A Solid-State NMR Experiment: Analysis of Local Structural Environments in Phosphate Glasses

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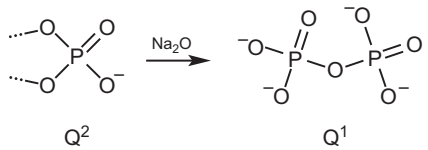
The importance of material sciences in the modern world cannot be overestimated. A variety of articles in recent years have been published in this *Journal* on the solid-state chemical and physical properties of inorganic materials. A number of experiments can be used to introduce undergraduate students to developments in the field *(1–9)*. While a large number of NMR experiments are available that utilize the capabilities of current instrumentation to study inorganic systems, all of these involve studying structure or chemical reactions in liquid solution *(10–28)* and are generally limited to observation of ^{1}H or ^{13}C nuclei. A few ^{19}F, ^{31}P, or ^{59}Co experiments are described. Some experiments introduce students to 2D techniques *(29)*.

Four-year colleges and universities increasingly have multinuclear FTNMR spectrometers available to undergraduate students. Many programs train their students in qualitative and quantitative analysis of organic compounds by NMR. We are not aware of any published experiments that introduce undergraduate students to the NMR spectroscopy of solids, with the possible exception of a recent inorganic lab experiment using ^{129}Xe to study adsorption of xenon gas on zeolites *(30)*. NMR spectroscopy of solids should be included in the undergraduate curriculum. This article is an attempt to fill that gap by introducing an experiment that can be used to directly study the local chemical environments of phosphorus in solid amorphous materials.

The study of phosphate glasses *(31–36)* has been important for the theoretical understanding of network solids and, more recently, in the development of fast ionic conductors, new optical lens materials, and materials with nonlinear optical properties. This experiment is appropriate for an advanced laboratory emphasizing the synthesis and characterization of typical glasses. It is also suitable for an instrumentation course with its emphasis on the quantitation of the chemical species present as well as its focus on principles of solid-state NMR spectroscopy.

The beauty of this experiment is that informative solid-state ^{31}P spectra can be obtained *on static samples* using high-field FTNMR instruments equipped with a multinuclear probe. The experiment does not require a magic-angle spinning (MAS) probe (rare in undergraduate teaching institutions), although this experiment could easily be extended to more powerful, high-resolution MAS techniques with a consequent increase in the quantity of information obtained. We observe wideline spectra with a typical high-resolution spectrometer and then analyze the spectra quantitatively to determine the relative contributions of local phosphate structures to the experimental lineshapes. Spectral analysis can be done with standard software supplied by most NMR manufacturers or even with commercial spreadsheets such as Microsoft Excel.



Scheme I. Reaction showing the effect of adding Na_2O.

The experiments we describe involve sodium phosphate glasses of the type $(Na_2O)_x(P_2O_5)_{1-x}$, which can be synthesized from melts over a range of x = 0.50–0.70. The glass network in this composition range is made up of singly-bridged pyrophosphate (Q^1) and doubly-bridged metaphosphate (Q^2) groups. Increasing the fraction of Na_2O breaks bridging bonds and converts one structure to the other as shown in Scheme I. Pure P_2O_5 containing three bridging oxygens is termed Q^3. With the help of ^{31}P NMR the proportion of these structural building-block units can be determined by adding together reference spectra of pure pyrophosphate and metaphosphate salts to simulate the observed spectrum of the glass.

Experimental

The purpose of this experiment is to familiarize students with the principles of solid-state NMR, to have them synthesize a simple phosphate glass, to observe the ^{31}P NMR spectrum, and to quantify the phosphate environments in the glass by deconvoluting this spectrum. The experimental procedure is outlined below.

Preparation of Phosphate Glasses

Phosphate glasses, $(Na_2O)_x(P_2O_5)_{1-x}$, with various compositions (mol%) are prepared, for example, 50% Na_2O–50% P_2O_5, 55% Na_2O–45% P_2O_5, and 60% Na_2O–40% P_2O_5. Appropriate quantities of Na_2CO_3 and $NH_4H_2PO_4$, to produce about 5 g of the glass, are weighed into a disposable porcelain crucible (or reusable graphite or platinum crucible). The mixture is heated at ~150 °C until gas evolution subsides. The reaction proceeds as follows:

$$x\mathrm{Na_2CO_3} + 2(1-x)\mathrm{NH_4H_2PO_4} \downarrow (\mathrm{Na_2O})_x(\mathrm{P_2O_5})_{(1-x)} + x\mathrm{CO_2} + 2(1-x)\mathrm{NH_3} + 6x\mathrm{H_2O}$$

The sample is then moved to a muffle furnace where it is heated above 800 °C until completely melted and held there

for 30–60 minutes. Since the melting point of each glass depends on composition, the temperature may need to be raised to 900 °C or higher until the melt flows easily. The resulting melts are rapidly poured onto a steel block to cool quickly and form the glasses.

NMR Experimental Details

Random incorporation of small quantities of Mn^{2+} does not affect the glass structure. The addition of 0.1–0.5% of $MnCO_3$ to each preparation speeds up the ^{31}P relaxation to facilitate more rapid acquisition of the spectra. These glasses are mildly hygroscopic and should be ground up and transferred to 5-mm NMR sample tubes in a nitrogen-filled glove bag. D_2O in sealed capillary tubes is placed in each sample tube to provide for an external lock. Pairs of students can be assigned a particular glass to synthesize and study. Spectra are obtained on a 300 MHz Bruker Avance spectrometer (^{31}P at 121.4 MHz) but procedures can be easily modified for other spectrometers *(37).* Solids generally require a Hahn echo 90-τ-180 protocol *(37, 38).* Sixteen acquisitions were enough to give spectra with excellent signal-to-noise ratios. All fid's are processed with a 200 Hz exponential multiplier before the Fourier transform.

Reference Spectra

Reference spectra are obtained for sodium pyrophosphate (corresponding to the Q^1 structure) and lithium metaphosphate (corresponding to the Q^2 structure).

Percent Composition

The percent composition is obtained by convolution using computer software. In this trial-and-error procedure, the reference spectra corresponding to Q^1 and Q^2 are added using the spectrum add–subtract command and varying the Q^2 multiplier by trial-and-error (DC parameter in Bruker software) until the added reference spectra match the glass spectrum.

A plot of experimental fractional component [e.g., DC/(1 + DC)] versus the percent molar ratio of Na_2O/P_2O_5 is prepared to compare the glasses. Appropriate conclusions are drawn from this plot. This last exercise requires that each pair of students share their results with the class. Students will discover that increasing the mol percent of Na_2O causes depolymerization of the fictitious P_2O_5 phosphate building blocks. A typical plot taken from class data is shown in Figure 1.

Hazards

Students need to exercise care in the use and disposal of the chemicals required, although they are relatively harmless materials. The greatest danger is from the synthesis of the glasses since muffle furnace temperatures of ~900 °C are used and students must manipulate the hot crucibles carefully.

Results and Discussion

Examples of spectra of glasses prepared by students are shown in Figure 2. Repeated syntheses and analysis of spectra gave results reproducible within 2%. The particular compositions were chosen so that there could be a direct

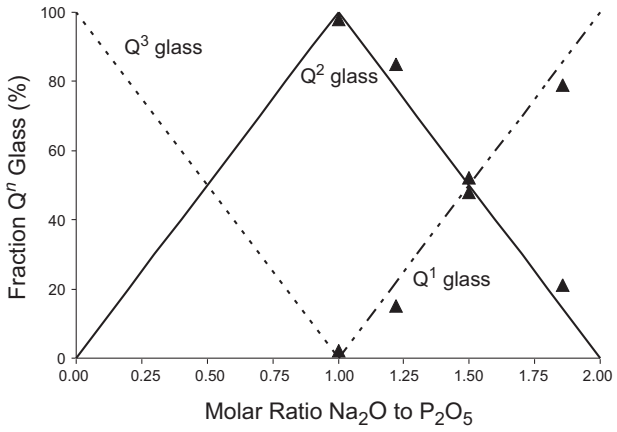


Figure 1. Class results for fractional composition versus the percent molar ratio of Na_2O/P_2O_5. Q labels refer to the solid and dashed theoretical composition lines.

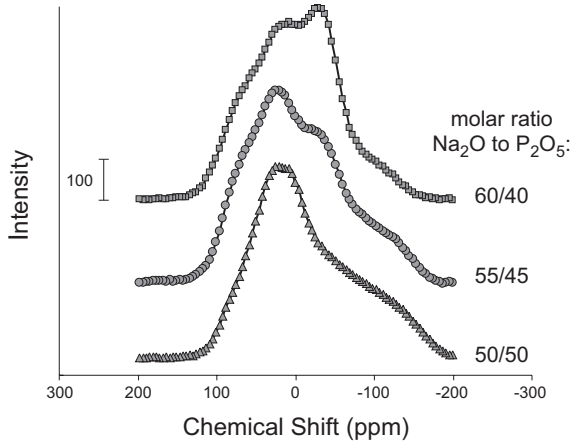


Figure 2. Wideline ^{31}P NMR spectra of various Na_2O/P_2O_5 glasses synthesized for this experiment.

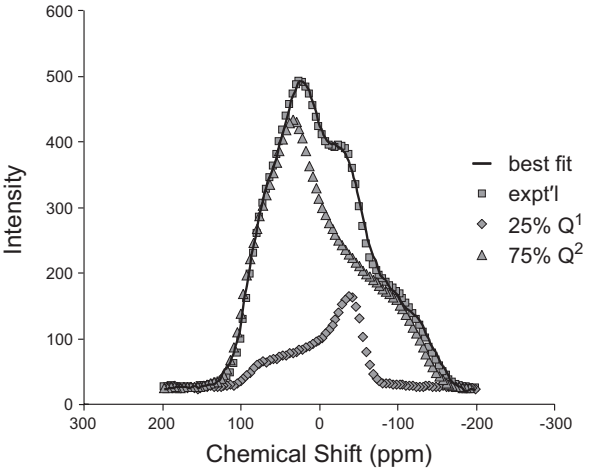


Figure 3. Best fit of observed 55% Na_2O/45% P_2O_5 glass spectrum from sodium pyrophosphate (Q^1) and lithium metaphosphate (Q^2) reference spectra gives 25% and 75% contributions, respectively.

comparison with literature values *(39)*. Depending on the size of the class, a wide range of compositions from x = 0.50–0.70 can be assigned for synthesis.

A typical fit for the glass of composition 55% Na_2O and 45% P_2O_5 that gives 25% Q^1 (pyrophosphate) and 75% Q^2 (metaphosphate) environments is shown in Figure 3. This is a good example of how well spectral components can be deconvoluted. An alternative procedure would be to digitize the printed spectrum using third-party software such as Unscan-it *(40),* import the ASCII file into a spreadsheet, and use the spreadsheet optimization tools to do a nonlinear least-squares fit of the reference spectra to the observed glass spectrum. The latter method gives very similar fits to the Bruker software, but requires considerably more manipulation of the data. Offline NMR data processing programs such as NUTS *(41)* are also useful, but again more numerical manipulation is required. It is instructive to have the student control the fitting process, but more time must be allotted to the analysis. We allowed one 4-hour lab period for the synthesis of the glasses, and a second 4-hour lab for the NMR data collection and analysis.

Student results obtained over a two-year period in several classes are within 2% of the literature values given in Table 1. This is a reasonable estimate of experimental error that includes variations in the synthesis of glasses as well as the fitting process. The correspondence is gratifying, especially considering that no adjustment was made to reference spectra linewidths, which undoubtedly would improve the fit.

Evaluations conducted at the completion of the course indicated a very positive experience for the students. Typical comments are reproduced in List 1. Students were challenged by the synthesis of the glass and were most enthusiastic about the application of NMR to solid-state analysis.

Table 1. Student Results for Phosphate Glasses

Composition ($\%Na_2O/\%P_2O_5$)	Wideline Results ($\%Q^1/\%Q^2$)	Literature (*39*)
50/50	3/97	4/96
55/45	24/76	22/78
60/40	43/57	43/57
65/35	71/29	—

List 1. Student Comments

This was a fun experiment! I enjoyed using the nitrogen glove bag, and learning more how NMR works.

Probably my favorite experiment. It was fun to learn about NMR and making the glasses was fun.

I liked being able to use the NMR more in depth.

Excellent lab that forced students to learn NMR.

This was our best experiment. I wouldn't change a thing.

Acknowledgments

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[W]Supplemental Material

Notes for the instructor, instructions for the students, an example of the lab report format, and a section on the fundamentals of NMR and high-resolution NMR are available in this issue of *JCE Online*.

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