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Solid State Nuclear Magnetic Resonance
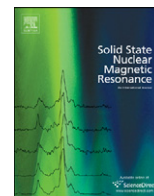
Rotational Resonance in milli-tesla fields detected by Field Cycling NMR

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ABSTRACT

Rotational Resonance (R^2) between different spin Zeeman levels in samples of adamantane $C_{10}H_{16}$ (homonuclear R^2) and a mixture of $C_{10}H_{16}$ and $C_{10}D_{16}$ (both homonuclear and heteronuclear R^2) has been studied. A Field Cycling NMR instrument was used to match the external field frequency v_0 to a fixed frequency of sample rotation v_r at $v_r = 40$, 50 or 60 kHz. Rotational Resonance is observed at rational frequency ratios of v_0/v_r, such as $\frac{1}{2}$, $\frac{2}{3}$, $\frac{3}{2}$ and 1. The method may prove to become a useful tool for the determination of spin–spin distances in condensed matter.

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1. Introduction

When rotating a sample of dipolar coupled spins at a frequency v_r around an arbitrary axis, the semi-classical dipolar interaction Hamiltonian for each spin pair is periodically modulated with frequency contributions at v_r and $2v_r$. Each interacting spin is, therefore, subject to fluctuating local fields generated by a mechanical motion. Due to their narrow frequency distribution, these local fields may be interpreted as photon modes with high photon numbers at energies hv_r and $2hv_r$ [1].

If the energy difference between two states of the coupled spin system is equal to the energy of such a photon, coherent spin-state transitions may occur. As in the case of nuclear magnetic resonance in the strict sense, i.e. the irradiation of a sample with an external magnetic field oscillating at the Larmor frequency, the oscillating field generated by sample rotation gives rise to a resonance effect called *Rotational Resonance* (R^2) at $\Delta v = kv_r$, with $k = 1,2$ for single-photon transitions and larger k for multi-photon transitions [2,3]. See Fig. 1 for an illustration of this phenomenon. R^2 is also closely related to *Rotary Resonance* [4,5].

Since the local field amplitude, which determines the timescale of the resonance effect, depends on the spin–spin-distance, observing the time evolution or lineshape under R^2 conditions yields information about the structure of the sample [3,6–8]. Theoretical approaches to solve the problem are Floquet theory [9–11] and multistep simulations [12].

In this paper, we will present measurements of R^2 between Zeeman levels of a coupled spin system. As mentioned above, this experiment is similar to a RF irradiation experiment using an oscillating local field rather than an external field generated by a coil to drive spin transitions. This analogy should not be pushed too far, however, as R^2 can create multi-quantum coherences while RF irradiation creates only single-quantum coherences.

In contrast to the conventional Rotational Resonance experiment, the full dipolar Hamiltonian has to be considered. In fact, the truncated Hamiltonian typically, used to describe R^2 in the high-field limit, is of little relevance at low fields (at least for the homonuclear case), as it does not couple eigenstates with a discernible energy difference. Instead, the "non-energy-conserving" terms of the Hamiltonian, which usually only have to be considered for longitudinal relaxation, drive the observed transitions between Zeeman levels.

2. Experiments

Observing Rotational Resonance between different Zeeman states of the spin system requires external fields at a Larmor frequency comparable to the rotation frequency. To achieve this, we used a home-built Field Cycling instrument [13] with an unusually large bore (30 mm diameter), that allowed us to use a custom probe with a Bruker 1.3 mm "Very Fast MAS" spinner capable of rotation frequencies of up to 70 kHz.

In our experiments, which were performed primarily in order to locate the frequencies of the occurring resonances, v_r was fixed to a certain value while the external field was varied. We chose to present spinning frequencies of $v_r = 40$, 50 and 60 kHz in this publication. v_r was not stabilized, but the fluctuations were smaller than 200 Hz, which is well below the resonance linewidth. The Larmor frequency $v_0 = \gamma B_0$, and with it v_r, should be large compared to the dipolar coupling strength v_D. As long as this condition is fulfilled, the value of v_r should not, and does not appear to, have a direct influence on the location of any resonance, which only depend on the ratio v_0/v_r.

As usual in Field Cycling relaxometry, for each accumulation, an equilibrium magnetization corresponding to a high external

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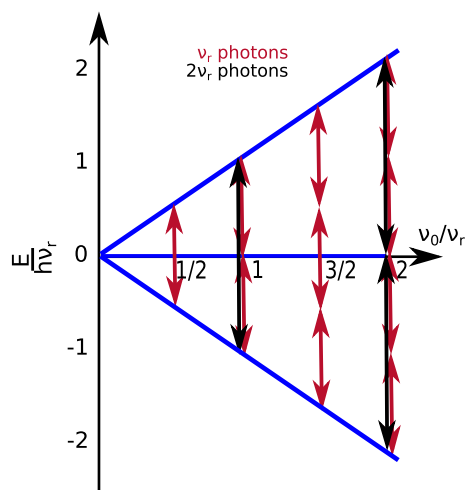
Fig. 1. Energy states of a coupled two-spin system with a small dipolar coupling strength. Photons generated by sample rotation connect the eigenstates at $v_0/v_r = n/2$.
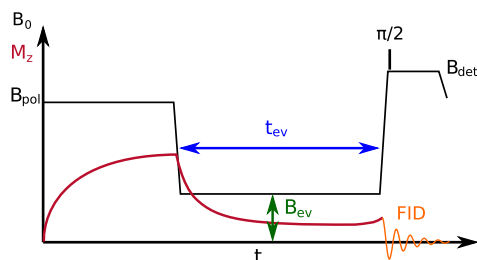

Fig. 2. The field cycle for a single accumulation.

field was first prepared, then the field was switched to the desired evolution field value, and last was switched up again for detection (see Fig. 2). By varying the evolution time, the time dependence of a chosen observable can be recorded for each evolution field.

As a sample substance, powdered adamantane $C_{10}H_{16}$ was used, a plastic crystal in which fast isotropic molecular rotation leads to an averaging of intramolecular dipolar coupling at room temperature, leaving only a weaker intermolecular coupling on the order of a few kHz [14]. Therefore, each adamantane molecule can be approximately considered as a collection of 16 independent spin-$\frac{1}{2}$ nuclei at the same location that interact only with spins at different crystal sites.

Since, in general, all terms in the dipolar coupling Hamiltonian depend on the angle θ between the axis of rotation and the external field axis, we performed measurements at different values of θ.

3. Results and discussion

From Fig. 3, Rotational Resonance lines may be identified beyond doubt at frequency ratios of

$$\frac{v_0}{v_r} = \frac{1}{4}, \frac{1}{3}, \frac{1}{2}, \frac{2}{3}, \frac{3}{4}, \frac{4}{5}, 1, \frac{5}{4}, \frac{4}{3}, \frac{3}{2}, \frac{5}{3}, 2, 3, \text{ and } 4.$$

To each resonance at a ratio of v_0/v_r, there exists an associated resonance at the double frequency $2v_0/v_r$ due to the availability of photons at $2v_r$ as well as v_r. All resonances can be readily interpreted in terms of single- or multi-photon transitions similar to those indicated in Fig. 1 (albeit in a much larger spin system). Resonances at ratios with a higher denominator indicate a higher spin transition number, e.g. a coherent 5-spin-flip for the resonance condition at $\frac{4}{5}$ (and also at $\frac{1}{5}$ and $\frac{2}{5}$). The shifts to lower frequency ratios of the resonances at very low fields (below 20 kHz) are indicative of the breaking down of the high-field approximation $v_0 \gg v_D$.

It should be mentioned that the loss of magnetization during Rotational Resonance is, for the largest part, not due to relaxation, but a result of destructive interference of a large number of single-spin signals, each of which has a complex time evolution with a frequency distribution that depends on the crystallite orientation and the angle θ as well as on the locations of neighboring spins. When perusing the experimental results, particular note should be made of the strongest resonances at $v_0/v_r = \frac{1}{2}$, 1 and 2. Here, R^2 eliminates the z-magnetization so quickly that it is lost during the short time the field is near the resonance while switching down to the evolution field. This time is difficult to estimate since it depends on the width of the resonance as well as the field switching characteristic of our instrument, but it is certainly less than 1 ms.

The measurements presented in Fig. 3 (b)–(d) agree qualitatively in that the resonances appear at the same frequency ratios, but increasing the spinning frequency and rotating around an axis close to the Magic Angle $\theta_M \approx 54.7°$ reduces the resonance linewidth and overlap of resonance lines at low fields. It follows that in the range of rotation frequencies and angles θ we chose, neither parameter has a qualitative influence on the experimental results.

4. Heteronuclear Rotational Resonance

We can select specific transitions between spins of different species by choosing an appropriate evolution field frequency. By selectively labeling a certain site in a molecule with an NMR active isotope, this could be exploited to observe only R^2 signals to which the labeled site contributes. To illustrate this *Heteronuclear Rotational Resonance* effect, consider a mixture of fully deuterated adamantane and natural abundance (i.e. protonated) adamantane. The mixture was prepared in a ratio of 1:1 by filling both powdered substances in a glass tube and repeatedly flipping the sample over a period of a few days. Since deuterons have a smaller magnetogyric ratio $\gamma_D = 0.1515 \, \gamma_H$ than protons, additional resonances occur in the proton signal as a result of transitions between coupled proton–deuteron states that involve a change in proton polarization, which can be observed in our experiment. An example is shown in Fig. 4.

In our experiment, additional resonances occur at approximately $v_0/v_r = 0.865$, 0.93, 1.08, 1.175 and 1.73. Due to the isotropic rotation, the quadrupolar interaction of each deuteron is averaged out at room temperature in the same manner as intramolecular dipolar coupling is. The expected values for these resonances, under the approximation that the energies are influenced only by Zeeman interaction with the external field, can be calculated in the model of photon-coupled states and reside at $v_0/v_r = 0.85$, 0.92, 1.08, 1.15 and 1.70. There is a significant systematic shift of these lines to higher frequencies compared to the homonuclear lines in the same measurement, which are at the predicted locations. This shift seems to increase the further the resonance is removed from 1. Note that the resonances at $v_0/v_r = 0.865$, 1.175 and 1.73, which are induced by the flip-flop term in the dipolar Hamiltonian via one-photon transitions, are the most pronounced ones of the additional lines.

5. Conclusions and outlook

To summarize, we would like to present the most notable differences between low-field R^2 and the conventional (high-field) case:

- We can observe transitions, and therefore measure distances, between different spin species, which is not possible in high fields with a large Zeeman interaction.