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# Exploring the limits of broadband excitation and inversion pulses

Kyryl Kobzar[a], Thomas E. Skinner[b], Navin Khaneja[c], Steffen J. Glaser[a], Burkhard Luy[a],*

[a] *Institut für Organische Chemie und Biochemie, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany*
[b] *Physics Department, Wright State University, Dayton, OH 45435, USA*
[c] *Division of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, USA*

## Abstract

The design of broadband excitation and inversion pulses with compensation of $B_1$-field inhomogeneity is a long standing goal in high resolution NMR spectroscopy. Most optimization procedures used so far have been restricted to particular pulse families to keep the scale of the problem within manageable limits. This restriction is unnecessary using efficient numerical algorithms based on optimal control theory. A systematic study of rf-limited broadband excitation by optimized pulses and broadband inversion by optimized pulses with respect to bandwidth and $B_1$-field is presented. Upper limits on minimum pulse lengths are set for different degrees of pulse performance.
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## 1. Introduction

The development of broadband excitation and inversion pulses has a long history. The hard pulse as the work horse of modern NMR spectroscopy is not compensated for $B_1$-field inhomogeneity and in the case of excitation causes a linear phase change with offset. While this phase variation can be compensated by a linear phase correction in one-dimensional experiments, more complex pulse sequences are expected to show significant improvements if pulses with uniform behavior over a range of offsets and rf-amplitudes could be used. Until now, the design of such pulses requires computer optimization, where the performance of a pulse can easily be simulated by rotations in three-dimensional space. However, optimization algorithms applied so far for broadband excitation and inversion only lead to satisfying results for a relatively low number of independent optimization parameters, typically on the order of 10–100 parameters that define the pulse shape. As a consequence the space of possible pulse shapes in an optimization had to be reduced to certain pulse families characterized by a relatively small set of parameters, such as phase-alternating pulses [1–4], symmetric pulses [5,6], pulses with constant amplitudes [7,8], Gaussian pulse cascades [9], Hermite polynomials [10], Fourier series-based pulses [11–13], spline interpolated pulse shapes [14], adiabatic pulses [15–18] or combinations thereof [19,20].

A different optimization procedure that was first used in magnetic resonance for the optimization of band-selective pulses in MRI [21–23] is based on optimal control theory. In this procedure a gradient towards better performing parameters is calculated efficiently based on an analytical formula that allows a significant increase in the number of independently optimized parameters.

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The adaptation of optimal control theory to the problem of broadband excitation pulses including the optimization with limited rf-amplitude was reported recently [24,25]. Because of the high efficiency of the algorithm the space of possible pulse shapes used in the optimization is not restricted to any pulse family. Its fast convergence allowed the coverage of 8000 independently optimized parameters in reasonable time [24]. In spin systems where the theoretical limits of quantum evolution were known [26–32], numerical algorithms based on principles of optimal control theory, provide pulse sequences which approach the physical limits [33–35].

An optimal control theory-based numerical algorithm therefore appears to be a well-suited tool to explore the physical limits for robust broadband excitation and inversion. In particular, we specify upper limits for the minimum durations of pulses as a functions of bandwidths and rf-variation.

## 2. Theory

Optimal control theory and its application to NMR spectroscopy is described in detail elsewhere [22–25,35]. The optimization algorithm used in the systematic studies of excitation and inversion pulses presented in this article is identical to the one used in [25] to limit the maximum rf-amplitude.

The quality factor or final cost $\Phi$ used in the optimizations is the transfer efficiency from the initial magnetization $\mathbf{M}(t_0) = \mathbf{M}_z$ to the target state $\mathbf{F}$ ($\mathbf{F} = \mathbf{M}_x$ for excitation and $\mathbf{F} = -\mathbf{M}_z$ for inversion pulses) averaged over all offsets and rf-amplitudes specified for a specific optimization. It can be written as

$$\Phi = \frac{1}{n_{off} n_{rf}} \sum_{i=1}^{n_{off}} \sum_{j=1}^{n_{rf}} \mathbf{M}_{ij}(t_p) \cdot \mathbf{F} \qquad (1)$$

with $i = 1 \ldots n_{off}$ being the offsets and $j = 1 \ldots n_{rf}$ the scaled rf-amplitudes calculated for each pulse of length $t_p$, e.g., to include the effects of rf-inhomogeneity or rf-amplitude misadjustments. In all cases, the nominal (unscaled) rf-amplitude was limited to 10 kHz using the method described in [25]. Sets of excitation and inversion pulses were calculated for bandwidths of 10, 20, 30, 40, and 60 kHz considering both ideal rf-amplitude (scale factor of 1) and a variation of ±20% in the factor used to scale the rf-amplitudes. Also sets of pulses for a fixed bandwidth of 20 kHz with variations $\vartheta$ of ±10, ±20, ±30, and ±40% in rf scale factor were optimized to test robustness against $B_1$-field inhomogeneity. For each set, pulse lengths $t_p$ were varied in ranges as listed in Table 1. Generally, pulse durations were incremented until the quality factor $\Phi$ exceeded 0.995. Each chosen bandwidth was divided into equal increments, with $n_{off} = 100$ for 10 kHz bandwidth, $n_{off} = 200$ for bandwidths of 20, 30, and 40 kHz and $n_{off} = 300$ for 60 kHz bandwidth. $n_{rf}$ was chosen equal to 5 with equidistant percentage amplitude changes whenever variations in rf-amplitude were included in the calculations. The time digitization for the optimized shapes was 0.5 μs in all cases.

One hundred randomized starting pulses were generated to start 100 optimizations for each data point in Figs. 1 and 2. As with all gradient-based optimizations, the optimal control algorithm can terminate at a local, rather than the global, extremum. The pulse found by the algorithm depends on the (random) pulse chosen to start the procedure. However, in contrast to conventional optimization procedures, a significant percentage of the optimal control trials converges to similar values, even in cases with tight constraints. In addition, the quality factors cited as establishing limits on pulse performance are very high, approaching the ideal value of

Table 1
Constraints used for BEBOP and BIBOP optimizations

| rf-limit (kHz) | $\Delta v^a$ (kHz) | $n_{off}$ | $v^b$ (%) | $t_p$ excitation (μs) | $t_p$ inversion (μs) |
|---|---|---|---|---|---|
| 10 | 10 | 100 | — | 2.5–85 | 2.5–122.3 |
| 10 | 20 | 200 | — | 2.5–142.5 | 2.5–182.5 |
| 10 | 30 | 200 | — | 2.5–217.5 | 2.5–247.5 |
| 10 | 40 | 200 | — | 2.5–267.5 | 2.5–312.5 |
| 10 | 60 | 300 | — | 2.5–422.5 | 2.5–457.5 |
| 10 | 20 | 200 | ±10 | 2.5–247.5 | 2.5–242.5 |
| 10 | 20 | 200 | ±20 | 2.5–337.5 | 2.5–307.5 |
| 10 | 20 | 200 | ±30 | 2.5–442.5 | 2.5–352.5 |
| 10 | 20 | 200 | ±40 | 2.5–667.5 | 2.5–417.5 |
| 10 | 5 | 100 | ±20 | 30–60 | 40–115 |
| 10 | 10 | 200 | ±20 | 50–125 | 50–170 |
| 10 | 20 | 200 | ±20 | 100–190 | 85–212.5 |
| 10 | 30 | 300 | ±20 | 150–285 | 200–250 |
| 10 | 40 | 300 | ±20 | 180–405 | 265–385 |
| 10 | 50 | 300 | ±20 | 200–540 | |

[a] $\Delta v$ is defined as the excitation/inversion bandwidth used in the optimization.
[b] $\vartheta$ is the range of rf-amplitude scaling incorporated in the optimization.
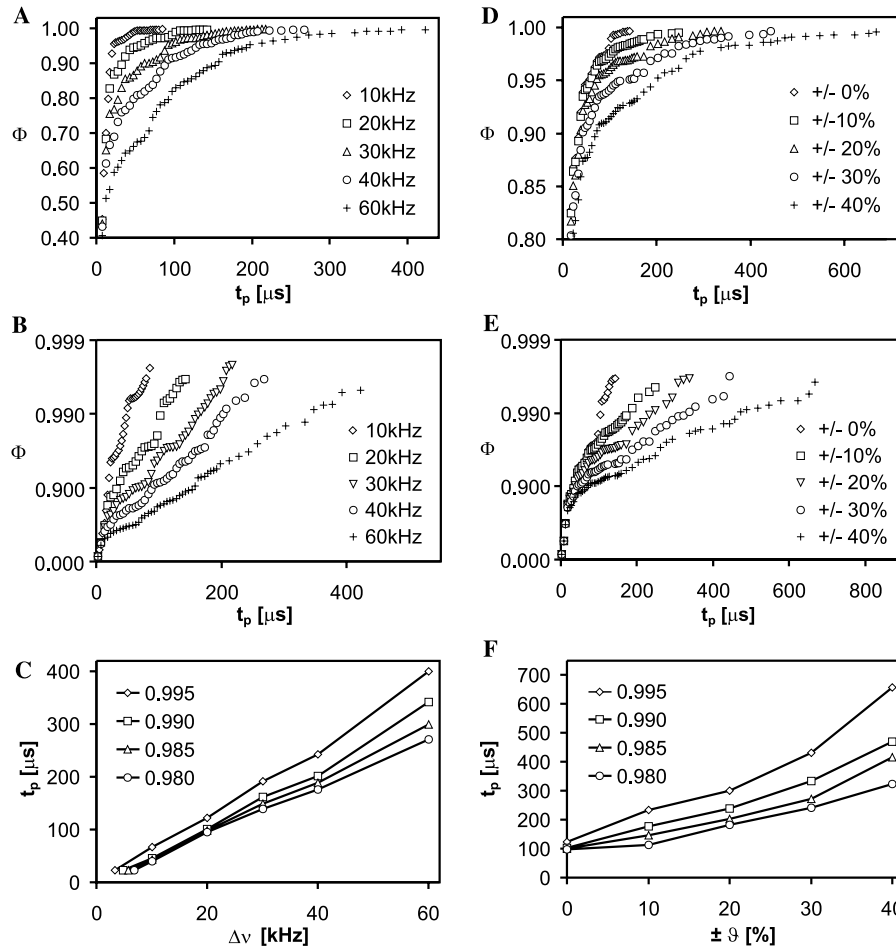
Fig. 1. Maximum quality factors reached for BEBOP with rf-amplitude limited to 10 kHz under various optimization constraints. The maximum quality factors $\Phi$ with respect to pulse duration is given for the five different bandwidths $\Delta\nu$ equal to 10, 20, 30, 40, and 60 kHz on a linear (A) and logarithmic scale (B). (C) The pulse lengths for quality factors of 0.98, 0.985, 0.99, and 0.995 are plotted as a function of the desired bandwidth and provide an estimate for the minimum pulse duration needed for specific requirements. The maximum quality factors $\Phi$ with respect to rf-variation are shown for no variation and rf-ranges $\vartheta$ of $\pm 10$, $\pm 20$, $\pm 30$, and $\pm 40\%$ on a linear (D) and logarithmic scale (E) for a fixed bandwidth of 20 kHz. (F) The minimum pulse duration $t_p$ are shown as a function of the rf variation $\pm\vartheta$ for quality factors $\Phi = 0.98$, 0.985, 0.99, and 0.995.

one (see Figs. 3 and 7). Any potential improvement in these limits will therefore be relatively small.

The convergence of every single optimization was very fast ranging from seconds for the shortest pulses to tens of minutes for the longest ones with larger $n_{\text{off}}$ and $n_{\text{rf}}$ on a single AMD Athlon 1500+ processor Linux-based PC.

## 3. Results

The results of the optimizations of excitation and inversion pulses are shown in Figs. 1 and 2, respectively: The performance of the optimized pulses described by the quality factor $\Phi$ is given as a function of pulse length on a linear scale in Figs. 1A, D and 2A, D. A logarithmic scale is used in Figs. 1B, E and 2B, E to show the differences at longer pulse durations more clearly. As expected, higher demands in terms of bandwidth or toler-

ance to rf-amplitude variation lead to reduced quality factors that can, however, be compensated by increased pulse lengths. In all cases pulses with more than 99.5% excitation or inversion over the entire offset and rf-amplitude ranges could be found for unexpectedly short pulse durations of significantly less than 700 μs. A question of considerable practical interest is the minimum pulse length needed to achieve an excitation or inversion of a given quality. This information is shown in Figs. 1C, F and 2C, F. The relation between the duration and bandwidth is roughly linear for both types of pulses for the investigated offset and rf ranges.

The dependence of the quality factor on the pulse duration is not a single smooth curve, but shows a step or wave-like behavior (c.f. Figs. 1A, D and 2A, D). A more detailed analysis reveals that steps are related to specific pulse families of optimal pulses. Representatives of such pulse families are shown in Fig. 4 for excitation. For very short pulses, optimal control theory found that hard
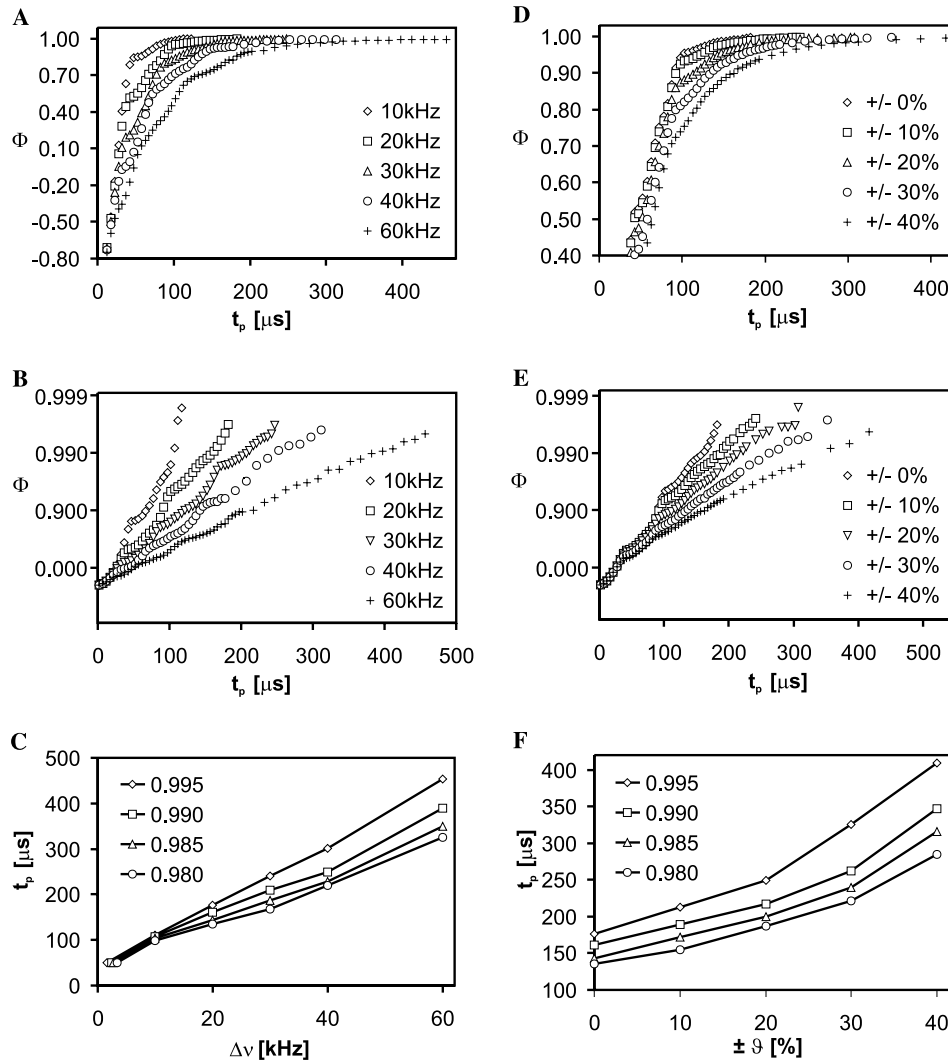
Fig. 2. Maximum quality factors reached for BIBOP with rf-amplitude limited to 10 kHz under various optimization constraints. Again, maximum quality factors $\Phi$ with respect to pulse duration are given for the five different bandwidths $\Delta v$ equal to 10, 20, 30, 40, and 60 kHz on a linear (A) and logarithmic scale (B). (C) The pulse lengths for quality factors of 0.98, 0.985, 0.99, and 0.995 are plotted as a function of the desired bandwidth and provide an estimate for the minimum pulse duration needed for specific requirements. The maximum quality factors $\Phi$ with respect to rf-variation are shown for no variation and rf-ranges $\vartheta$ of $\pm 10$, $\pm 20$, $\pm 30$, and $\pm 40\%$ on a linear (D) and logarithmic scale (E) for a fixed bandwidth of 20 kHz. (F) The minimum pulse duration $t_p$ are shown as a function of the rf variation $\pm \vartheta$ for quality factors $\Phi = 0.98$, 0.985, 0.99, and 0.995.



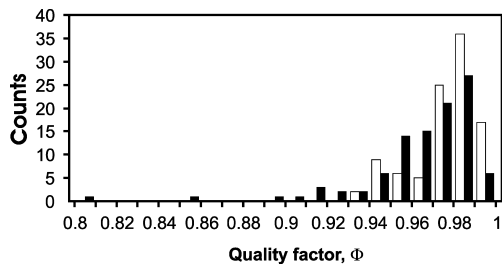Fig. 3. Histogram distribution of quality factors $\Phi$ obtained for 100 optimizations for excitation pulses of 20 kHz bandwidth, of 300 μs duration, and $\pm 20\%$ rf-variation (open bars); 600 μs duration and $\pm 40\%$ variation in rf-amplitude (black bars). A significant percentage of the optimizations is close to the maximum quality factors of 0.9955 and 0.9957, respectively.

pulses with constant amplitude and phase provided the best performance. For longer pulses, the algorithm introduced 180° phase shifts resulting in pulses very similar to phase-alternating composite pulses with one, two, and three phase jumps. If the pulse length increases further, the phase jumps 'morph' into more continuous phase changes. As was shown in [25], even longer pulses will have significant amplitude modulation, interspersed with periods of maximum rf-amplitude. If the pulse is sufficiently long, the amplitude will not necessarily reach the rf limit [24]. The pulse families shown in Fig. 4 each correspond to a 'step' in Figs. 1A, D.

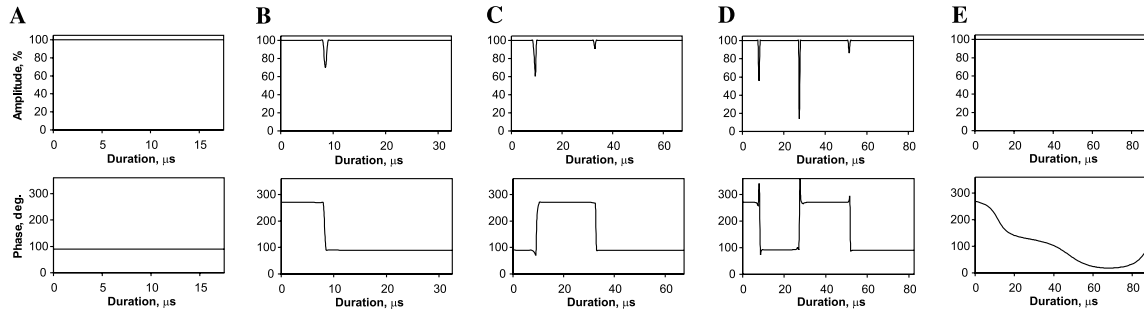Pulses optimized for inversion all show constant rf-amplitude over the entire length, but the observed

Fig. 4. Amplitude and phase for optimized excitation pulses of various durations found in the optimization for a bandwidth of 30 kHz and no rf-variation. Although no restrictions to the pulse shape were made, phase-alternating composite pulses are found for pulse durations of up to 82.5 μs (pulses shown in A–D roughly correspond to $63°_y$, $\{29°_{-y}, 88°_y\}$, $\{32°_y, 85°_{-y}, 126°_y\}$, and $\{29°_{-y}, 68°_y, 88°_{-y}, 112°_y\}$), while smooth phase-modulations were found for longer pulses.

step-like behavior still corresponds to certain pulse patterns. As for excitation, hard pulses and pulses with a single 180° phase jump give best results for very short pulse durations and bandwidths up to 30 kHz. As an example, for a bandwidth of 20 kHz and assuming no variation in rf-amplitude, Fig. 5B shows the numerically optimized pulse with a total duration of 67.5 μs, which represents a phase-alternating composite pulse $\{52°_x, 191°_{-x}\}$. For this bandwidth, such two component phase-alternating pulses of the general form $\{\alpha_x, \beta_{-x}\}$ are found to be optimal for pulse durations between 52.5 and 72.5 μs. In this range, the flip angle $\beta$ of the numerically found optimal pulses is approximated by $\beta \approx \alpha + 145°$. Hence, the overall on-resonance flip angle $\alpha - \beta$ of these pulses is only about 145° for this family of short pulses, which achieve the best possible *average* inversion over the full 20 kHz offset range. For a bandwidth of 30 kHz, two-component phase-alternating pulses $\{\alpha_x, \beta_{-x}\}$ are found for durations between 52.5 and 62.5 μs with $\beta \approx \alpha + 125°$. For a bandwidth of 10 kHz, two-component phase-alternating pulses are found for durations between 52.5 and 87.5 μs with $\beta \approx \alpha + 165°$, e.g., for a duration of

87.5 μs, the numerically optimized pulse is $\{76°_x, 239°_{-x}\}$, which is similar to the well-known pulse $\{90°_x, 270°_{-x}\}$ [36,37]. For longer pulse durations and broader bandwidths, a pulse family with smoothly modulated phase is found to be superior to phase-alternating composite pulses (c.f. Figs. 5C–E for a bandwidth of 20 kHz). The number of modulations in the phase marks different subclasses that again correspond to slight steps in Figs. 2A, D. Although no symmetry constraints were imposed in the optimization, pulses of this class are perfectly symmetric around the pulse center. In Fig. 6 the phase and frequency of three such pulses is shown. The central smooth frequency sweep is strongly reminiscent of adiabatic pulses, which have a high degree of tolerance to rf inhomogeneity or miscalibration. However, the class of pulses derived here has constant maximum amplitude and therefore shows very low adiabaticity at the pulse edges. Instead, a pronounced frequency swing is observed that seems to achieve a similar effect as the amplitude modulation at the edges of adiabatic pulses. In general, the optimized pulses are similar to BIP pulses derived in [20] with only slightly improved inversion properties.
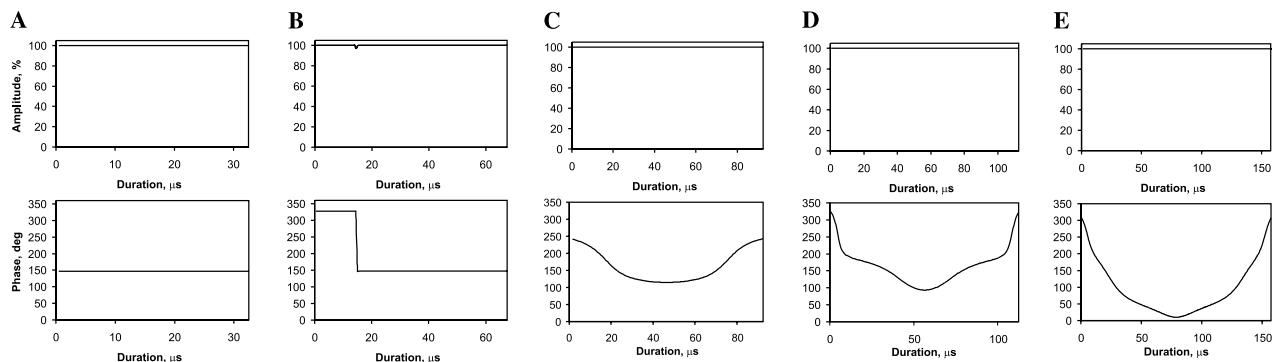


Fig. 5. Amplitude and phase behavior for optimal inversion pulses of various durations found for an optimization bandwidth of 20 kHz and no rf-variation. Constant amplitude pulses were obtained for all pulse lengths. While hard and phase-alternating composite pulses appear to be optimal for very short durations (pulses shown in A and B correspond to $112.5°_x$ and $\{52°_x, 191°_{-x}\}$), a symmetric class of pulses with smooth phase modulations seems to be optimal for pulse lengths longer than 70 μs.
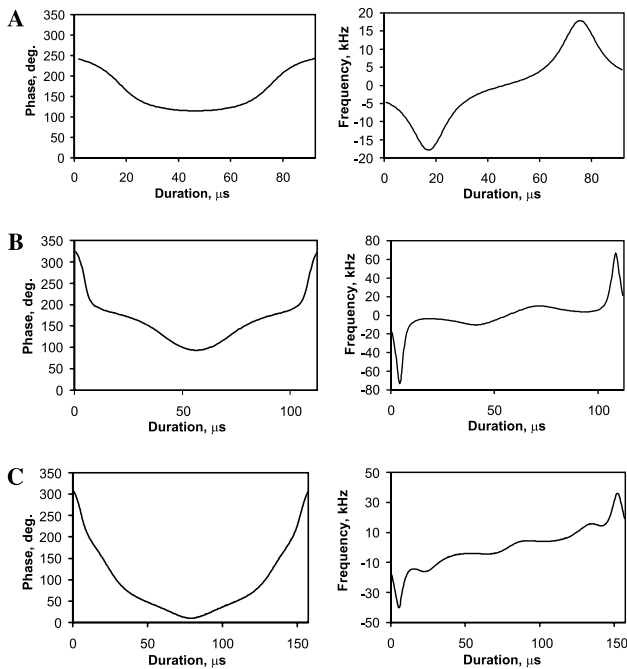
Fig. 6. The phase behavior of the pulses shown in Figs. 5C–E has been converted to frequency modulation for comparison. A symmetric nonlinear frequency sweep is observed. While the frequency sweep observed in the pulse center is reminiscent of adiabatic pulses, the swings at the pulse edges are not of high adiabaticity.

We also studied pulses only optimized for on resonant excitation (data not shown). The inclusion of $B_1$-field compensation in the optimization result-ed in pulses with smooth phase modulations for pulses shorter than a 90° hard pulse. For slightly longer pulses even amplitude modulation can be observed.

For comparison of the broadband excitation by opti-mized pulses (BEBOP) and broadband inversion by op-timized pulses (BIBOP) with already known excitation and inversion pulses we calculated the quality factor $\Phi$ for a large number of short published pulses. In all cases we set the maximum rf-amplitude to 10 kHz for consis-tent results. In addition, we set up comparisons without considering rf-amplitude variation and considering a variation $\vartheta$ of ±20%. For all pulses we numerically de-termined the maximum bandwidth in which the quality factor $\Phi$ reaches 0.98. Composite pulses we used for comparison were taken from [1,3,6] for excitation and from [1,4,6–8,39] for inversion. In addition we derived optimum sech/tanh and tanh/tan adiabatic pulses for several bandwidths as described in [40] and implemented most of the BIP inversion pulses [20]. The results are shown in Fig. 7: In the case of excitation no pulse reach-es the performance of BEBOP pulses; considering varia-tions in rf-amplitude none of the tested pulses does reach a quality factor of 0.98 (Figs. 7A, B). In the case of broadband inversion, only the $90_y240_x90_y$ pulse [1] achieves the limit when no rf-variation is considered (Fig. 7C). As shown in Fig. 7D, the BIP pulses [20] closely approach the limits found by our algorithm if rf-amplitude variations of ±20% are included in the cal-culations.
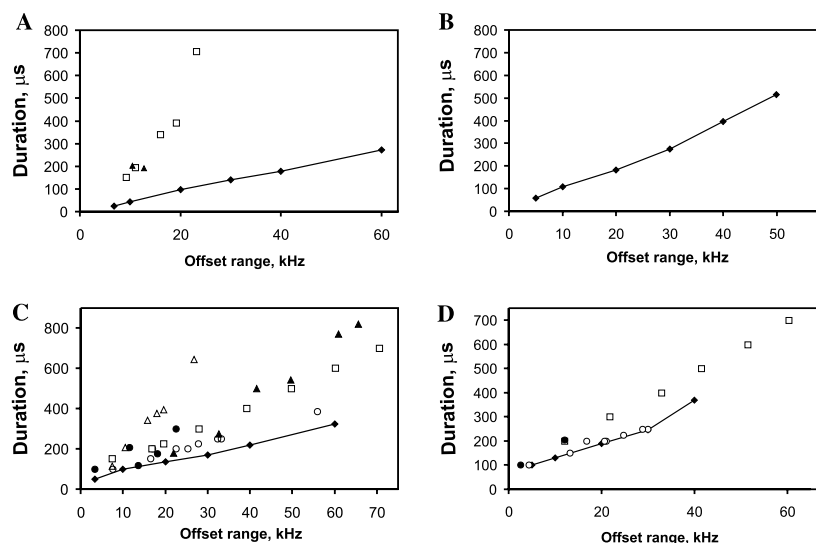


Fig. 7. Comparison of the maximum bandwidths with a quality factor $\Phi$ of 0.98 for previously reported broadband excitation (A,B) and inversion pulses (C,D) relative to BEBOP and BIBOP obtained here. BEBOP and BIBOP are indicated by filled diamonds which are connected by solid lines. (A) For excitation, BEBOP were compared with pulses from [6] (squares) and other pulses cited in [38] from original references [1,3] (filled triangles). (B) By taking a rf-variation of ±20% into account, none of the composite pulses reached a quality factor of 0.98. (C) Inversion pulses compared to BIBOP were taken from [39] (filled triangles), [6] (open triangles), [20] (open circles), [40] (open squares), and other inversion pulses cited in [38] from original references [1,4,7,8]. Only a $90_y240_x90_y$ pulse reaches the performance of BIBOP. (D) The same comparison including ±20% rf-variation. Only a few composite pulses, adiabatic and BIP pulses reach a quality factor of 0.98. The shapes of the BIP pulses [20] are almost identical to the optimum BIBOP.

## 4. Discussion

Modern high resolution NMR spectrometers with very high magnetic fields result in large offset ranges that have to be covered by pulse sequences. Especially ^{13}C and ^{19}F nuclei with their large offset ranges pose problems to conventional hard pulses. But also weak ^{15}N pulses of common triple resonance probeheads, for example, make it impossible to cover the whole nitrogen spectrum of uniformly labeled nucleic acids. The increased offset ranges could in principle be covered by stronger hard pulses, but high spectrometer frequencies close to 1 GHz limit the technically available maximum rf-amplitude. An effective alternative to the hard pulse for covering the necessary bandwidth therefore is urgently needed.

The development of cryogenic probe heads allows NMR measurements with significantly improved signal-to-noise ratios. However, the large temperature gradient in such a probehead leads to a coil design with significantly increased $B_1$-field inhomogeneity compared to conventional probeheads. As a consequence the sensitivity gain due to the cryogenic cooling is reduced with every uncompensated pulse. With robust pulses that are compensated for strong variations in rf-amplitude this loss in sensitivity could be strongly reduced.

Optimal control theory is an ideal tool for the design of pulses that fulfill the needs of modern NMR spectroscopy. The results shown in this article are the first systematic studies without restrictions to the pulse shape that allow the exploration of physical boundaries of the performance of excitation and inversion pulses. With better bounds to these limits known it seems possible to optimize tailored pulses for specific needs in a reasonable time.

Some of the limitations to the applicability of the presented BEBOP and BIBOP should be pointed out. All pulses are optimized starting with initial $\pm\mathbf{M}_z$ magnetization. The pulse is not defined for any other starting magnetization. However, if a BEBOP pulse shall be used to transfer $\mathbf{M}_x$ magnetization to $\mathbf{M}_z$, the time reversed pulse shape can be used. In addition, as with most other optimized excitation and inversion pulses, BEBOP and BIBOP do not result in uniform unitary rotations. Initial magnetization components different from $\mathbf{M}_z$ will not be transferred as they would for a hard pulse. BIBOP therefore cannot be used as refocussing pulses. The refocussing of a single transverse magnetization component (e.g., $-\mathbf{M}_x$) can be achieved by the application of two pulses, first a time-reversed and 180° phase shifted BEBOP and then the original BEBOP. In this case the magnetization component is refocussed in two steps: $-\mathbf{M}_x \rightarrow \mathbf{M}_z \rightarrow \mathbf{M}_x$. The development of pulses that act as uniform unitary rotations will be the subject of future research.

BEBOP and BIBOP are, of course, scalable in the same way as conventional pulses. A pulse applied with twice the rf-amplitude will have half the duration and cover twice the bandwidth of the original pulse with the same robustness with respect to relative variations of the rf-amplitude. The data presented will therefore be useful as an estimate for most pulse requirements.

Besides practical aspects on the application of pulses in modern spectroscopy some theoretical aspects of the work presented should be noted. The length of an excitation pulse that is well compensated for $B_1$-field inhomogeneity exceeds the time of an equally well-compensated inversion pulse. We therefore conclude that a controlled phase in the transverse plane in the presence of $B_1$-field inhomogeneity is a rather difficult task especially if the bandwidth exceeds the maximum allowed rf-amplitude. This complies with the results obtained for BEBOP optimized for on resonant excitation only which show the pure effect of $B_1$-field compensation on excitation pulses (data not shown). Compensation for variation in rf-amplitude introduces phase modulation already for pulses of the length of a hard 90° pulse and amplitude modulation for slightly longer pulses. It seems that the phase-alternating composite pulses obtained from broadband studies therefore are a result of the bandwidth only, while $B_1$-compensation could be better achieved by smooth phase and amplitude changes.

Finally, for relatively short inversion pulses a symmetric class of pulses with constant amplitude appears to be optimal. The pulses show a frequency sweep similar to adiabatic pulses in the center but a distinct 'frequency swing' at the pulse edges and closely resemble the BIP pulses [20].

## 5. Conclusion

A very efficient algorithm based on optimal control theory was used to explore the physical limits of excitation and inversion pulses. It does not impose any restrictions to the pulse form except for limiting the maximum rf-amplitude and the temporal digitization of the pulses. Steps in the form of abrupt changes in the performance of pulses that were observed with respect to pulse length appear to be related to certain types of pulses, including a class of relatively short inversion pulses with good compensation for variations in rf-amplitude. Correlations of the minimum pulse length required with respect to excitation/inversion bandwidth and compensation for $B_1$-field inhomogeneity are given. For almost all pulse lengths improvements relative to already published pulses could be achieved. The pulses will be made available for download on the website http://org.chemie. tu-muenchen.de/people/bulu.

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