THE UNIVERSITY of TENNESSEE KNOXVILLE

Department of Chemistry
NMR Facilities
Director: Dr. Carlos A. Steren

NMR NEWS December 2012

* To check on the **instrumental status** and **reservation system**, and find tutorials, links and more, visit our website www.chem.utk.edu/nmr

* Student operators at the NMR Facilities.

Mr. Chris Murdock, cmurdock@utk.edu, Varian 300 and AC250

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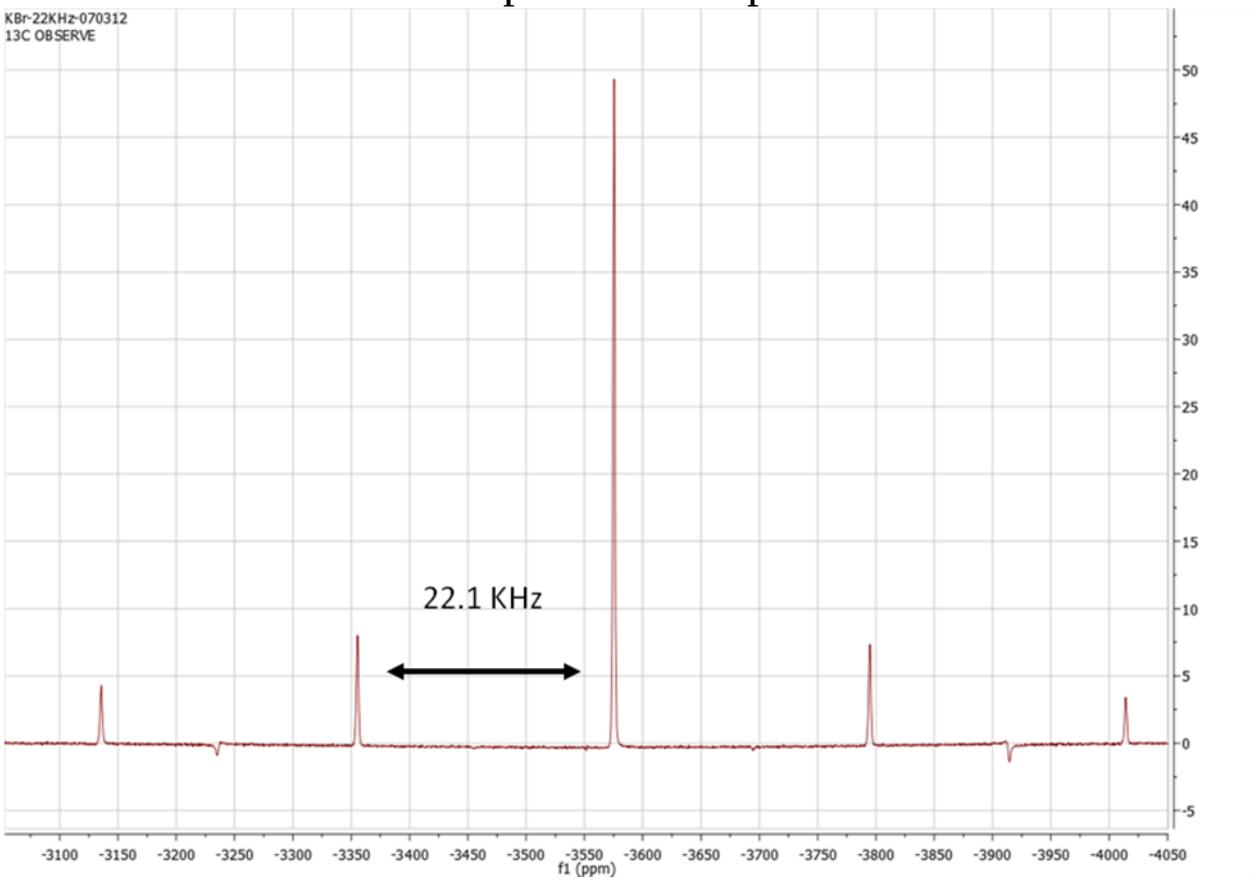
* New Solid State CPMAS probe.

Thanks to contributions from several groups in the Department and a SARIF grant, a new Solid State MAS probe was purchased. It is a Doty, two channels, ^{1}H/X, 4mm probe. The maximum spinning speed is 24 KHz. The frequency range of the low band channel is from ^{31}P (161.9 MHz) to ^{15}N (40.54 MHz).

The Chemagnetics probe will remain as the default probe. Still, the new probe is available to all users. A request in advance is needed in order for us to install and have it ready for the user.

The ^{79}Br spectrum of a KBr sample displayed below was acquired with the new probe. It demonstrates that samples indeed spin that fast! The distance between the spinning side bands in Hz is the actual speed of the spinner.

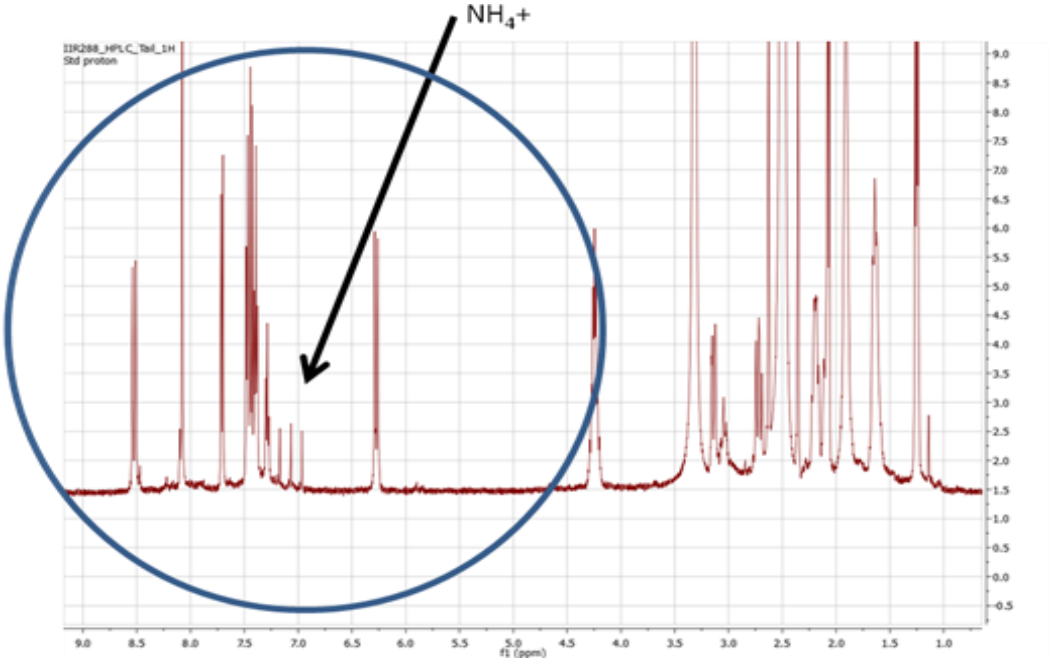


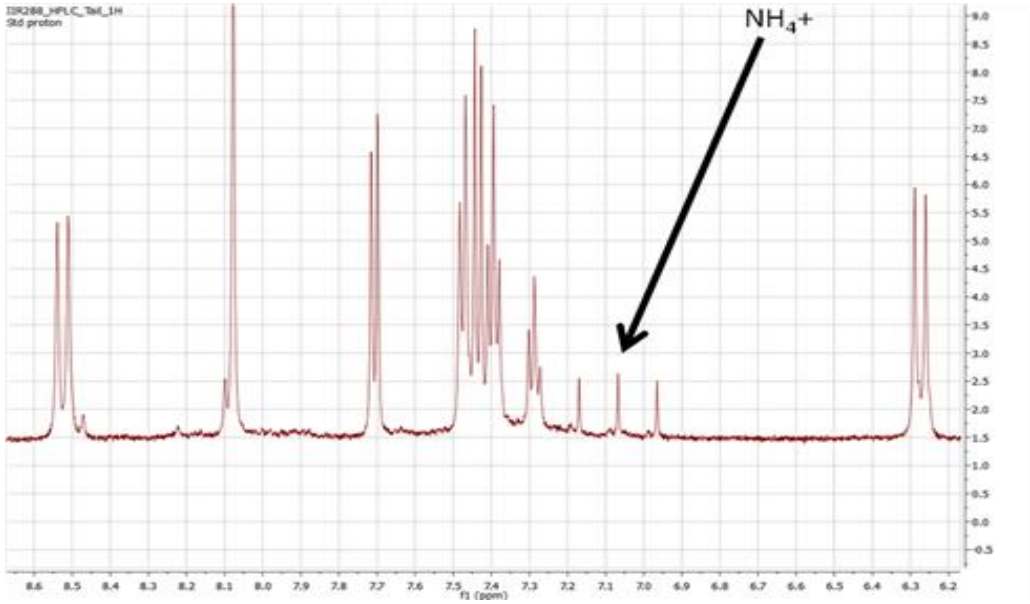
* ^{14}Nitrogen J coupling.

^{14}N is the most natural abundant nitrogen isotope, 99.6 %. It has a spin I=1. If coupled to a ^{1}H, NH, the ^{1}H line should split into (2I+1)=3 lines with equal intensities.

Most of the time though, due to quadrupolar relaxation effects, no ^{14}N splitting of the ^{1}H line is observed.

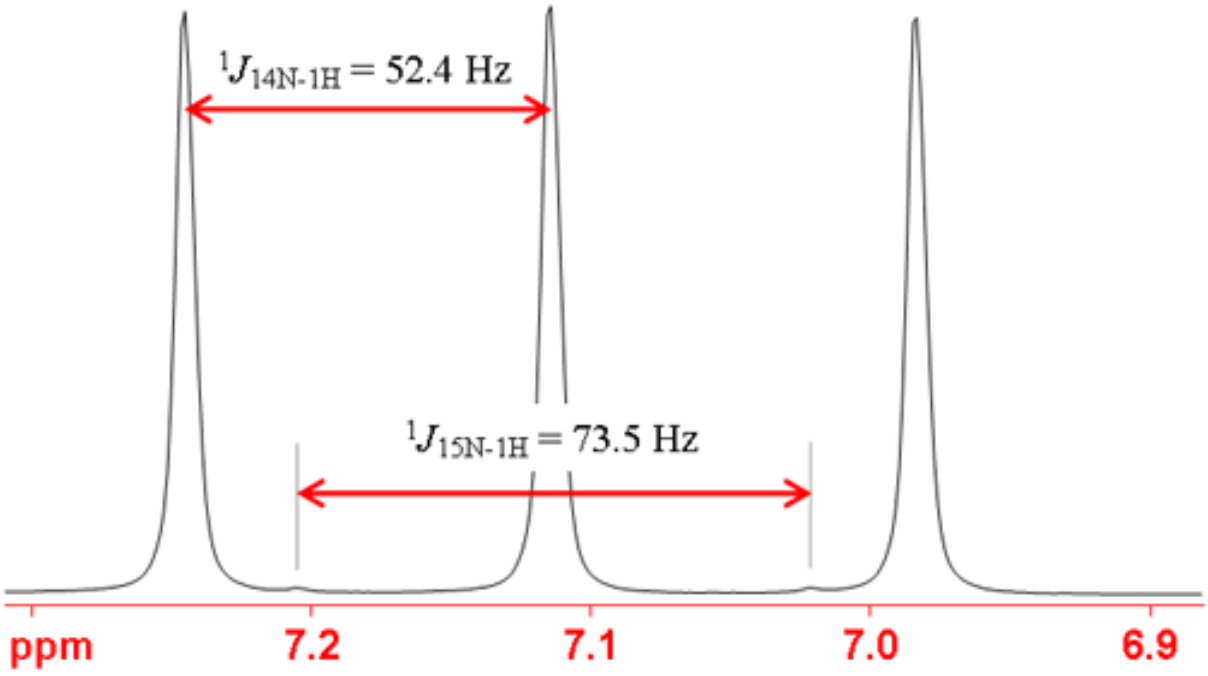
Now, when N is in a highly symmetric environment, like NH_4+, the ^{14}N splits the proton signal into a triplet as shown in the following spectrum,





The following information on N-H couplings was found in the literature,

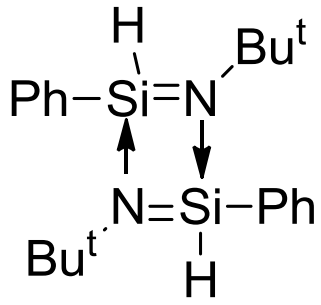
^{1}H spectrum of natural abundance NH_4Cl (1.5 M) in 1M HCl/H_2O showing coupling to ^{14}N as a (spin 1) triplet and coupling to ^{15}N as a weak doublet. Note that the ^{14}N coupling constant is smaller than that of ^{15}N because of ^{14}N's lower resonant frequency.



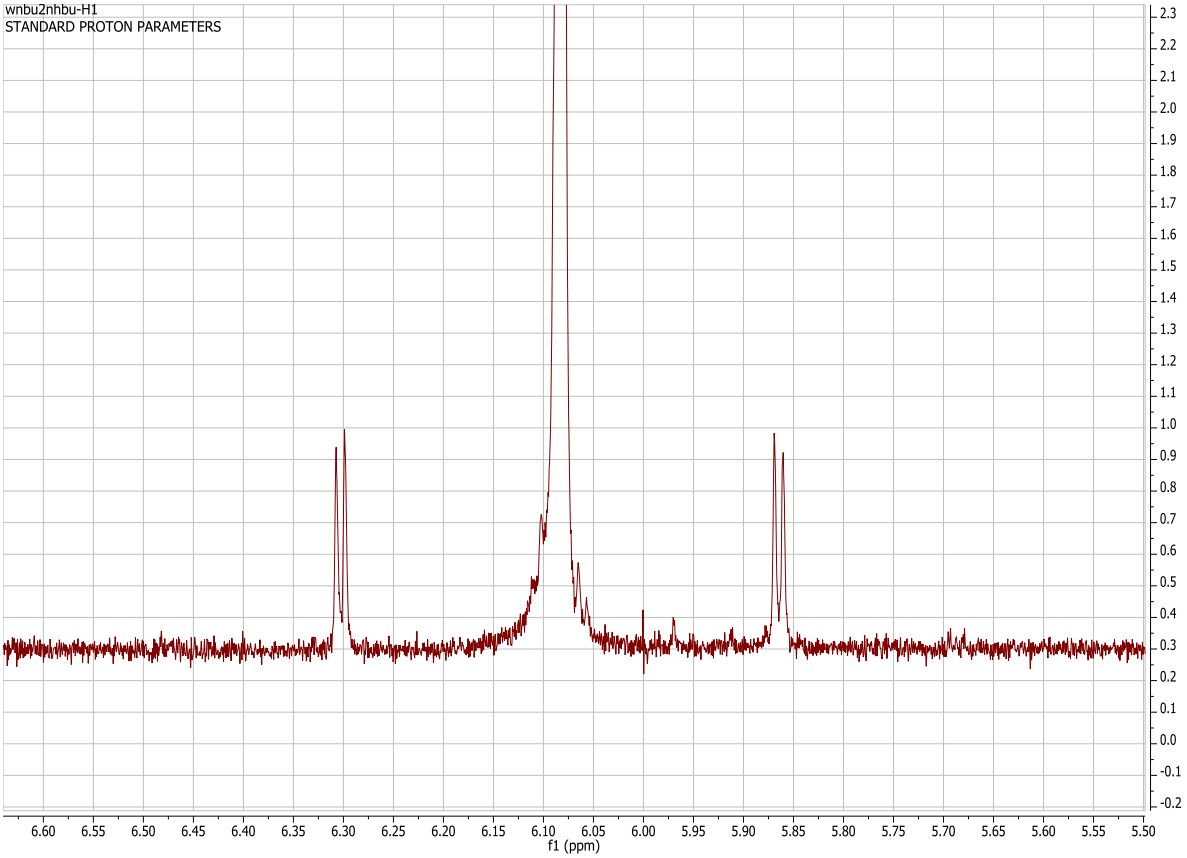
Many thanks to Dr. Mike Quinn and Dr. Kabalka for lending us the spectrum.

* ^{29}Si Satellite lines.

The ^{1}H NMR line of the H-Si group of the complex

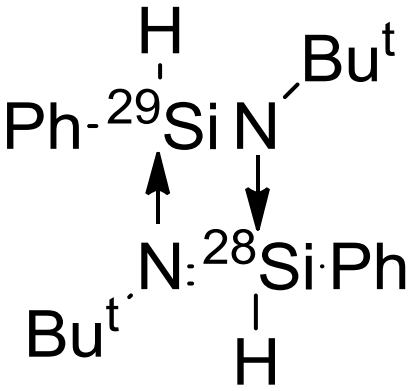


is shown below.



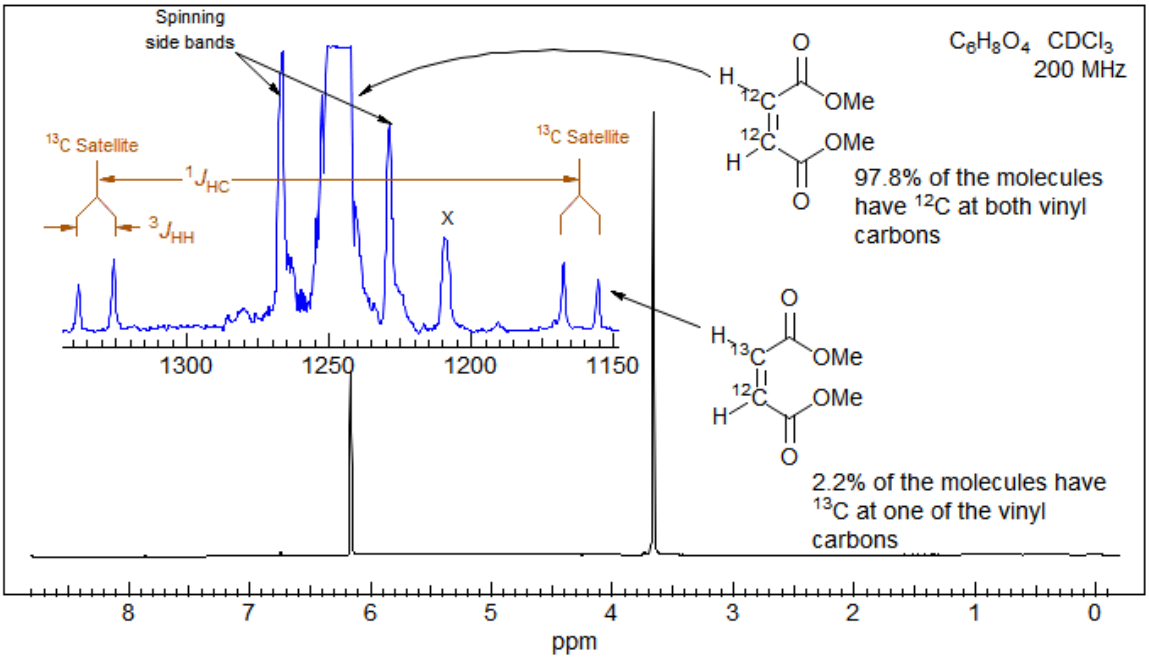
What is puzzling in this spectrum is the shape of the ^{29}Si satellite lines. Due to the symmetry of the molecule, a single satellite line on each side of the main ^{1}H signal was expected. Instead, doublets with different intensities (roof effect) are observed.

It turns out that in the molecule the NMR is detecting, the two protons are magnetically non-equivalent. This molecule has two different Si isotopes, and thus one ^{1}H is J coupled to ^{29}Si but the other ^{1}H, is bonded to ^{28}Si, and lacks a J coupling to Si. Hence, the two protons are magnetically non-equivalent and there is a J coupling between them that causes the satellite lines to split into doublets.



As a result what is observed is like an AB system, with the roof effect.

An example from literature explains the effect in detail,



Many thanks to Dr. Mauzhang Miao and Dr. Xue for lending us the spectrum.