Using phase incremented echo train acquisition (PIETA) Experiments to measure J-Couplings in Phosphate glasses.

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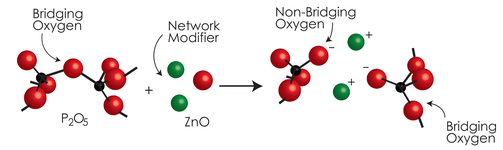
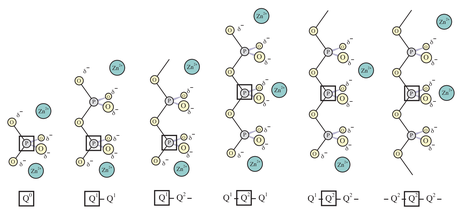
Abstract & Introduction

The scalar (J) couplings were measured in a series of phosphate glasses using the newly developed ^{31}P magic-angle spinning (MAS) phase incremented echo train acquisition (PIETA) method. In other kinds of chemical systems these J-couplings may be used to measure structural parameters such as molecular bond angles, in our case we hope to measure the P–O–P bond angle distribution in these glasses. Samples of the pyrophosphate ($P_2O_2^{4-}$) composition were prepared with tin, lead, zinc, cadmium, barium, and cesium counter cations and were quenched rapidly from the melt above 900˚C. After grinding and packing samples in the dry air box, the J-coupling distributions were measured with PIETA and then simulated using a C computer program written at Berea College.

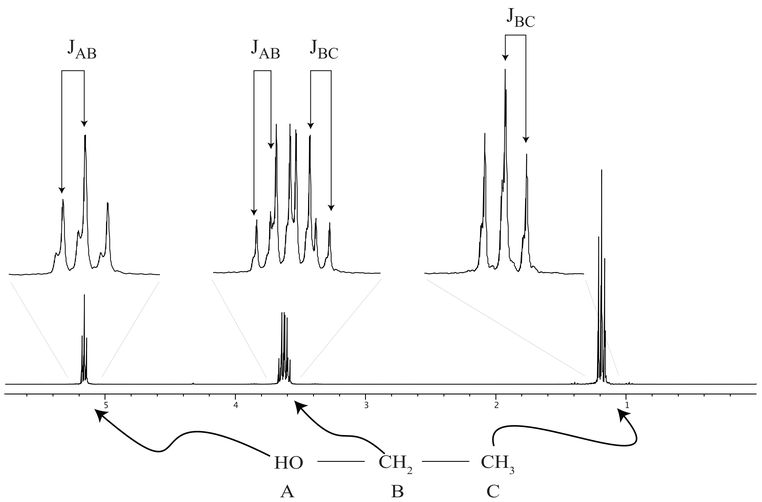
Phosphate Q-Speciation

Phosphate glasses are composed of linked PO_4 tetrahedra that could be bonded to one ($Q^{(1)}$ species), two ($Q^{(2)}$ species) and three ($Q^{(3)}$ species) other tetrahedra through the formation of corner shared P-O-P bonds. Since it is difficult to separate the $Q^{(n)}$ species in the phosphate glass by using MAS experiments alone, we used the PIETA methodology to extract the $Q^{(n)}$ speciation and J-coupling information.



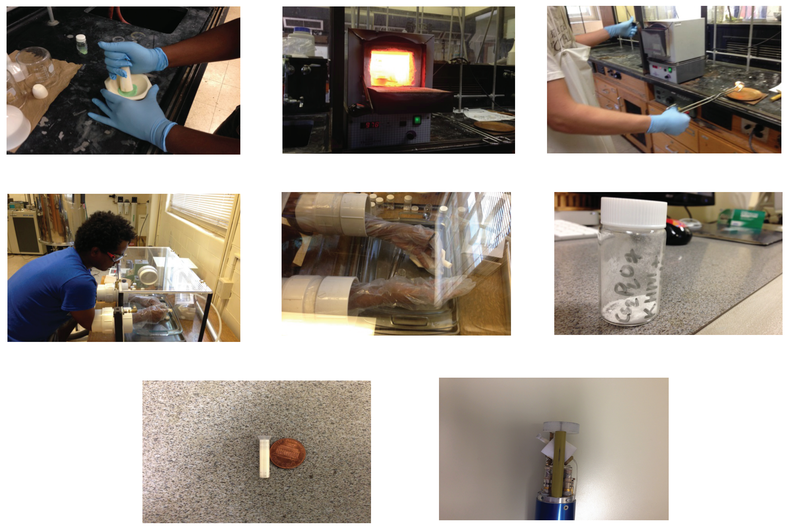


Homonuclear J-Coupling



Homonuclear scalar (J) couplings arise when the nuclear magnetic dipole moment of a near by spin is carried via the bonding electrons to a neighboring atom. This changes the local magnetic field for this atom based on the number of spin up and spin down neighbors. This produces a characteristic splitting pattern (N+1 rule from organic chemistry, see the example of Ethanol shown above). The measured J-coupling constants themselves have been used in other work to determine local strucure, for example the famous Karplus relation used to measure dihedral angles in proteins. We hope our ^{31}P homonuclear couplings can provide similar useful information.

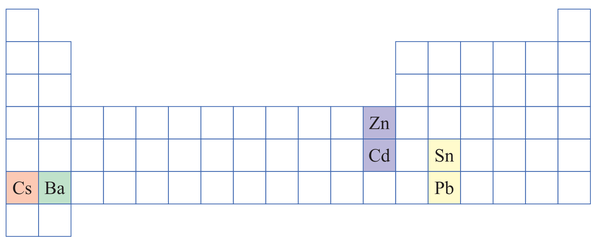
Sample Preparation & NMR Setup



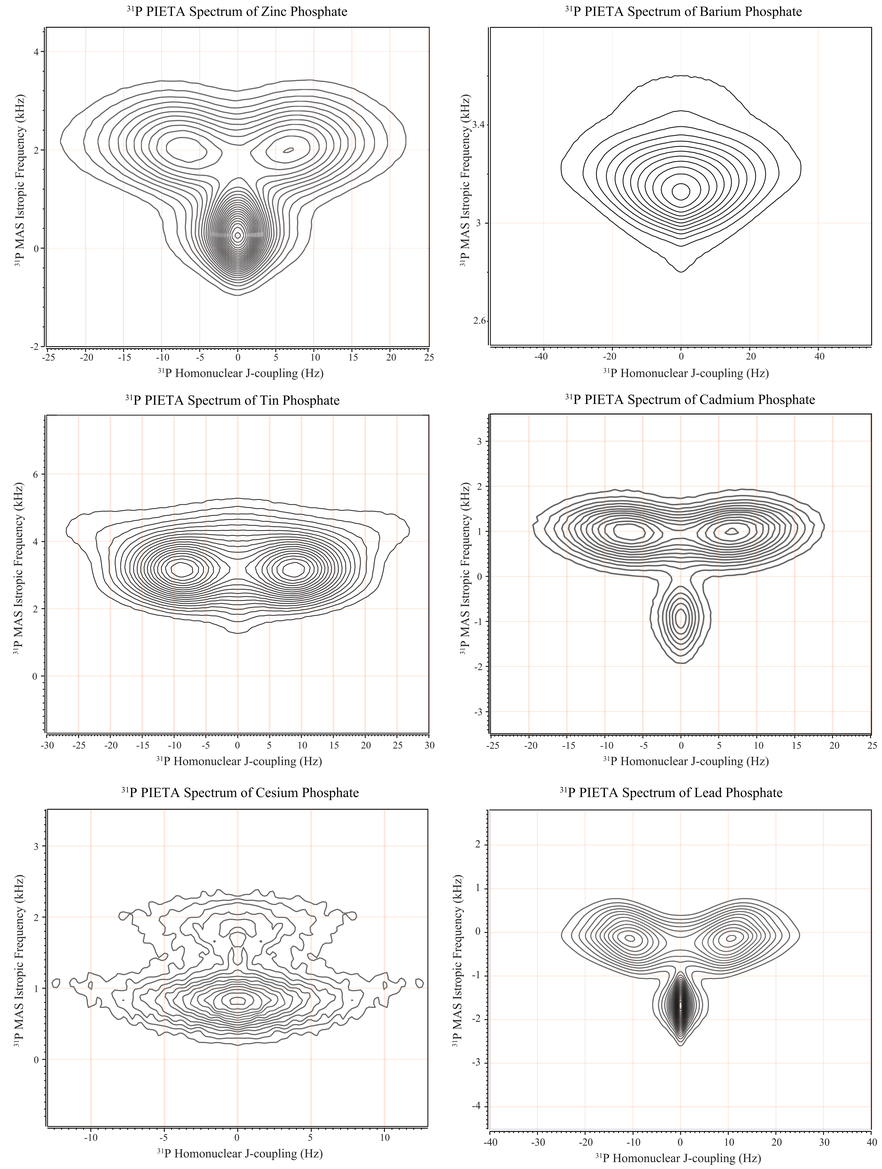
Measured Homonuclear J-Coupling Constants

Sample	Average J-coupling	Families
Tin phosphate	18 Hz	IV A
Lead phosphate	22 Hz	IV A
Zinc phosphate	15 Hz	II B
Cadmium phosphate	14 Hz	II B
Barium phosphate	5 Hz	II A
Cesium phosphate	< 5 Hz	I A

PIETA data (shown to the right) were acquired and simulated using a computer program written by Jay Baltisberger. The fits allowed an adjustable J-coupling average value, a distribution width of J-coupling values, and an overall slope for the coupling as a function of isotropic position in the MAS spectrum. The resulting simulations match the data exceptionally well and give the average J-coupling constants shown in the table above.



Results and Discussion



Conclusion

The results of these PIETA experiments indicate that the size of the cation is much less important than the group membership. This indicates the overall chemical bonding present is more of a structural determinant than the size of the cation (as you might expect from simple Pauling ionic radii rules). At this point we cannot distinguish if the distribution of bond angles is controlling the average J-coupling or if the average J-coupling is dependent upon the degree of ionic bonding between the cations and the phosphate units. In the future, calculations will be performed using GAUSSIAN03 to model the effects of bond-angle and cation type in these glasses and deconvolute this problem.