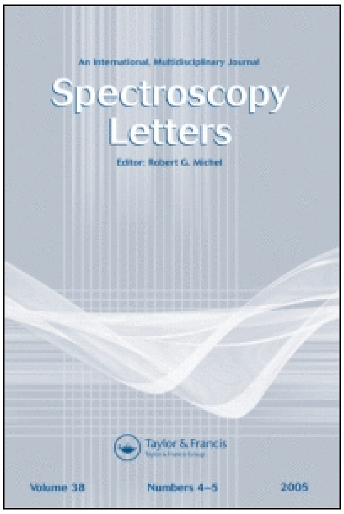

Spectroscopy Letters

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Dual-Compensating Composite Inversion Pulses for NMR

Xujie Yang[a]; Zhengliang Zhi[a]; Xiaobo Huang[a]; Baohua Gao[a]; Lude Lu[a]; Xin Wang[a]; B. C. Sanctuary[b]
[a] Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing, P. R. China
[b] Department of Chemistry, McGill University, Montreal, Quebec, Canada

To cite this Article Yang, Xujie , Zhi, Zhengliang , Huang, Xiaobo , Gao, Baohua , Lu, Lude , Wang, Xin and Sanctuary, B. C.(1998) 'Dual-Compensating Composite Inversion Pulses for NMR', Spectroscopy Letters, 31: 8, 1665 — 1676

To link to this Article: DOI: 10.1080/00387019808007444

URL: http://dx.doi.org/10.1080/00387019808007444

SPECTROSCOPY LETTERS, 31(8), 1665–1676 (1998)

Dual-Compensating Composite Inversion Pulses for NMR

Xujie Yang, Zhengliang Zhi, Xiaobo Huang, Baohua Gao, Lude Lu and Xin Wang*

Materials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, *P. R. China*

B. C. Sanctuary

Department of Chemistry, McGill University, 801 *Sherbrooke Street West, Montreal, Quebec H*3*A* 2*K*6, *Canada*

ABSTRACT Dual-compensating composite inversion pulses described as Wigner rotation matrix has been proposed for NMR optimization. The main FORTRAN program was modified to carry out optimization of the composite pulses, and the subroutine DULSJ and DSLEQ were programed instead of "IMSL" library DBCLSJ to calculate Jacobian and Levenberg-Marquardt iteration equations. Pulse and phase angles with respect to positive and negative resonance off-set were optimized on the multidimensional surface in search for the optimal parameters. It was found that the results obtained by the proposed method are better than other exsisting pulse sequences.

* Author to whom correspodence should be addressed

INTRODUCTION

Composite pulse sequences have been proven to be very use in NMR studies. Among the successful composite pulse sequences are WALTZ-16 [1] for hetronuclear decoupling of spin-$\frac{1}{2}$ nuclei in solution, COMARO-4 [2] for dipolar decoupling in solid, and for broadband population inversion in solid state NMR [3]. They are also adopted in many other NMR experiments, including improvements in excitation or inversion bandwidts in isotropic liquids [4,5], two-dimensional nuclear magnetic resonance experiments [6], homo- and hetro-nuclear TOCSY experiments [7,8].

Optimizing composite pulse sequence has been performed by computer simulation numerically and analytically, for instance, pulse-sequence optimization with analytical derivatives has been proposed in oriented phases [9], optimization in widehand spin inversion [10-12], and in studying optimal detection of ^nJ (^1H—^{119}Sn) coupling by 1D and 2D spectroscopy [13].

In this paper a new method using dual-compensating composite π pulses is presented. A computer program uses a geometical model of the spin system to optimize flip angles and phases with respect to resonance offset ($\Delta\omega/\omega_1$).

THEORY

A pure δ-pulse applied to a single spin system I can be described by the Hamitonian

$$\mathscr{H} = \mathscr{H}_{zeeman} + \mathscr{H}_{rf} = -\gamma h I \cdot H(t) \quad (1)$$

where H(t) is given by

$$H(t)=H_1\cos(\omega t-\varphi)x-H_1\sin(\omega t-\varphi)y+H_zZ \quad (2)$$

On the multiple basis, this Hamiltonian is represented by [14]

$$\mathscr{H}=\mathscr{H}_{zeeman}+\mathscr{H}_{rf}=-\gamma h\sqrt{I(I+1)/3}\sum_q \mathscr{Y}^{1q}(I)H_1q(t) \quad (3)$$

Where $\mathscr{Y}^{1q}(I)$ is the sperical tensors, q the sperical component. For the system of isolated spin-$\frac{1}{2}$ nuclei or systems of higher spins, $q=0, \pm 1$, the components are defined by [15]

$$\mathscr{Y}^{1\pm1}(I)=\sqrt{\frac{3}{I(I+1)}}\left(\mp\frac{i}{\sqrt{2}}\right)(I_x\pm iIy)$$

$$\mathscr{Y}^{10}(I)=\frac{\sqrt{3}}{\sqrt{I(I+1)}}iI_z \quad (4)$$

and $H_{1\pm1}(t)=\pm\frac{i}{\sqrt{2}}H_1e^{\pm i(\omega t-\varphi)}$, $\quad H_{10}=iH_z$

Substituting this Hamiltonian into the quantum Liouville equation leads to the defining set of first-order differential equations for the time behaviour of the $(2I+1)^2$ polarizations [16], in the rotation frame of the Larmor frequency ω_0

$$\frac{\partial}{\partial t}\hat{\Phi}_q^k=\frac{i\omega_1}{2}\cdot e^{i(\Delta\omega-\varphi)}\sqrt{(k-q+1)(K+q)}\hat{\Phi}_{q-1}^k$$
$$+\frac{i\omega_1}{2}\cdot e^{-i(\Delta\omega-\varphi)}\sqrt{(k+q+1)(k-q)}\Phi_{q+1}^k \quad (5)$$

The solution to equation (5) is given by

$$\hat{\Phi}_q^k(t)=\sum_{q'}D_{qq'}^{(k)}(\Omega)\cdot\hat{\Phi}_{q'}^k(0) \quad (6)$$

where k is the tensor rank, and Ω the Eular angle which could be shown as

$$\Omega=(\alpha+\varphi,\ \beta,\ \alpha-\varphi+\Delta\omega+\pi) \quad (7)$$

with

$$\cos\beta=\frac{1}{\Omega^2}[\Delta\omega^2+\omega_1^2\cos(\Omega t)]$$

$$\sin\beta=\frac{2\omega_1}{\Omega}\sin\left(\frac{\Omega t}{2}\right)\left[1-\frac{\omega_1^2}{\Omega^2}\sin^2\left(\frac{\Omega t}{2}\right)\right]^{\frac{1}{2}}$$

$$\sin\alpha = -\cos\left(\frac{\Omega t}{2}\right)\left[1-\frac{\omega_1^2}{\Omega^2}\sin^2\left(\frac{\Omega t}{2}\right)\right]^{-\frac{1}{2}} \tag{8}$$

$$\cos\alpha = -\frac{\Delta\omega}{\Omega}\sin\left(\frac{\Omega t}{2}\right)\left[1-\frac{\omega_1^2}{\Omega^2}\sin^2\left(\frac{\Omega t}{2}\right)\right]^{-\frac{1}{2}}$$

and

$$\Omega = \sqrt{(\Delta\omega^2+\omega_1^2)}$$

$$\Delta\omega = \omega - \omega_0$$

$$\omega_0 = \gamma H_z, \qquad \omega_1 = \gamma H_1$$

The above solution permits one to follow the effects of pulses, both on- and off- resonance, for any spin I. This result is of particularly convenient in that the flip angle β and the azimuthal angle α are parameterized in terms of experimentally controlled variables $\Delta\omega$ and ω_1, which will prove to be useful in exploiting the properties of composite pulses.

For n composite pulses, equation (6) could be written as following form

$$\hat{\Phi}_q^k(t) = \sum_{\text{all } q} \mathscr{D}_{qq_1}^{(k)}(\Omega_1)\cdot\mathscr{D}_{q_1q_2}^{(k)}(\Omega_2)\cdots\mathscr{D}_{q_{n-2}q_{n-1}}^{(k)}(\Omega_{n-1})\cdot \mathscr{D}_{q_{n-1}q_n}^{(k)}(\Omega_n)\hat{\Phi}_{q_n}^k(0) \tag{9}$$

where $\mathscr{D}_{qq'}^{k}(\Omega)$ are the elements of the Wigner rotation matrix.

For the system of isolated spin-$\frac{1}{2}$ nuclei or systems of higher spins, in which the Zeeman or dipolar polarization $\hat{\Phi}_0^1$ dominates, this means that $k=1$, $q=0, \pm 1$, and only elements of the rotation matrix $\mathscr{D}_{qq'}^1$ need to be considered, with the generation function for the reduced matrix elements $\mathscr{D}_{qq'}^1(\Omega)$ as given by Edmonds [17]

$$\mathscr{D}_{qq'}^1(\alpha+\varphi, \beta, \alpha-\varphi+\Delta\omega+\pi) = e^{iq(\alpha-\varphi+\Delta\omega+\pi)}d_{qq'}^1(\beta)e^{iq'(\alpha+\varphi)} \tag{10}$$

where the $d_{qq'}^1(\beta)$ are the matrix elements, given by [17]

$$d^1_{qq'}(\beta)=\begin{vmatrix} \frac{1}{2}(1+\cos\beta) & \frac{1}{\sqrt{2}}\sin\beta & \frac{1}{2}(1-\cos\beta) \\ -\frac{1}{\sqrt{2}}\sin\beta & \cos\beta & \frac{1}{\sqrt{2}}\sin\beta \\ \frac{1}{2}(1-\cos\beta) & -\frac{1}{\sqrt{2}}\sin\beta & \frac{1}{2}(1+\cos\beta) \end{vmatrix} \quad (11)$$

expansion of the equation (9) using relationship between equation (10) and (11) will obtain a 3×3 matrix. An n dual-compensating composite π pulse can be optimized for flip angles (β_i) and phase angles (φ_i) with respect to resonance off-set ($\Delta\omega/\omega_1$) by using computer algorithm for the pulse sequences.

A composite pulse with N components is described by 2N parameters, being the flip angle β and phase φ of each component pulse. They maybe written as a 2N-dimensional vector, which can be defined as [18]

$$F(\mathbf{x})=\sum_{i=1}^{m}[f_i(\mathbf{x})]^2 \qquad \mathbf{x}=(\beta_1,\beta_2,\cdots\beta_n;\ \varphi_1,\varphi_2,\cdots\varphi_n) \quad (12)$$

where $m\geqslant n$. Minimizing $f(\mathbf{x})$ with respect to the parameters $\mathbf{x}$ and resonance off-set ($\Delta\omega/\omega_1$) will yield the optimum flip and phase angles. Altering the resonance off-set ($\Delta\omega/\omega_1$) will mould more efficient parameters so that pulse sequences could be designed according to the prevailing experimental imperfections, and composite pulses could compensate the verious inadequacies of a pure δ-pulse.

In reference [19], we reported composite pulses with phase distortion, in which the "IMSL" library DBCLSJ [20], solving the non-linear least square problems, has been used as subroutine to carry out calculation on IBM/3600 computer to minimize flip and phase angles with respect to a range of resonance off-set

Table 1 Optimizing Procedures of Dual-Compensating 3-composite Pulses

```
STARTING GUESSES ARE:
 .7700000D+02  .1560000D+03  .2740000D+03  .2060000D+03  .5600000D+02

NUMBER OF PTS IS 12  NUMBER OF PULSES IS  3
NUMBER OF OBJECTS IS  5

GRADIENTS OF THE ANGLES ARE:
 -.3175372D-04  .1391481D-03 -.1162701D-03  .1376826D-03 -.3996004D-04

THE RESIDUES ARE:

              RESIDUES         DEL

           .2698226D-01  .0000000D+00
           .1093906D-01  .1000000D+00
           .1401256D-01  .2000000D+00
           .1600041D-01  .3000000D+00
           .9064342D-02  .4000000D+00
           .8149340D-03  .5000000D+00
           .2996492D-02  .6000000D+00
           .1669228D-01  .7000000D+00
           .2860626D-01  .8000000D+00
           .2453352D-01  .9000000D+00
           .1151185D-01  .1000000D+01
           .3043489D-01  .1100000D+01

FSUMSQ IS  .4149525D-02   FITTED ANGLES ARE:
 .7672542D+02  .1561681D+03  .2744184D+03  .2061014D+03  .5599434D+02

************************************************************************

STARTING GUESSES ARE:
 .7670000D+02  .1562000D+03  .2744000D+03  .2061000D+03  .5600000D+02

NUMBER OF PTS IS 13  NUMBER OF PULSES IS  3
NUMBER OF OBJECTS IS  5

GRADIENTS OF THE ANGLES ARE:
 -.7339678D-04  .1299619D-03 -.1605981D-03 -.1058873D-04 -.7242936D-04

THE RESIDUES ARE:

              RESIDUES         DEL

           .3787303D-01  .0000000D+00
           .1501496D-01  .1000000D+00
```

.1946017D-01	.2000000D+00
.2378379D-01	.3000000D+00
.1612269D-01	.4000000D+00
.3576135D-02	.5000000D+00
.9940854D-03	.6000000D+00
.1478797D-01	.7000000D+00
.3492616D-01	.8000000D+00
.4250754D-01	.9000000D+00
.2896473D-01	.1000000D+01
.1355861D-01	.1100000D+01
.4491776D-01	.1200000D+01

FSUMSQ IS .9163708D-02 FITTED ANGLES ARE:
.7741306D+02 .1396265D+03 .2639954D+03 .2131225D+03 .7215460D+02

****

STARTING GUESSES ARE:
.7740000D+02 .1396000D+03 .2640000D+03 .2131000D+03 .7220000D+02

NUMBER OF PTS IS 14 NUMBER OF PULSES IS 3
NUMBER OF OBJECTS IS 5

GRADIENTS OF THE ANGLES ARE:
.8298800D-04 .3210145D-04 .1717470D-03 .1981582D-03 .7209062D-04

THE RESIDUES ARE:

RESIDUES	DEL
.4729348D-01	.0000000D+00
.2104183D-01	.1000000D+00
.2753940D-01	.2000000D+00
.3369425D-01	.3000000D+00
.2485300D-01	.4000000D+00
.7894660D-02	.5000000D+00
.7789248D-04	.6000000D+00
.1228917D-01	.7000000D+00
.3846607D-01	.8000000D+00
.5880584D-01	.9000000D+00
.5544930D-01	.1000000D+01
.3096892D-01	.1100000D+01
.1722734D-01	.1200000D+01
.6686394D-01	.1300000D+01

FSUMSQ IS .1914321D-01 FITTED ANGLES ARE:
.7992082D+02 .1248218D+03 .2549897D+03 .2178233D+03 .8584590D+02

($\Delta\omega/\omega_1$). In this study, the subroutines DULSJ and DSLEQ have been programed instead of the "IMSL" library DBCLSJ.

CALCULATIONS AND RESULTS

Calculations were carried out on a COMPAQ 586 personal computer. Pulse angles and phases with respect to a range of resonance off-set ($\Delta\omega/\omega_1$) were optimized on the multidimensional surface of $F(\mathbf{x})$ in search for the global minimum corresponding to the "best" set of parameter values. Minimization routines using modified Levenberg-Marquardt algorithm [21] were adopted to solve the non-linear least square problems. The optimized steps involving numerical and geometical method are summarized as follows.

(1) modify the main FORTRAN program for optimizing dual-compensating composite π pules and program subroutines DULSJ and DSLEQ are used to calculate the mxn Jacobian matrix ($J_{ij}=\partial f_i/\partial \mathbf{x}_j$) of function $F(\mathbf{x})$ and Levenberg-Marquardt iteration equations

$$\begin{cases} X_{k+1}=X_k+P_k \\ P_k=-(J_k^T J_k+\mu_k I)^{-1}\{J_k^T \cdot f(\mathbf{x}_k)\} \end{cases}$$

where μ_k is a damping factor of some non-negative value, and I unit matrix.

(2) input initial guess pulse angles (β_i) and phase angles (φ_i, set $\varphi_1=0$) and optimize the pulse angles and phases with respect to a range of resonance off-set ($\Delta\omega/\omega_1$), being termed DEL. The optimized pulse and phase angles would be obtained.

(3) repeat step(2) and input the optimized pulse and phase angles obtained from step(2) by increasing the resonance off-set

Table 2 Optimized Dual-Compensating Composite Inversion Pulse

Composite pulses pulse/phase angles (deg.)	DEL ($\Delta\omega/\omega_1$)	Total length compared with a simple pulse	Ref.
180(0)	±0.12	1.0	18
180(0)	±0.15	1.25	This paper
198(0) 382(204)	±0.7	5.8	11
192.1(0) 379.9(208.8)	±0.7	5.8	This paper
79(0) 276(106) 79(0)	±0.4	3.3	18
84(94) 251(0) 84(44)	±0.55	4.6	22
90(0) 240(90) 90(0)	±0.6	5.0	23,24
86(0) 160(180) 260(9)	±1.25	10.4	19
79.9(0) 125.2(217.4) 255.0(85.1)	±1.3	10.8	This paper
64(0) 146(185) 320(310) 77(192)	±0.4	3.3	18
180(0) 180(105) 180(210) 360(59)	±0.6	5.0	3
52.5(0) 72.8(226.7) 72.3(122) 197.6(26)	±1.45	12.1	19
46.9(0) 92.9(219.0) 73.7(113.7) 217.1(19.9)	±1.5	12.5	This paper
64(32.2) 122(96) 310(0) 122(96) 64(32.2)	±0.6	5.6	22
45(0) 180(90) 90(180) 180(90) 45(0)	±0.8	6.7	3
98.6(0) 140.9(144.8) 140.8(390.7) 216.3(133.2) 160.4(34.7)	±1.1	9.2	This paper
14(0) 257.8(99.5) 329.6(306.3) 121.4(143.8) 222.6(0)	±1.3	10.8	This paper
52(0) 94(139) 66(196) 323(251) 143(159) 63(10)	±0.47	3.9	18
107.6(0) 177(209) 68.6(107.6) 54.1(339.4) 109.8(190.3) 298.8(37.2)	±2.0	16.7	19
107(0) 176.7(209.1) 69.4(108.2) 54.1(339.3) 110.1(190.1) 299.3(36.5)	±2.0	16.7	This paper
54(0) 135(163) 177(295) 381(11) 177(295) 135(163) 54(0)	±0.5	4.2	18
88.8(0) 91.8(117.4) 89.3(313) 296.2(139.5) 128.7(220.3) 68.7(248.2) 180.4(21.2)	±2.1	18	19
89(0) 95.2(117.4) 91.5(316.9) 305.2(145.7) 135.3(224.5) 71.2(249.6) 189.1(19.8)	±2.1	18	This paper
77.2(0) 75(147) 74(349.3) 201.8(203) 110.7(92) 116(273.7) 67.6(91.8) 266.1(23.4)	±2.4	20	19
77.2(0) 75(147) 74(349.3) 201.8(203) 110.7(92) 116(273.7) 67.6(91.8) 266.1(23.4)	±2.4	20	This paper
47.9(0) 67.5(57) 67.1(281) 164.1(187.2) 65.7(48.1) 65.6(259.7) 80.3(127.7) 268.4(0)	±2.3	19.2	This paper

($\Delta\omega/\omega_1$), until the "best" values are obtained. The optimizing procedures of a three dual-compensating composite π pulse 77. 0 (0) 156. 0(206. 0) 274. 0(56. 0) are listed in Table 1, which is good to $|(\Delta\omega/\omega_1)|$ of about 1. 3.

(4) within the optimization procedures, the other pulse and phase angles of dual-compensating composite π pulses were optimized by means of above steps, the final results are summarized in Table 2. As can be seen, the results are better than other exsisting dual-compensating composite π pulses.

ACKNOWLEDGMENTS

The support of this work by grants from the Natural Science Foundation of Jiangsu (China), and the Provincial Government of Quebec (Canada) is gratefully acknowledged.

REFERENCES

[1] A. J. Shaka, J. Keeler, R. Freeman, *J. Magn. Reson.*, **52**, (1983), 335

[2] D. Suter, A. Pines, G. Drobny, *Chem. Phys. Lett.*, **144**, (1988), 324

[3] R. Tycko, E. Schneider, A. Pines, *J. Chem. Phys.*, **81** (**2**), 1984, 680

[4] M. H. Levitt, *J. Magn. Reson.*, **50**, (1982), 95

[5] A. J. Shaka, *Chem. Phys. Lett.*, **120**, (1985), 201

[6] R. P. E. Kanters, B. W. Char, A. W. Addison, *J. Magn. Reson.* **101**, (1993), 276

[7] J. Briand, R. R. Ernst, *Chem. Phys. Lett.*, **185**, (1991), 276

[8] L. R. Brown, B. C. Sanctuary, *J. Magn. Reson.*, **91**, (1991), 413

[9] T. O. Lerante, T. Bremi, R. R. Ernst, *J. Magn. Reson.*, Series **A 121**, (1996), 167

[10] E. Kupce, R. Freeman, *J. Magn. Reson.*, Series **A 118**, (1996), 299

[11] X. J. Yang, M. A. Keniry, B. C. Sanctuary, *J. Magn. Reson.*, **105A**, (1993), 295

[12] X. J. Yang, L. D. Lu, X. Wang, *Spectroscopy Letts.*, **28** (**8**), (1995), 1191

[13] J. C. Martins, F. Kayser, M. Biesmans, *J. Magn. Reson.*, **124**, (1997), 218

[14] B. C. Sanctuary, *Mol. Phys.*, **48**, (1983), 1155

[15] B. C. Sanctuary, T. K. Halstead, P. Osment, *Mol. Phys.*, **49**, (1983), 753

[16] R. Freeman, M. H. Levitt, *J. Magn. Reson.*, **43**, (1981), 65

[17] A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, 1974, Princeton University Press, Princeton, New Jevsey, Ch. 4

[18] D. J. Lurie, *J. Magn. Reson.*, **70**, (1986), 11

[19] X. J. Yang, L. D. Lu, X. Wang, *Spectroscopy Letts.*, **29** (**7**), (1996), 1417

[20] IMSL Mathematics/Library FORTRAN Subroutines for Mathematical Applications, (1987), 882(IMSL Inc.)

[21] J. E. Dennis, B. C. Robert, *Numerical Methods for*

Unconstrained Optimization and Nonlinear Equations , (1983), Prentice-Hall, Englewood Cliffs, New Jersey

[22] J. Baum, R. Tycko, A. Pines, *J. Chem. Phys.* , **79**, (1983), 4643

[23] A. Box, D. G. Davis, *J. Magn. Reson.* , **65**, (1985), 355

[24] R. Freeman, S. P. Kempsell, M. H. Levitt, *J. Magn. Reson*, **38**, (1980), 453

Date Received: June 1, 1998
Date Accepted: July 10, 1998