Simulation of Magic-Angle Turning Spectra

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Abstract/Introduction

My work during the summer of 2014 had two major projects being conducted by two students (Solomon Tesfamichael and Kyaw Hpone Myint) at Berea College. The first project (involving primarily Kyaw Hpone Myint) was a continuation of the work we started last summer with Mikiyas Assefa to simulate two-dimensional XCS and MAT/PASS datasets of ^{31}P and ^{29}Si glasses. The second project (involving both students) was to measure J-resolved spectra (primarily using the phase-incremented echo train acquisition, PIETA, method) for ^{31}P sites in new phosphate glasses (this summer we added cadmium, tin and cesium cations). These results were presented as separate posters at the Berea Undergraduate Reseach Symposium in October 2014 and will be shown at the Kentucky Academy of Sciences conference in November 2014. We are in the process of writing up the J-coupling PIETA results for submission later this fall. I will give more specific details about each project in the following sections.

Chemical Shift Anisotropy Experiments

Reliably measuring the ^{31}P chemical shift anisotropy (CSA) in amorphous samples such as these modified pyrophosphate glasses in the past has been accomplished primarily by either magic-angle flipping experiments where isotropic magic-angle spinning (MAS) spectra are correlated with CSA patterns. The other approach has been to do sideband simulations of slow speed MAS spectra, sometimes using the MAT experiment. We have worked to improve the MAT experiment to allow collection of multiple echoes for enhanced sensitivity using the PIETA method as well as improved spinning sideband simulations (see figure 1 for an example of this method applied to $Cs_4P_2O_7$). This involved adapting a high speed Fourier Transform method developed by Malcolm Levitt along with a CSA tensor distribution coming from an extended Czjzek distribution. My student Kyaw worked on the C program we developed this summer generating first a flow chart for our one-dimensional simulation program written last year. Second he helped modify the code to simulate a two-dimensional MAT-PIETA dataset. As the summer

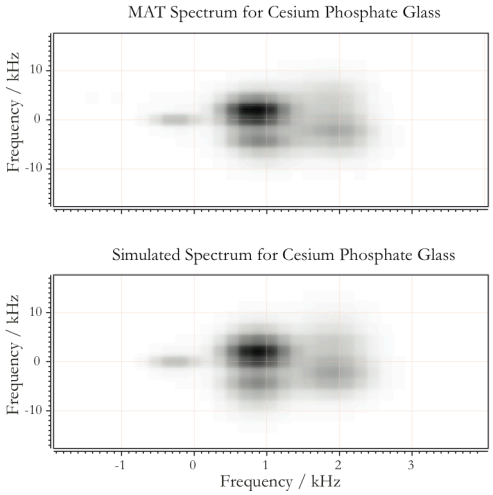

Figure 1: Example of MAT-PIETA (top) and simulation (bottom) for a $Cs_4P_2O_7$ glass with a gray density plot showing intensity at different frequencies.

came to a close, I was able to help him add (and later finish) the addition of the Czjzek distribution to this program. One of the difficulties of this is trying to develop an efficient algorithm to numerically calculate the distribution of CSA tensors. Since the extended-Czjzek distribution does not have an analytical solution, we had to use a Monte-Carlo method to sample the five dimensional Gaussian distriubtions and appropriately divide these amplidutes in an appropriate number of CSA distribution bins to feed into the sideband simulation part of the program. An example of how a Czjzek distribution changes the spinning sideband pattern is shown in figure 2.

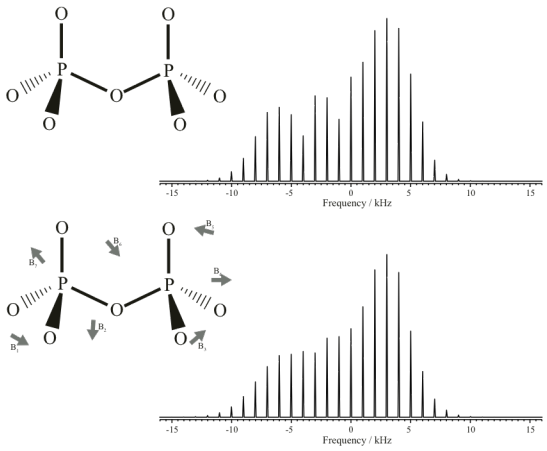

Figure 2: Effect of Czjzek distribution of random magnetic fields on a CSA sideband pattern.

Kyaw was able to run some simulations on data we acquired this summer and we have preliminary results on the various pyrophosphates we synthesized both during the summer of 2013 and 2014. The pulse sequence used to generate the data is show in figure 3. The data is given in table 1 showing that the various glasses have a number of similarities in the values for the CSA tensors. The next step in this research would be to run more MAT-PIETA experiments on additional samples with different cations as well as different compositions. With enough data we will then begin to try to model the CSA tensors with structural models that might be able to identify what differences are present that lead to differences in tensor parameters. This would mostly involve running simulations using *ab initio* quantum mechanical computational software such as GAUSSIAN03.

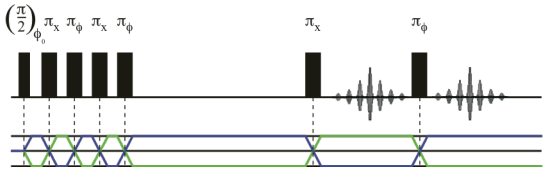

Figure 3: Magic-angle turning (MAT) PIETA pulse sequence used to acquire spectra.

J-Coupling Experiments

The second major project of the summer was to continue measuring J-coupling distributions in the same pyrophosphate glasses used in the CSA studies. This is a continuation of work we started a few years ago with Pyae Phyo and was continued this summer mostly by Solomon Tesfamichael. Most of the work this summer really came in trying to make new phosphate glasses. We had some trouble with platinum crucibles in the past reacting with samples at 1100˚C and this year we tried a change to alumina (Al_2O_3) crucibles. These have the advantage of being much less expensive ($50 per alumina crucible versus $500

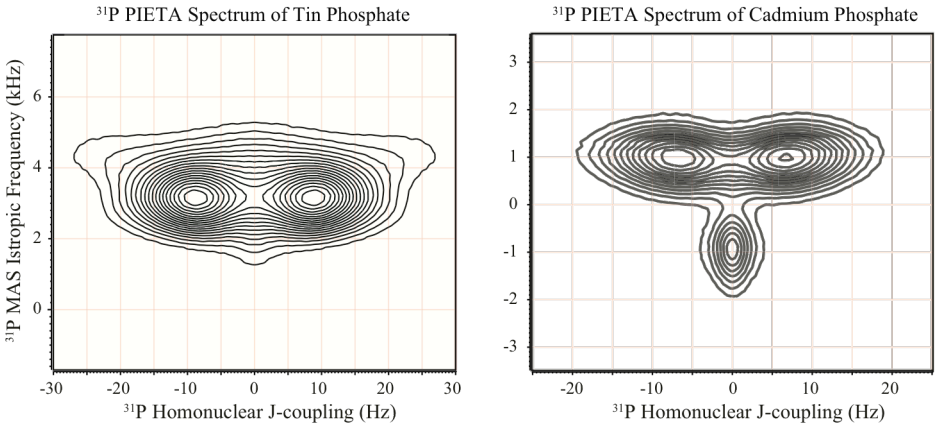

Figure 4: MAS-PIETA data for two different glasses. The tin sample shows mostly a strong doublet at 3.1 kHz in the isotropic dimension with a minor triplet at 4.7 kHz with a very strong nearly 20 Hz coupling. The cadmium sample has more cations and thus a singlet at –1 kHz and a doublet at 1 kHz with a weaker 15 Hz coupling.

or more for a Pt crucible). However even the alumina crucibles show signs of reaction with the starting materials and thus we need to consider either lower melting point materials or perhaps a shift to other crucible materials such as graphite, however this would necessitate inert atmosphere work. The pulse sequence is the same PIETA approach we have used before and has been extensively tested already on both ^{31}P and ^{29}Si glasses. Some examples of the data taken this summer are show in figure 4. Simulations of these spectra lead to minimal residuals (difference between simulation and data) indicating that the model has appropriate complexity to describe the data (results also in table 1). Our model has both an average coupling and coupling distribution width that is linearly related to the isotropic shift. What we are yet to do is begin to build a model that correlates the measured J-coupling parameters with an actual glass structure. We will undertake this in the future in combination with the CSA models mentioned in the previous section.

Sample	Site	ζ/ppm	η	J-coupling/Hz
Zinc Phosphate	$Q^{(1)}$ $Q^{(2)}$	78.3 –135.8	0.41 0.26	15.0
Cesium Phosphate	$Q^{(1)}$ $Q^{(2)}$	75.1 -80.9	0.40 0.33	< 5.0
Tin Phosphate	$Q^{(1)}$ $Q^{(2)}$	74.2 -94.0	0.41 0.78	18.0
Cadmium Phosphate	$Q^{(1)}$	81.4	0.42	14.0
Lead Phosphate	$Q^{(1)}$	-	-	22.0
Barium Phosphate	$Q^{(1)}$	-	-	5.0

Table 1: CSA and J-Coupling parameters for various glasses studied.

Conclusion and Future

We continue to make progress in developing new tools to analyze glass structure. We have enough J-coupling data that we can begin to write a preliminary journal article detailing these results. We also now

have enough tools to really test the comparisons between MAT and MAF experiments for measuring CSA distributions (especially those with an extened Czjzek model). I continue to collaborate with my colleagues at CEMTHI in Orleans, France (Fayon, Deschamps, Florian) and at the Ohio State University (Grandinetti) and I am optimistic there will be more productive travels to both locations in the future.