Improvement of the F1 Resolution in Two-Dimensional Nuclear Magnetic Resonance Using a Purged Half-Gaussian Pulse

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Generally, most of the pulse sequences used in modern two-dimensional nuclear magnetic resonance (2D NMR) spectroscopy comprise non-selective pulses, which excite the entire spectrum of resonances in a molecule. A two-dimensional plot of the data results in a map of the correlations of various spin networks throughout a molecule. To obtain the degree of resolution necessary for interpreting the fine structure of the cross peaks, however, an excessively large memory and long experimental time are required with these pulse sequences.

Often, any elucidation of the molecular structure can be done sufficiently from specific spectral regions if they are highly resolved to show the fine structures in the cross peaks of interest. To achieve this, pulses of the sequence can be shaped so as to provide selectivity in the excitation of just the resonance lines of interest, since a shaped pulse can exhibit both frequency selectivity and excellent phase behavior.¹ The generation of shaped pulses has now become a feature of commercial spectrometers.

In our study we showed the usefulness of a purged half-Gaussian pulse for improving the F1 resolution in phase-sensitive double-quantum filtered correlation spectroscopy (DQF-COSY).

Experimental

Experiments were carried out on a General Electric Omega 400 spectrometer (400 MHz). A numeric table of the half-Gaussian function was incorporated in a source file in the native pulse sequence language. The truncation level was set to 0.1% of the maximum amplitude, and the time resolution was 400 points at full width. The table was compiled into the wave-form memory and the half-Gaussian pulse was generated by a pulse sequence generator (PSG) module.

For the experiment, 45 mg of strychnine dissolved in 0.5 ml of CDCl₃ was used as a typical sample. The structure is shown in Fig. 1.

Excitation profiles were simulated by numerical computation based on the classical Bloch equations.

Fig. 1 Structure of strychnine. Molecular weight=334.42.

The program was developed by us and was run on SUN Microsystems' Sparcstation.

Results and Discussion

Property of a purged half-Gaussian pulse

Half-Gaussian and purged half-Gaussian pulses are shown in Figs. 2(a) and (b), respectively. As illustrated in the excitation profiles in Fig. 3, the half-Gaussian affords excellent selectivity for the positive M_x component, except for dispersive effects of the M_y component. In the purged half-Gaussian pulse the dispersive component, however, can be self-cancelled by applying a 90° non-selective pulse just after the half-Gaussian pulse. The non-selective pulse must be phase shifted by $\pm 90^\circ$. Summation of the two scans leads to a cancellation of the M_y and M_z components. The net effect is to remove or purge the dispersive component, as shown in Fig. 3. The uniform phase and excellent selectivity properties of the purged half-Gaussian pulse have shown its usefulness in 1D-NOESY, 1D-ROESY, 1D-TOCSY and semisoft-TOCSY according to the work of Kessler *et al.*²

It should be noted that since the use of a purged half-Gaussian pulse as an excitation pulse would result in no evolution of operators during the first t_1 interval in a 2D experiment, a small phase distortion in the spectrum of F1 would be expected.

Fig. 2 Half-Gaussian (a) and purged half-Gaussian (b) pulses.

Application to phase-sensitive DQF-COSY

The first excitation pulse of a conventional sequence was replaced by a purged half-Gaussian pulse. Although the basic phase cycle was the same as the conventional one, the experiment requires twice as many accumulations. A proton (2.34 ppm) at the 15 position of the structure in Fig. 1 was selectively excited and the evolution time was incremented by 2 ms at each step among 256 steps. These conditions defined a spectral bandwidth of 500 Hz in F1 with a digital resolution of 1.95 Hz/point without zerofilling. The raw data were halved two times in order to produce three data sets, which had 64, 128 and 256 t_1 increments, respectively. Zerofilling was then applied to each set in order to fill identical 2k×512 data plots for a comparison (Fig. 4). The F1 resolution in normal DQF-COSY experiments corresponds to (a) in Fig. 4, where the fine structures of the diagonal and cross peaks are not fully resolved. Doubling the number of data points, however, allows the fine structure to become apparent, as in (b), while the full set of 256 points permits the fine structure to be clearly

Fig. 3 Simulated excitation profiles of half-Gaussian and purged half-Gaussian pulses.

Fig. 4 F1 resolution dependence of the DQF-COSY spectrum. The upper numbers are the positions of protons coupled with 15 protons (Fig. 1). The chemical shifts are indicated in ppm. F2 resolution: 3.90 Hz. F1 resolution before zero-filling: (a) 7.80 Hz, (b) 3.90 Hz, (c) 1.95 Hz. Window function: sinesquare, 45° shifted for both dimensions. Each final data size is made the same by zero-filling to 2k×512 real points.

seen. This implies that these techniques can be used to reduce the experimental time in order to obtain high-resolution spectrum, compared with that from conventional DQF-COSY experiment.

Cavanagh *et al.* have reported on the application of phase-sensitive DQF-COSY using a Gaussian pulse.³ The data (Fig. 4) exhibit a smaller phase distortion than that shown in the work of Cavanagh *et al.* The use of a purged half-Gaussian pulse seems to have improved the F1 phase properties.

In conclusion, the incorporation of a purged half-Gaussian pulse in phase-sensitive DQF-COSY sequences increases the F1 resolution, thus allowing observations of the fine structure for a short time.

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