Optimal phase modulation in stored waveform inverse Fourier transform excitation for Fourier transform mass spectrometry. II. Magnitude spectrum smoothing

Shenheng Guan[a)]
Department of Chemistry, University of California, Irvine, California 94143

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A smoothing method for generating optimal SWIFT (stored waveform inverse Fourier transform) excitation waveforms used in Fourier transform mass spectrometry (FT-ICR or FTMS) was previously proposed to substitute time-domain waveform apodization procedures. This work gives a detailed analysis of the simple smoothing procedure. The effect of the smoothing procedure on magnitude spectral edges can be easily expressed in analytical format so that the frequency resolution of excitation can be easily analyzed. The relation between the time domain apodization and the smoothing of magnitude spectra in the frequency domain is established. This provides a convenient method to estimate the time duration required for accommodation of excitation power leakage from the power distribution limits. A method for generating nonconstant frequency resolution excitation waveforms is proposed.

I. INTRODUCTION

Fourier transform techniques have revolutionized the field of spectroscopy. A general scope of this area can be found in a recent text.[1] Excitation methods play a very important role in applications of the Fourier transform mass spectrometry (FTMS) technique. The various excitation methods used in Fourier transform mass spectrometry have been discussed elsewhere.[2,3] The stored waveform inverse Fourier transform (SWIFT) excitation method introduced by Marshall *et al.*[4–9] has demonstrated high mass selectivity and uniform excitation power which are essential for high resolution MS/MS and for quantitative experiments. In principle, the SWIFT method allows one to generate a time-domain waveform with an arbitrarily desired excitation profile. This enhances the capability of Fourier transform mass spectrometry for ion manipulation.

In the SWIFT method, the desired excitation magnitude spectrum and an additional phase function are specified. The time-domain waveform is synthesized from the magnitude and phase spectra by inverse Fourier transformation. The magnitudes of the responding ion signals (or radii of the ion orbitals) are approximately proportional to the excitation magnitude (or the magnitude spectrum). The phase portion of the excitation waveform controls only the relative phases among the ion signals which in most applications have little physical significance. Therefore, one can choose a phase function for synthesis of a SWIFT excitation waveform to meet additional conditions. An optimal phase modulation algorithm for generating SWIFT (stored waveform inverse Fourier transform) excitation waveforms has been proposed previously[2] to solve excitation dynamic range and resolution problems. The central idea in the algorithm is using the phase function to distribute the excitation power evenly in a limited time period.[3] The excitation waveform with distributed power has reduced dynamic range and the power of excitation outside the distribution power decreases monotonically. In the previous work[2] we showed for a waveform with a square magnitude spectrum that the profile of the waveform outside of the power-distributing time period decreases as $1/t$. If the waveform is transmitted within a limited time duration, the waveform is truncated and the power loss from the truncation causes the Gibbs oscillations in the final excitation spectrum. The power loss can be reduced by smoothing the excitation magnitude spectrum before inverse Fourier transformation. Therefore the Gibbs oscillations in the final excitation profile can be greatly diminished. This work provides detailed examination of the effect of the smoothing filter on both magnitude spectra and resulting time domain waveforms. A definition for the resolution of FTMS excitation is proposed. The relation between the smoothing procedure and time domain apodization is established. The frequency resolution of the smoothing filter is not limited to be constant. An example for using nonconstant frequency resolution excitation is given to demonstrate the flexibility of the smoothing procedure.

II. SMOOTHING FILTER AND ITS EFFECT ON EXCITATION MAGNITUDE PROFILES

Desirable FTMS excitation spectra are essentially band limited (nonzero over a finite frequency range). According to the uncertainty principle of Fourier analysis, a band-limited signal is unlimited in the time domain. Therefore in principle, it is impossible to generate a time-limited excitation waveform with a truly band-limited spectrum. The task is how to produce time-limited waveforms with final excitation spectra which are as close as possible to what is

[a)]Present address: Department of Pharmaceutical Chemistry, University of California, San Francisco, CA 94143.

desired. One of the advantages of SWIFT excitation is high frequency resolution. The high resolution implies sharp transitions in excitation spectra. Because of the complementary nature of the Fourier transform, sharp variations in the frequency domain result in slow changes in the corresponding time domain waveforms. Therefore a long time duration is needed for accommodation of slowly changing waveforms for high resolution applications. For convenience, most commonly used FTMS excitation profiles consist of magnitude-mode square wave spectral segments. There are discontinuities at the edges of the square waves. These discontinuities represent the infinitely high frequency resolution which cannot be realized in real applications. A smoothing filter was proposed[2] to transform the vertical edges into continuous transitions. The smoothing filter is defined as

$$F_1(\omega) = 1/(2\Delta\omega) \int_{\omega - \Delta\omega/2}^{\omega + \Delta\omega/2} F(y)dy. \quad (1)$$

Here $\Delta\omega$ is the filter bandwidth. The smoothed function $F_1(\omega)$ can also be expressed as convolution of the original function $F(\omega)$ and a rectangular function $\Pi_{\Delta\omega}(\omega)$,

$$F_1(\omega) = \int_{-\infty}^{\infty} \Pi_{\Delta\omega}(y) F(\omega - y)dy. \quad (2)$$

Here

$$\Pi_{\Delta\omega}(\omega) = \begin{cases} 1/\Delta\omega, & -\Delta\omega/2 < \omega < \Delta\omega/2 \\ 0, & \text{otherwise} \end{cases}, \quad (3)$$

since most commonly used SWIFT excitation magnitude spectra are a collection of square waves. We now examine the effect of the filter on this type of function. Apparently, the smoothing filter has no effect on the continuous part of these excitation profiles. However, a large effect near the discontinuous points is expected. For simplicity, we examine the effect on a step function

$$U(\omega) = \begin{cases} 1, & \omega > 0 \\ 0, & \omega \leqslant 0 \end{cases}. \quad (4)$$

If the bandwidth of the filter is $\Delta\omega$, the function $U(\omega)$ is transformed by the filter into

$$U_1(\omega) = \begin{cases} 1, & \Delta\omega/2 < \omega \\ (\omega + \Delta\omega/2)/\Delta\omega, & -\Delta\omega/2 < \omega \leqslant \Delta\omega/2 \\ 0, & \omega \leqslant -\Delta\omega/2 \end{cases}. \quad (5)$$

The discontinuous point of the step function $U(\omega)$ at $\omega = 0$ now becomes a linear curve $U_1(\omega)$, over the interval $[-\Delta\omega/2, \Delta\omega/2]$. Although the smoothed function $U_1(\omega)$ has become continuous, its derivative $dU_1(\omega)/d\omega$ has two discontinuous points at $-\Delta\omega/2$ and $\Delta\omega/2$. This discontinuity can be further removed by running the filter for the second time. The resulting function $U_2(\omega)$ is continuous in its first derivative

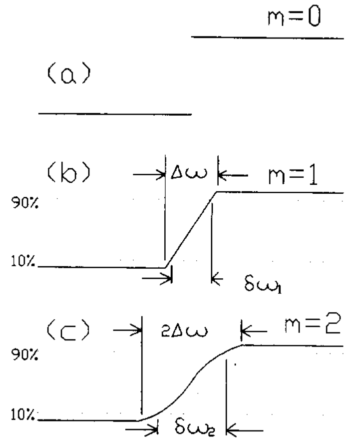

FIG. 1. Proposed definition for excitation resolution. (a) A step function $U(\omega)$; (b) the smoothed function $U_1(\omega)$, notice that the function is affected in the region $\Delta\omega$ by the filter and the excitation resolution is defined as $\delta\omega_1$; and (c) the doubly smoothed function, the resolution is $\delta\omega_2$.

$$U_2(\omega) = \begin{cases} 1, & \Delta\omega < \omega \\ 1 - (\omega - \Delta\omega)^2/2\Delta\omega^2, & 0 < \omega \leqslant \Delta\omega \\ (\omega + \Delta\omega)^2/2\Delta\omega^2, & -\Delta\omega < \omega \leqslant 0 \\ 0, & \omega \leqslant -\Delta\omega \end{cases}. \quad (6)$$

This process can go on to achieve any order of smoothness for the excitation profile.

Although the term, excitation resolution, can be seen quite often in the literature, there is no clear definition for the improvement parameter for the FTMS excitation waveforms. Here we propose a simple one and examine the relation between the defined frequency resolution and the filter bandwidth. A very simple definition for frequency resolution ($\delta\omega$) is the frequency width needed for a transition from 10% to 90% of the full spectral magnitude. Before the smoothing filter is performed, the magnitude variations are "vertical". This means that the frequency resolution is zero ($\delta\omega_0 = 0$, in which the subscript denotes the number of the filter performed). If the function is subjected to the smoothing filter once ($m = 1$), it takes a duration of 0.8 $\Delta\omega$ for the transition from 10% to 90% of the full level [Fig. 1(b)]. Therefore, the frequency resolution is now equal to 0.8 $\Delta\omega$. If the function is smoothed twice ($m = 2$), the frequency resolution can be derived from Eq. (6) as $2(1-0.2^{1/2})\ \Delta\omega$ (or $\delta\omega_2 = 1.106\Delta\omega$) [see Fig. 1(c)]. Using the filter one more time only degrades the frequency resolution (by this definition) by less than an additional 40%.

III. EFFECT OF THE SMOOTHING FILTER ON THE TIME-DOMAIN WAVEFORM

A SWIFT excitation waveform $f(t)$ is synthesized from a specified magnitude spectrum $F(\omega)$ and a phase spectrum $P(\omega)$. The waveform $f(t)$ can be expressed from the inverse Fourier transformation of $F(\omega)$ and $P(\omega)$,

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(\omega) e^{jP(\omega)} e^{j\omega t} d\omega. \quad (7)$$

In order to obtain a real time-domain waveform, $F(\omega)$ should be symmetrical about the origin and $P(\omega)$ is antisymmetrical. In general, $P(\omega)$ is a complicated function.

Here only a simple case is given consideration, however the conclusion from the analysis for the smoothing effect is general.

We first consider synthesis of a waveform with a square magnitude spectrum and zero phase [$P(\omega)=0$]. The magnitude spectrum can be written as

$$F(\omega)=\begin{cases}1, & -\Omega<\omega<\Omega\\ 0, & \text{otherwise}\end{cases}. \tag{8}$$

In this simplest case, the time-domain waveform is a sinc function

$$f(t)=\sin(\Omega t)/\pi t. \tag{9}$$

Since the function $\sin(\Omega t)$ is only a phase factor, the profile of the waveform is described by $1/\pi t$. This means that the amplitude of the waveform decreases as the same power of t. Now let us examine the effect of the smoothing filter on the decreasing rate of the amplitude of the time-domain waveform. The inverse Fourier transformation of $\Pi_{\Delta\omega}(\omega)$ [defined in Eq. (3)] is $\sin(\Delta\omega t/2)/\pi\Delta\omega t$. According to the convolution theorem of Fourier analysis, the time-domain waveform or the inverse Fourier transformation of the smoothed $F_1(\omega)$ is equal to the product of the individual inverse FT's of $F(\omega)$ and $\Pi_{\Delta\omega}(\omega)$,

$$f_1(t)=2\pi[\sin(\Delta\omega t/2)/\pi\Delta\omega t]\sin(\Omega t)/\pi t.$$

Using the inductive method, one can prove the following equation for any number of m (the number of filtering processes performed):

$$f_m(t)=\sin(\Omega t)\sin^m(\Delta\omega t/2)/[\pi(\Delta\omega t/2)^m t]. \tag{10}$$

The factor of $\sin(\Omega t)\sin^m(\Delta\omega t/2)$ in the above equation is bounded within ± 1 and oscillates throughout the entire time axis. Therefore the profile of $f_m(t)$ is described by the function, $1/[(\Delta\omega t/2)^m\pi t]$ when t is far from the origin. Since the profile of the original waveform (a sinc function) is $1/\pi t$ ($|t|\gg 0$), the smooth filtering of m times on the magnitude spectrum is equivalent to applying an apodization function of $1/(\Delta\omega t/2)^m$ to the time-domain waveform. It is not surprising that the filter has no effect on the original waveform near the time origin ($t=0$). In this simple case, there is not phase modulation or no time shift. However, it can be proved that the smoothing filter produces the same effect on phase-modulated cases.[10]

The advantage of using the filter more than once can be seen clearly here since the power leakage can be greatly suppressed by the increasing orders of the "apodized function" without loss of large amount of resolution (see last section).

IV. NONCONSTANT FREQUENCY RESOLUTION EXCITATION

The bandwidth ($\Delta\omega$) of the smoothing filter does not have to be a constant. This results in nonconstant frequency resolution in the final excitation magnitude spectrum. Here, we present an example to demonstrate the flexibility of the technique by using this property.

In general, the mass-to-charge ratio (m) is a complicated function of the frequency (ω),

$$m=g(\omega). \tag{11}$$

The frequency resolution ($\Delta\omega$) is related to the mass resolution (Δm) with

$$\Delta\omega=\Delta m/g'(\omega). \tag{12}$$

Here, $g'(\omega)$ is the derivative of $g(\omega)$. For simplicity, the mass-to-charge ratio (m) of an ion is considered to be

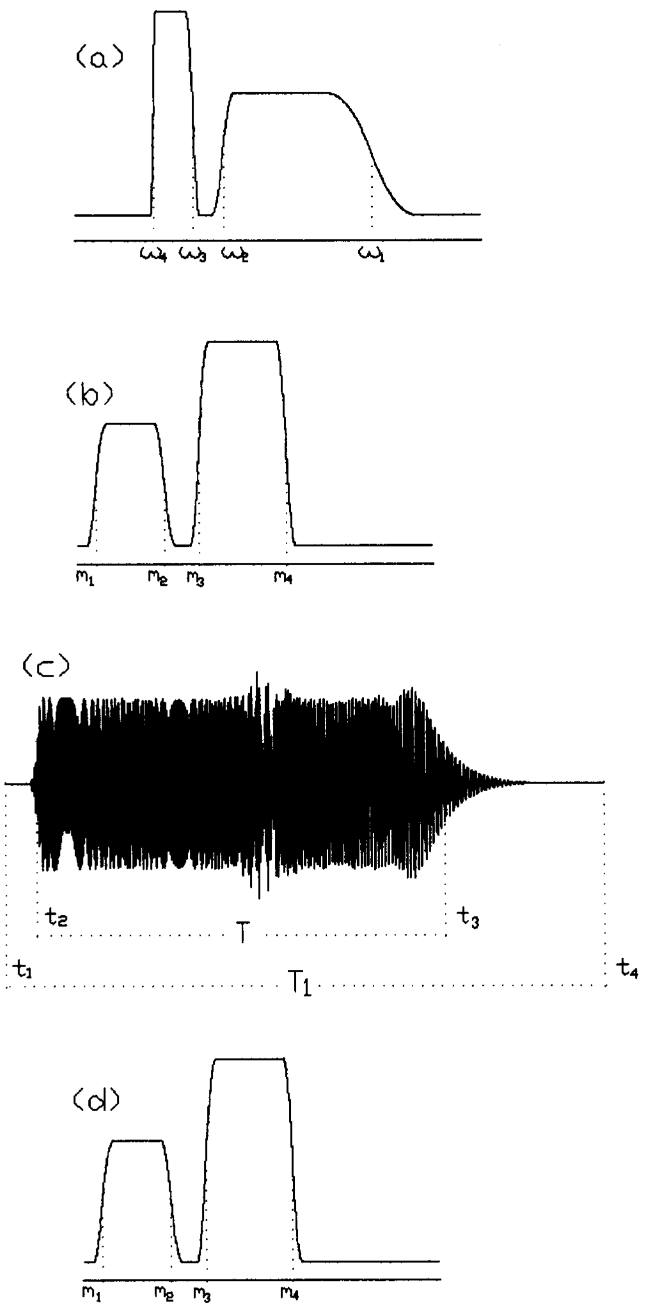

FIG. 2. Constant mass resolution excitation. (a) The magnitude spectrum smoothed by the filter with a nonconstant frequency bandwidth ($\Delta\omega=a\omega^2$, a is a constant); (b) the corresponding mass spectrum [rescaled from the magnitude spectrum (a)]; (c) the time-domain waveform; and (d) the "true" mass spectrum obtained by one zero filling of the waveform (c), FFT, and rescaling as (b). T_1 is the time length of the waveform and T is the time duration in which the power of the excitation is distributed (Ref. 2).

inversely proportional to its resonance frequency (ω) only ($m = a/\omega$, a is a proportional constant). In this case,

$$\Delta\omega = \Delta m \omega^2/a. \quad (13)$$

If the mass resolution is constant ($\Delta m = \text{const}$), the frequency resolution ($\Delta\omega$) is proportional to the square of the frequency. This relationship between mass resolution and frequency resolution was first deduced by Comisarow and Marshall.[11]

The potential applications of this method include spontaneously selective excitation or(/and) ejection of isotopic ions. Figure 2(a) shows the smoothed excitation magnitude spectrum with a constant mass resolution. Notice the resolution at the lower frequency (ω_4) is about 14 times higher than that at the higher frequency (ω_1). However, the mass resolution in the corresponding mass spectrum [Fig. 2(b)] is uniformly distributed (at $\Delta m_1 = \Delta m_2 = \cdots = \Delta m_4$). The excitation time domain waveform is shown in Fig. 2(c). Since the magnitude spectral variation at ω_4 in the magnitude spectrum is quite sharp, it requires a long time duration ($t_4 - t_3$) to accommodate the power leakage from the limit of the power distribution period (t_3). In contrast, much shorter time ($t_2 - t_1$) is needed for a slow transition (at ω_1). Since sufficient time periods are provided and at the limits of the waveform the amplitude is near zero, the waveform has a "true" mass spectrum [Fig. 2(d)] which is virtually the same as was specified.

V. CONCLUSIONS

By analyzing the effect of magnitude spectral smoothing, a frequency resolution for FTMS excitation is proposed. It is hoped that this would provide a universal measurement for FTMS excitation techniques. The application of the smoothing filter to magnitude spectra has been shown to be equivalent to apodization of $1/t^m$ type of functions to the corresponding waveforms. This provides an analytical method to estimate the decreasing rate of amplitude of waveforms. Therefore the time duration required for accommodation of power leakage can be evaluated. Finally an example for using nonconstant frequency resolution excitation shows the unique capability of the method.

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