2D PASS-CPMG: A New NMR Method for Quantifying Structure in Non-crystalline Solids

A Thesis

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By

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ABSTRACT

Quantifying the distribution of $Q^{(n)}$ species in silicate glasses has been of particular interest to researchers interested in the structure of silicate glasses. Previously, $^{29}$Si MAS NMR experiments have been used to quantify the $Q^{(n)}$ species assuming that the overlapping isotropic chemical shift distribution of $Q^{(n)}$ species is Gaussian. However, due to strong overlap of the $Q^{(n)}$ resonances this technique has considerable uncertainty. In this thesis we introduce 2D PASS-CPMG, a new method for the quantification of $Q^{(n)}$ species. In this method we obtain a correlation between the spinning sidebands and the fast spinning MAS spectrum. By adding CPMG to the 2D PASS we are able to increase the sensitivity and investigate inexpensive, unenriched $^{29}$Si samples.

In the first chapter of this thesis, the importance of glasses and a brief overview on the structure of glasses is discussed. Next, a few of the previous studies that have been done and the previous methodologies used in quantifying the $Q^{(n)}$ species are also discussed. In chapter two, the new 2D PASS-CPMG experiment is discussed. Experimental data on a silicate glass with the composition of $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ is presented.
This is dedicated to my parents, Jesse and Patty Farley, without them I would not be the person that I am today.
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I would like to thank everyone who helped, encouraged, and inspired me to complete my thesis.

I must begin by thanking God for all His guidance and blessings in my life. My husband, Joey Vickers, whose love and support has gotten me this far. I could not have made it through this experience without him. I must also thank my family for their love and encouragement. It is their constant belief in me that makes me continually strive to be a better person. I am truly blessed to have such a wonderful support system.

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CHAPTER 1

Introduction

1.1 Materials

Non-crystalline or glassy materials are found everywhere in our society. Glasses are used in everything from windows to fiber optics. Since glass plays such an important role in our lives, it is important to understand its structure and properties. However, the structure of even vitreous silica, one of the most extensively studied glasses, is still not well understood beyond the basic tetrahedral structural unit. In 1932 Zachariasen said, “It must be frankly admitted that we know practically nothing about the atomic arrangement in glasses [4].” Surprisingly even today, there is significant room to improve our understanding of the atomic level structure of glasses. Improving our understanding of this will give us the ability to modify their properties to fit our needs and can have great impact on fields such as waste containment glass technology [5] and glassy ionic conductors [6].

Zachariasen predicted the presence of well-defined corner-sharing SiO$_4$ tetrahedra that are connected in a continuous infinite three-dimensional network having no long-range order [4]. For A$_m$O$_n$ to be a glass, it must follow four rules: 1) An oxygen atom can be linked to no more than two atoms of A. 2) The oxygen coordination around A is small. 3) The cation polyhedral share corners, not edges or faces. 4) At least three
corners are shared. This prediction was later confirmed in 1936 by Warren using X-ray diffraction techniques [7]. In 1985, Greaves predicted a Modified Random Network model [8]. This model postulates the existence of nano-scaled zones composed of pure v-SiO$_2$ surrounded by alkali channels. When a network modifier, such as Na$^+$, is introduced into SiO$_2$ the network of corner-sharing SiO$_4$ tetrahedra is broken up as more negatively charged non-bridging oxygens (oxygen connected to one silicon and several network modifying cations) are created.

Figure 1.1: Comparison of the atomic level structure of (A) a crystalline structure with the formula A$_2$O$_3$ and (B) a glassy structure with the formula A$_2$O$_3$ (Adapted from W. H. Zachariasen. *J. Am. Chem. Soc.*, 1932, **54**, 3841).
Researchers interested in the structure of silicate glasses often focus on measuring the statistical distribution of the type of silicate tetrahedral species present. There are five different types of silicate tetrahedra characterized by the number of oxygen that are corner-linked to other tetrahedra. The types of silicate tetrahedral are commonly denoted as $Q^{(n)}$, where $n$ (ranging in value from 0-4) represents the number of bridging oxygen per tetrahedron. Quantifying the distribution of $Q^{(n)}$ species in silicate glasses is essential for any structure-based model of thermodynamic or transport properties of silicate melts [9, 10] and glasses [6]. A large number of papers have been published that show the populations of $Q^{(n)}$ species can be estimated from peak intensities in Raman spectroscopy [11–15]. More recently, it has been shown these populations can be estimated from $^{29}$Si nuclear magnetic resonance (NMR) spectra [16–24]. Since $^{29}$Si NMR is more quantitative than Raman spectroscopy, it has provided the most convincing evidence that the $Q^{(n)}$ distribution is not random but closer to binary meaning it contains a maximum of two $Q^{(n)}$ species, with a sequential appearance of $Q^{(n-1)}$ species as the alkali content increases. This information has been important in the testing of thermodynamic models of alkali silicate glasses [25, 26]. One popular model, used in understanding the energetic and thermodynamic mixing properties of silicate melts [9, 10], and suggested as part of a mechanism for alkali ion transport in alkali silicate glasses [6, 27], involves the disproportionation equilibria between $Q^{(n)}$ species,

$$2Q^{(n)} \rightleftharpoons Q^{(n-1)} + Q^{(n+1)}.$$  \hspace{1cm} (1.1)

This disproportionation reaction has the equilibrium constant at the glass transition temperature,

$$k_n = [Q^{(n+1)}][Q^{(n-1)}]/[Q^{(n)}]^2.$$

(1.2)
The equilibrium constant ranges from $k_n = 0$ for a highly ordered distribution of silicate anionic species to $k_3 = 0.375$, $k_2 = 0.439$, and $k_1 = 0.311$ for a completely random distribution [28, 29]. This thermodynamic model, along with $^{29}$Si magic angle spinning (MAS) NMR, has been used to predict reasonable activation energies for ionic transport [6]. However, the $^{29}$Si MAS $k_n$ values are based on the fitting of heavily overlapping lines whose detailed shapes are unknown, and could be biased by the common assumption that the MAS NMR lineshapes are Gaussian [16].

1.2 Previous NMR Material Investigation

Each $Q^{(n)}$ species exhibits an anisotropic NMR line shape under static or off-magic angle spinning. These anisotropic NMR lineshapes are shown in Figure 1.3 and are due to the anisotropy of the NMR chemical shift interaction (CSA) that arises from the magnetic shielding produced by the electron cloud surrounding the nucleus and therefore reflects the nature and directionality of the bonding. The line shape anisotropy is categorized by three parameters: isotropic position ($\delta_{iso}$) which reflects the mean silicon environment, axiality ($\Delta$) which measures the extent of the distortion of the electron cloud, and an asymmetry parameter ($\eta$) that expresses the departure from a cylindrically symmetric environment. Therefore, the width of the anisotropy is dependent on the magnitude of $\Delta$, while the line shape is determined by $\eta$. $Q^{(0)}$ and $Q^{(4)}$ sites have highly symmetrical environments and therefore have the smallest axiality of the five $Q^{(n)}$ species. The rest of the sites possess relatively large axialities; the axialities are opposite in sign for $Q^{(1)}$ and $Q^{(3)}$ sites. Since there is an axial symmetry to the environments of the $Q^{(1)}$ and $Q^{(3)}$ sites, they have low asymmetry.
Figure 1.3: (A) One-dimensional $^{29}\text{Si}$ anisotropic NMR lineshapes spinning at 90° angle for the five $Q^{(n)}$ species. The lineshape parameters are based on the typical values found in crystalline compounds [1, 2]. (B) On the left is the one-dimensional $^{29}\text{Si}$ anisotropic NMR lineshape spinning at 90° angle and on the right is the one-dimensional $^{29}\text{Si}$ MAS NMR lineshape for 2Na$_2$O·3SiO$_2$ (Adapted from P. Zhang, C. Dunlap, P. Florian, P. J. Grandinetti, I. Farnan, and J. F. Stebbins. J. Non-Cryst. Solids, 1996, 204, 294).

parameters. $Q^{(2)}$ sites have a divergence from axial symmetry and therefore have an intermediate asymmetry parameter.

Using Magic Angle Spinning (MAS) conditions removes the anisotropic broadening (i.e. the information on $\Delta$ and $\eta$). Under these conditions the $Q^{(n)}$ species are primarily identified by their isotropic position, $\delta_{iso}$, which ranges from approximately -70 ppm for $Q^{(0)}$ to approximately -100 ppm for $Q^{(4)}$ [30]. In crystalline silicates the
isotropic line shapes are generally on the order of 1 ppm or less, often making it possible to not only resolve different \( Q^n \) species but also crystallographically distinct \( Q^n \) species of the same type (having the same \( n \)). In glasses, each \( Q^n \) site possess a continuous structural distribution arising from second coordination sphere disorder such as a distribution of Si-O-Si bond angles, variations in non-bridging oxygen-alkali distances and higher coordination sphere structure. This disorder results in a continuous distribution of isotropic chemical shifts causing the isotropic line widths to be inhomogeneously broadened to over 10 ppm. This broadening creates a considerable overlapping of the \( Q^n \) resonances in the MAS and static NMR spectra making it difficult to quantify the relative \( Q^n \) populations from isotropic MAS line shapes.

Using one-dimensional MAS experiments to quantify the relative \( Q^n \) species populations in silicate glasses, requires a least-squares analysis of the MAS lineshape to be performed with the common assumption that the MAS lineshape is a superposition of Gaussian lineshapes, one for each \( Q^n \) species present. Unfortunately, the strong overlap of \( Q^n \) resonances in the MAS spectra leads to large covariances between best fit intensity parameters resulting in significant uncertainties in the relative populations of \( Q^n \) species. One-dimensional static \(^{29}\text{Si}\) NMR experiments have been used to improve the precision of \( Q^4 \) quantification by exploiting the high symmetry of the \( Q^4 \) site [20, 22]. However, the problem still exists that assumptions about the \( Q^n \) lineshapes must be made and relatively large covariances between best fit intensity parameters still exist.
1.3 Previous NMR Methodologies

1.3.1 Measuring CSA

In liquid state NMR, the resonances are very narrow because of the rapid isotropic tumbling of the molecules which averages away the anisotropic parts of the chemical shift, dipole, and quadrupolar interactions. In solids, the NMR resonances are considerably broadened due to the anisotropic motion of the molecules. The chemical shift anisotropy (CSA) is a significant broadening in the NMR spectra of solids. In order to get site resolution, the CSA must be removed. It was found that spinning a powder sample along an axis orientated at the magic angle ($54.7^\circ$) with respect to the applied field will average the CSA to zero. In order to have complete averaging, the spinning speed must exceed the span of the chemical shift anisotropy. While fast MAS has high resolution, the CSA information is lost in this method.

One option to obtain CSA information is to spin the sample slowly. When the spinning speed is reduced to less than the chemical shift anisotropy, the isotropic line of the NMR spectrum is flanked on either side by sidebands spaced at the spinning frequency. The intensities of these spinning sidebands are related to the chemical shift anisotropy and can be analyzed to retrieve the CSA from each site. Herzfeld and Berger derived general integral and series expressions for the intensities of sidebands seen in the magic angle spectra of inhomogeneously broadened $I = 1/2$ systems [31]. These expressions were used to construct graphical and numerical methods for obtaining the principle values of the chemical shift tensors from the intensities of a few sidebands. Taking the CSA interaction as a function of time arising from sample rotation we obtain:
\[ H_c = \sum_{i} \sum_{p=1}^{3} I_{iz} B \sigma_{ip} [\cos^2 \beta \cos^2 \chi_{ip} + 2 \cos \beta \sin \beta \cos \chi_{ip} \sin \chi_{ip} \cos(\omega_r t + \psi_{ip}) + \sin^2 \beta \sin^2 \chi_{ip} \cos^2(\omega_r t + \psi_{ip})]. \]  \hspace{2cm} (1.3)

The CSA interaction contains terms that are periodic with frequency \( \omega_r \). It has been shown that this time-dependence gives rise to a series of echoes separated by a time interval in the free induction decay (FID). When the FID is Fourier transformed, these echoes give rise to spinning sidebands separated from the central isotropic line at frequency intervals equal to the spinning frequency. The expression for the FID of a powder sample in the MAS experiment is:

\[ S(t) = \frac{1}{8\pi^2} \int_{0}^{2\pi} \int_{0}^{\pi} \int_{0}^{2\pi} \exp \left[ i \int_{0}^{t} \omega(t') dt' \right] d\alpha \sin \beta d\beta d\gamma. \] \hspace{2cm} (1.4)

Herzfeld and Berger have shown through an analysis of Equation (1.3) that the sideband intensities are indeed related to the principal values of the CSA tensor, and they have developed graphs to assist in making the analysis of these sidebands [31]. This analysis is done by first identifying the intensity of the \( N^{th} \) sideband, \( I_N \), by varying the rotor frequency and identifying \( I_N \) as the line that shifts by a frequency interval of \( \omega_r \). Next, a ratio of \( I_N/I_0 \) (\( I_0 \) being the unshifted isotropic line) is found and used to identify the correct curve on the appropriate graph. The abscissa and ordinate, \( \mu \) and \( \rho \) are defined by:

\[ \mu = (\gamma B)(\sigma_{33} - \sigma_{11})/\omega_r \] \hspace{2cm} (1.5)

and

\[ \rho = (\sigma_{11} + \sigma_{33} - 2\sigma_{22})(\sigma_{33} - \sigma_{11}), \] \hspace{2cm} (1.6)
where the three principle values of the chemical shielding tensor components have been taken in the order

\[ \sigma_{33} > \sigma_{22} > \sigma_{11}. \]  \hspace{1cm} (1.7)

One then simply superimposes the graphs and identifies as many sidebands as possible. With values of \( \mu \) and \( \rho \) and the isotropic value of \( \sigma \) given by

\[ \sigma = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3, \]  \hspace{1cm} (1.8)

\( \sigma_{11}, \sigma_{22}, \) and \( \sigma_{33} \) can be determined. The problem is that as the number of sites increases, the Herzfeld and Berger analysis becomes intractable. Therefore, two-dimensional (2D) methods for correlating CSA and high resolution spectra are more desirable.

### 1.3.2 Magic Angle Hopping

One such 2D method was developed by Bax et al. [32]. In 1983 they introduced a 2D Fourier transform (FT) technique that correlates the isotropic shifts to the chemical shift anisotropies by magic-angle hopping. In this experiment, the isotropic average chemical shift is presented in one frequency dimension (F1) and the static CSA powder pattern is presented along the other frequency dimension (F2). Rather than continuously spinning the sample, the experiment is performed using hops in 120° increments about the magic-angle axis. Hopping in 120° increments about the magic angle is mathematically equivalent to spinning at the magic-angle and no spinning side bands are produced in the spectrum. This technique is useful in obtaining powder patterns for individual peaks of complex molecules were a static experiment would give only broad bands of overlapping powder patterns. The challenge of this experiment is that achieving the hopping for the experiment can be a challenge technically and the
time required for the hopping to occur must be hidden from the $t_1$ evolution. Also, since the detection occurs on a static sample, the signal decays more rapidly causing the sensitivity to suffer compared to a normal MAS experiment.

### 1.3.3 Magic Angle Flipping

Bax et al. [33] also developed another 2D approach for obtaining anisotropic information in which the spinning axis of the sample is flipped from $90^\circ$ to $54.74^\circ$ between the evolution and detection periods. In this experiment, the sample is spun at an axis $90^\circ$ to the static magnetic field. The sample is then flipped so the spinning axis of the sample is at the magic angle and spun faster than the width of the anisotropy patterns so that the spinning sidebands are removed. The advantage to this experiment is that the anisotropy information is obtained in a very straightforward way with minimal distortion. The disadvantage of this technique is that while the sensitivity is rather good it is lower than that of the conventional MAS experiment. Also, there is the technical challenge of flipping the sample between $90^\circ$ and the magic angle.

### 1.3.4 Anionic Species Determination Using 2D $^{29}$Si NMR

Zhang et al. [34] investigated an enriched silicate glass sample of composition $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ with a modified approach based on the magic-angle-flipping experiment by Bax et al. [33] previously discussed. In the experiment performed by Zhang et al. [34], the NMR spectrum while spinning at the magic angle is correlated with that while spinning at an axis perpendicular to the magnetic field. As shown in Figure 1.3, when spinning perpendicular to the magnetic field the static sample anisotropic line shapes are scaled [35] by a factor of -0.5. The sequence used by Zhang et al. [34] differed from the original experiment by Bax et al. [33] by the addition of an additional
Figure 1.4: Stacked plot of $^{29}$Si 2D correlation spectrum for a $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ sample (Adapted from P. Zhang, C. Dunlap, P. Florian, P. J. Grandinetti, I. Farnan, and J. F. Stebbins. J. Non-Cryst. Solids, 1996, 204, 294).

$\pi$ pulse before $t_2$ in order to improve sensitivity and to give pure absorption mode line shapes. The $2\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ sample was chosen because it is expected to contain both $Q^{(2)}$ and $Q^{(3)}$ type sites. It is also well established that deviations from a binary distribution will result in the presence of $Q^{(4)}$ sites. A stacked plot of the $^{29}$Si 2D ($90^\circ$, $54.74^\circ$) correlation spectrum for this sample is shown in Figure 1.4.

Using the characteristic anisotropic lineshapes shown in Figure 1.3, it is seen from the $90^\circ$ dimension that the low intensities of the MAS lineshape near -100 ppm are dominated by $Q^{(4)}$, the MAS lineshape intensities around -88 ppm are dominated by $Q^{(3)}$, and the MAS lineshape intensities around -75 ppm are dominated by $Q^{(2)}$. Figure 1.5 shows a comparison of the one-dimensional (1D) MAS Gaussian deconvolution
Figure 1.5: Comparison of the 1D MAS Gaussian deconvolution on the left with the decomposition of the $^{29}$Si MAS spectrum using the anisotropic cross-sections of the 2D NMR spectrum (Adapted from P. Zhang, C. Dunlap, P. Florian, P. J. Grandinetti, I. Farnan, and J. F. Stebbins. *J. Non-Cryst. Solids*, 1996, 204, 294).

with the decomposition of the MAS spectrum using the anisotropic cross-sections of the two-dimensional NMR spectrum.

From this data, it can be seen that the 2D approach is more than an order of magnitude more precise in quantifying $Q^{(n)}$ species distributions than is the fitting of the 1D MAS spectra only. Therefore, Zhang *et al.* were successful in presenting a 2D isotropic / anisotropic correlation experiment that significantly enhanced the precision of the determination of species concentrations.
\[ Q^{(4)} = 0.0113 \pm 0.0001 \]
\[ Q^{(3)} = 0.2414 \pm 0.0053 \]
\[ Q^{(2)} = 0.5468 \pm 0.0034 \]

\[ Q^{(1)} = 0.1933 \pm 0.0028 \]
\[ Q^{(0)} = 0.0072 \pm 0.0013 \]

\[ k_1 = \frac{[Q^{(2)}][Q^{(0)}]}{[Q^{(1)}]^2} = 0.105 \pm 0.019 \]
\[ k_2 = \frac{[Q^{(3)}][Q^{(1)}]}{[Q^{(2)}]^2} = 0.156 \pm 0.005 \]
\[ k_3 = \frac{[Q^{(4)}][Q^{(3)}]}{[Q^{(4)}]^2} = 0.106 \pm 0.022 \]

\[ \text{Isotropic } ^{29}\text{Si chemical shift (ppm)} \]

\[ \text{Charge Balance} \]
\[ (\text{Ca/Si}) = 0 \cdot [Q^{(4)}] + 0.5 \cdot [Q^{(3)}] + 1 \cdot [Q^{(2)}] + 1.5 \cdot [Q^{(1)}] + 2 \cdot [Q^{(0)}] \]

Expected from Composition: \( (\text{Na/Si})_{\text{composition}} = 1 \)
Calculated from 2D NMR: \( (\text{Ca/Si})_{\text{NMR}} = 0.972 \pm 0.006 \)

Figure 1.6: Decomposition of the \(^{29}\text{Si} \) MAS spectrum using the anisotropic cross-sections of the 2D NMR spectrum (Adapted from P. Zhang, P. J. Grandinetti, and J. F. Stebbins. \textit{J. Phys. Chem. B}, 1997, \textbf{20}, 4004). 

Zhang \textit{et al.} [36] also performed this experiment on a CaSiO\(_3\) sample. They found that for this sample the conventional approach of fitting the 1D MAS spectrum with overlapping Gaussian line shapes would lead to significant errors in the quantification of \( Q^{(n)} \) species. The results from this experiment shown in Figure 1.6 indicates that compared to alkali silicate glass, alkaline earth silicate glasses have a significantly greater deviation from a binary model of \( Q^{(n)} \) species disproportionation.
This experiment was the first to exploit isotropic / anisotropic correlation to unravel the $Q^{(n)}$ species distribution. However, the need for a special magic angle flipping probe has prevented this technique from being applied in other labs. A technique is needed that can be performed on probe designs that are commonly available.

1.3.5 2D PASS

One technique that can be used on a commonly available probe design is the 2D PASS experiment. In 1982, Dixon introduced the PASS (phase-adjusted spinning sidebands) sequence [37]. The PASS sequence uses a sequence of four $\pi$ pulses to prepare the magnetization components of a powder sample such that well-defined sideband phase shifts are introduced. By combining spectra with different sideband phase shifts, it is possible to separate all sidebands by order. It is also possible to demonstrate spinning-sideband-free and spinning-sideband-only NMR spectra.

The problem with Dixon’s method is that the pulse sequences with different sideband phase shifts vary considerably in overall duration. This leads to an incomplete separation of the spinning sidebands for finite transverse relaxation. In 1995, Antzutkin et al. [3] developed a 2D PASS pulse scheme using sequences containing five $\pi$ pulses. These sequences contain five $\pi$ pulses in order to give all the PASS sequences the same overall duration independent of the sideband phase shift. The timings of the five $\pi$ pulses are varied during the 2D experiment according to the solution of the PASS equations. This 2D PASS experiment allows for a complete separation of spinning sideband manifolds with a negligible loss in the signal intensity. This allows for the use of the sideband amplitudes to determine the CSA eigenvalues.
It has also been shown that the sidebands may be superimposed to obtain a spectrum with only isotropic shift peaks with a higher signal-to-noise ratio than a conventional 1D spectrum at the same spinning speed.

This technique has the advantage of being a 2D correlation spectrum that can be done on a commonly available NMR probe design. However, increasing the number of spinning sidebands can cause a decrease in the sensitivity compared to the fast MAS spectrum.

1.3.6 CPMG

Improving sensitivity has been a major obstacle for NMR spectroscopists. The experiments discussed previously improve upon the ability to measure the chemical shift anisotropy at the expense of a loss of signal intensity. While the Carr-Purcell-Meiboom-Gill (CPMG) experiment [38, 39] was originally used to measure transverse relaxation times [40], it has become a way for experimenters to enhance the sensitivity of anisotropically broadened spectra of spin half nuclei and half-integer quadrupolar nuclei [41]. The experiment consist of a $\pi/2$ pulse followed by a series of $\pi$ pulses. This sequence leads to a FID followed by a train of echoes. The train of echoes created leads to an increase in the amount of signal in the time domain; therefore, leading to an increase in sensitivity in the frequency domain. Larsen et al. [41] claimed that the application of CPMG led to a sensitivity enhancement of up to about 30 for the samples studied in their experiment.

1.4 Overview of Thesis

Chapter 2 discusses the coupling of CPMG with the 2D PASS experiment. In performing this experiment, the obstacles faced by the experiments in Section 1.3 can be
overcome. The 2D PASS allows for an isotropic / anisotropic correlation spectrum that can be performed on an NMR probe design that is readily available unlike the Magic Angle Flipping and Magic Angle Hopping experiments that require a special probe design. Coupling CPMG to the 2D PASS experiment overcomes the problem of loss of sensitivity in the conventional 2D PASS experiment. The CPMG also provides a gain in sensitivity over the conventional 2D PASS spectrum. The added enhancement provided allows for the use of inexpensive, natural abundance $^{29}$Si samples unlike the $^{29}$Si-enriched samples used by Zhang et al. [34].
CHAPTER 2

Anionic Species Determination Using 2D PASS-CPMG

2.1 Introduction

In spite of all the experiments that have been performed on glassy materials, there is still significant room to improve our understanding of the atomic level structure of glasses. In order to create structure-based models of thermodynamic or transport properties of silicate glasses, the distribution of $Q^{(n)}$ species must be quantified [6]. Many papers have been written showing that the populations of $Q^{(n)}$ species can be estimated from $^{29}$Si nuclear magnetic resonance (NMR) spectra [16–24]. However, these experiments suffer from heavy overlapping lines whose shapes are unknown, making analysis of the data difficult. Two-dimensional methods correlating the CSA to a high resolution spectra such as Magic Angle Hopping [32] and Magic Angle Flipping [33] have also been used. However, these methods require a special probe design that is not readily available to other labs. Another problem with these methods is that they have a loss of sensitivity when compared to a conventional MAS experiment and require enriched $^{29}$Si samples.

In this chapter, we discuss the coupling of the 2D PASS and the CPMG experiments. As discussed in Chapter 1, the 2D PASS sequence allows for complete
separation of spinning sideband manifolds allowing the CSA eigenvalues to be calculated from the sideband amplitudes. The 2D PASS experiment can be performed on probes that are commercially available, making it easy to implement in other labs across the world. In these initial experiments, we show that coupling CPMG to the 2D PASS pulse sequence gives a 1.68 signal to noise ratio gain over simple 2D PASS. This provides a reduction in the signal averaging time by a factor of about 3, allowing unenriched $^{29}$Si samples to be investigated.

As discussed earlier, each $Q^{(n)}$ species exhibits an anisotropic NMR line shape under static or off-magic angle spinning. Each $Q^{(n)}$ species also exhibits its own unique spinning sideband pattern as shown in Figure 2.1. The separated sideband patterns in the 2D PASS-CPMG experiment can be analyzed to obtain the relative concentration for each of the $Q^{(n)}$ species present in the sample. From these concentrations, the equilibrium constant at the glass transition temperature can be calculated.

### 2.2 Experimental

The $2Na_2O$-$3SiO_2$ sample used in this study was synthesized from $Na_2CO_3$ and natural abundance $SiO_2$ with 0.2 wt % $Gd_2O_3$ added to reduce the spin-lattice relaxation time. The sample was allowed to decarbonate at 770°C overnight, before being melted at 1200°C for approximately 12 hours and then rapidly quenched. The sample had to be ground and packed in the rotor in a sealed glove bag under nitrogen gas to prevent it from absorbing water. Experiments were performed at 9.4 T on a Bruker DMX 400 Spectrometer, using a 7 mm MAS probe spinning at 1 kHz. $^{29}$Si spectra were acquired at 79.588547 MHz. The 90° and 180° pulses were calibrated using a crystalline clinoenstatite sample. The pulse sequence is shown in Figure 2.3. The
Figure 2.1: (A) One-dimensional $^{29}\text{Si}$ anisotropic NMR lineshapes for the five $Q^{(n)}$ species. The lineshape parameters are based on the typical values found in crystalline compounds. (B) On the top is the one-dimensional $^{29}\text{Si}$ slow spinning (1kHz) MAS NMR lineshape and on the bottom is the one-dimensional $^{29}\text{Si}$ fast spinning (4kHz) MAS NMR lineshape for 2Na$_2$O·3SiO$_2$. 
timings for the PASS sequence are given in Table 2.1. The PASS echo was shifted by 2 ms and the duration between the CPMG \( \pi \) pulses was 4 ms. The recycle delay, \( d_1 \), was set to 25 s.

### 2.3 Theory of 2D PASS / CPMG

The 2D PASS sequence used in this work is shown in Figure 2.2. The timings for the pulse spacings in this experiment are in Table 2.1 for a 16 step experiment and Table 2.2 for a 32 step experiment. These timings are derived as follows. The NMR frequency can be written

\[
\Omega(t, \phi_0) = \sum_{l=0}^{\infty} \omega_{l,0} + \sum_{l=0}^{\infty} \sum_{m \neq 0} \omega_{l,m} e^{im(\Omega R t + \phi_0)}, \quad (2.1)
\]
Figure 2.2: (A) Pulse sequence for the 2D PASS experiment with a coherence pathway diagram. (B) Sampling trajectory (blue lines) of the 2D PASS experimental data in the 2D $t_1 - \Theta$ coordinate system. Identical data sets run parallel in the 2D plane and are separated by $\tau_R$ and $2\pi$ in the $t_1 - \Theta$ coordinate system. (C) Sheared 2D data set that correlates $t_1$ and $\Theta$. 
Figure 2.3: (A) 2D PASS-CPMG experiment with coordinate definitions and timings. (B) Sampling trajectory (blue lines) of the 2D PASS-CPMG experimental data in the 2D $t_1 - \Theta$ coordinate system. Identical data sets run parallel in the 2D plane and are separated by $\tau_R$ and $2\pi$ in the $t_1 - \Theta$ coordinate system. (C) Sum of all the echoes in the 2D PASS-CPMG experiment. (D) Sheared 2D data set that correlates $t_1$ and $\Theta$. 

\[ \Theta \]

\[ 0 \]

\[ \pi \]

\[ \pi/2 \]

\[ \pi \]

\[ \pi \]

\[ 4\tau \]

\[ \pi \]

\[ 4\tau \]

\[ 4\tau \]

\[ 4\tau \]

\[ \pi \]

\[ t_1 \]

\[ 0 \]

\[ \pi \]

\[ 2\pi \]

\[ 3\pi \]

\[ 4\pi \]

\[ 5\pi \]

\[ 6\pi \]

\[ 7\pi \]

\[ 8\pi \]

\[ 9\pi \]

\[ 10\pi \]

\[ 11\pi \]

\[ 12\pi \]
Table 2.2: Timings for the 2D PASS-CPMG Experiment with 32 Steps.

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where $\phi_0$ is the initial rotor phase and $\Omega_R$ is the rotor speed. After a single pulse, the phase of the MAS signal has the form

$$\Phi(t, \phi_0) = W_0t - \sum_{l,m \neq 0} iW_{l,m}e^{im\phi_0}[e^{im\Omega_Rt} - 1],$$  

(2.2)

where we have defined

$$W_0 = \sum_{l=0}^{\infty} \omega_{l,0} \quad \text{and} \quad W_{l,m} = \frac{\omega_{l,m}}{m\Omega_R}.$$  

(2.3)

A multipulse experiment allows the phase of the MAS signal to be manipulated into one of several desirable forms. One method for manipulating the phase is to use a series of $\pi$ pulses placed at time $\tau_j$ after the excitation pulse. As first demonstrated by Dixon [37], the signal phase at $\tau_{n+1}$ after the $n$th $\pi$ pulse is

$$\Phi_n = (-1)^n \sum_{j=0}^{n} (-1)^j \int_{\tau_j}^{\tau_{j+1}} \Omega(s) ds - \sum_{l,m \neq 0} iW_{l,m}e^{im\phi_0} \left[ -\sum_{j=0}^{n} (-1)^j e^{im\theta_{j+1}} - e^{im\theta_j} \right],$$  

(2.4)

where $\tau_0 = 0$ and $\theta_j = \Omega_R \tau_j$. Equation (2.4) can be arranged to

$$\Phi_n = W_0 \left[ (\tau_{n+1} - 2(-1)^n \sum_{j=0}^{n} (-1)^j \tau_j) \right]$$

$$- \sum_{l,m \neq 0} iW_{l,m}e^{im\phi_0} \left[ 1 - (-1)^n - e^{im\theta_{n+1}} + 2(-1)^n \sum_{j=0}^{n} (-1)^j e^{im\theta_j} \right].$$  

(2.5)

In the PASS experiment, the number of $\pi$ pulses and pulse spacing are manipulated until the signal phase has the form

$$\Phi_{\text{PASS}} = -\sum_{l,m \neq 0} iW_{l,m}e^{im\phi_0}[e^{im\Omega_R t+\Theta} - 1],$$  

(2.6)
where $\Theta$ can be varied independent of $t$. This phase leads to the signal

$$S_{PASS}(t, \Theta) = \sum_{N_1, N_2} A_{N_1} A_{N_2}^* e^{-iN_1(\Omega_R t + \Theta)} e^{i(N_2 - N_1)\phi_0}.$$  

(2.7)

By equating Equations (2.5) and (2.6), the following equations are obtained:

$$t = \tau_{n+1} - 2(-1)^n \sum_{j=1}^{n} (-1)^j \tau_j = 0,$$

(2.8)

and

$$[e^{im(\theta_t + \Theta)} - 1] = 1 - (-1)^n e^{im\theta_{n+1}} + 2(-1)^n \sum_{j=1}^{n} (-1)^j e^{im\theta_j},$$  

(2.9)

where $\theta_t = \Omega_R t$. Further substitution yields the first PASS equation

$$\theta_t = \theta_{n+1} - 2(-1)^n \sum_{j=1}^{n} (-1)^j \theta_j = 0,$$

(2.10)

and the second equation

$$e^{im\Theta} = 2 - (-1)^n e^{im\theta_{n+1}} + 2(-1)^n \sum_{j=1}^{n} (-1)^j e^{im\theta_j}.$$  

(2.11)

From Equations (2.10) and (2.11), one can solve for the necessary $\pi$ pulse spacings, $\tau_j$, for the PASS solutions. By setting $n = 5$ and $\theta_6 = 2\pi$, Equations (2.10) and (2.11) can be simplified to

$$2\pi + 2 \sum_{j=1}^{5} (-1)^j \theta_j = 0,$$

(2.12)

and

$$e^{im\Theta} + 1 + 2 \sum_{j=1}^{5} (-1)^j e^{im\theta_j} = 0.$$  

(2.13)

Solving these simplified equations give us the values calculated in Tables 2.1 and 2.2 [3].

A Fourier transform of Equation (2.7) with respect to $\Theta$ yields the spinning side-band intensities, whereas a Fourier transform of Equation (2.7) with respect to $t$ yields
the fast spinning MAS spectrum. In 2D PASS the signal is acquired as a function of both Θ and t, as shown in Figure 2.2 (B). After a shearing transformation the signal can be double Fourier transformed to obtain a 2D spectrum correlating the MAS spectrum at infinite Ω_R with the sideband intensities at Ω_R, as shown in Figure 2.2 (C).

When adding CPMG to the 2D PASS sequence, only the CPMG echoes after even π pulses can be acquired since they are the only ones that satisfy Equations (2.10) and (2.11). The odd echoes do not satisfy these PASS solutions, and are not shown in the 2D PASS-CPMG experiment as shown in Figure 2.3 (A). The 2D PASS-CPMG echoes are then summed by converting the 1D CPMG data into a 2D data set as shown in Figure 2.3 (B). The proper matched filter must be applied to both dimensions, and then a 2D Fourier transform is performed. The summed spectrum is obtained by taking the cross-section at ω_1 = 0 ppm. Finally a shear is applied in order to correlate t_1 and Θ, as shown in Figure 2.3 (D).

2.4 Results and Discussion

In Figure 2.4 is a 29Si 2D PASS-CPMG spectrum of the 2Na_2O·3SiO_2 glass. This spectrum is compared to a normal 2D PASS spectrum of the same sample in order to see the enhancement that comes from adding CPMG. The sites are more defined in the 2D PASS-CPMG spectrum and the amount of noise has been significantly reduced. By combining CPMG and 2D PASS, we obtain a sensitivity increase of 1.68. While the sensitivity enhancement is significant, it is possible that even greater enhancement could be obtained for samples having longer, T_2, spin-spin relaxation times. The T_2 in this sample may have been shortened by the addition of Gd_2O_3, which was added
Figure 2.4: Comparison of (A) a 2D PASS spectrum of $^{29}$Si in $2Na_2O-3SiO_2$ glass sample to (B) a 2D PASS-CPMG spectrum of the same sample. The contour lines are drawn at 10 equally spaced levels ranging from 3 to 93 % of the maximum intensity in the spectrum.

to reduce the $T_1$, spin-lattice relaxation time and thus reduce the time needed for the magnetization to re-equilibrate between acquisitions. Unfortunately, Gd$_2$O$_3$ can also reduce $T_2$, and reduce the number of echoes that can be obtained in a CPMG experiment. Further work is needed to determine the optimum doping level of Gd$_2$O$_3$, that minimizes the reduction of $T_2$ while maximizing the reduction of $T_1$.

The 2D PASS-CPMG spectrum is shown in Figure 2.5 along with the sideband dimension cross section for different isotropic positions. Comparing the characteristic sideband patterns shown in Figure 2.1 with Figure 2.5, it is clear from the sideband dimension that the low intensities of the MAS lineshape near -100 ppm are dominated by $Q^{(4)}$, the intensities around -88 ppm are dominated by $Q^{(3)}$, and the intensities around -75 ppm are dominated by $Q^{(2)}$. These results are consistent with what has been found in previous studies. Some differences in sidebands seen in the 2D
Figure 2.5: 2D PASS-CPMG spectrum of $^{29}$Si in 2Na$_2$O·3SiO$_2$ glass sample. The left hand side of the spectrum shows the contour plot of the 2D PASS-CPMG data processed with our modified data processing method. The right hand side spectrum shows the sideband dimension cross section for different isotropic positions. The spinning speed was 1 kHz and inter $\pi$ pulse delay for CPMG was 4 ms.
PASS-CPMG spectrum may be caused by a field inhomogeneity. It was discovered after the experiment that the shims of the magnet were off causing the field to be inhomogeneous. We can see from the simulated data in Figure 2.1 that the $Q^{(4)}$ site should only have one sideband at -100 ppm. In our experimental spectrum we see symmetrical sidebands on either side of the peak at -100 ppm thought to be caused by the field inhomogeneity. We also see some differences in sidebands between the simulations and the $Q^{(3)}$ as well as the $Q^{(2)}$ sites.

The sideband patterns can be analyzed to obtain the $Q^{(n)}$ site populations. Unfortunately, software for fitting the intensities is still under development and not yet ready for use. Once the fitting program has been finished, the $Q^{(n)}$ contribution to each isotropic frequency in the MAS spectrum can be found. Once the $Q^{(n)}$ populations have been obtained, the equilibrium constant for the disproportionation reaction $2Q^{(n)} ⇌ Q^{(n-1)} + Q^{(n+1)}$ can be calculated at the glass transition temperature according to

$$k_n = [Q^{(n+1)}][Q^{(n-1)}]/[Q^{(n)}]^2,$$

and used to study the thermodynamics of this important reaction in silicate melts.

Overall, we have successfully shown that 2D PASS and CPMG can be combined to provide enhanced sensitivity for quantifying $Q^{(n)}$ species in non-crystalline solids. As pointed out, there are a number of additional improvements that can be made to the method. The first thing that must be done is to correct the field inhomogeneity problem mentioned earlier and rerun the experiment. This should solve the problem of the sideband distortions seen in Figure 2.5. Another improvement that can be made is to lower the amount of Gd$_2$O$_3$ used in the sample to see if the enhancement can be increased. Additionally, running the experiment at lower spinning speeds using
the 32 step PASS pulse spacings calculated in Table 2.2 would provide better contrast between the CSA of the $Q^{(n)}$ sites making the analysis easier.

2.5 Summary

We have been able to successfully acquire a 2D PASS CPMG spectrum that has an increase in signal noise ratio of 1.68 over normal 2D PASS. This increase in sensitivity allows for the use of unenriched $^{29}\text{Si}$ samples to be investigated. Comparing the simulated sideband patterns to the sideband dimension cross sections taken from our spectrum we have seen that the intensities of the MAS lineshape near -100 ppm is dominated by $Q^{(4)}$, the intensities around -88 ppm are dominated by $Q^{(3)}$, and the intensities around -75 ppm are dominated by $Q^{(2)}$.

Future studies would include the analysis of the sideband order cross-sections once the fitting program has been completed. From this we could obtain the equilibrium constant for the $Q^{(n)}$ disproportionation reaction at the glass transition temperature. Additionally, running the experiment at lower spinning speeds using the 32 step PASS pulse spacings could prove to be beneficial by providing better contrast between the CSA of the $Q^{(n)}$ sites. As mentioned earlier the experiment should be re-run with the proper shimming to confirm that the sideband distortions are coming from a field homogeneity, and the optimum doping level of $\text{Gd}_2\text{O}_3$ should be found. Ultimately, applying this new method to glasses of varying composition could provide further insight into the structure of silicate glasses.
BIBLIOGRAPHY


