$(P$_2$O$_5$)$_{1-x}$]. (From Reference 96).
very low $M_2(\text{^31P-^31P})$ values at low P content and a linear increase with increasing P content. These results (including the comparison with the spin echo data measured on the amorphous AlPO$_4$) indicate that despite the Al–O–P connectivity preference, the orthophosphate species are widely dispersed and do not form AlPO$_4$-like clusters in this compositional domain. In glasses with compositions exceeding the Al/P ratio of unity ($x > 0.15$), the strength of the $\text{^31P-^31P}$ dipole–dipole coupling remains more or less constant. In this compositional domain, both AlPO$_4$-like environments as well as metaphosphate ($Q^2$)-like environments with P–O–P linkages are present. As both species are characterized by comparable $\text{^31P-^31P}$ interaction strengths, no strong compositional change is observed here.

The extent of P–O–Al connectivity in this glass system was extracted from $^{27}\text{Al}\{\text{^31P}\}$ REDOR and $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR experiments. The average number of P atoms linked to aluminum, $n_p(\text{Al})$, is estimated by comparing the $M_2(\text{^{27}Al\{^31P\}})$ values to that measured ($4.7 \times 10^6$ rad$^2$/s$^2$) for sol-gel prepared AlPO$_4$ glass, in which each aluminum atom is tetrahedrally surrounded by four P atoms. For the low-aluminum glasses (Al/P < 1), these $M_2$ values are of similar magnitude, albeit always by a factor $\beta = 0.8$ to 0.85 smaller, suggesting that $n_p(\text{Al}^{IV})$ always remains somewhat below the maximum value of four. In a similar vein, the $M_2(\text{^{27}Al\{^31P\}})$ values measured for the Al$^V$ and Al$^VI$ species are comparable to, but somewhat lower than those measured in ternary aluminophosphate glasses with Al/P ratios < 1 [98]. Assuming that the same scaling factor $\beta$ applies for the Al$^V$ and Al$^VI$ species in this composition domain as determined for the Al$^{IV}$ species, we can estimate $n_p(\text{Al})$ from the expression

$$n_p(\text{Al}) = (f(IV) \times 4 + f(V) \times 5 + f(VI) \times 6) \times \beta$$

where $f(IV)$, $f(V)$, and $f(VI)$ represent the fractional contributions of the various aluminum coordination states, as determined via $^{27}\text{Al}$ MAS-NMR peak integration. For glasses with Al/P > 1, no such site-resolved second moment information is available; thus $n_p(\text{Al})$ is approximated by the formula

$$n_p(\text{Al}) = 4 \times M_2(\text{^{27}Al\{^31P\}_exp}) / M_2(\text{^{27}Al\{^31P\}_AlPO4})$$

Analogously the average number of Al atoms linked to phosphorus, $n_{\text{Al}}(\text{P})$, can be extracted from $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR experiments (see Figure 9.21). While in this case no second moment analysis is possible, $n_{\text{Al}}(\text{P})$ can be estimated by interpolating the simulated REAPDOR curves for 0 < $n$ < 4, so as to make a satisfactory fit to the experimental data. Following this approach, $n_{\text{Al}}(\text{P})$ is close to one in the sample with $x = 5\%$, and about 2.3 for the sample with $x = 10\%$. For higher $x$ values, $n_{\text{Al}}(\text{P})$ remains approximately constant close to 3, that is, distinctly below the number 4 expected for AlPO$_4$ glass. Figure 9.21 illustrates that the REAPDOR dephasing of the latter reference material is indeed significantly stronger than for any of the present glasses. The bottom of this figure summarizes the total numbers of P–O–Al linkages, $n_{\text{P-O-Al}}$, obtained either by multiplying $n_p(\text{Al})$ with the aluminium content $2x$, or by multiplying $n_{\text{Al}}(\text{P})$ with the phosphorus content $2 \times (30 - x)$. Note that these values, obtained via two independent experiments, are in excellent agreement with each other, thereby validating the above
Figure 9.21. Top and middle: $^{31}$P($^{27}$Al) REAPDOR curves for the $\text{Al}_2\text{O}_3:$(30-x)$\text{P}_2\text{O}_5:70\text{SiO}_2$ glasses. The experimental data are compared with simulations based on P interacting with one, two, and three $^{27}$Al neighbors (two-spin, three-spin, and four-spin system, respectively). Experimental data for glassy sol-gel-prepared AlPO$_4$ glass are also included. Bottom: Total number of P–O–Al linkages $n_{\text{P-O-Al}}$ as extracted from $^{27}$Al($^{31}$P)REDOR (circles) and $^{31}$P($^{27}$Al) REAPDOR analysis (open triangles). Solid curves illustrate the prediction from the extreme aluminum phosphate cluster scenario. See plate section for a color version of this figure. (From Reference 96).
Figure 9.22. One-dimensional $^{31}$P refocused INADEQUATE (right) and $^{31}$P single-pulse MAS-NMR spectra (left) of glasses in the system $[\text{K}_2\text{O}]_{1/3}[(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}]_{2/3}$, measured at 7.1 T and MAS-rotor frequencies of 14.0 kHz. Spinning sidebands have been omitted. Experimental spectra are displayed in black, their total fits in red, and the individual fitting components are shown as dashed lines [110].

analysis. In Figure 9.21, these values are compared to a clustering scenario, which maximizes the number of Al–O–P linkages. It is evident that the numbers $n_{\text{P-O-Al}}$ are always consistently lower than those predicted by the cluster scenario, suggesting that the glass structure is more homogeneous than that predicted from an AlPO$_4$ segregation scenario.

Studies of this kind, addressing the structural role and connectivity of aluminum species, have been reported for numerous other Al-containing phosphate glasses, prepared either via melt-cooling or sol-gel methodology [97–102]. In all cases, a distinct Al–O–P connectivity preference has been noted. As described in detail in Reference 1, in the case of the system 50K$_2$O–xAl$_2$O$_3$–(50–x)P$_2$O$_5$, a complete P–O–P and P–O–Al connectivity analysis in terms of the various $Q^{(n)}_{m\text{Al}}$ species was possible based on $^{27}\text{Al}\{^{31}\text{P}\}$ REDOR, $^{31}\text{P}\{^{27}\text{Al}\}$ REAPDOR, CP-HETCOR, and $^{31}\text{P}$-$J$-resolved spectroscopy [101,102]. If Al$_2$O$_3$ is replaced by Ga$_2$O$_3$, completely analogous behavior is observed [103]. A detailed examination of glasses in the system NaPO$_3$-Ga$_2$O$_3$ by $^{71}\text{Ga}\{^{31}\text{P}\}$ REDOR indicates that the number of Ga–O–P linkages is close to the
maximum number possible. Ga can be considered a network modifier, resulting in the successive transformation \( P^2 \rightarrow P^1 \rightarrow P^0 \) as \( x \) increases. Furthermore, the Ga coordination number appears to be controlled by the type of phosphate species present. While Ga(VI) dominates in the region of small \( x \), where the majority of phosphate is present as \( P^2 \) or \( P^1 \) units, it is successively transformed to Ga(IV) as the number of \( P^0 \) units increases [103]. The composition \( x = 0.25 \) corresponds to the maximum value for which a structure can be formed consisting entirely of Ga(IV)–O–P linkages. For glasses with higher \( x \) values up to the glass-forming border (\( x = 0.35 \)), \(^{71}\)Ga\{\(^{31}\)P\} REDOR results evidence the formation of Ga–O–Ga linkages. Homo- versus heteroatomic connectivity distributions were also analyzed in a number of aluminoborate glasses by \(^{11}\)B\(^{27}\)Al) and \(^{27}\)Al\(^{11}\)B) REDOR experiments [104–107]. For sodium aluminoborate glasses, these experiments indicate a rather chemically ordered structure. The conversion of the network follows the hierarchy \( \text{Al}_4 \rightarrow \text{B}_4 \rightarrow \text{B}_2 \). No higher coordinated Al is formed unless the Al/Na ratio exceeds one. The anionic \( \text{B}^4 \) and \( \text{Al}_4 \) units are preferentially linked to neutral \( \text{B}^3 \) species. There is a particularly strong avoidance of \( \text{B}^4–\text{O–Al}_4 \) connectivity, as can be rationalized based on bond valence considerations [104]. Aluminoborate glasses containing alkaline earth or rare-earth ions as network modifiers do not show such behavior and contain larger amounts of higher coordinated Al atoms over the entire composition range [105–107]. A predominance of \( \text{Al–O–B} \) connectivity can be noted here as well, however.

### 9.5.3 Speciation and Connectivity Distributions in Borophosphate and Thioborophosphate Glasses

The large majority of technically relevant ion-conducting glasses are based on more than one network former species. The combination of several network formers usually offers the possibility of fine-tuning physical property combinations to special technological demands and in certain cases the interaction between the various network former components results in improved physical properties. For example, the ionic conductivities of alkali borophosphate glasses along the compositional series \([\text{Na}_2\text{O}]_y(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x})_1^{-y}\) are significantly higher than those of either the binary alkali borate or the alkali phosphate glass systems having the same concentration of network modifiers, \( y \) [108]. During the past few years, detailed solid state NMR experiments have given a quantitative structural explanation for such trends on the basis of the local environments of the borate and phosphate network former species, their bond connectivities, and their overall competition for the network modifier [109–117].

The preceding chapter already reviewed some important structural insights obtained for glasses in the system \([\text{Na}_2\text{O}]_{0.40}(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x})_{0.60}\) (0.0 ≤ \( x \) ≤ 1.0) on the basis of \(^{31}\)P and \(^{11}\)B MAS-NMR results [109]. That information is complemented with \(^{11}\)B\{\(^{31}\)P\} and \(^{31}\)P\{\(^{11}\)B\} REDOR results, obtained within a more recent study of the compositionally closely related system \([\text{M}_2\text{O}]_{0.33}(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x})_{0.67}\) (0.0 ≤ \( x \) ≤ 1.0; \( M = \text{Li, K, Cs} \)) [110]. The single-pulse NMR data reveal similar spectra and essentially the same compositional trends as the earlier work on the \( y = 0.40 \) system. In the most recent study, double quantum filtering by the Refocused INADEQUATE method was used as an additional spectral editing method. Owing to the absence of
P–O–P linkages, the lineshape components attributed to the P$_2$B and P$_3$B units are not observed in such experiments, making it possible to (i) refine their lineshape parameters by difference spectroscopy, and (ii) remove ambiguities in the lineshape deconvolution of the remaining signal. Based on this work, a complete analysis of the $^{31}$P NMR spectra in terms of the individual P$_n^m_B$ units ($0 \leq n \leq 4$; $m \leq n$) was possible. The results are summarized in Figure 9.23. The structural transformation caused by the successive replacement of the network former P$_2$O$_5$ by B$_2$O$_3$ can be summarized as follows: Up to $x = 0.5$, metaphosphate, P2 units are successively replaced by anionic tetrahedral B$_4$ species. The dramatic increase of ion mobility in this compositional domain can be attributed to the change in the nature of the charge compensating species. The B$_4$ units offer more effective charge dispersal, as the negative charge is delocalized over four bridging oxygen atoms, rather than two non-bridging oxygen atoms in the case of P$_2$ units. Bond valence considerations show further that in the case of B$_4$–O–P$_3$ linkages (which are prevalent particularly for $x < 0.5$); the charge is actually spread out over the non-bridging oxygen atoms of the P$_3$ units. These delocalization mechanisms result in shallower Coulomb traps than in case of the binary metaphosphate glasses, thus increasing the probability of cation jumps. Beyond $x = 0.5$, where the ionic conductivity remains independent of composition, the NMR results show that the principal change is the substitution of neutral P$_3$ species by neutral B$_3$ species.

Figure 9.24 summarizes typical results from the $^{11}$B{${}^{31}$P} REDOR NMR measurements on this system, indicating that the B$_4$ and the B$_3$ units differ significantly with regard to the $^{11}$B–$^{31}$P dipolar coupling strengths, as previously observed for other alkali and silver borophosphate glass systems [113–115]. The numerical $M_2(11B{^{31}P})$ values extracted from these data via Eq. 9.8 and shown in the bottom part of the figure express the extent of P–O–B connectivity, with a contribution of about $4 \times 10^6$ rad$^2$/s$^2$ per B–O–P linkage. The data reflect the expected decrease of B–O–P connectivity from
predominantly $B_4^{4p}$ units at low $x$ values, $P_2O_5$ rich glasses, to predominantly $B_4^{0p}$ units at high $x$ values, $B_2O_3$ rich glasses, along with the decreasing P/B ratio. Assuming $m = 4$ for $x = 0.1$ and based on $m = 0$ for $x = 1.0$, estimates of $m$ for the $B_4^{mp}$ units can be obtained from the measured $M_2$ values by interpolation. As illustrated by Figure 9.24c, these values are generally well-correlated with those estimated from the average $^{11}B$ NMR chemical shifts of the $B_4$ species (as discussed in the preceding chapter).

Based on the boron and phosphorus speciations and the REDOR data, total concentrations of P–O–P, B–O–P, and B–O–B linkages can be derived. Figure 9.25 compares these results with two distinct structural scenarios. The dashed curves in this plot represent the distribution according to a random linkage scenario, which is clearly not applicable here. Rather, heteroatomic P–O–B connectivities are strongly preferred over homoatomic P–O–P and B–O–B linkages, despite the fact that as suggested by Figure 9.24c, only few $B_3^{3–O–P}$ linkages appear to exist in these glasses. Alternatively, the solid lines in Figure 9.25 show the predicted numbers of B–O–P linkages under
Figure 9.25. Connectivity distribution of the bridging oxygen atoms in $[\text{K}_2\text{O}]_{1/3}(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}l_{2/3}$ glasses derived from NMR data and comparison with different linkage scenarios. Dashed curves, random linkage scenario; solid curves, scenario corresponding to the maximum possible number of B$^4$–O–P linkages excluding the formation of B$^3$–O–P linkages [110]. See plate section for a color version of this figure.

the assumption that no B$^3$–O–P linkages occur and the number of B$^4$–O–P linkages always corresponds to the maximum number possible based on the composition. This scenario is in excellent agreement with the experimental data. This study concludes that B$^4$–O–P linkages, particularly those of the B$^4$–O–P$^3$ type, have special stability and are thus preferentially formed in this glass system. While previous $^{31}$P/$^{11}$B REDOR studies had further suggested the absence of B$^3$–O–P connectivity, their presence has been subsequently suggested on the basis of heteronuclear dipolar and J-based experiments [116, 117]. Furthermore, two different types of B$^4$ species could be discriminated based on the extent of B–O–B connectivity as probed by $^{11}$B double quantum NMR spectroscopy [116].

Similar studies have been published for a number of other oxide-based mixed-network former (MNF) systems in recent years [61, 118–122]. Heteroatomic bond formation is also favored in the $(\text{Na}_2\text{O})_{0.33}(\text{P}_2\text{O}_5)_{1-x}(\text{Ge}_2\text{O}_4)_{x}l_{0.67}$ [118], NaPO$_3$–GeO$_2$ [119] and NaPO$_3$–MoO$_3$ systems [120], whereas the bond distribution is close to random in NaPO$_3$–TeO$_2$ glasses [121, 122]. Finally, a number of recent dipolar NMR applications have focused on the characterization of phase separation phenomena in glasses and partially crystallized glass ceramics [123–127]. Here solid state NMR can furnish quite specific information of domain sizes, chemical segregation phenomena, and the medium range order of residual glassy phase.

Phase separation phenomena are also omnipresent in mixed-network-forming chalcogenide glasses. Quantitative details regarding the concentrations of individual local environments, their connectivities and the partitioning of the network modifier $M_2S$, where $M$ is an alkali, between the various network former components were elaborated for the system $[\text{Na}_2\text{S}]_{2/3}(\text{B}_2\text{S}_3)_{x}(\text{P}_2\text{S}_5)_{1-x}l_{1/3}$, $0.0 \leq x \leq 1.0$ [128]. Figure 9.26 summarizes the $^{31}$P solid state MAS-NMR spectra of the glasses. At low thioborate
Figure 9.26. $^{31}\text{P}$ MAS-NMR spectra of $[\text{Na}_2\text{S}]_{2/3}[(\text{B}_2\text{S}_3)_x(\text{P}_2\text{S}_5)_{1-x}]_{1/3}$ glasses [128]. Black curves show experimental spectra and red curves display simulations, with individual deconvolution components shown as dashed curves.

With increasing thioborate content, $x \leq 0.3$, three overlapping contributions near 93, 84, and 107 ppm are observed. The nature of these species was further explored by homonuclear J-resolved spectroscopy (Figure 9.27). The 84 ppm peak, which forms a singlet in the second frequency domain, is attributable to an isolated $\text{PS}_4^{3-}$ unit, while the 93 ppm peak, which forms a doublet in the second frequency domain ($J \sim 20$ Hz), can be assigned to a pyrothiophosphate, $\text{P}_2\text{S}_7^{4-}$ moiety. The downfield component near 107 ppm is correlated with a second doublet characterized by a substantially larger spin–spin coupling constant ($J \sim 80$ Hz). Based on the chemical shift and the size of this coupling constant, this species can be unambiguously assigned to a hexahypothiophosphate, $\text{P}_2\text{S}_6^{4-}$ species, in which a phosphorus–phosphorus bond is present. These results are further corroborated by the Refocused INADEQUATE spectrum of a glass with composition $[\text{Na}_2\text{S}]_{2/3}[(\text{B}_2\text{S}_3)_{0.3}(\text{P}_2\text{S}_5)_{0.7}]_{1/3}$, Figure 9.27, right. Note that in the double-quantum filtered spectrum, the dominant resonance attributed to $\text{PS}_4^{3-}$ groups is eliminated and only those species are being detected that are involved in P–P or P–S–P linkages. Overall, aided by the assignment made via the results of Figure 9.27, Figure 9.26 shows that with increasing thioborate content the monomeric $P^0$ units at 84 ppm become increasingly dominant. Qualitatively, these results illustrate that the thiophosphate
groups function as an alkali metal scavenger species, accumulating a higher negative charge and attracting more network modifier than would be expected on the basis of proportional sharing of the network modifier. Consistent with these findings P–S–B linkages are not detected in either $^{11}$B{$^{31}$P} or $^{31}$P{$^{11}$B} REDOR experiments. Figure 9.28 shows the $^{11}$B{$^{31}$P} REDOR results obtained on a sample with $x = 0.5$, B/P = 1:1. The comparison of these curves to those in Figure 9.24 indicate that the heteronuclear magnetic $^{11}$B–$^{31}$P dipole–dipole interactions are extremely weak, and the $M_2(^{11}$B{$^{31}$P})
values of $0.2 \times 10^{-6} \text{ rad}^2/\text{s}^2$ and $0.3 \times 10^{-6} \text{ rad}^2/\text{s}^2$ for B$^4$ and B$^3$ units, respectively, are one order of magnitude lower than expected in the case of B–S–P linkages.

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