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Abstract

Despite the high natural abundance of ^{75}As (100%), there have been a limited number of solid-state NMR spectroscopy investigations involving arsenic. Previous NMR investigations for this quadrupolar nuclei ($I = 3/2$) have involved the direct detection of ^{75}As in very symmetric environments using either static or MAS NMR, or the observation of quadrupolar coupled ^{13}C [1], or ^{11}B [2] MAS NMR line shapes for a few select compounds. This laboratory has recently investigated the use of solid-state $\{^1\text{H}$ - ^{13}C CPMAS $\}^{13}\text{C}$ - ^{75}As TRAPDOR NMR experiments as a method for the identification of organo-arsenic compounds. For example, dimethyl arsenic acid, DMA(V) (also known as cacodylic acid) is shown to have a very strong ^{13}C - ^{75}As double resonance effect. The magnitude of the ^{13}C - ^{75}As TRAPDOR signal was investigated as a function of spinning speed and ^{75}As irradiation offset for DMA(V). In contrast, the arsenic compound betaine (a dimethyl arsenic analog) shows a very weak ^{13}C - ^{75}As TRAPDOR effect. Preliminary results on biologically relevant samples is also presented to address the utility of the ^{13}C - ^{75}As TRAPDOR method.

[1]. D.L. Sastry, A. Naito, C. A. McDowell, (1988), *Chem. Phys. Lett.*, 146(5), 422-427.
[2]. S. Wi, V. Frydman, L. Frydman, (2001), *J. Chem. Phys.*, 114(19), 8511-8519.

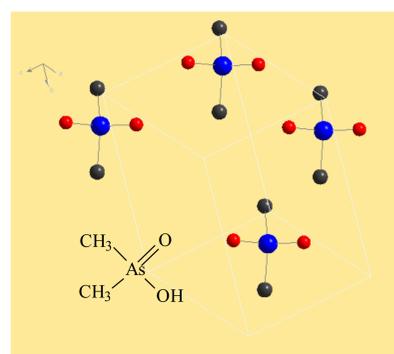
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NMR Experimental

All solid-state MAS NMR spectra were obtained on a Avance 400 WB system at resonant frequencies of ^1H (400.2 MHz), ^{13}C (100.6 MHz), and ^{75}As (68.5 MHz). TRAPDOR experiments were performed on a 4 mm triple resonance MAS probe, spinning between 3 and 5 kHz. Typical CPMAS conditions were 1k scan averages, 1 ms contact time and 5 s recycle delay. The ^{75}As irradiation ($\nu_r = 38.5$ kHz) was included only in the first half of the rotor-synchronized echo sequence giving the signal intensity S , while spectra without ^{75}As irradiation (120 dB) gave rise to the signal intensity S_0 . The resulting ^{13}C spectra were individually phased and then subtracted to obtain the TRAPDOR fraction $(S_0 - S)/S_0$. The variation of the TRAPDOR fraction was determined as a function of ^{75}As irradiation time and offset.

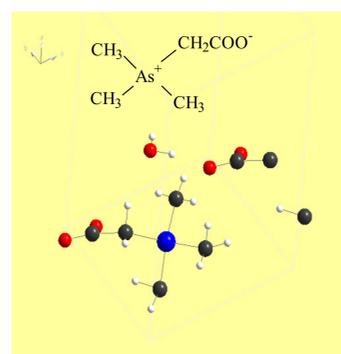
Compounds

Dimethyl Arsenic Acid – DMA(V)



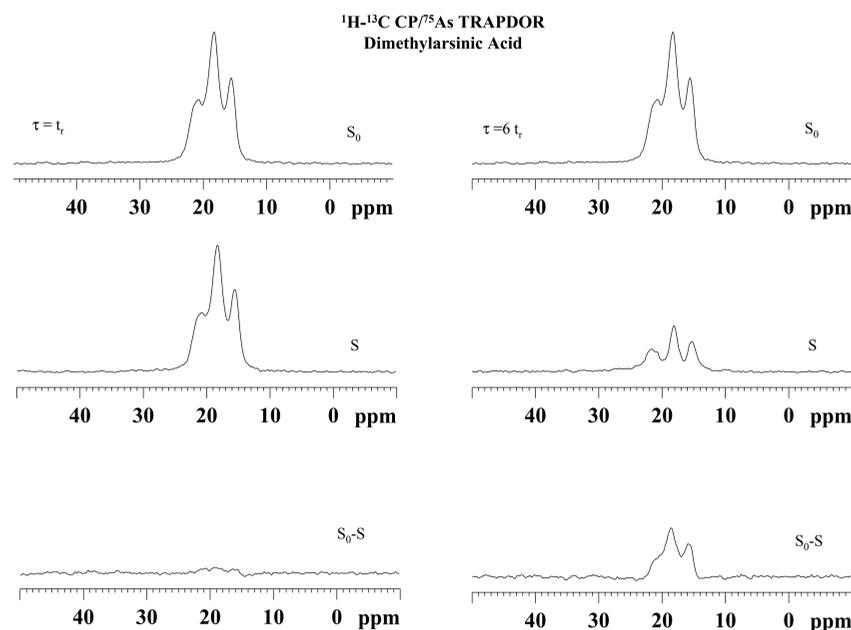
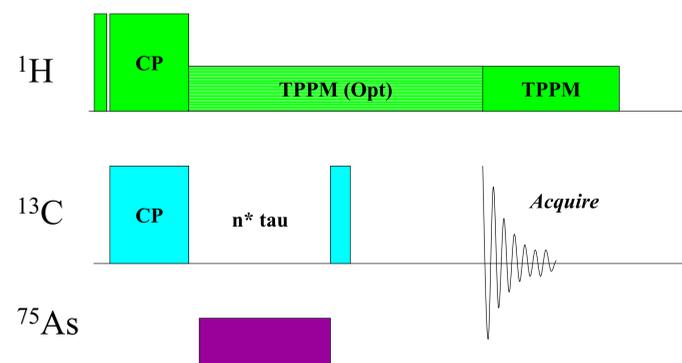
$d(^{13}\text{C}$ - $^{75}\text{As}) = 1.91 \text{ \AA}$
QCC ~ 91 MHz

Arsenobetaine

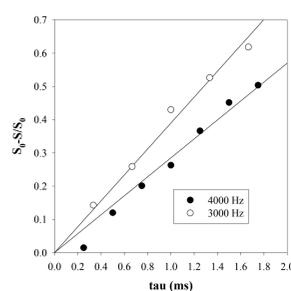


$d(^{13}\text{C}$ - $^{75}\text{As}) = 1.84, 1.91(2), 1.92 \text{ \AA}$
QCC $\sim ??$ MHz

$\{^1\text{H}\}^{13}\text{C}$ - ^{75}As TRAPDOR NMR



TRAPDOR BUILDUP for DMA (V)

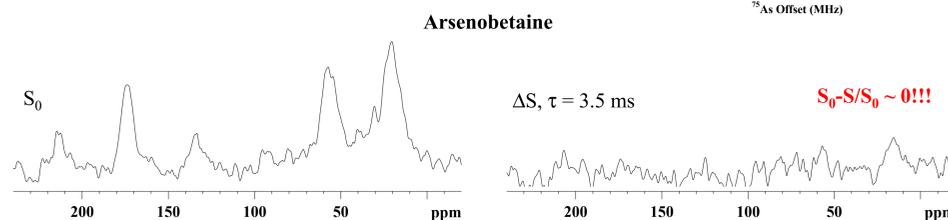
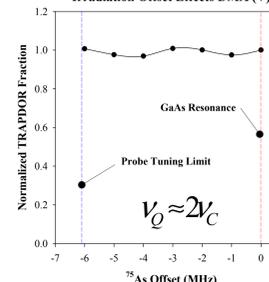


Adiabaticity Parameter

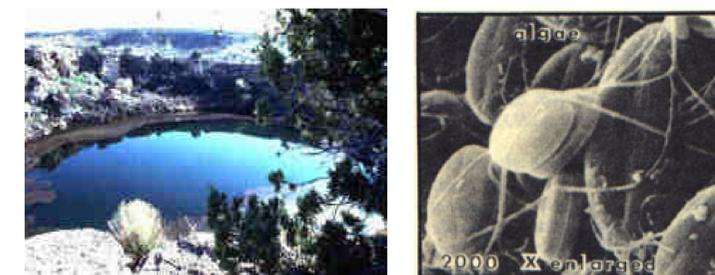
$$\alpha' = \nu_{rf}^2 / \nu_r \nu_Q$$

- Variation in TRAPDOR fraction with spinning speed shows we are NOT in the adiabatic limit.
- Cutoff offset frequency (ν_c) can give estimate of ν_Q . In this case probe limited! $\nu_Q \gg 12$ MHz!.

Irradiation Offset Effects DMA (V)

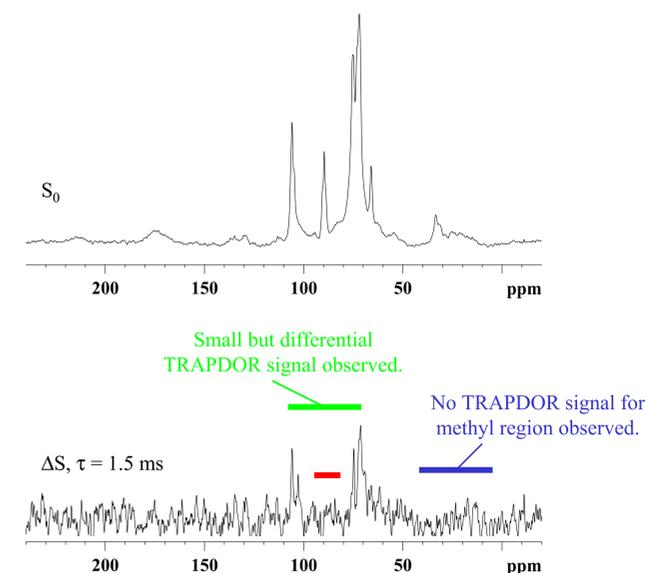


Montezuma Well – Algae



Montezuma Well in Northern Arizona is a unique closed ecosystem that contains elevated concentrations of geogenic arsenic. The natural arsenic levels in the well water are 100 $\mu\text{g/l}$. Studies show that for moss/algae in the well there is an average of 50 $\mu\text{g/g}$ of plant material.

^{13}C - ^{75}As TRAPDOR - Algae



Conclusions

- For the first time ^{13}C - ^{75}As TRAPDOR MAS NMR experiments are demonstrated.
- In DMA(V) these ^{13}C - ^{75}As TRAPDOR effects are very significant.
- The efficiency of the TRAPDOR experiment is highly dependent on the organo-arsenic compound identity. Most likely these variations are the result of large changes in QCC and the corresponding adiabaticity parameter α' .
- Preliminary results on an environmental sample are promising; showing heteronuclear double resonance effects with carbons that are NOT DMA(V) based arsenic compounds.