Comment on: Is multiple quantum nuclear magnetic resonance spectroscopy of liquid water real?

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COMMENTS

Comment on: Is multiple quantum nuclear magnetic resonance spectroscopy of liquid water real?

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Recently, McCoy and Warren[1] have obtained very interesting results by performing simple 2D NMR experiments on a water sample. These consisted in an "MQT-like" experiment, including a fixed mixing period τ_m,

$$(90)_x - \tau_m - (90)_x - t_1 - (90)_{-x} - t_2.$$

2D spectra of water were then obtained, by setting the carrier at an offset $\Delta\omega$. Very surprisingly, these spectra exhibited several peaks separated by $\Delta\omega$ in the ω_1 dimension, which were assumed to be coherences evolving at multiples of the Larmor frequency during the evolution period. According to the authors, the delay τ_m is to be thought of as a mixing time allowing multiple-spin one-quantum operators to occur, via a coupling between the spins and the coil (i.e., via the phenomenon of radiation damping[2-4]), which are subsequently transformed into multiple-spin multiple-quantum coherences by the second pulse. We could reproduce the same results in our laboratory, using the sequence mentioned above; in addition, we have performed similar experiments, conserving only two pulses, thus leading to the "COSY-like" sequence,

$$(90)_x - t_1 - (90)_{-x} - t_2.$$

We could then observe exactly the same results, i.e., a series of peaks in the ω_1-dimension, spaced by $\Delta\omega$. We constantly tried to thouroughly eliminate experimental artifacts that could give rise to those images. In particular, we obtained similar spectra by using low power pulses, or by attenuating the detected signal before the receiver. A substantial delay was imposed before each scan in order to avoid artifacts due to incomplete relaxation; detuning the probe allowed us to record spectra exhibiting the same characteristics.

These results do not seem to be in agreement with the previous studies. Although it is well known that a semiclassical treatment is valid[4,5] in the field of magnetic resonance, we will use in this paper a quantized field framework, following the suggestion of McCoy and Warren, to show that radiation damping cannot account for those experimental results. In a quantized field framework, the Hamiltonian describing the evolution of an ensemble of spins interacting with a single mode ω of the radiation field can be written as follows:[5-7]

$$\mathbf{H} = \omega_0 \mathbf{I}_z + \omega a^+ a + \lambda(a^+ \mathbf{I}_- + a\mathbf{I}_+), \tag{1}$$

where a and a^+ are the photon anihilation and creation operators of the interacting mode, and $\mathbf{I}_z = \Sigma \mathbf{I}_{kz}$, $\mathbf{I}_- = \Sigma \mathbf{I}_{k-}$, $\mathbf{I}_+ = \Sigma \mathbf{I}_{k+}$ represent the collective spin operators. In NMR experiments, the field present in the sample is always generated by the coil, during an rf pulse as well as during the detection period (in the latter case, the field is induced by the precession of the spins). The constant λ is the coupling constant between the spins and the rf field, related to the macroscopic intensity of the field ω_1 and to the mean photon number n by[5,6]

$$\omega_1 = \lambda n^{1/2}. \tag{2}$$

In this framework, the spin density operator, ρ_{spin}, will be

$$\rho_{\text{spin}} = \text{Trace}_{\text{field}}\rho, \tag{3}$$

where ρ is the total density operator, describing the evolution of the system {spin + field}. Now in order to give a more complete description of the processes that govern the evolution of the spins, we have to take into account the radiation damping phenomenon, i.e., the energy exchange between the rotating magnetization and the coil. This phenomenon has long been studied[2,3] by analogy of two coupled electrical circuits, one of them describing the magnetization of the spins, and the other one the circuit of the probe. On the other hand, in a quantized field framework, radiation damping can be considered as a relaxation phenomenon[7] of the interacting field. This has been extensively studied in the case of the interaction of a laser beam with an atom in a cavity,[8,9] and we will only recall the main results here. It can be viewed as a small system (the interacting field mode) coupled to a field reservoir, the evolution of which is described by a Hamiltonian term, H_f, describing the "free evolution" of the field mode, and a Liouvillian term, Λ_f, accounting for dissipative processes, thus leading to the evolution equation of the density operator of the field ρ_f,

$$\frac{d\rho_f}{dt} = -i[H_f, \rho_f]_+ \Lambda_f \rho_f. \tag{4}$$

The relaxation phenomenon of the considered field mode corresponds to the leakage of the photons from the interacting mode towards other modes of the radiation field, as well as the population of the interacting mode with photons coming from others modes of the reservoir, these processes occuring through the interaction with the coil. The particular form of the field relaxation operator depends upon the type of interactions accounting for the dissipative processes, but the evolution equation for the interacting field density operator ρ_f can be shown to take the general form,[9]

$$\frac{d\rho_f}{dt} = -\frac{\omega}{2Q}[a^+a,\rho_f] + \frac{\omega}{Q}a\rho_f a^+ - \frac{\omega}{2Q}\frac{n}{n+1}[aa^+,\rho_f] + \frac{\omega}{Q}\frac{n}{n+1}a^+\rho_f a, \tag{5}$$

where Q is a phenomenological temperature-dependent quality factor, and n is the mean occupation number of the reservoir energy levels, i.e., the average blackbody photon number per mode. The two first terms describe energy transfer to the reservoir, whereas the two last ones account for absorption of blackbody radiation of the reservoir.

The global evolution of the system can be described by the superposition of the two independant evolutions of the spins and of the field, provided that the time required for the coupling between them is much greater than the correlation time of the relaxation processes between the field and the field reservoir (i.e., the field relaxation processes are not affected by the coupling with the spins). The evolution equation of the {spin + rf field} density operator ρ then takes the form

$$\frac{d\rho}{dt} = -i\left[\omega_0 \mathbf{I}_z + \omega a^+a + \frac{\lambda}{2}(a^+\mathbf{I}_- + a\mathbf{I}_+),\rho\right] - \frac{\omega}{2Q}[a^+a,\rho] + \frac{\omega}{Q}a\rho a^+ - \frac{\omega}{2Q}\frac{n}{n+1}[aa^+,\rho] + \frac{\omega}{Q}\frac{n}{n+1}a^+\rho a. \tag{6}$$

We now return to our main concern in this article. In the various experiments mentioned above, resonance peaks were found in the ω_1 dimension, which revealed an oscillatory behavior of the spins, reminding that of multiple spin coherences. The question is to find out if the quantized field theory described above, which includes a description of the (improperly called) radiation damping, is likely to account for the presence of those peaks. It is easy to show that the presence of the field relaxation operator Λ_f is unable to produce any oscillation frequency of the system; its effect will manifest itself only through an attenuation of the already existing oscillations; it then suffices, for our purpose, to study the particular case of an infinite quality factor Q. The behavior of the system described here is a collective one, as far as radiation damping is concerned, i.e., the coupling of the spins with the coil causes an indirect coupling of the spins among themselves, creating strong correlations, and the system is shown[10] to behave like a angular momentum $J = N/2$, where N is the number of spins in the sample, rather than a two-level system. After the simplification mentioned above, the evolution equation becomes

$$\frac{d\rho}{dt} = -i\left[\omega_0 \mathbf{I}_z + \omega a^+a + \frac{\lambda}{2}(a^+\mathbf{I}_- + a\mathbf{I}_+),\rho\right] = -i[\mathbf{H},\rho] \tag{7}$$

the solution of which is

$$\rho(t) = \sum_{i,j} A_i A^*j \exp[-i(E_i - E_j)t] \;\; |i\rangle\langle j|, \tag{8}$$

where the $|i\rangle$ are the eigenstates of $\mathbf{H}$, with the corresponding energies E_i.

The exact determination of the evolution frequency necessitates the diagonalization of the Hamiltonian, which becomes rapidly difficult. However, it has been shown (Ref. 5 of Ref. 9) that, for a large number of spins N, the dressed states levels are almost equally spaced by an energy $\lambda N^{1/2}$; this shows that the evolution frequencies of the system are of the order of $\lambda N^{1/2}$ and its multiples, which are not likely to be equal to ω_0 or its multiples. Furthermore, this oscillatory behavior is conditioned, in the general case of a noninfinite Q, to $\omega/Q \ll \lambda N^{1/2}$, which can be shown not to be fulfilled in the NMR experiments we are presenting here. Thus, we have seen that in spite of the fact that, theoretically, an oscillatory behavior of the spin system could be observed, radiation damping is unable to yield coherences that evolve at multiples of the Larmor frequency ω_0, in the experiments described above.

In conclusion, we have seen that some interesting "COSY-like" experiments have been performed, which exhibit unexpected features, namely, the presence of resonance peaks in the ω_1 dimension on spectra of water, and have received no convincing explanation so far. Unlike what had been suggested before, we have shown that a quantized field theory of radiation damping cannot account for those peaks.

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[1] M. A. McCoy and W. S. Warren, J. Chem. Phys. **93**, 858 (1990).
[2] N. Bloembergen and R. V. Pound, Phys. Rev. **95**, 8 (1954).
[3] S. Bloom, J. Appl. Phys. **28**, 800 (1957).
[4] A. Abragam, *Principles Of Nuclear Magnetism* (Clarendon, Oxford, 1961).
[5] C. Cohen-Tannoudji, J. Dupont-Roc, and G. Grynberg, Processus d'interaction entre photons et atomes, Interéditions/Editions du CNRS (1988).
[6] S. Haroche, Ann. Phys. Fr. **6**, 189, 327 (1971).
[7] William H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1973).
[8] S. Haroche and J. M. Raimond, Adv. At. Mol. Phys. **20**, 347 (1985).
[9] S. Haroche, in *New Trends In Atomic Physics* (Les Houches Summer School Lecture Notes), edited by R. Stora and G. Grynberg (North-Holland, Amsterdam, 1984).
[10] R. Dicke, Phys. Rev. **93**, 99 (1954).