

“Cooking the sample”: Radiofrequency induced heating during solid-state NMR experiments

Jean-Baptiste d’Espinose de Lacaillerie^{a,*}, Benjamin Jarry^a, Ovidiu Pascui^b, Detlef Reichert^b

^aLaboratoire de Physique Quantique, UMR CNRS 7142 SIEN, Ecole Supérieure de Physique et de Chimie Industrielles de la Ville de Paris, 10 rue Vauquelin, 75231 Paris, Cedex 05, France

^bFachbereich Physik, Martin-Luther-Universität Halle-Wittenberg, Friedemann-Bach-Platz 6, 06108 Halle, Germany

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Abstract

Dissipation of radiofrequency (RF) energy as heat during continuous wave decoupling in solid-state NMR experiment was examined outside the conventional realm of such phenomena. A significant temperature increase could occur while performing dynamic NMR measurements provided the sample contains polar molecules and the sequence calls for relatively long applications of RF power. It was shown that the methyl flip motion in dimethylsulfone (DMS) is activated by the decoupling RF energy conversion to heat during a CODEX pulse sequence. This introduced a significant bias in the correlation time–temperature dependency measurement used to obtain the activation energy of the motion. By investigating the dependency of the temperature increase in hydrated lead nitrate on experimental parameters during high-power decoupling one-pulse experiments, the mechanisms for the RF energy deposition was identified. The samples were heated due to dissipation of the energy absorbed by dielectric losses, a phenomenon commonly known as “microwave” heating. It was thus established that during solid-state NMR experiments at moderate B_0 fields, RF heating could lead to the heating of samples containing polar molecules such as hydrated polymers and inorganic solids. In particular, this could result in systematic errors for slow dynamics measurements by solid-state NMR.

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1. Introduction

In a standard NMR experiment, the description of the radiofrequency (RF) field’s effect on a sample typically considers the perturbation caused by the oscillating B_1 magnetic field but neglects the effects of the electric field E_1 propagated by the RF wave. However, the tendency to work at higher static B_0 fields and, therefore, at higher RF frequencies and higher RF powers combined with the increasing sophistication and length of the multiple pulse sequences used in modern solid-state NMR leads to a configuration where significant amounts of RF electric field energy are brought to the sample. Partial conversion to heat due to RF losses might thus be a legitimate concern.

In magnetic resonance imaging, the dissipation of power within the imaged body has been studied since the early days of this technique [1]. The issue is not only one of sensitivity but also of safety due to the expected physiological effects of internal thermal loads on humans [1–4]. Within this context, four main physical phenomena can be associated with heating. First, there is the ohmic (Joule) effect associated with the circulation of charges within conductors. In this category fall the current generated by the amplifiers through the emitting coil during the pulse and the eddy currents within the receiving coils (or metallic implants) especially during the rapid switching of magnetic gradients. Second, when applying an oscillating electrical field, free charge carriers within the sample are put in motion and, again, resistive losses occur. Third, electric dipoles couple with the oscillating field and react accordingly; but this fluctuation is impeded by their environment, and energy is drawn from the field (dielectric

*Corresponding author. Fax: +33 01 40 79 47 44.

E-mail address: Jean-Baptiste.dEspinose@espci.fr (J.-B. d’Espinose de Lacaillerie).

losses). When the electric dipole is permanent, as in the case of polar molecules, the dielectric losses are called dipolar losses. They constitute the physical basis of dielectric spectroscopy and microwave heating which depend on the occurrence and density of polar entities within the sample. Finally, to be complete, one cannot ignore the very basis of NMR, that is, the absorption of the resonant magnetic field by the spin. However, at room temperature and NMR frequencies, the energy deposited by coupling with the magnetic field can be safely neglected against thermal energy [5].

In liquid-state ^{13}C NMR also, heating of the sample when employing excessive decoupling power is a well-known artifact [6]. Direct coil heating can be considered minimal in NMR spectroscopy because of the poor thermal contact between the coil and the sample. Most of the RF heating is thus attributed to resistive losses in electrolyte solutions. Dipolar losses are also of concern for molecules with a high permanent electric dipole moment [7]. They have gained in importance with the generalization of high magnetic fields in which the Larmor frequency approaches the microwave absorption range of the solvents. High-field spectrometers operate at proton Larmor frequencies between 750 and 900 MHz while water, for example, has a broad dielectric absorption range between 1 and 300 GHz with a maximum at 16.7 GHz (a microwave oven operates at 2.45 GHz) due to interaction with the fluctuating hydrogen network [8]. The situation is particularly problematic in the case of biological samples in ionic aqueous solutions: both the resistive and the dipolar losses contribute to the heating and can spoil the precious samples. This realization has prompted the development of experimental measures to reduce this effect [9].

On the contrary, in solid-state MAS NMR, the issue of sample heating due to RF losses has been rarely of explicit concern and only then in the specific cases of particularly lossy materials. Heating due to resistive losses has been evidenced in a conductive graphite [10]. Dipolar losses have also been addressed in heat sensitive samples with a high density of mobile permanent dipole moments, such as polar liquid crystal samples [11,12] and more recently hydrated lipid membranes [13]. It remains that solid samples are commonly neither totally free of charge carriers (or those of reasonable mobility) nor of mobile solvent molecules that could have an appreciable effect on heating by conductive or dipolar losses. Indeed, the recent drive for MAS NMR studies of biological macromolecules at very high fields (above 17 T) has also prompted the development of probe designs to compensate [14] or minimize [15] RF heating.

We have incidentally realized the occurrence of RF heating in MAS NMR of solids, even at moderate fields (below 12 T). While evaluating solid-state dynamic NMR methods to measure the correlation time of molecular dynamic processes in solid organic molecules, it appeared to us that the results depended crucially on the applied proton-decoupling power. This observation, unexpected to

us, prompted a more detailed investigation of RF losses in hydrated lead nitrate in order to explore quantitatively the importance of the phenomenon during standard MAS NMR, to estimate its relevance to the study of hydrated inorganic materials, and, finally, to apprehend its physical origin.

2. Experimental

Dimethyl sulfone ($\text{CH}_3)_2\text{SO}_2$ (DMS) and lead nitrate $\text{Pb}(\text{NO}_3)_2$ were commercial samples from Aldrich. Controlled amounts of water were added as needed using a volumetric syringe. DMS was used as-received or vacuum dried for 24 h at room temperature.

^{207}Pb one-pulse MAS NMR was performed with continuous wave (CW) irradiation at the nominal frequency of protons for a period preceding and including acquisition (Fig. 1a). The CW irradiation on the decoupler channel had no spectroscopic purpose but served to carry RF power to the sample in a flexible manner. The spectra were acquired on two Bruker spectrometers: an ASX500 (11.7 T) and an ASX300 (7.04 T) equipped each with their commercial Bruker BL7 CPMAS probes. The bearing and drive pressure settings necessary to reach the spinning frequency of 4 kHz for the zirconia rotors were identical on both systems, and the external (bearing gas) temperature was set at 288 K. A $\pi/2$ pulse duration of 1 μs , CW irradiation during T_C 202 ms (including the 102 ms acquisition time), 80 dummy scans, and eight acquisitions were used. The CW power level ($\nu_1^H = \Omega_1^H/2\pi$) was varied between 0 and 55 kHz. The duty cycle was varied by changing the pre-scan delay between 2 and 20.6 s. The chemical shift was referenced to a 0.1 M aqueous solution of $\text{Pb}(\text{NO}_3)_2$ at -2941 ppm from $\text{Pb}(\text{CH}_3)_4$. Sample temperature increases were measured using the well-established dependence of the ^{207}Pb isotropic chemical shift of dry $\text{Pb}(\text{NO}_3)_2$ with temperature: 0.753 ppm/K. [16] It was verified that this relation held also on hydrated samples by using the well-described heating effect of spinning: the relationship between spinning rate and chemical shift was the same on all samples regardless of the hydration level. Since the heating was then solely due to the spinning and was therefore the same on all samples, the 0.753 ppm/K relationship for dry lead nitrate held true within 10% for hydrated samples.

^{13}C Center-band Only Detection of Exchange (CODEX) [17] experiments were performed on a Varian INOVA 400 spectrometer (9.4 T) and on a UNITY 200 (4.7 T) equipped, respectively, with a Varian and a Doty 7 mm CPMAS probe. The pulse length for ^1H and ^{13}C were about 4 μs . The CP amplitude was kept constant to satisfy Hartman–Hahn matching but the CW level varied for each spectra and was applied during the evolution and acquisition period for a total time of 30 ms. The recycle delay was 1 s, the spinning speed 3 or 4 kHz and the set temperature of 288 K calibrated with the chemical shift of an external $\text{Pb}(\text{NO}_3)_2$ reference. The sequence is represented in Fig. 1b.

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