Raman Magnetic Resonance

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A method for continuous coherence transfer in magnetic resonance is proposed and demonstrated with real-time detection of a double-quantum NMR coherence. The technique, which has implications for a broad range of magnetic resonance experiments, is related to effects observed in the study of coherent optical transients.

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Over the last few years, a variety of magnetic resonance experiments have required detection of the time evolution of coherences which are not directly observable. A recent example is a multiple-quantum transition which is dipole forbidden in first order.[1] Despite the apparent inaccessibility of such a transition, it is possible to monitor the state of the evolving coherence by use of a "read" pulse to transfer the information to an allowed, and therefore detectable, transition.[2] The pulse method achieves maximum coherence transfer, but destroys the evolving coherence, and forces the experiment into a point-by-point mode.[1,2] This can become very time consuming if one step in the experiment is very long. For example, each point requires a nuclear polarization period which is orders of magnitude longer than the rest of the experiment. When many points are required to define the time evolution sufficiently, it would be advantageous to have a method for the observation of these coherences continuously, as is done for allowed transitions.

In this communication, we report a method which permits continuous observation of forbidden magnetic resonances, and demonstrate the technique with real-time detection of a double-quantum coherence.[3] A weak, continuous-wave (cw) field is used to stimulate a Raman response from a spin system in which the coherence of interest has been generated. This is an effect which has heretofore only been associated with optical[4] or mixed optical-magnetic[5] three-level systems, and in all these experiments, optical detection was used. The experiment described in the Letter was carried out on a three-level system in which the energies and responses were determined solely by magnetic interactions among nuclear spins. Thus, the method can be viewed as a magnetic analog of coherent Raman spectroscopy in the optical regime,[6,7] and the signals observed as coherent magnetic Raman beats.

The double-quantum transition was observed in a three-level NMR system composed of the dipole-perturbed Zeeman states of two identical spins. Difluorotetrachlorethane was dissolved in a nematic liquid-crystal solvent. The liquid crystal becomes partially aligned in the external field (1.4 T) used for the NMR experiment, and the solute becomes oriented in the liquid crystal so that the dipolar interaction between the two ^{19}F spins is not motionally averaged to zero as it would be in an isotropic medium.[8] The dipolar perturbation shifts the Zeeman levels of the ^{19}F nuclei, resulting in the three-level system shown in Fig. 1(a). The corresponding ^{19}F NMR spectrum, shown in Fig. 1(b), is a doublet with splitting $a = 1016$ Hz. The stimulated coherent Raman beat is generated by mixing of the two-quantum coherence at $2\nu_0$ with a weak cw probe field at

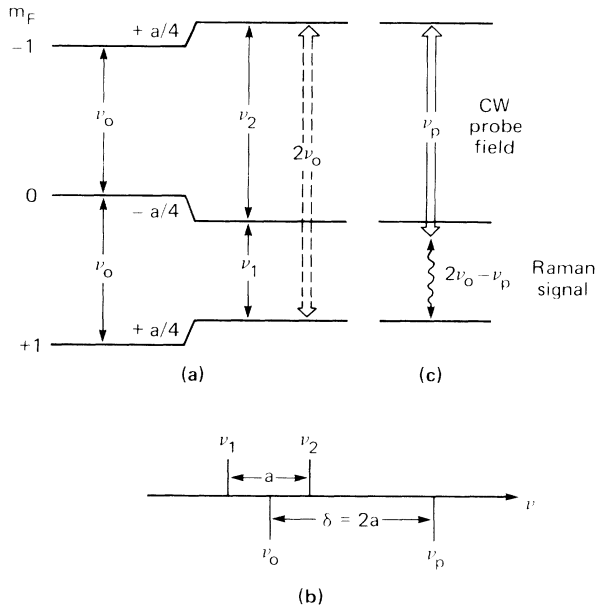

FIG. 1. (a) Three-level system for two coupled ^{19}F spins, showing Zeeman levels separated by $\nu_0 = 56.4$ MHz and dipole shifted by $\pm a/4$, leading to a doublet spectrum with frequencies ν_1 and ν_2, and double-quantum coherence at twice the Larmor frequency ($2\nu_0$). The states are labeled by the Zeeman sublevel quantum number. (b) Single-quantum spectrum showing the position of the cw probe field (ν_p) offset from the resonance frequency (ν_0) by δ. (c) Raman signal at $2\nu_0 - \nu_p$ generated by mixing of the double-quantum coherence and weak off-resonance cw probe field.

ν_p to produce the Raman signal at $2\nu_0 - \nu_p$, as shown in Fig. 1(c).

Double-quantum coherence is first generated by well-known methods which use the pulse pair shown at the beginning of the sequence in Fig. 2[9]: The radio-frequency carrier is set off resonance at ν_p by twice the splitting in the single-quantum spectrum [Fig. 1(b)]. A nonselective 90° pulse is applied, and the single-quantum magnetizations are allowed to precess freely for a time $(2a)^{-1}$, when they are 180° out of phase with each other. A second nonselective 90° pulse is then applied, which converts all the single-quantum coherence into double-quantum coherence at $2\nu_0$.[1] The phase of the pulse pair is cycled in order to minimize the amount of single-quantum coherence generated.[9] At the end of the second pulse ($t=0$, Fig. 2), the double-quantum coherence begins to evolve in time. A weak cw "probe" field is immediately applied at ν_p,[10] and the receiver is turned on simultaneously so that signal induced by the cw field can be acquired in real time.[11] The evolving two-quantum coherence mixes with the weak probe field to produce Raman signals at $2\nu_0 \pm \nu_p$. The spectrometer was tuned to detect the low-frequency beat at $2\nu_0 - \nu_p$ shown schematically in Fig. 1(c),[12] and the signal actually observed is shown in Fig. 3(a). The spectrum obtained after Fourier transformation of the acquired signal [Fig. 3(b)] has the following major features: two resonance lines at 1561 and 2583 Hz, 180° out of phase with each other, and a third resonance at 4143 Hz. The two low-frequency lines, separated by 1022 Hz, constitute the single-quantum spectrum, while the third line occurs at twice the resonance offset (2δ), as expected for a two-quantum response.[1,13] If the same sequence is used, but without the initial pulse pair, only single-quantum lines are observed, showing that the line at 2δ must be due to the prepared two-quantum coherence. The width of an inhomogeneously broadened two-quantum line should be double that of a one-quantum line.[1] We have tested for this by spoiling the homogeneity of the external field, and have observed widths of 21 and 42 Hz for the lines at 1561 (or 2583) and 4133 Hz,

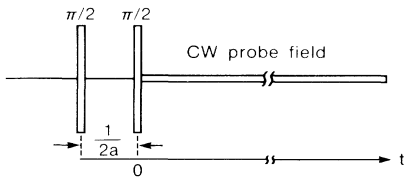

FIG. 2. Pulse sequence used for creation and detection of double-quantum coherence. The pulse pair (two 3-μsec pulses separated by 490 μsec) is used to create the coherence at $2\nu_0$, while the cw probe field stimulates a Raman response which faithfully reflects the time dependence of this coherence. The strength of the probe field (4.7 μT) is almost three orders of magnitude less than the strength of the pulse field (2 mT).

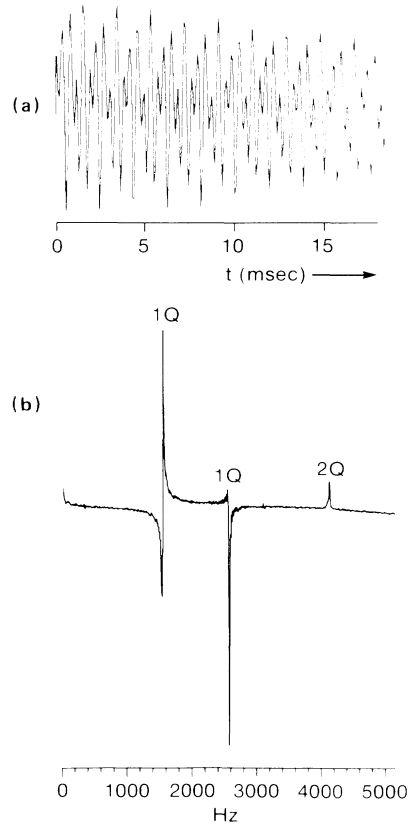

FIG. 3. (a) cw signal stimulated by the probe field. Only the first part of the data is shown (the decay lasts for over 200 msec) so that the beat structure is visible. (b) Fourier transform of the signal shown in (a). The antiphase signals at 1561 and 2583 Hz constitute the single-quantum (1Q) spectrum, while the two-quantum (2Q) signal is at 4133 Hz, twice the offset of the probe field from the center of the dipolar doublet.

respectively. The spectrum shown in Fig. 3(b) was actually obtained in a relatively uniform external field, and in this case, the widths of the one- and two-quantum transitions will be determined by competing effects: (1) variation in the degree of solute orientation, which makes the one-quantum line broader without affecting the two-quantum line,[1] and (2) external field homogeneity, which makes the two-quantum line twice as broad as the one-quantum line. These considerations account for the widths of the lines shown in Fig. 3(b): 10 Hz for the single-quantum (1Q), and less than twice this, 17 Hz, for the double-quantum (2Q) transition.

The rotating-frame Hamiltonian which describes the evolution of the two-quantum coherence in the presence of the cw probe field is given by

$$\mathcal{H} = aI_{1z}I_{2z} + \delta(I_{1z} + I_{2z}) + (\omega_1/2\pi)(I_{1x} + I_{2x}), \quad (1)$$

where a is a reduced dipolar coupling constant equal to

one-half of the doublet splitting,[14] δ is the resonance offset, and $\omega_1 = \gamma_F B_{1p}/2$ is the strength of the cw probe field. The cw signal, calculated in first order,[13] is given by

$$\langle I_y \rangle \sim \frac{\omega_1}{2\pi}\left\{\left[\delta-\frac{a}{2}\right]^{-1}\cos\left[\delta+\frac{a}{2}\right]t - \left[\delta+\frac{a}{2}\right]^{-1}\cos\left[\delta-\frac{a}{2}\right]t + \left[\left[\delta+\frac{a}{2}\right]^{-1}-\left[\delta-\frac{a}{2}\right]^{-1}\right]\cos 2\delta t\right\}. \quad (2)$$

The first two terms on the right are single-quantum oscillations, while the third term is the two-quantum oscillation. Equation (2) predicts, and the experimental results show, that the cw probe field stimulates single- as well as double-quantum responses. Furthermore, we find that the relative phases and amplitudes of the single- and double-quantum signals as functions of the resonance offset are in accord with Eq. (2). The double-quantum signal accounts for 20% and 30% of the total signal intensity with settings of $\delta = a$ and $\delta = 2a$, respectively. For a fixed value of δ/a, Eq. (2) indicates that the double-quantum signal intensity should increase linearly with the strength of the probe field (ω_1). Second-order line broadening should limit this increase,[13] and although we never reached this theoretical limit, receiver noise did become a practical limitation as the cw level was increased.

The use of a weak cw field for the detection of forbidden transitions in magnetic resonance represents a marked departure from the prevalent strategy of the use of a "hard" pulse to monitor such a coherence,[1,2] but introduces a general method for continuous coherence transfer. Viewed within the framework of two-dimensional spectroscopy,[15] the cw approach introduced here contracts evolution, mixing, and detection into a single time period. Therefore, such a "one-shot" experiment[16] holds promise for sensitivity improvement over the point-by-point method. Although we have chosen to demonstrate the technique on a three-level NMR system, the Raman method of detection has implications for a broad range of magnetic resonance experiments, including electron spin-echo modulation[17] and optical detection of coherence effects in triplet states.[18] We are currently exploring the use of the Raman beat method in both of these areas, and are also developing a comprehensive theoretical treatment of the phenomenon.

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[10]In principle, the frequencies of the probe field and pulse pair are independent; in these initial experiments, it was experimentally convenient to use the same carrier frequency for both. The resonance offset was actually 2072 Hz, somewhat greater than $2a$ (2032 Hz), resulting in a negligible reduction of double-quantum coherence (Ref. 9). The strength of the probe field (4.7 μT) was 0.25% of the strength of the pulse field (2 mT).

[11]The experiment was carried out in cw mode with a cross-coil probe; the inner solenoidal coil was used for the nonselective pulse pair and detection, while the outer saddle-shaped coil was used for the weak probe field.

[12]The Raman signal at $2\nu_0 + \nu_p$ [not shown in Fig. 1(c)] would be too weak to detect.

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