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Radiation damping on cryoprobes

Dmitry Shishmarev, Gottfried Otting *

Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

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ABSTRACT

Radiation damping on 600 and 800 MHz cryoprobes was investigated. The phase angle β between a vector 90° phase shifted to the precessing magnetization and the rf field induced in the coil was found to depend markedly on whether an FID was being acquired or not. The magnitude of the radiation damping field was sufficiently strong to restore 95% of the equilibrium water magnetization of a 90% H_2O sample in a 5 mm sample tube within about 5 ms following a 165° pulse. This can be exploited in water flip-back versions of NOESY and TOCSY experiments of proteins, but care must be taken to limit the effect of the radiation damping field from the water on the H^{α} protons. Long water-selective pulses can be applied only following corrections. We developed a program for correcting pulse shapes if β is non-zero. The WATERGATE scheme is shown to be insensitive to imperfections introduced by radiation damping.

1. Introduction

Radiation damping is associated with very intense NMR signals, e.g. the ^{1}H NMR resonance of water in an aqueous solution. By coupling the magnetization with the circuit of the radio-frequency (rf) coil, radiation damping returns transverse magnetization back to equilibrium much faster than T_1 relaxation processes. The phenomenon is well understood [1–4] and many ingenious ways have been designed to suppress radiation damping effects, including active feedback circuits [5–7], pulse shape compensation [8], bipolar gradients [9–11], trim pulses [12] and *Q*-switches [13]. The effect has also been exploited to achieve selective water flip-back, e.g. during the mixing times of NOESY and ROESY experiments [14,15], and for selective water excitation [16–18]. Controlling radiation damping is important, because it can perturb resonances with similar frequencies [16,18–21].

Radiation damping increases with the quality factor of the rf coil and therefore is particularly strong with cryogenic probes which achieve improved sensitivity by an increased quality factor compared with room temperature probes. To understand the peculiar appearance of FIDs measured for samples of 90% H_2O/10% D_2O on different cryoprobes, we determined the radiation damping parameters from indirectly and directly detected signals. While data were obtained using Bruker TCI cryoprobes, the effects from strong radiation damping apply to any probe with very high quality factor. The results show that different parameters apply during signal acquisition compared with free precession delays, that a strong water signal overloads the cold preamplifier and that radiation damping is sufficiently strong to be used for water flip-back in improved NOESY and TOCSY experiments.

2. Theory

Radiation damping of a single NMR signal can be described by [22]:

$$\omega_{+}^{RD}(t) = -i\alpha M_{+}(t)e^{-i\beta}\cos(\beta). \quad (1)$$

where $\omega_{+}^{RD}(t) = \omega_{x}^{RD}(t) + i\omega_{y}^{RD}(t)$ and $M_{+}(t) = M_x(t) + iM_y(t)$ are the complex forms of the radiation damping field and the transverse magnetization, respectively, α is the coefficient of proportionality between the transverse magnetization and the resulting radiation damping field and β is the phase angle between a vector orthogonal to the precessing magnetization and the rf field induced in the coil. When the probe is tuned exactly at electrical resonance, the RD field is at perfect quadrature with the transverse magnetization, i.e. $\beta = 0$. Since probe tuning usually minimizes reflected power rather than putting the probe at exact electrical resonance [23], β can be non-zero.

In the case of several resonances subject to radiation damping, the modified Bloch equations take the following form [22]:

* Corresponding author. Fax: +61 2 61250750.
E-mail address: gottfried.otting@anu.edu.au (G. Otting).

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$$\frac{M_i^x(t)}{dt} = -\omega_i M_i^y(t) - R_2^i M_i^x(t) - \alpha\cos^2(\beta) M_i^z(t) \times \sum_j^N M_j^x(t) - \alpha\cos(\beta)\sin(\beta) M_i^z(t) \sum_j^N M_j^y(t);$$

$$\frac{M_i^y(t)}{dt} = \omega_i M_i^x(t) - R_2^i M_i^y(t) - \alpha\cos^2(\beta) M_i^z(t) \sum_j^N M_j^y(t) + \alpha\cos(\beta)\sin(\beta) M_i^z(t) \sum_j^N M_j^x(t);$$

$$\frac{M_i^z(t)}{dt} = R_1^i\left(M_0^i - M_i^z(t)\right) + \alpha\cos(\beta)\left(\cos(\beta) M_i^x(t) - \sin(\beta) M_i^y(t)\right) \sum_j^N M_j^x(t) + \alpha\cos(\beta)\left(\cos(\beta) M_i^y(t) + \sin(\beta) M_i^x(t)\right) \sum_j^N M_j^y(t) \quad (2)$$

where R_1 and R_2 are the longitudinal and transverse relaxation rates and the indices i and j identify resonances at different frequencies. In these equations, α is in units of rad/s. In the following, we specify this radiation damping parameter in Hz, i.e. $\alpha_{Hz} = \alpha/2\pi$.

3. Results

3.1. Measurement of the radiation damping parameters α and β

3.1.1. RD parameters of a FID – isopropanol

The radiation damping parameters α and β prevailing during acquisition of an FID can be estimated from the appearance of the 1D NMR spectrum of a sample of 90% isopropanol/10% DMSO-d_6 measured after a small flip-angle excitation pulse. The RD fields from each of the two doublet components of the methyl resonance mutually affect their time evolution in a manner that yields a symmetrical methyl resonance only when $\beta = 0$ [22].

Fig. 1 shows that the intense RD field of a cryoprobe severely affects the appearance not only of the doublet of the isopropanol methyl resonance but also of its ^{13}C satellites. The lineshapes could readily be simulated with a Python script (provided in the Supporting Information) using Eq. (2) for six resonances (two doublet components and four satellite lines). A 10° change in β significantly changes the appearance and symmetry of the doublet. Following tuning of the probe as recommended by the manufacturer (using the Bruker "wobb" command) to produce a maximal Q factor on resonance (599.991 MHz), the RD parameters were determined to be $\alpha_{Hz} = 35$ Hz and $\beta = 44°$. Repeating the experiment on a 800 MHz Bruker Avance NMR spectrometer equipped with the same type of cryoprobe (manufactured in 2005) yielded $\alpha_{Hz} = 32$ Hz and $\beta = 30°$ when tuned to the Larmor frequency (800.126 MHz). This means that neither probe is at exact electrical resonance following tuning to the ^1H Larmor frequencies. Nonetheless, measurements of signal-to-noise performed with a standard ethylbenzene sample at different tuning frequencies confirmed that tuning to the exact Larmor frequency produced the maximal sensitivity (data not shown).

3.1.2. RD parameters of a FID – water

To determine the sample dependence of the α and β parameters, we also measured the time domain signals of water ^1H magnetization after an inversion pulse for a range of H_2O/D_2O samples containing between 90% and 10% H_2O. Following calculation of the magnitude values of the FIDs, it is particularly easy to visualize the increase and decrease of transverse magnetization as radiation damping rotates the magnetization back to equilibrium.

Fig. 2 shows such magnitude FIDs for three samples containing 90%, 30% and 10% of H_2O on the 800 MHz spectrometer. Notably, the maximal signal observed for the 90% H_2O sample was not nine times greater than the maximal signal observed for the 10% H_2O sample. In addition, the FID of the 90% H_2O sample displayed a flat top that could not be reproduced in simulations using Eq. (2), whereas the FID of the 10% H_2O sample could readily be simulated. The result did not change when we placed an attenuator in the acquisition signal path. We believe that the cold preamplifier of the cryoprobe no longer operates in a linear regime when challenged by a large H_2O signal.

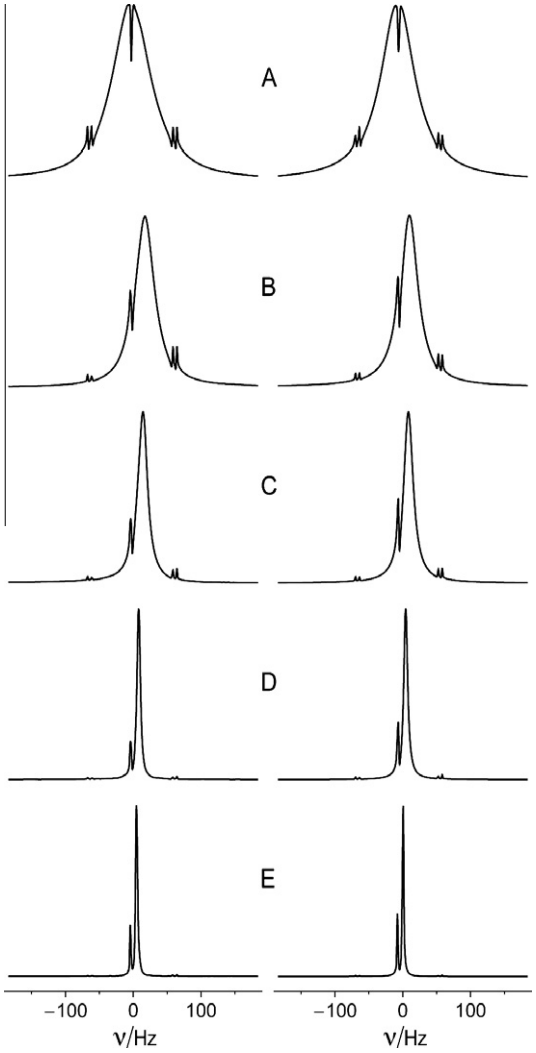

Fig. 1. Experimental 600 MHz ^1H NMR spectra of the isopropanol methyl doublet including its ^{13}C satellites of a 90%/10% v/v mixture of isopropanol/DMSO-d_6 in a 5 mm sample tube recorded after a 9° excitation pulse at different tuning frequencies (TF). The data were recorded on a Bruker Avance 600 NMR spectrometer equipped with a triple-resonance $^1H/^{13}C/^{15}N$ TCI cryoprobe with single-axis gradient coil (built in 2007). The left and right panels display the experimental and simulated spectra, respectively. The simulated spectra were calculated using $\alpha_{Hz} = 35$ Hz throughout, whereas the phase angles β were adjusted for a best fit between the simulated and experimental data. $T_1 = 7$ s and $T_2 = 5$ s as in Barjat et al. [22]. The spectra were scaled to the same height of the maximum point. (A) TF = 599.345 MHz, $\beta = 3°$; (B) TF = 599.991 MHz, $\beta = 44°$; (C) TF = 600.448 MHz, $\beta = 58°$; (D) TF = 601.686 MHz, $\beta = 71°$; (E) TF = 602.552 MHz, $\beta = 81°$.

The best fit of the FID obtained with the 10% H_2O sample using Eq. (2) gave $\alpha_{Hz} = 25.4 \pm 0.6$ Hz and $\beta = 35.0 \pm 1.1°$. This shows that the β angle is only to a small degree sample dependent. For the samples with higher H_2O content, the strength of the RD field can be estimated by the width of the trace (the time τ_{rec}) at a height, where the cold preamplifier would not be overloaded (Fig. 2). As a consequence of a non-zero β parameter, the magnetization changes its phase in a non-linear manner during its return to the z-axis.