



Method Development of ^2H Rotating Frame Relaxation Under Static Conditions for Studies of Molecular Dynamics

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Introduction

This work is focused on demonstrating feasibility of static deuterium rotating frame NMR relaxation measurements for characterization of slow time scales motions in powder systems. Using a model compound, dimethyl sulfone- d_6 , we show that these measurements yield conformational exchange rates and activation energy values in accordance with results obtained with other techniques. Further, we demonstrate that the full Liouvillian approach as opposed to the Redfield approximation is necessary to analyze the experimental data.

Experimental

The $R_{1\rho}$ is performed with the quadrupolar echo scheme using a two-step phase cycle and a heat compensation block between 73 and 5 °C.[1] We utilized the 600 MHz spectrometer at NHMFL and the wide-line low-E probe. Spin lock times varied between 10 μs and 50 ms and powers varied from 14 to 42 kHz. New matlab-based programs were developed for simulations involving the full Liouvillian treatment.

Results and Discussion

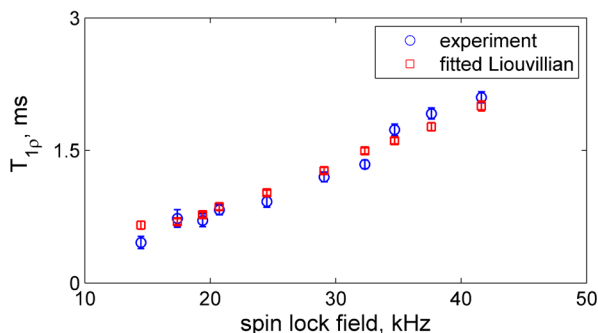


Fig. 1. Sample relaxation dispersion profiles for the fast relaxing component, $T_{1\rho}$ versus spin lock field strengths.. Experimental results from the two-exponential approximation (blue circles) and the best-fit simulation according to the Liouvillian approach (red squares) with the inclusion of $\pm 5\%$ averaging due to B_1 inhomogeneity. Data corresponds to the horn positions of the powder pattern.

Conclusions

We have demonstrated the feasibility of static deuterium $R_{1\rho}$ relaxation measurements for determining slow motional rate constants in powder samples. We discussed data treatment using a simple two-exponential approximation to the decay curves and a more sophisticated treatment that explicitly takes into account coherent oscillations. Both yield very similar results in regards to the conformational exchange rate. Additionally, we discussed the limits of validity of the Redfield theory as opposed to the full Liouvillian approach for the data analysis. This work builds a foundation for the extension of deuterium $R_{1\rho}$ relaxation measurements toward biological samples under static conditions as well as potentially under magic-angle spinning applications.

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References

[1] Vugmeyster, L., *et al.*, Chemphyschem., **21(2)**, 333-342 (2019).