Structural Insights from the NMR Spectroscopy of Quadrupolar Nuclei: Exploiting Electric Field Gradient and Spin-Spin Coupling Tensors

Frédéric A. Perras

U.S. DOE Ames Laboratory, Ames, IA, USA, 50011

Solid-state NMR spectroscopy (SSNMR) is one of the two main structural solution tools, along with diffraction, that are used in the characterization of materials, and the most powerful technique to study non-crystalline materials. Impressive advancements have been made, particularly in recent years, in using SSNMR to solve the crystal structures of organic materials, zeolites, and aluminophosphates. Unlike diffraction, however, the approaches used in solving solid structures by SSNMR need to be tailored to the class of materials that are studied. This fact has slowed the introduction of NMR crystallography to inorganic materials as these are generally composed of elements whose NMR active nuclei are quadrupolar ($S > 1/2$).

Unfortunately, the extraction of structural information from the NMR spectra of quadrupolar nuclei is often far from trivial. In many cases, only the quadrupolar coupling can be measured; which is difficult to relate to structure. Contrary to this, however, with the use of PAW DFT it is relatively straightforward to predict the EFG tensor for a given crystal structure. We have then developed a least-squares method that combines accurate DFT prediction of EFG tensors and experimentally-determined ones in order to directly refine crystal structures against the NMR data in a way akin to the Rietveld approach.[1] We have shown that this approach can produce crystal structures that often rival those obtained from single crystal diffraction and are of higher quality than those produced from DFT alone. This method was applied to solve high quality crystal structures for a near-zero thermal expansion material and a non-linear optical material, for example.[2]
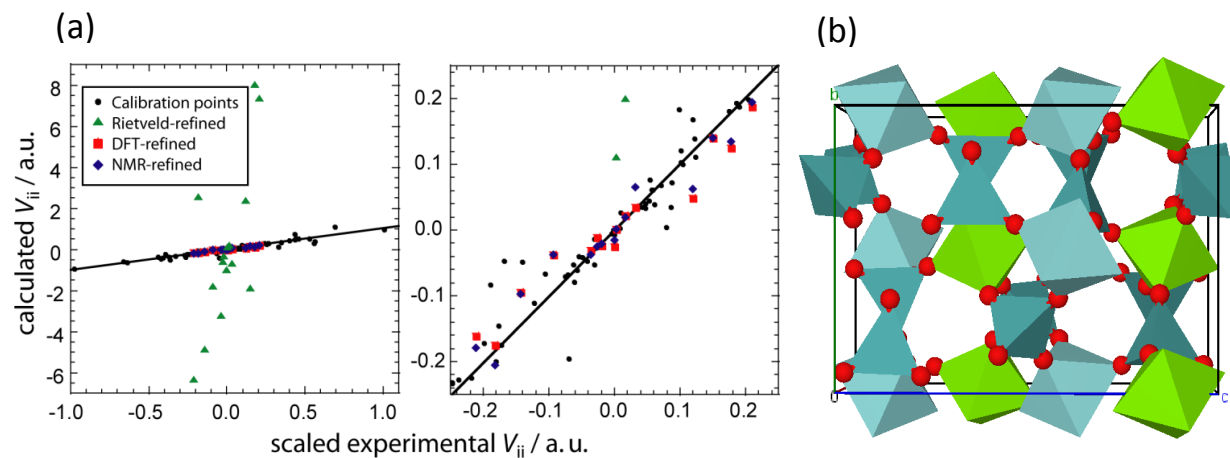

Figure 1. Results from an EFG-based crystal structure refinement of the near-zero thermal expansion material $ZrMgMo_3O_{12}$. In (a) the agreement between experimental and DFT-

predicted EFG tensor components are plotted for structures refined using PXRD (green triangles), DFT (red squares), or NMR (blue diamonds). The final NMR crystallographic structure is depicted in (b).

The quality of the structures obtained by such an approach of course depends on the accuracy of the EFG tensor measurements. Commonly, these parameters are obtained by fitting the spectra with the use of the high field approximation, which treats the quadrupolar interaction as a small perturbation to the Zeeman interaction. The quadrupolar interaction, however, can rival in size with the Zeeman interaction and an exact treatment of the combined Zeeman-Quadrupolar Hamiltonian is needed. We have developed a user-friendly, graphical, and fast program to simulate the NMR lineshapes of quadrupolar nuclei exactly from the complete range covering NQR to high-field NMR.[3] This free program, known as QUEST (QUadrupolar Exact SofTware) has been used to analyze the NMR spectra of numerous nuclides including ^{14}N, ^{33}S, $^{35/37}Cl$, $^{79/81}Br$, ^{87}Sr, ^{91}Zr, ^{121}Sb, ^{127}I, ^{139}La, and $^{185/187}Re$.[4]

When available, the most direct structural information that can be obtained from SSNMR corresponds to the spin-spin coupling (dipolar and J). Measuring these spin-spin coupling interactions is particularly difficult in pairs of quadrupolar nuclei due to their unfavorable spin dynamics and broad line shapes. We have shown that both dipolar and J coupling can be measured with the use of double-rotation (DOR) with which higher resolution allows for the observation of the complex multiplet structure of the resonances.[5,6] A surprising discovery from this study is that the J coupling multiplets are still observable in pairs of magnetically equivalent nuclei if they happen to be quadrupolar. The observed multiplet structure is nevertheless unusual.

In order to simplify the measurement of spin-spin coupling between quadrupolar nuclei we developed a series of J-resolved type experiments that enable the resolution of the J interaction with the use of broadly available MAS probes.[7,8,9] Since only the central transition ($m = \frac{1}{2}$ to $-\frac{1}{2}$ transition) can be accurately manipulated, the use of a double-quantum filter is necessary in these experiments in order to removes signals arising from spins that are coupling to the satellite states of another spin. Along the lines of the previous DOR work, we found that the doublet measured by these experiments is amplified when the spins are magnetically equivalent.[10,11] This useful feature can not only be used as a structural restraint but can also be used in order to access smaller J coupling constants. The J-resolved experiment can also be performed in static samples where it then enables the measurement of both the J and the dipolar coupling in pairs of quadrupolar nuclei possessing large quadrupolar coupling.[12]
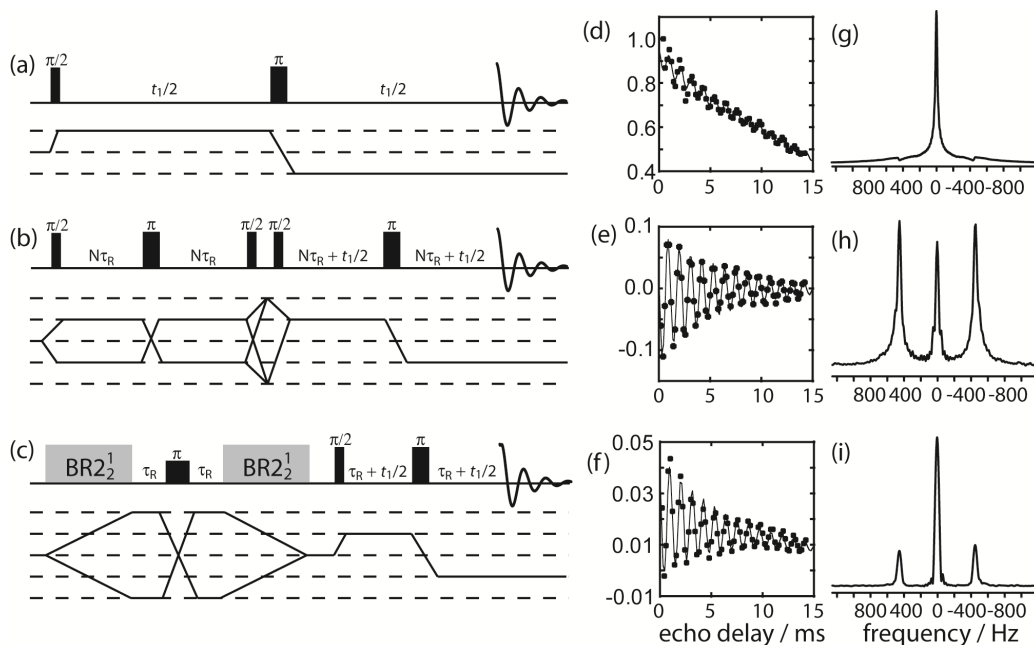
Figure 2. The pulse sequences and coherence transfer pathways for the ordinary (a), *J*-based double quantum filtered (b) and dipolar-based double quantum filtered *J*-resolved experiments are depicted. The time domain (d-f) and frequency domain (g-i) responses are also shown for dimanganese decacarbonyl demonstrating the need for the application of a central-transition selective double-quantum filter in order to observe the splitting caused by *J* coupling.

Lastly, applications of dynamic nuclear polarization (DNP) in order to enhance the sensitivity of difficult experiments involving quadrupolar nuclei are presented. Notably we found that the PRESTO polarization transfer technique is a good alternative to cross-polarization when performing indirect DNP experiments on quadrupoles. The improved sensitivity of PRESTO and DNP enabled the measurement of 1D and 2D ^{17}O SSNMR spectra of surface sites at natural abundance.

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