**17O & 2H MAS NMR of XO4 Anions & CD3 Dynamics in a CD3- Silicate & 4-Phenanthrene**

Jakobsen, H.J.; Bildsoe, H.; Jensen, S.K. (Aarhus U., Chemistry); Brorson, M. (Haldor Topsoe); Gan, Z. and Hung, I. (NHMFL)

**Introduction**

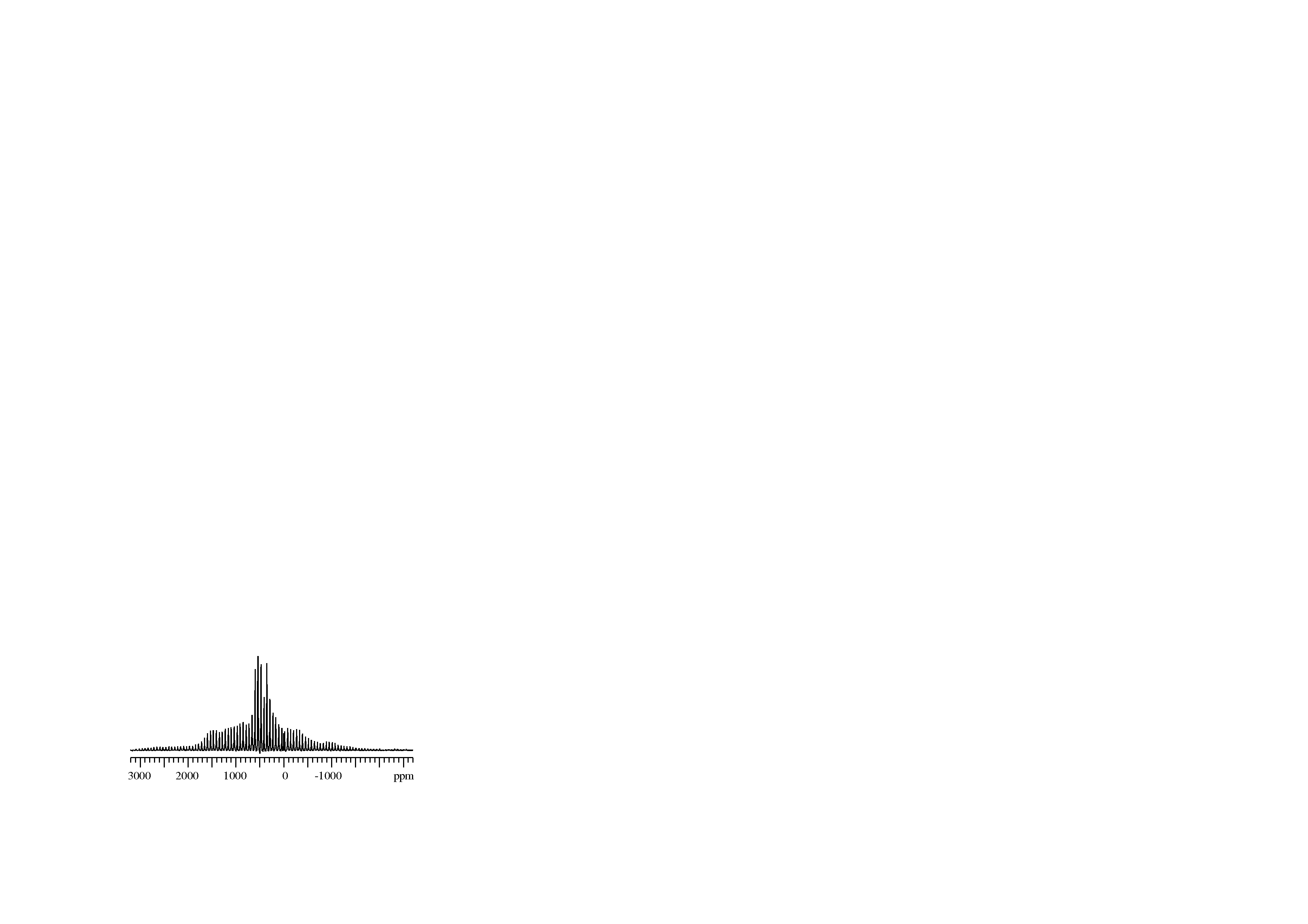
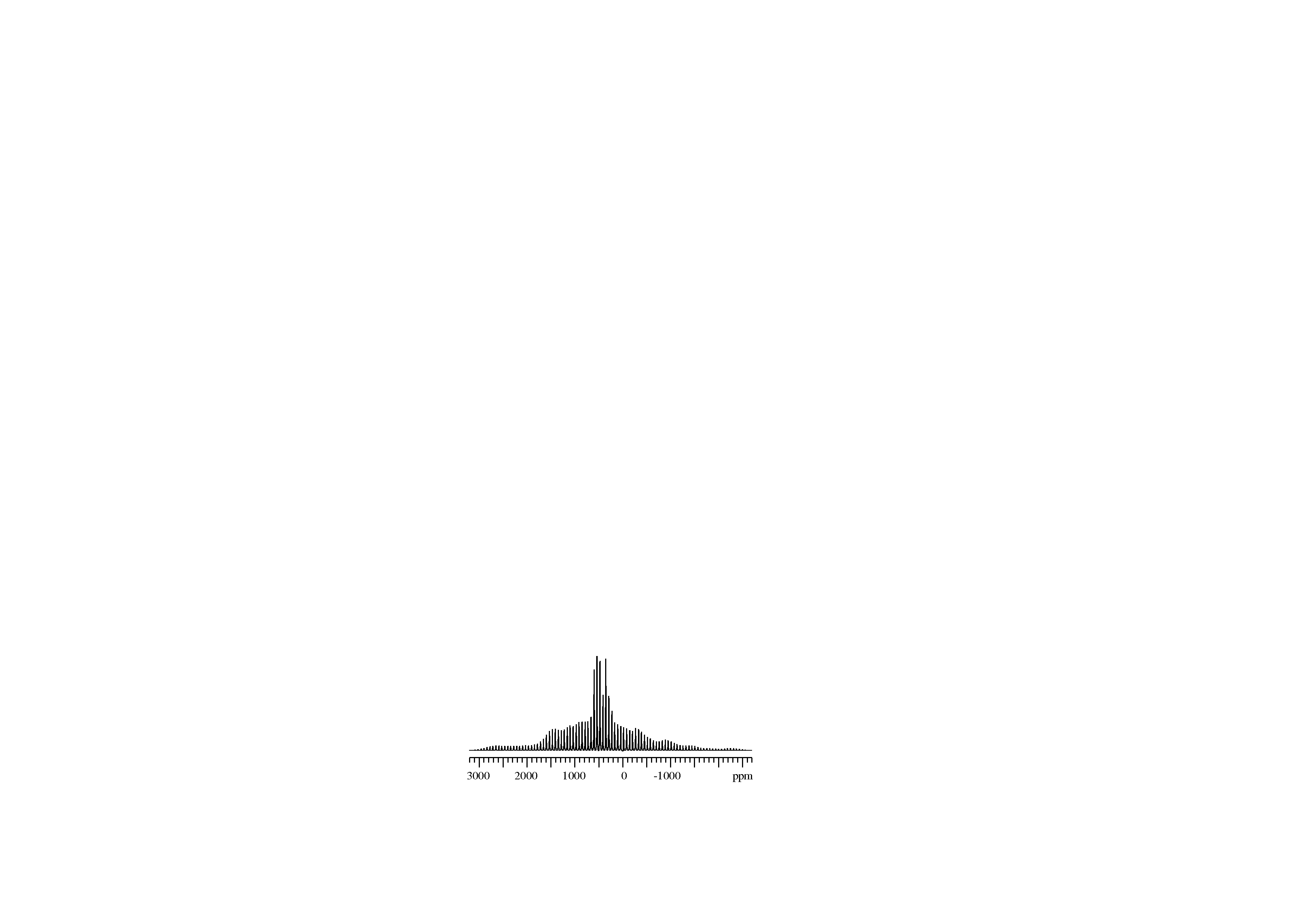
Continuing our solid-state 17O VT MAS NMR dynamic studies of XO4 anions [1] this study reports preliminary results for RbMnO4, CsMnO4, and CaWO4. Moreover, using 2H MAS the dynamics of CD3 rotation for a CD3–Si≡ silicate have been studied. This CD3–Si≡ silicate originates from a mechanical tumbling experiment intended to mimic the winds on planet Mars [2]. The result will be compared to the CD3 dynamics for CD3-*L*-alanine [3] and to that determined here for 4-CD3-phenanthrene. Furthermore, the results will be compared to the 13C-{1H} CP/DP (Cross-Polarization/De-Polarization) zero-crossing data obtained for the corresponding three CH3-materials.

**Experimental**

17O VT/RT MAS NMR spectra of the 17O-enriched (~10%) materials were recorded at 21.15 T (122.0 MHz)/ 19.6 T (112.8 MHz). 2H VT MAS spectra were recorded at 14.1 T (92.12 MHz) using a Bruker low-temp (LT) MAS DNP probe, without microwave irradiation, in the temperature range –170 to –30 ºC.

**Results and Discussion**

The 17O VT MAS NMR spectra of RbMnO4 (I) and CsMnO4 (II) exhibit fairly similar behavior and spectral features as we observed earlier for KMnO4 (III) [1a], i.e., a narrow singlet resonance at RT which separates into two groups of 2:2 resonances at LT. Thus, variable temperature spectral analysis followed the procedure as for KMnO4 (III)[1a] and led to activation energies Ea ~40 kJ/mol for the XO4 rotation for (I & II) compared to Ea ~7 kJ/mol for (III).

 The 17O RT MAS spectra of CaWO4 (mineral Scheelite), shown in Fig. 1a & b (60% cut-off for tallest peak), were analyzed for comparison with the spectral parameters recently determined for the Scheelite structures (I41/a) of the periodates NaIO4 and KIO4 [1b] and the dynamics and parameters for Cs2WO4 and K2WO4 [1a]. The RT spectra and spectral parameters (not shown) show that dynamics don’t affect the spectra and the determined parameters when compared to those reported for the periodates [1b] and for K2WO4 (RT) and Cs2WO4 (LT) [1a].

**Fig.1a.** Experimental 17O MAS NMR spectrum of CaWO4. **Fig.1b.** Simulated 17O MAS NMR spectrum of CaWO4.

The CH3–Si≡ silicate isolated from the tumbling experiment exhibit a very short 13C-{1H} CP/DP zero-crossing time of 120 μs, i.e., similar to the value for *L*-alanine (125 μs) and 4-CH3-phenanthrene (165 μs), both known to exhibit highly restricted CH3-rotation [3]. However, to our surprise the 2H MAS spectra of the CD3–Si≡ silica material at RT and –170 ºC are quite identical. We are presently seeking an explanation for this observation.

**Conclusions**

17O and 2H VT MAS NMR has proved useful in dynamic studies of inorganic and organic solid materials.

**Acknowledgements**

We acknowledge the NHMFL, which is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the State of Florida. In addition, we acknowledge the NMR facilities at Aarhus University.

**References**

[1] Jakobsen, H.J., *et al*., [1a] J. Phys. Chem. C., **118**, 20639-20646 (2014) and [1b] **119**, 14434-14442 (2015).

[2] Jensen, S.J.K., *et al*., Icarus, **236**, 24-27 (2014).

[3] Beshah, K., *et al*., J. Chem. Phys., **86**, 4730-4736 (1987).