



Synthesis and Characterization Alkali Metal Salts Containing Trapped Hydrino

Performed at Rowan University
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Summary

In this work, potassium chloride and potassium iodide salts containing a new form of hydrogen (hydrino) were synthesized. Characterization using solid state MAS ^1H NMR of potassium chloride salt containing the hydrino hydrogen (KH^*Cl) gave spectral features at -4.50 ppm and 1.20 ppm relative to tetramethylsilane (TMS) while liquid ^1H NMR gave less intense peaks at 1.20 ppm versus TMS. MAS ^1H NMR of potassium iodide salt containing the hydrino hydrogen (KH^*I) gave an intense broad peak at approximately -2.45 ppm relative to TMS while liquid ^1H NMR showed a very intense peak at approximately 1.258 ppm. These unusual upfield shifted peaks relative to the respective ordinary molecular hydrogen (4.5 ppm in liquid NMR) and hydride (0.8 and 1.1 ppm in MAS ^1H NMR) ^1H NMR peak locations are similar to those reported by BLP. Samples synthesized using chemicals provided by BLP also yielded similar MAS ^1H NMR spectral features. BLP has attributed these peaks to lower energy hydrogen (hydrino) as hydride ions (-4.5 and -2.45 ppm in MAS ^1H NMR) and molecular hydrino gas (1.2 ppm in liquid ^1H NMR). Neutron diffraction studies indicate the possibility of trapped interstitial atoms although the exact nature of these could not be established unambiguously. Elemental analysis on these salts containing hydrino hydrogen showed negligible amounts of Be, Cr, Mn, Ni, Co, Zn, As, Ag, Cd, Sb, Ba and Pb. These results are supportive of the possibility of having lower electronic states of hydrogen.

Introduction

BLP has made claims of the existence of a hydrogen where the single electron resides in a lower energy state called *hydrinos* [1-8]. The transition to such a state is induced by the presence of a catalyst and atomic hydrogen [1-8]. It has been claimed that the alkali metal halide is capable of trapping this lower energy hydrogen as a high binding energy hydride ion also called the hydrino hydride ion. If these claims are verified then it is reasonable to envision a potentially novel and revolutionary energy source.

In this work, we have used chemicals supplied by BLP and synthesized several alkali halide hydrides, (KH*X, X= Cl and I) containing hydrino hydride ions trapped in the lattice of the alkali halides. The procedure is outlined below. We also purchased our own chemicals and synthesized in-house samples of these compounds. Synthesis of KH*X included the reaction of KCl or KI with hydrogen in the presence of catalysts [2-5, 7, 8]. These reactions were carried at temperatures in the range of 500°C to 600°C in a kiln for 68 hours. BLP has claimed that the high binding energy hydrides have a smaller radius relative to the normal hydride which in turn enhance the shielding. The observed upfield shifts in the NMR spectra has been attributed to the increased shielding.

The objective of the work at the Chemistry and Biochemistry Department at Rowan was to synthesize and characterize hydrino-hydride ions trapped in the lattice of alkali halides and compare the results with those obtained from BLP materials

Synthesis of Alkali Salts with Trapped Hydrino

Chemicals and Procedures

KCl and KI (both with a purity better than 99.5%) were procured from VWR, potassium sticks from Strem Chemicals, and nickel screen (Ni, 20x20 mesh plain, 0.014 inch in diameter) was purchased from the Unique Wire Weaving Company. K_2CO_3 and H_2O_2 were also purchased from VWR.

In preparation for the reaction, the salts were first dried in a flask under a vacuum of approximately 50 mTorr at 200°C for 14 hours and then transferred to the glove box. The potassium sticks were washed three times with anhydrous hexane inside the glove box. Nickel screen was washed with a water solution containing 20 wt % K_2CO_3 and 5 % H_2O_2 and then with deionizer water and dried at 100 °C overnight.

For the synthesis of KH^*Cl , a clean stainless steel reactor was transferred to the glove box after drying in the oven overnight at 120°C and lined with about 43 grams of nickel screen. A stainless steel crucible was then placed in the reactor. The oxide layer on the surface of potassium was peeled off with a penknife. About 1.6 g of the shiny potassium was weighed and placed on the bottom of stainless steel crucible. 20 grams of KCl was then weighed and placed in the stainless steel crucible to cover the potassium. The reactor was tightly closed and was checked for any leaks before placing the reaction was started. The reactor was pumped down to a final vacuum of < 30 mTorr.

For synthesis of KH^*I , 15.0 grams of dry Raney Ni 2800 was weighed inside the glove box and placed in the stainless steel crucibles. Approximately 1.0 g of potassium metal was also weighed inside the glove box and placed in a smaller stainless steel crucible. 20 grams of KI was then weighed and spread over the potassium metal inside the smaller crucible. The crucible was subsequently transferred to the larger crucible and placed on the bottom of the reactor before sealing and evacuation. The reaction temperature for this synthesis was 500°C . The rest of the procedure was similar synthesis of KH^*Cl .

After evacuation of the reactors, hydrogen gas (5 PSIG pressure) was slowly introduced and the temperature was gradually increased to 600°C . The reactor pressure was maintained at 5 PSIG for the next 68 hours. In some experiments, the pressure was checked and more hydrogen added every 30 minutes if needed to maintain 5 PSIG. After the completion of the experiment, the kiln was shut down and allowed to cool naturally. At about 300°C , the kiln's lid was opened to hasten the cooling. The reactor was pressurized with helium after the reactor temperature had dropped to 50°C .

The reactor assembly was transferred to the Ar-filled glove box after closing all the valves. The hydrogen containing salts were retrieved and placed in a vial. Nearly 1.0 gram of the sample was sent out for solid state MAS ^1H NMR studies. This procedure was repeated several times to ensure the reproducibility during the months of January to May. Liquid NMR studies of these samples were taken at Rowan University. Solid state MAS ^1H NMR results, liquid ^1H NMR, as well as elemental analysis, and neutron diffraction studies were carried out.

For solution ^1H NMR measurements, KH^*X samples were first washed in DMF-d_7 solvent in a glove box. The clear liquid, just above the solid material, was transferred to an NMR tube (attached to a vacuum line for sealing) and then flame-sealed for NMR analysis. Proton NMR was recorded using a 400 MHz Varian Oxford AS400 NMR system. Solution ^1H NMR spectra of these salts were obtained in the DMF-d_7 solvent. All NMR spectra were relative to TMS.

Elemental analysis of the salt was done using inductively coupled plasma mass spectrometry (Agilent 7500, ICP-MS) and using standard analytical procedures.

Results and Discussions

Characterization of Hydrino Containing KCl Salts

Figure 1 shows the solid state MAS ^1H NMR spectrum of KH^*Cl sample prepared using chemicals provided by BLP using the procedure described above. Two peaks were observed, one intense peak at around -4.469 ppm and another less intense centered at 1.197 ppm. Other samples synthesized using BLP chemicals yielded similar spectra.

Figure 2 shows the MAS ^1H NMR spectrum of the KCl salt purchased by Rowan from VWR. Two peaks with low intensity centered at around 1.13 ppm and at 4.298 ppm were observed, and no peaks upfield of TMS were detected. BLP reported that the MAS ^1H NMR of mixtures of KCl and KH show an H_2 peak at 4.3 ppm and KH in two chemical environments at 1.1 and 0.8 ppm [3,5]. KH is air sensitive and not present in KCl. The peak at 1.1 ppm has been found only in salts that contain a hydrino catalyst [2] and H_2 . The peak at 1.1 ppm has been observed by other researchers who could not assign it [9]. It is observed along with the known H_2 peak at about 4.3 ppm. BLP attributes the peak to interstitial $\text{H}_2(1/4)$ [2]. MAS ^1H NMR spectra of some additional KH^*Cl salts synthesized using Rowan procured reagents are shown in Figures 3 and 4. Two intense peaks were obtained, one at -4.5 ppm and another at 1.201 ppm. All syntheses showed considerable reproducibility as each sample yielded the similar spectra.

Solid State ^1H NMR clearly shows an upfield shifted peak at -4.50 ppm and a peak at 1.20 ppm which BLP has attributed to hydrino hydride ion and molecular hydrino, $\text{H}_2(1/4)$, respectively. The unusual upfield shifted peaks were consistently observed at these positions in the samples as

repeated runs yielded similar spectra. We cannot assign negative upfield shifted peaks to any known compound from the literature as ordinary alkali hydrides alone or when mixed with alkali halides only show down-field shifted peaks.

Solution ^1H NMR spectrum of KH^*Cl in DMF-d_7 as the solvent is shown in figure 5. Four peaks were observed, a singlet at 8.030ppm and two solvent peak quintets centered at 2.907 ppm, and 2.715 ppm. Another singlet is also visible at 3.379 ppm due to presence of residual water in DMF. There was no clear upfield shifted peak at -3.80 ppm that was observed by BLP [2]; although, a less intense peak at 1.25 ppm assigned to $\text{H}_2(1/4)$ by BLP [2] was apparent (Figure 5 insert).

Neutron diffraction studies of KH^*Cl and KCl used in the synthesis indicated that interstitial atoms could be trapped in the KCl lattice. Figure 6 shows the neutron diffraction pattern KCl while figure 7 shows the neutron diffraction pattern of KH^*Cl . This initial result leads us to believe that indeed hydrogen could be the atom in the salt but exactly in what form is still not clear to us. We have planned more neutron diffraction studies.

Elemental analysis of KH^*Cl using ICP-MS yielded the following results: Be (less than 1 ppb) , Cr (3.0 ppb) , Mn (less than 1.0 ppb), Ni (less than 1.0 ppb) , Co (< 1.0 ppb) , Zn (about 1.0 ppb) , As (about 1.6 ppb), Ag (7.4 ppb), Cd (< 1.0ppb), Sb (1.8 ppb), Ba (<1.0 ppb) and Pb (0.3 ppb). These concentrations were too low to influence the reaction or the NMR results.

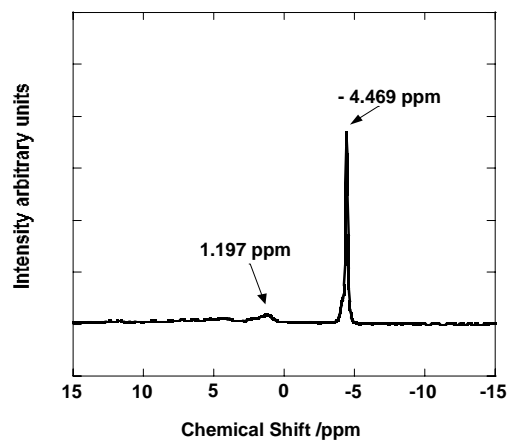


Fig. 1. Solid state MAS ^1H NMR spectrum of sample prepared using BLP chemicals.

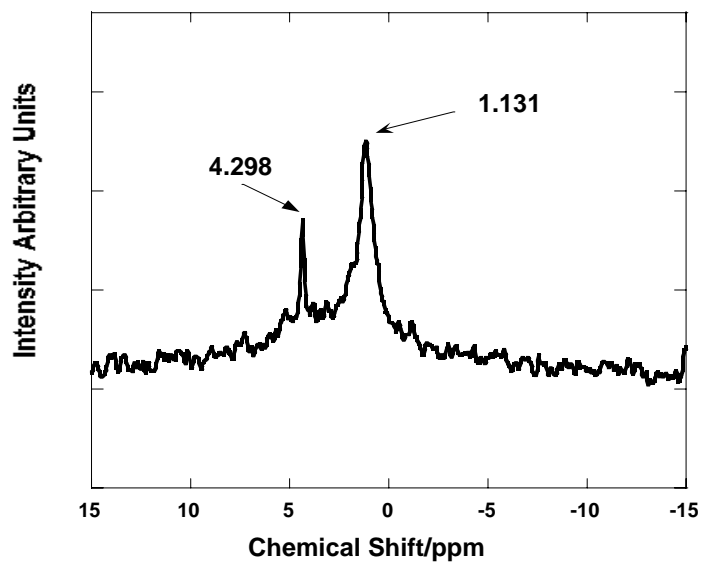


Fig. 2. MAS ^1H NMR spectrum of KCl bought from VWR.

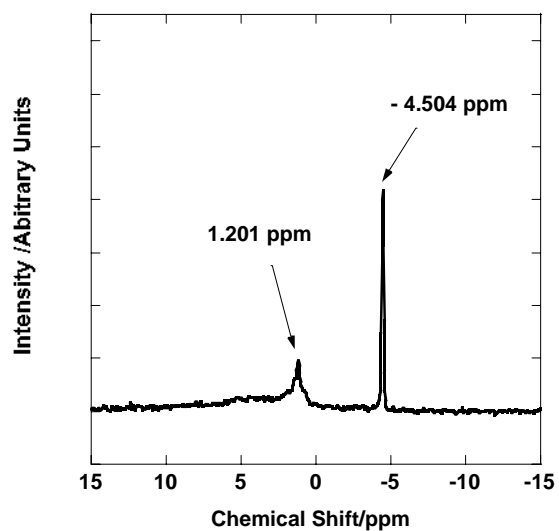


Fig. 3. MAS ^1H NMR spectrum of KH^*Cl synthesized using chemicals purchased by Rowan.

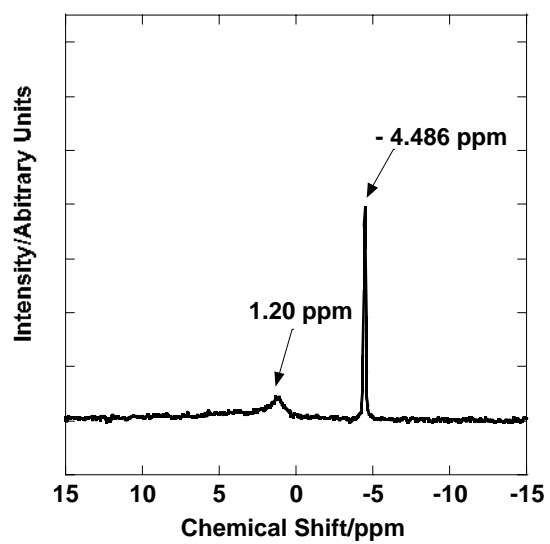


Fig. 4. MAS ^1H NMR spectrum of KH^*Cl synthesized on Feb 24, 2009 using chemicals procured by Rowan.

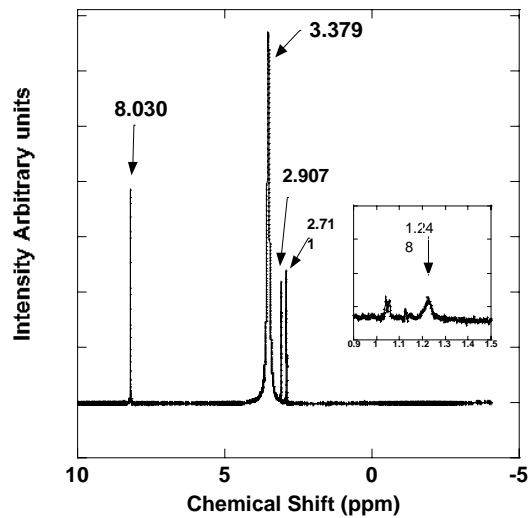


Fig. 5. Liquid ^1H NMR spectra of KH^*Cl synthesized on April 14, 2009 using chemicals procured by Rowan.

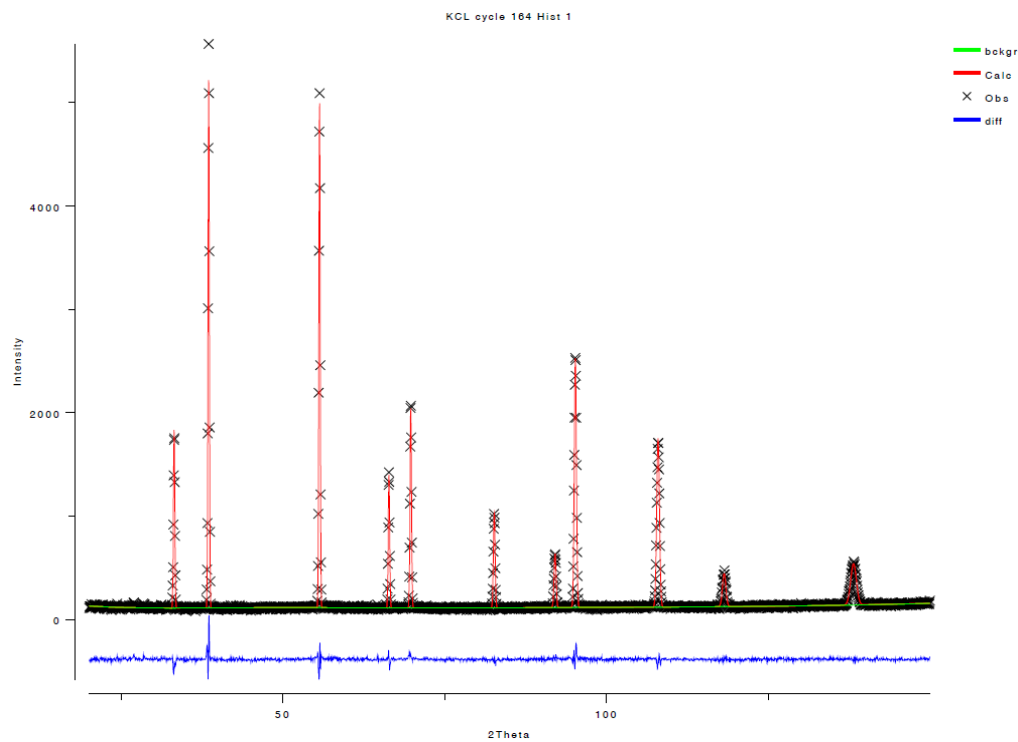


Fig. 6. Neutron diffraction spectra of KCl.

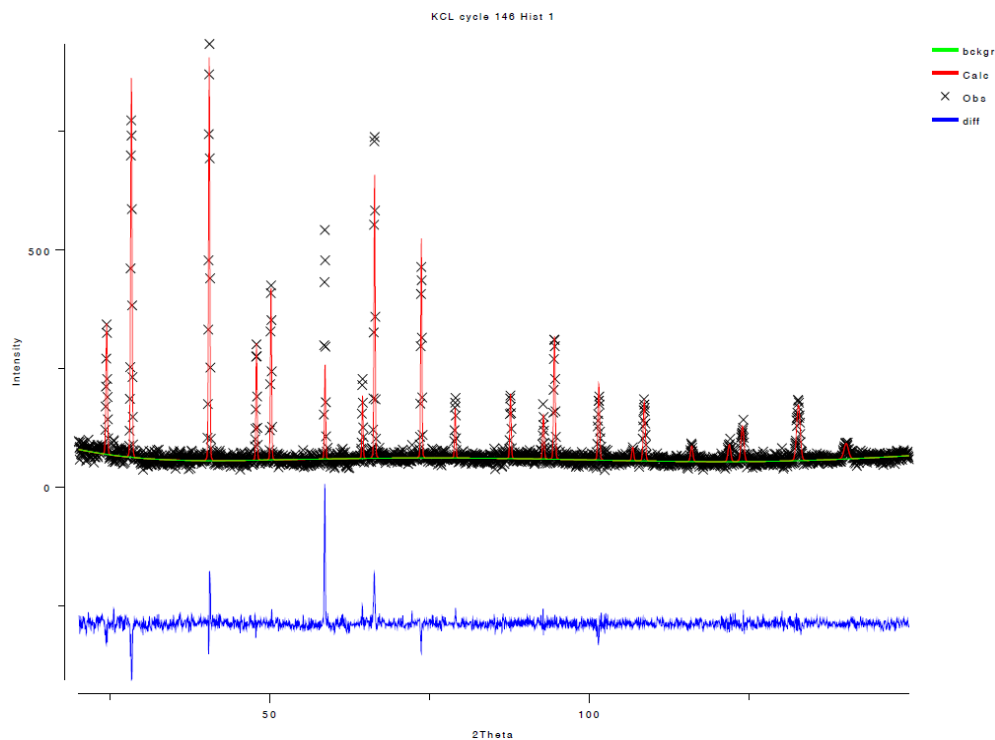


Fig.7. Neutron diffraction pattern of KH*Cl.

Characterization of Hydrino Containing KI Salts

Figure 8 shows the solid state MAS ^1H NMR spectrum of a KH*I sample prepared using chemicals provided by BLP using the procedures discussed previously. One broad intense peak at around -2.4 ppm, a less intense 1.051 ppm and broad peaks centered at -19.1 ppm and 13.9 ppm, which are the side bands of -2.4 ppm peak, were observed. Other samples synthesized using BLP chemicals yielded similar spectra.

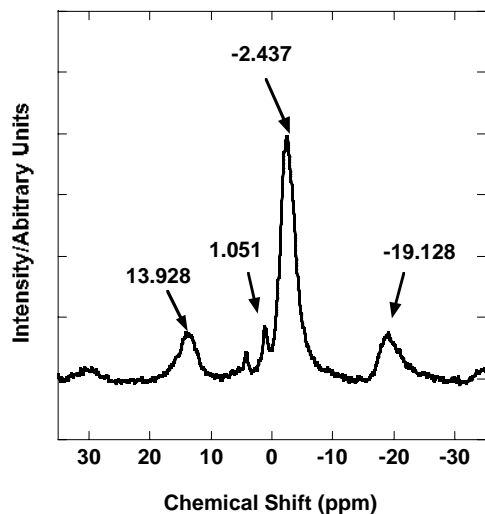


Fig. 8. MAS ¹H NMR spectra of KH*I sample prepared using chemicals provided by BLP.

Using our own chemicals and protocols discussed previously, we synthesized KH*I. MAS ¹H NMR spectra of some of the KH*I salts synthesized are shown in Figures 9 and 10. One broad intense peak was obtained, at between -2.3 ppm and -2.7 ppm. A less intense broad peak was observed at approximately 1 ppm. The sidebands of the about -2.4 ppm peak were observed at about -19 ppm and 13 ppm. The synthesis was reproducible as repetition of sample synthesis yielded the same spectra.

Previously BLP published results show MAS ¹H NMR spectra with broad peaks at around -2.31 ppm and 1.13 ppm versus TMS. According to BLP, the upfield shifted peak at around -2.31 ppm is due to a hydrido hydride ion, H⁻(1/4) shifted compared to the -4.4 ppm peak in KH*Cl by a matrix effect that also broadens the peak, whereas the peak at around 1.05 ppm is due to trapped molecular hydrido gas H₂(1/4). Other than the halide, the main hydrogen dissociator used in this synthesis was Raney Ni as opposed to Ni screen in the synthesis of KH*Cl. KH*Cl gives very sharp peaks (Figures 1, 3, and 4). The narrow peak width obtained with KH*Cl points to a free ion rotating. In the literature no compounds have been found with the kind of protons contained in these

compounds. We are planning to carry out neutron diffraction studies of this salt to identify any interstitial atoms present.

The solution ^1H NMR spectrum of KH^*I synthesized in our lab using DMF-d_7 as the solvent is shown in Figure 11. Four solvent peaks were observed, a singlet at 8.030 ppm and two quintets centered at 2.898 ppm, and 2.686 ppm. Another singlet is also visible at 3.498 ppm due to presence of residual water in DMF. There was also a huge peak at 1.258 ppm which was not due to the DMF solvent. Samples synthesized using BLP chemicals and our own chemicals have shown consistent unusual liquid ^1H NMR peaks at approximately 1.258 ppm. BLP's published results also include another less intense peak at -3.79 ppm in addition to the peak at 1.21 ppm [2]. BLP has attributed the upfield shifted peaks at -3.79 ppm to $\text{H}^-(1/4)$ while the one at approximately 1.21 is assigned to $\text{H}_2(1/4)$. Our liquid ^1H NMR spectra did not show the less intense peaks at -3.79 ppm but an unusually large peak at 1.258 ppm was obtained which matched the $\text{H}_2(1/4)$. This huge peak may also be formed through conversion of $\text{H}^-(1/4)$ to hydrino gas $\text{H}_2(1/4)$.

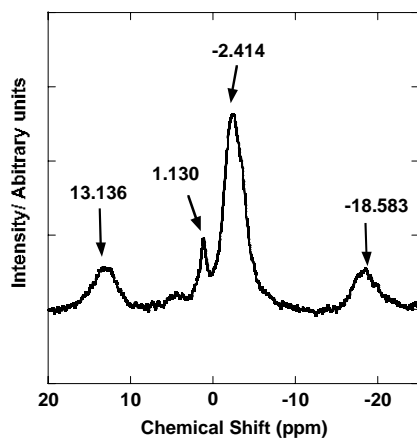


Fig. 9. MAS ^1H NMR spectrum of KH^*I synthesized on April 15, 2009 using chemicals procured by Rowan.

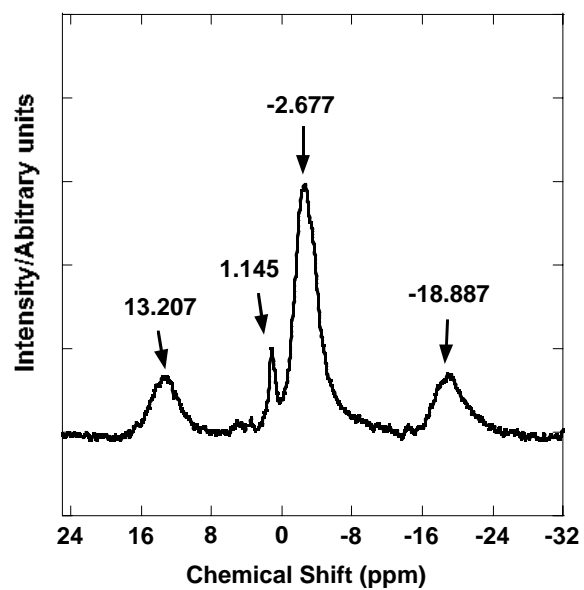


Fig. 10. MAS ¹H NMR spectrum of KH*I synthesized on April 28, 2009 using chemicals procured by Rowan.

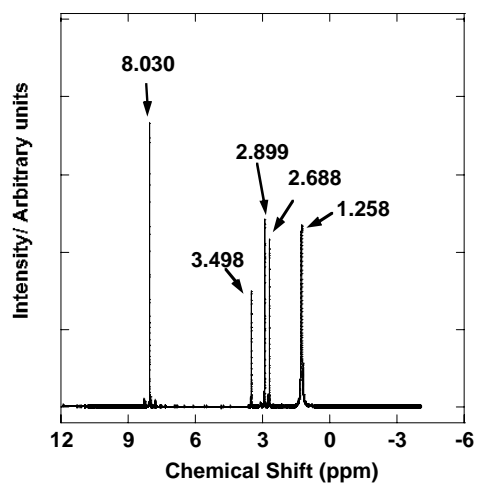


Fig. 11. Liquid ¹H NMR spectrum of KH*I synthesized on April 28, 2009 using chemicals procured by Rowan.

Conclusions and Further Work

The solid state MAS ^1H NMR spectra of KH^*Cl and KH^*I synthesized using chemicals purchased by Rowan and those provided by BLP have shown similar and consistent unusual upfield shifted peaks relative to those of ordinary H species. From KH^*Cl we observed peaks at around 1.20 and -4.50 ppm while KH^*I shows broad, high intensity peaks at around -2.3 to -2.7 ppm. BLP has attributed these upfield shifted peak at -4.50 ppm and -2.3 ppm to $\text{H}(1/4)$ while the ones at approximately 1.21 ppm and 1.1 ppm to $\text{H}_2(1/4)$ [2]. Liquid ^1H NMR studies show less intense peaks at 1.248 ppm for KH^*Cl while strong peaks were observed for KH^*I at 1.258 ppm.

Neutron diffraction studies on these samples point to presence of trapped atoms in the crystal lattice of these salts. According to our elemental analysis results using ICP-MS, we do not see significant amount of other elements that could play a role in the synthesis. Accordingly, we have ruled out the role of other elements in these reactions. Although we have not concluded our work in the area of characterization, we are not aware of any hydride compounds in the literature based on elemental analysis that gives these upfield-shifted peaks. This gives credence to presence of hydrinos trapped in these salts.

To precisely confirm the presence of hydrino hydride ions and molecular hydrino in these salts we plan to perform further neutron diffraction. After obtaining the diffraction pattern, we plan to drive off the trapped interstitial atoms through heating and obtain the pattern again. The pattern should resemble either KCl or KI, after driving off the hydrino gas.

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