

Chemical Bonding of Lead in Glasses through Isotropic vs Anisotropic Correlation: PASS Shifted Echo

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When observing spin $I = \frac{1}{2}$ nuclei with important chemical shift anisotropy in disordered materials, the distribution of isotropic shift can become so large that no accessible spinning rate is able to provide a resolved spectrum. This is the case of ^{207}Pb in glasses where static and high-speed MAS spectra are nearly identical. It is still possible in such a case to rebuild a spinning sideband free spectrum using a shifted echo modified PASS sequence. This makes it possible to discuss isotropic and anisotropic chemical shifts of lead in phosphate glasses, to characterize its structural role and its chemical bonding state. © 1999 Academic Press

Key Words: solid state NMR; MAS; PASS; ^{207}Pb ; glass.

INTRODUCTION

High-resolution nuclear magnetic resonance has proved to be a useful tool for the investigation of local structure and chemical bonding in crystalline phases, but also in disordered solids: amorphous powders or glasses. Lead (^{207}Pb) is an attractive NMR nucleus, with a reasonable sensitivity and an $I = \frac{1}{2}$ nuclear spin, but, as mentioned earlier (1–4), ^{207}Pb suffers from a very wide range of chemical shift (7000–8000 ppm) with very large chemical shift anisotropy (more than 2000 ppm) due to its high number of electrons and high polarizability. Its characterization by NMR is currently regaining interest (5). From a systematic MAS NMR study of oxide compounds we showed that the chemical shift tensor parameters, both isotropic and anisotropic (mostly measured from sideband intensities (6)) can be correlated to the bonding environment of lead (4). In ionic bonding environments, lead has large coordination numbers and long Pb–O distances corresponding to low isotropic chemical shifts with low chemical shift anisotropy in the NMR spectrum. In covalent bonding environments, lead has small coordination numbers (down to 3 to 4) with short Pb–O distances in a typically pyramidal geometry with the Pb atom at the apex and O at the base. In this case, ^{207}Pb NMR spectra show large spans with high isotropic chemical shift values. Resulting from this large chemical shift anisotropy, the moderate field (7.04 T) high-speed (15 kHz) ^{207}Pb NMR MAS spectra of covalent crystalline compounds exhibit a very large array of spinning sidebands in which the determination of the isotropic positions can be problematic. Further-

more, the spectrum can become so wide that there is incomplete excitation even under high-power conditions (7, 8). These difficulties, which are partly overcome in the case of a crystalline compound because of its narrow linewidth, become a major obstacle to obtaining resolved MAS spectra for disorder-bearing materials such as glasses due to severe overlap of a large number of spinning sidebands, which are unavoidable under currently accessible spinning rates. In such a case, static spectra, eventually acquired in pieces, were used to characterize the lead environment. Using ^{207}Pb static spectra, in agreement with L_{III} Pb edge XAFS analysis and ^{29}Si NMR, we showed that lead is in a covalent bonding environment in SiO_2 –PbO glasses with low coordination numbers and that it plays the role of a network former (7, 8). The aim of this contribution is to show that, even in the case of an unresolved MAS spectrum, it is possible to experimentally separate the isotropic and anisotropic part of the chemical shift tensor using a shifted echo (9) modification (PASS-SE) of the 2D-PASS sequence proposed by Antzutkin *et al.* (10). From the obtained two-dimensional isotropic/anisotropic correlation dataset it becomes possible to better describe the lead bonding environment in P_2O_5 –PbO glasses.

EXPERIMENTAL

The P_2O_5 –PbO samples have been prepared by quantitative precipitation from aqueous solutions of ammonium hydrogen phosphate and lead nitrate. The $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_2\text{P}_2\text{O}_7$, $\text{Pb}_3\text{P}_4\text{O}_{13}$, and $\text{Pb}(\text{PO}_3)_2$ crystalline phases were obtained by annealing at high temperature and the 3PbO – $2\text{P}_2\text{O}_5$ glass by quenching from the liquid phase.

All the solid-state NMR experiments have been carried out using a Bruker DSX 300 spectrometer operating at 7.04 T with a Larmor frequency of 62.6 MHz for ^{207}Pb . The $\pi/2$ pulse duration was 1.7 μs ($\omega_1/2\pi = 147$ kHz). The spinning frequency was stabilized to ± 10 Hz for MAS and PASS experiments. Timings for the PASS sequence corresponding to 16 pitch increments are given in Table 1. These 16 pitch increments allow a complete sideband separation of the ^{207}Pb spectra at high spinning frequency (10 kHz). The pulse phases were cycled by steps of 120° to fulfill the coherence pathway of Fig.

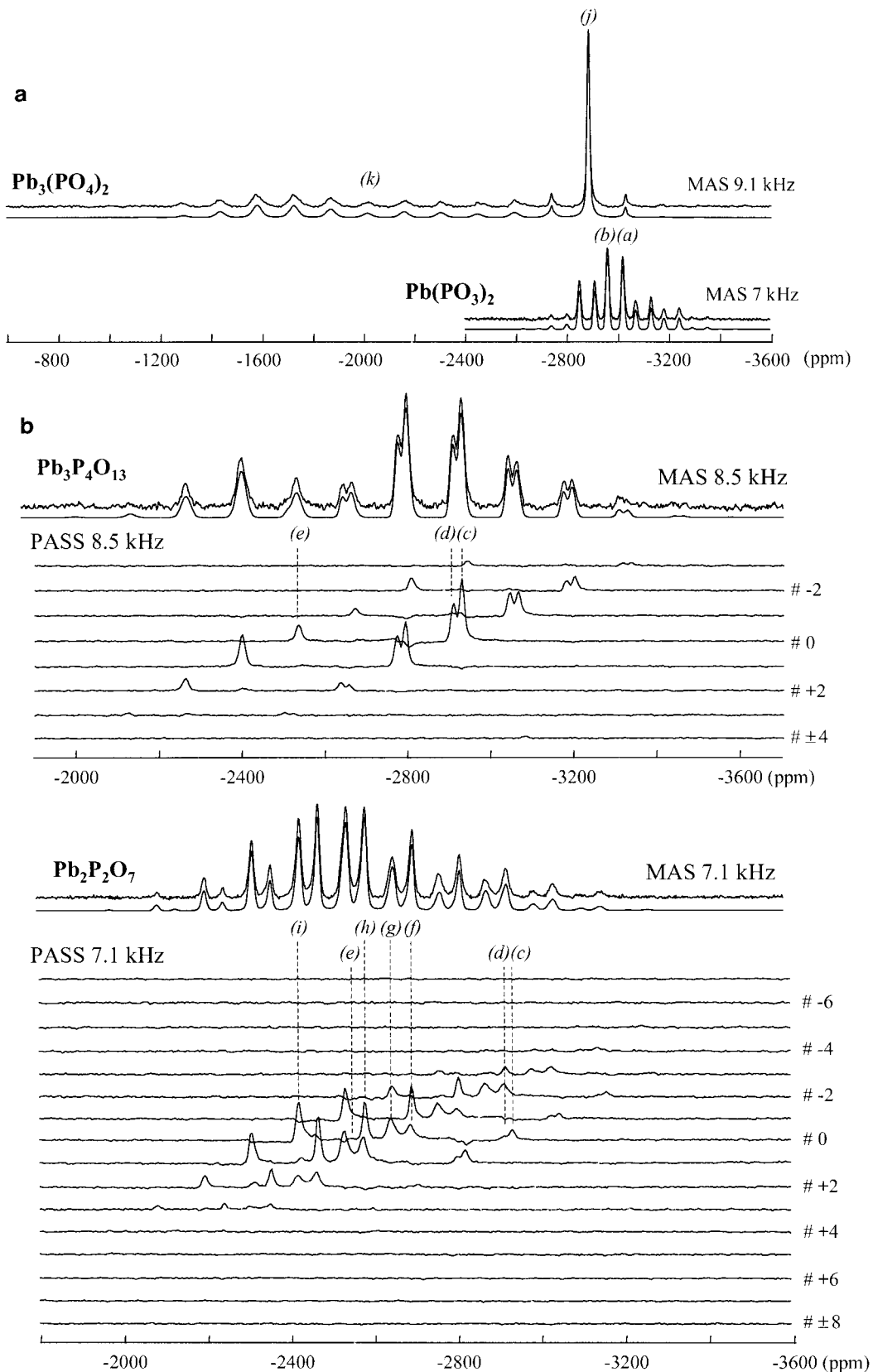


FIG. 1. (a) ^{207}Pb MAS spectra of crystalline $\text{Pb}(\text{PO}_3)_2$ and $\text{Pb}_3(\text{PO}_4)_2$. (b) ^{207}Pb MAS and 2D PASS spectra of crystalline $\text{Pb}_3\text{P}_4\text{O}_{13}$ (height pitch increments, 486 transients per slice) and $\text{Pb}_2\text{P}_2\text{O}_7$ (16 pitch increments, 972 transients per slice).

TABLE 1
Delays between Pulses Used for the 2D PASS Experiments
(Measured in Sample Revolution Angles)

Increment	$\Delta\theta_1/2\pi$	$\Delta\theta_2/2\pi$	$\Delta\theta_3/2\pi$	$\Delta\theta_4/2\pi$	$\Delta\theta_5/2\pi$	$\Delta\theta_6/2\pi$
1	0.16667	0.16667	0.16667	0.16667	0.16667	0.16667
2	0.18989	0.17512	0.15541	0.17615	0.15470	0.14873
3	0.21668	0.17874	0.14270	0.18365	0.14062	0.13761
4	0.24453	0.17549	0.12896	0.18947	0.12651	0.13504
5	0.26915	0.16096	0.15737	0.19608	0.11511	0.14297
6	0.28147	0.12931	0.11053	0.21004	0.10800	0.16065
7	0.26731	0.09195	0.13166	0.22798	0.10102	0.18008
8	0.23472	0.07687	0.17459	0.22846	0.09069	0.19467
9	0.20979	0.08043	0.20978	0.20979	0.08043	0.20978
10	0.19467	0.09069	0.22846	0.17459	0.07687	0.23472
11	0.18008	0.10102	0.22798	0.13166	0.09195	0.26731
12	0.16065	0.10800	0.21005	0.11052	0.12934	0.28144
13	0.14297	0.11511	0.19608	0.11574	0.16095	0.26915
14	0.13504	0.12651	0.18947	0.12896	0.17549	0.24453
15	0.13761	0.14062	0.18365	0.14270	0.17875	0.21667
16	0.14874	0.15469	0.17615	0.15541	0.17512	0.18989

3a (10). Chemical shifts were referenced to tetramethyl lead $\text{Pb}(\text{CH}_3)_4$ at 0 ppm, using a 1 M aqueous lead nitrate solution as a secondary reference (11).

RESULTS

The ^{207}Pb static NMR or MAS (10 kHz spinning) spectra of the $3\text{PbO}-2\text{P}_2\text{O}_5$ glass, both acquired as full echo (rotor synchronized in the case of the MAS spectrum), are identical. This indicates that the distribution of isotropic chemical shift (width of the individual spinning sidebands) is greater than the spinning rate (10 kHz \sim 160 ppm). These spectra exhibit an asymmetric lineshape that contains both isotropic and anisotropic contributions and cannot be modeled without information on the related crystalline compounds. By analyzing the spinning sideband intensities in the MAS experiment (6), we independently measured the chemical shift anisotropy parameters of ^{207}Pb in 11 different structural positions in four crystal structures: $\text{Pb}_3(\text{PO}_4)_2$, $\text{Pb}_2\text{P}_2\text{O}_7$, $\text{Pb}_3\text{P}_4\text{O}_{13}$, and $\text{Pb}(\text{PO}_3)_2$ (Table 2). The ^{207}Pb experimental MAS and PASS spectra of these crystalline compounds are shown in Fig. 1. In these crystalline structures lead–oxygen coordination numbers varying from 7 to 10 are difficult to discern in the NMR spectrum. Figure 2 shows the ^{207}Pb static NMR spectrum of the glass together with the modeled static spectra of the four crystalline lead phosphate compounds. Considering the shape of the crystalline compound spectra, it clearly appears that there is no unambiguous interpretation of the spectrum obtained for the glass sample without characterizing the chemical shift tensor distribution. To determine the ^{207}Pb isotropic chemical shift distribution which is related to the local glass structure, it would be necessary to acquire a spinning sideband free spectrum by spinning at 50 to 60 kHz, which is impossible with today's probe-

TABLE 2
Isotropic and Anisotropic ^{207}Pb Chemical Shifts of the Four Crystalline Lead Phosphates $\text{Pb}(\text{PO}_3)_2$, $\text{Pb}_3\text{P}_4\text{O}_{13}$, $\text{Pb}_2\text{P}_2\text{O}_7$, and $\text{Pb}_3(\text{PO}_4)_2$ ($\delta_{\text{iso}} \pm 2$ ppm, $\Omega \pm 10$ ppm, $K \pm 0.05$) with $\Omega = \delta_{11} - \delta_{33}$, $K = 3(\delta_{22} - \delta_{\text{iso}})/\Omega$ (21)

Compound	δ_{iso} (ppm)	Ω (ppm)	K	δ_{11} (ppm)	δ_{22} (ppm)	δ_{33} (ppm)	
$\text{Pb}(\text{PO}_3)_2$	(a)	-3023	450.5	0.53	-2837.5	-2943.5	-3288
	(b)	-2962	387.5	0.87	-2824.5	-2849.5	-3212
$\text{Pb}_3\text{P}_4\text{O}_{13}$	(c)	-2926	595	0.53	-2681	-2821	-3276
	(d)	-2906	695	0.20	-2582	-2860	-3276
	(e)	-2533	840	0.75	-2218	-2323	-3058
$\text{Pb}_2\text{P}_2\text{O}_7$	(f)	-2680	861	0.38	-2303	-2571	-3165
	(g)	-2635	675	0.43	-2346	-2539	-3020
	(h)	-2571	657	0.24	-2269	-2518	-2926
$\text{Pb}_3(\text{PO}_4)_2$	(i)	-2412	573	0.04	-2129	-2405	-2702
	(j)	-2886	210	-0.64	-2758.6	-2930.8	-2968.6
	(k)	-2016	1781	0.64	-1315	-1638	-3096

head hardware. Spinning sideband suppression techniques (TOSS (12–14); SELTICS (15)) can give spinning sideband free spectra; however, they have limited utility since the obtained isotropic spectrum is not quantitative: i.e., the sites with large chemical shift anisotropy have lowered contributions. One possible solution is to separate the different spinning sidebands using a multiple pulse experiment so as to recon-

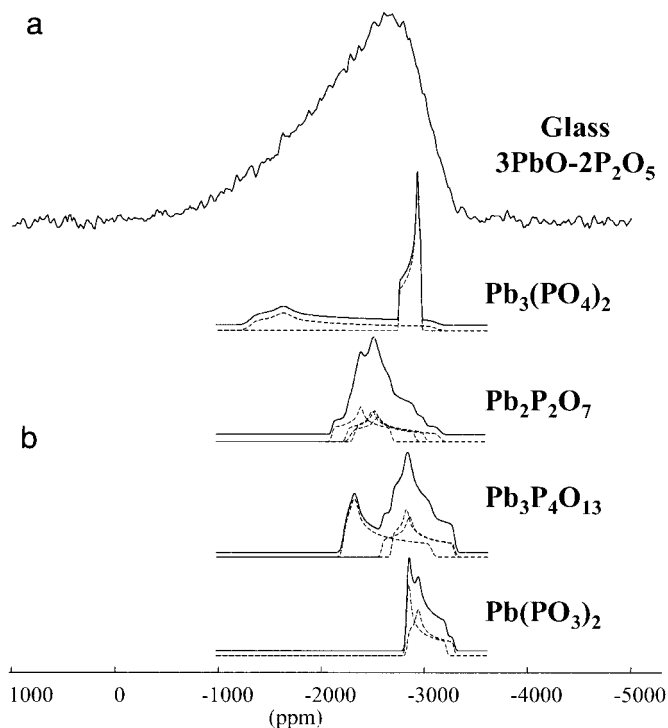


FIG. 2. (a) ^{207}Pb static NMR spectrum of the $3\text{PbO}-2\text{P}_2\text{O}_5$ glass, (b) modeled static NMR spectra of the four crystalline lead phosphates $\text{Pb}(\text{PO}_3)_2$, $\text{Pb}_3\text{P}_4\text{O}_{13}$, $\text{Pb}_2\text{P}_2\text{O}_7$, and $\text{Pb}_3(\text{PO}_4)_2$.

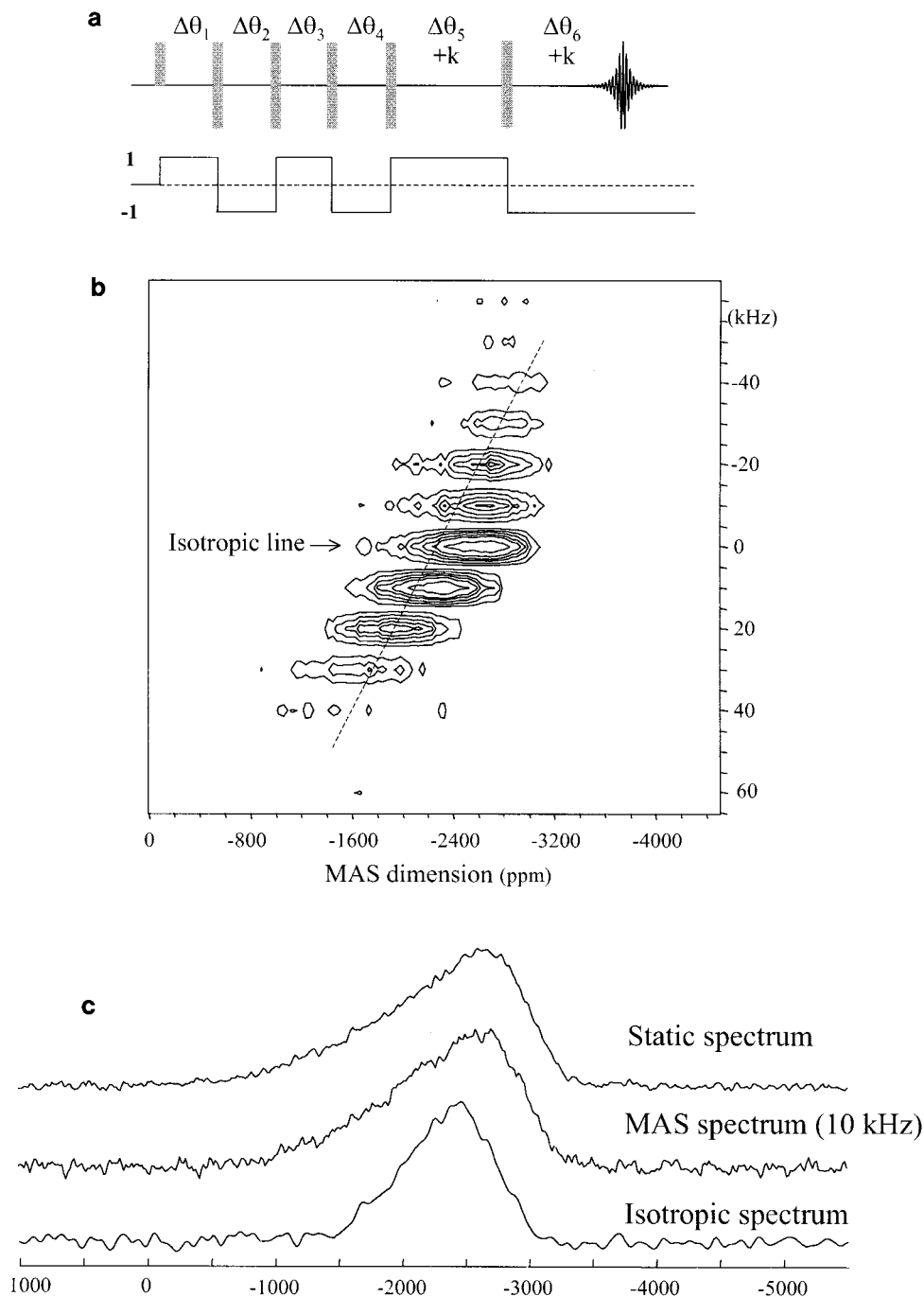


FIG. 3. (a) Pulse sequence and coherence pathway used for the two-dimensional PASS-SE experiment (small pulse is $\pi/2$ and large ones are π pulses); delays between pulses are given in Table 1 (10). An integer number of rotor periods is added to the last delay to acquire a full echo. (b) ^{207}Pb 2D PASS spectrum (10 kHz) of $3\text{PbO}:2\text{P}_2\text{O}_5$ glass represented as a contour plot. Sixteen pitch increments were taken, each the sum of 4131 transients. For clarity, data were concatenated in the F_1 dimension to generate spinning sideband separation by null slices. (c) Stack plot of the ^{207}Pb static, MAS (10 kHz), and isotropic NMR spectra of the $3\text{PbO}:2\text{P}_2\text{O}_5$ glass.

struct the *infinite spinning rate* sideband-free spectrum. To achieve this aim we have implemented a modified PASS experiment (10, 12). This experiment, designed for an $I = \frac{1}{2}$ nuclear spin subject to chemical shift anisotropy, uses a train of 5π pulses placed in the spinning period to encode the phase of

each spinning sideband by a pitch variable. Double Fourier transformation, according to the t_2 (acquisition time) and pitch variables, results in a two-dimensional spectrum in which spinning sidebands are sorted by number in the F_1 dimension. From this dataset it becomes possible to reconstruct the side-

band free isotropic spectrum correlated to an anisotropic dimension. The obstacle to directly applying the PASS sequence to our ^{207}Pb spectrum lies in the very short duration (very large bandwidth) of the lead signal (FID). As described in the case of the QPASS experiment (16), it is possible to add an integer number of rotor periods in the last evolution period (between the fourth and fifth pulses—Fig. 3) which results in shifting the echo out of the last pulse and thus enables the acquisition of a full echo (PASS-SE: PASS-shifted echo), as used in static echo experiments (7, 8, 17) but also in DAS (9) or MQ-MAS (18). Using a full echo acquisition results in unambiguous phasing of the pure absorption mode two-dimensional spectrum and improves the signal-to-noise ratio by a factor of up to $2^{1/2}$ (9).

Figure 3 presents the PASS-SE pulse sequence and the results obtained for the $3\text{PbO}-2\text{P}_2\text{O}_5$ glass. The two-dimensional spectrum shows very wide spinning sidebands which were summed to give the isotropic spectrum shown at the bottom of the figure together with the MAS and static spectrum. This isotropic spectrum has a width of 830 ppm (~ 52 kHz) covering the whole range of isotropic chemical shift positions observed in crystalline phases of the $\text{PbO}-\text{P}_2\text{O}_5$ system. Furthermore, it has a Gaussian shape and can be ascribed to a continuous distribution of isotropic chemical shift centered at -2320 ppm with a width of 830 ppm. A similar approach could have been worked out using MAT experiments (19, 20). The advantage of the PASS sequence is that it provides resolution with a minimum number of pitch increments, thus minimizing the whole experimental acquisition time.

By shearing the obtained two-dimensional spectrum we can transform this representation to a more conventional isotropic vs anisotropic correlation (10), from which we can now discuss the anisotropic part of the chemical shift tensor across the isotropic line. This is presented in Fig. 4. It becomes clear in this representation that there exists a correlation between the isotropic and anisotropic parts of the chemical shift tensor. The lower chemical shift part has a lower chemical shift anisotropy while the higher chemical shift part of the line has a higher chemical shift anisotropy. This shows that the bonding environment of lead in this glass varies from a more ionic environment (longer Pb–O bond lengths, low anisotropy) to a more covalent bonding environment (shorter Pb–O bond lengths, more pronounced lone pair effect, and high anisotropy (4)) across the isotropic line. Using these results it becomes possible to identify the structural role of lead in these phosphate glasses and to show that it changes from a network modifier role in the phosphate-rich composition to a mixed former-modifier role with increasing lead content. This will be illustrated in a forthcoming publication.

CONCLUSION

Even in the case of severe anisotropic broadening of NMR spectra, which leads to unresolved magic angle spinning spectra, it is possible to reconstruct an *infinite spinning rate* spec-

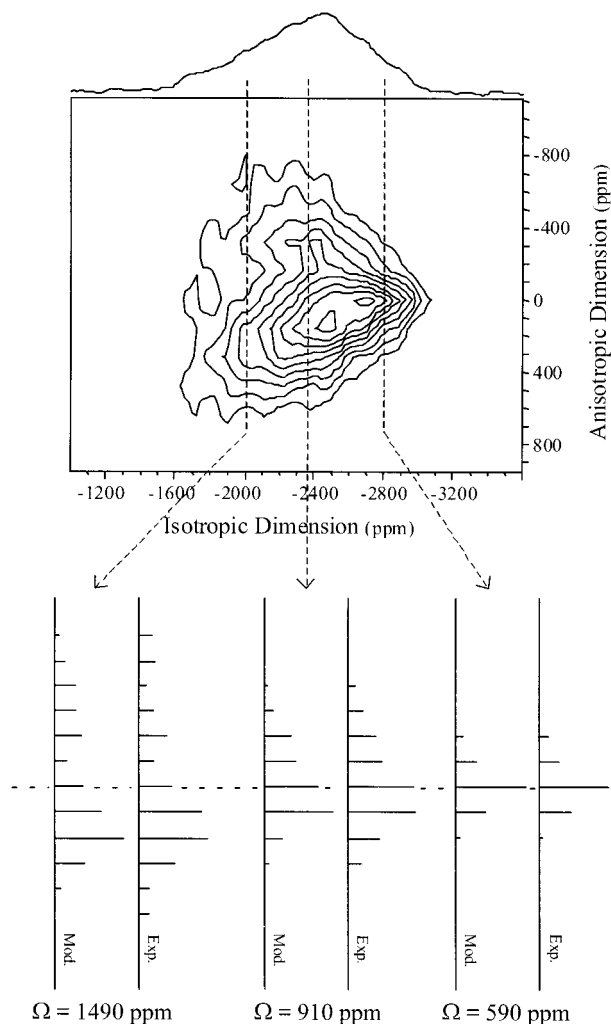


FIG. 4. ^{207}Pb 2D PASS sheared spectrum (10 kHz) of $3\text{PbO}:2\text{P}_2\text{O}_5$ glass represented as a contour plot.

trum that gives an accurate measure of the distribution of isotropic chemical shifts and enables the separation of isotropic and anisotropic parts of the chemical shift interaction. In the case of ^{207}Pb NMR, the PASS-SE experiment reveals a continuous distribution of the lead environment in lead phosphate glasses from more ionic to more covalent bonding environments, thus revealing the mixed network former/network modifier role of Pb^{2+} in $\text{P}_2\text{O}_5-\text{PbO}$ glasses. This experimental scheme could be of much interest in the NMR study of heavy metals such as Sn, Cd, and Hg, which all have large chemical shift anisotropy, in amorphous materials or glasses.

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