Crafted Pulses for the Uniform Suppression of a Region in a Coherent Spectrum

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We have theoretically derived and experimentally demonstrated "narrow reject" pulses which give a uniform $\pi/2$ excitation off resonance, and zero excitation in a sharp hole directly on resonance. They are also insensitive to relaxation effects. This shape is symmetric and has only amplitude modulation, and so it can be implemented on most commercial NMR spectrometers or with laser modulators. It can replace conventional broadband $\pi/2$ pulses in most NMR or laser pulse sequences, in order to give solvent suppression or measure spectral diffusion.

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We report a method, readily applicable to pulsed NMR or coherent laser spectroscopy, for suppressing a range of frequencies in the middle of a uniformly excited spectrum, even when the excitation is sufficiently strong to make linear-response theory inaccurate. This method relies on the use of modified or crafted pulse shapes, and has several advantages over those previously reported.[1-4] This single "narrow-reject" pulse maintains undistorted intensities and phases in the excited spectrum, produces a uniform hole, and compensates for T_1 and T_2 relaxation. Such pulses are likely to be extremely valuable in such fields as biological NMR, where suppression of the water peak is necessary to observe much weaker protein signals. They also provide a powerful tool in laser spectroscopy for measuring spectral diffusion processes, such as velocity-changing collisions in a gas.[5]

These pulse envelopes are based on polynomials multiplied by the difference of two Gaussians. In our previous work[6,7] we demonstrated pulse shapes which retain phase coherence, give a uniform 90° or 180° rotation of magnetization (or pseudopolarization, the equivalent mathematical construct for an optical system) over a specified frequency range, and produce little effect outside of that range. We found these simple, symmetric, single-phase pulse shapes (a quadratic equation multiplied by a Gaussian) by a new and rapidly convergent perturbation expansion which corrects for even the gross nonlinearity of π-pulse excitation (complete inversion). Assume that the pulse shape is described by the function $\omega_1(t)$, and extends from $t=-T/2$ to $t=+T/2$. Define

$$\rho_{\rm in}(0)=\exp(-i\Delta\omega I_z T/2)\rho(-T/2)\exp(+i\Delta\omega I_z T/2),\quad \rho_{\rm fin}(0)=\exp(+i\Delta\omega I_z T/2)\rho(T/2)\exp(-i\Delta\omega I_z T/2),$$

where $\Delta\omega$ is the resonance offset. $\rho_{\rm in}(0)$ is the density matrix which would have been observed at $t=0$ if the pulse had, in fact, been omitted, and $\rho_{\rm fin}(0)$ is the final prepared density matrix translated back in time to $t=0$. Then

$$\rho_{\rm fin}(T/2)=e^{-i\bar{A}}\rho_{\rm in}(T/2)e^{+i\bar{A}},\qquad \bar{A}=\bar{A}^{(0)}+\bar{A}^{(1)}+\bar{A}^{(2)}+\ldots,\qquad \bar{A}^{(0)}=I_x\left(\int_{-T/2}^{+T/2}\omega_1(t)\cos(\Delta\omega t)\,dt\right),$$

$$\bar{A}^{(1)}=-\tfrac{1}{2}I_z\int_{\tau=-T/2}^{+T/2}\left(\int_{t=-T/2}^{T/2}\omega_1(t)\omega_1(t+\tau)\,dt\right)\sin(\Delta\omega\tau)\,d\tau=-\tfrac{1}{2}I_z\int_{-T/2}^{+T/2}G(\tau)\sin(\Delta\omega\tau)\,d\tau.$$

$\bar{A}^{(0)}$ is the Fourier transform of the pulse shape; $\bar{A}^{(1)}$ is the sine Fourier transform of the pulse autocorrelation function $G(\tau)$. $\bar{A}^{(2)}$ and higher-order terms can usually be neglected, as shown in Ref. 6. The pulse shapes of Refs. 6 and 7 use the combined effects of $\bar{A}^{(0)}$ and $\bar{A}^{(1)}$ to create a sharper inversion than would be possible from Fourier-transform arguments alone.

In this Letter we address the opposite problem: Instead of generating a narrow-band excitation with no effect far from resonance, can we generate a broadband excitation with no effect near resonance? Starting with our crafted narrow-band shapes, one quickly comes up with two different approaches for such "narrow reject" pulses. The first is to modulate the pulse with a sine or cosine wave, thus redistributing its Fourier components to either side of the exact resonance. But this approach disperses the autocorrelation function ($\bar{A}^{(1)}$) as well, and thus does not tend to give sharp edges. In addition, sine modulation gives a 180° phase shift upon crossing the suppressed region (as do most of the standard water suppression sequences) and cosine modulation does not give the pulse zero area (required for exactly zero excitation on resonance).

The second approach is to center a strong and short pulse on a weak and long crafted narrow-band pulse. Since the time scales of the two pulses are very different the autocorrelation function is relatively simple.

For experimental reasons we restricted ourselves to pulse shapes which could be adequately described by a 256-point digital approximation. We started with the coefficients that we developed for 90° narrow-band pulses and had a computer search the region around those coefficients.[5] The actual pulse envelope we used (Fig. 1) is described by

$$\omega_1(t) = [1.017 - 0.3332T^2 + 0.3719T^4 - 0.1488T^6]\exp[-T^2] - [0.01700 - 0.005552t^2 + 0.006199t^4 - 0.002479t^6]\exp[-t^2], \quad T = 60t,$$

where $\omega_1(t)$ is scaled to a maximum of 1. The coefficients with T give the short pulse, and the coefficients with t give the long pulse.

The pulse shape produces a spectrum which has a hole in the middle with a width in hertz of 1.04/FWHM (full width at half maximum of the long part of the pulse) and an excitation width which is equal to (24 Hz^2)/FWHM, over which the peak intensities are distorted by less than 2% (Fig. 2). If one is willing to have 5% distortion of intensities the excited region has a width of (33 Hz^2)/FWHM. The area of the pulse is exactly zero so that the excitation on resonance is always exactly zero, independent of rf homogeneity.

The theory used to generate and optimize this pulse shape did not explicitly include T_1 and T_2 relaxation. However, such relaxation normally plays a critical role in determining the maximum pulse length. Thus, for example, solvent-suppression sequences in biological NMR have been generally limited to pulses of a few

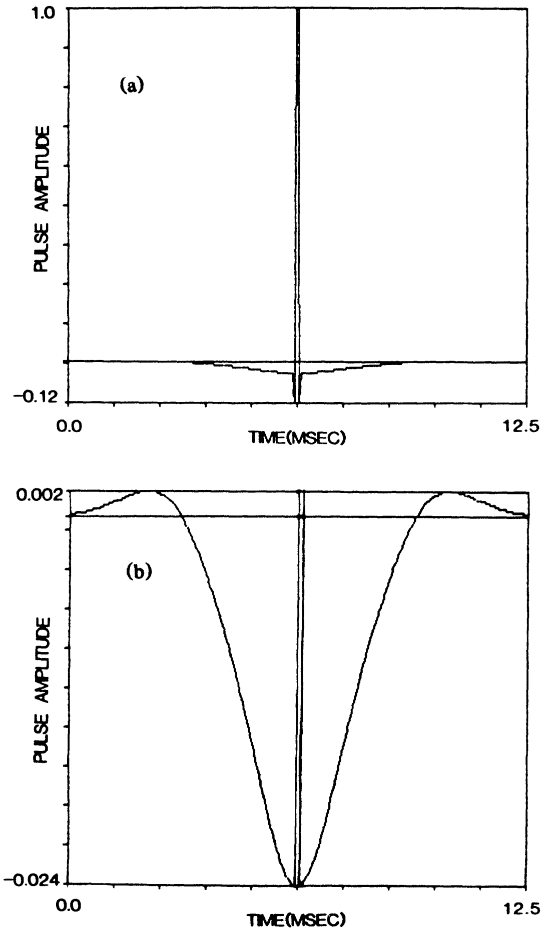

FIG. 1. Narrow-reject pulse shape. This shape can be viewed as the combination of two simpler $\pi/2$ pulses, each of which is a polynomial multiplied by a Gaussian. The short and strong pulse gives complete excitation off resonance, but this excitation is canceled by the long and weak pulse near resonance. The total area is zero.

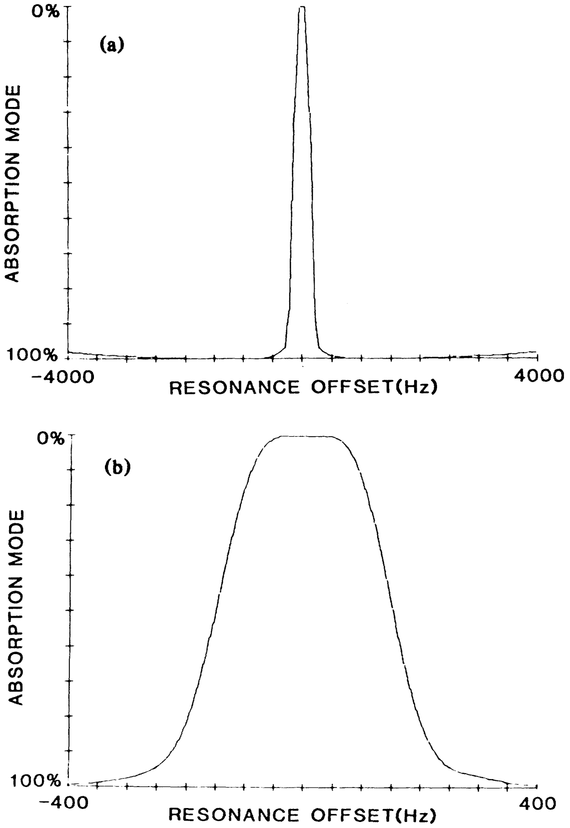

FIG. 2. Calculated excitation profile for the pulse shape in Fig. 1. The pulse gives a complete $\pi/2$ excitation with no phase shifts over a wide region far from resonance, with no excitation in a flat region near resonance. The frequency scale may be adjusted arbitrarily by just a change in the pulse length (see text).

milliseconds duration, for two reasons. First of all, rectangular pulse excitation gives distorted phases far from resonance, but this problem is corrected by our shapes. More significantly, if $T_2 = 500$ msec, 10% of the water molecules will relax during a 50-msec pulse sequence, and they will generally end up giving a spurious signal because they saw only part of what should have been a complete solvent-suppression sequence. However, it turns out that the excitation profile from our pulse shapes is remarkably insensitive to T_1 and T_2 effects. This can be understood by recognition that the high symmetry of the pulse shape guarantees that for every spin that relaxes at time τ after the middle of the pulse (giving a nonzero value for $\langle I_x \rangle$ or $\langle I_y \rangle$) a nearly equal number will relax at time τ before the middle of the pulse (giving exactly the negative values for $\langle I_x \rangle$ and $\langle I_y \rangle$). This insensitivity is verified by numerical solutions of the differential Bloch equations with use of a predictor-corrector method[8] with $T_1 = T_2$ (Fig. 3). Relaxation times that are on the order of 25 times the pulse length (FWHM) do not perceptibly distort the excitation profile. Relaxation times on the order of only 2.5 times the pulse length (FWHM) caused nearly uniform, approximately 50% attenuation in the signal, and the appearance of only about a 0.25% excitation in the exterior two-thirds of the suppressed region. This is a substantial improvement which allows hole widths comparable to T_1 and T_2, and gives resolution enhancement in crowded spectra.

The single narrow-reject pulse was generated with a 256-point approximation as described in our previous communication.[7] In essence, a pulse shape is fed to a double-balanced mixer, which is inserted before the final amplifier. The pulse was truncated at the level corresponding to 1/2048 of the maximum intensity of the pulse. The spectra displayed in Fig. 4 were taken on a JEOL FX90Q FT NMR, which for technical reasons could not be made to give a pulse longer than 12 msec. Suppression of the aromatic region of 3-bromopropyl

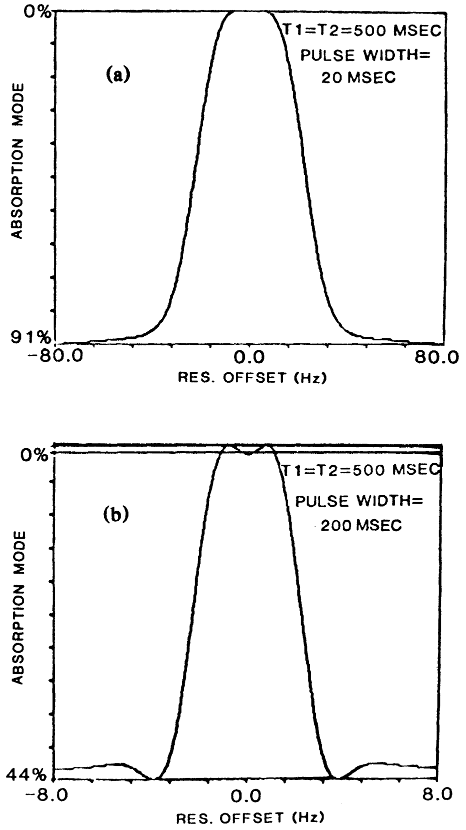

FIG. 3. Effects of T_1 and T_2 relaxation on narrow-reject pulses. Even pulse lengths comparable to these relaxation times give uniform excitation off resonance and zero excitation directly on resonance. Minor shape modifications can improve this profile further. This leads to substantial resolution enhancement if the pulse is very long.

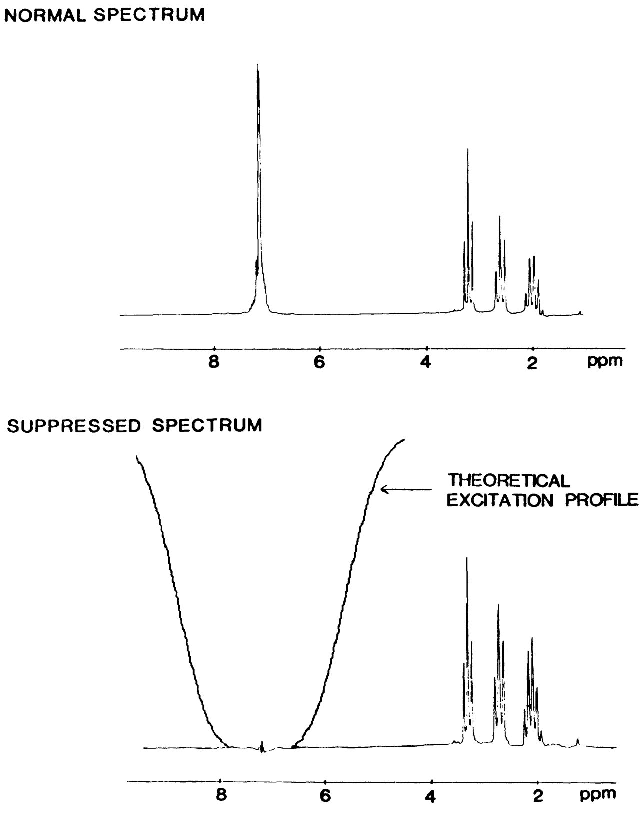

FIG. 4. Experimental spectra of (3-bromopropyl)-benzene at 90 MHz. We chose to suppress the entire aromatic region, which has J couplings and a chemical shift range. Solvent suppression is much easier. These phase-sensitive spectra show no distortions in the aliphatic region. The residual excitation on resonance is primarily due to amplifier nonlinearities, which could be corrected (see text).

benzene was chosen as a sensitive test, since this region consists of multiple peaks. As can be seen, the aromatic peak in the sample was almost completely suppressed. No attempt was made to compensate for amplifier nonlinearity, but this would certainly have further improved the suppression. The excited spectrum has no measurable dispersive component or amplitude distortions, and agrees well with our theoretical predictions.

Our results show that it is relatively easy to suppress a region of the NMR spectrum cleanly without significantly modifying the unsuppressed region of the spectrum and without having to worry about the relaxation times of the sample, even if they are on the order of the pulse length. The ease with which this method is implemented and the quality of the results should make it the method of choice for solvent suppression. A more complete suppression of a region of the spectrum can undoubtedly be obtained with further adjustments or a better spectrometer. For example, the ability to use more points on the digitized pulse not only will improve the results, but will allow the strong part of the pulse to be shorter in relation to the long part so that a narrower part of the spectrum may be suppressed while having uniform excitation over the same broad region.

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