Optimal phase modulation in stored wave form inverse Fourier transform excitation for Fourier transform mass spectrometry. I. Basic algorithm

Shenheng Guan and Robert T. McIver, Jr.
Department of Chemistry, University of California at Irvine, Irvine, California 92717

(Received 2 October 1989; accepted 2 February 1990)

A new signal processing method has been proposed for generating optimal stored wave form inverse Fourier transform (SWIFT) excitation signals used in Fourier transform mass spectrometry. The excitation wave forms with desired flat excitation power can be obtained by using the data processing steps which include: (1) smoothing of the specified magnitude spectrum, (2) generation of the optimal phase function, and (3) inverse Fourier transformation. In contrast to previously used procedures, no time domain wave form apodization is necessary. The optimal phase functions can be expressed as an integration of the specified power spectral profiles. This allows one not only to calculate optimal phase functions in discrete data format, but also to obtain an analytical expression (in simple magnitude spectral cases) that is for theoretical studies. A comparison is made of the frequency sweeping or "chirp" excitation and stored wave form inverse Fourier transform (SWIFT) excitation. This shows that chirp excitation and SWIFT excitation with a square magnitude spectrum and a quadratic phase are counterparts of the Fourier transformation. Therefore, the results of theoretical work on chirp excitation can be used for the analysis of the time domain excitation wave forms in the SWIFT technique.

I. INTRODUCTION

Fourier transform mass spectrometry (FT-ICR or FTMS) is a powerful technique for mass analysis and for the study of ion–molecule reactions. The principles and applications of FT-ICR have been reviewed.[1] The most important features are its capability of detecting all the ions simultaneously and its power to manipulate trapped ions. The excitation methods used for FT-ICR play a central role for realization of these capabilities. The fundamental goal is to produce a wave form with the desired excitation power spectrum (or magnitude spectrum). In order to detect all the trapped ions, an excitation wave form with a bandwidth of 3 orders of magnitude (from kHz to MHz) has to be generated. The large bandwidth of the excitation is a technically difficult problem. Several excitation methods have been proposed and tested.[2] Among them, frequency sweeping or "chirp" excitation[2c] is most commonly used, although it neither provides flat excitation power nor is convenient to use.

The stored wave form inverse Fourier transform (SWIFT) excitation method introduced by Marshall *et al.*[3] has provided high mass selectivity and uniform excitation power. In the SWIFT method, the desired excitation magnitude spectral profile and the corresponding phase function are specified. They are then subjected to inverse Fourier transformation to give the time domain excitation wave form. In most experiments, magnitude spectra (mass spectra) of ion transient signals are used to measure the ion populations, and the phase portion of the frequency domain of the transient signal, which does not contain useful chemical information, is discarded. This gives one the freedom to choose the phase function without concern for its influence on the resulting mass spectra. The development of the SWIFT excitation technique has focused on selection of the proper phase functions to obtain more uniform excitation power and reduce the dynamic range needed for the time-domain excitation wave form. If a constant or a linear phase function is used, a dynamic range problem results because of the phase coherence of all the frequency components. This results in a very sharp peak in the time-domain excitation wave form that requires high dynamic range digital and analog devices to generate and process the excitation signals.[4] In order to reduce the dynamic range, the phase coherence must be destroyed. Using "random phase" is the simplest way to accomplish this, and it reduces the needed dynamic range by a factor of 10.[3] However, the excitation power of the wave form produced by random phase randomly covers all the transmission time period. This causes the power to leak outside the specified time limits for the excitation wave form. The actual magnitude spectrum becomes very nonuniform due to the uneven Gibb's effect[5] By experimenting with different types of phase functions, a "quadratic phase" function was found to be superior to the random function.[6]

Recently, we described a general phase modulation algorithm[7] for generating excitation wave forms with desired excitation magnitude spectra and reduced dynamic range. We also demonstrated that a quadratic phase function is the theoretically optimal phase modulation for square excitation spectra. Although the general algorithm can be used to reduce the dynamic range, there are a few problems with the algorithm. First, the area under power spectral profiles (not magnitude spectra) should be used to determine the time shift distance so that the excitation power can be evenly distributed. The uniformity of the resulting magnitude spectrum also remains unanswered. Recently, Goodman has proposed a new method to generate SWIFT excitation wave forms.[8] By using the group delay concept, optimal phase functions can be generated in a discrete data format that are similar to our general algorithm. He further introduced expanded windows to accommodate the power leak (for all the group delay) at the transitions. Although the method can produce optimal time domain excitation wave forms for arbitrary excitation power profiles, it requires three Fourier transform steps and additional data processing steps that make the method very complicated and time consuming.

In this paper, our previous work is extended to solve the nonuniform excitation problem. A general analytical expression for the optimal phase function is derived. A signal processing algorithm is proposed to generate optimal excitation wave forms with only one inverse Fourier transform step. The most distinctive feature of the algorithm is that no time domain wave form apodization is needed. The Gibb's effect commonly found in SWIFT excitation spectra can be greatly suppressed by smoothing the specified magnitude spectra. Comparison of the chirp and SWIFT methods shows that there are intrinsic relations between the two. The profiles for time domain wave forms with square magnitude spectra and quadratic phase are expressed in term of Fresnel integrals from which the maximum dynamic range reduction can be estimated.

II. ANALYTICAL EXPRESSION FOR OPTIMAL PHASE FUNCTIONS

We first consider how to generate a time-domain wave form with a broadband magnitude spectrum [$F(\omega)$ from ω_I to ω_F] and distribute its power evenly in a time period (from t_0 to t_1). According to the analysis given in the previous work,[7] the width of a wave packet dt is proportional to the area under the *power* spectral profile,

$$dt = cG(\omega)d\omega,$$

where $G(\omega) = |F(\omega)|^2$ and c is a proportionality constant. Since the power spectrum has physical significance of power density (volt^2/radian), the equation above can be interpreted as distributing the power contribution in $d\omega$ to a time interval dt. Integration of the above equation gives

$$t - t_0 = c \int_{\omega_0}^{\omega} G(y)dy. \tag{1}$$

Now, c can be determined by taking the integration to its limit

$$c = \frac{t_1 - t_0}{\int_{\omega_0}^{\omega_1} G(y)dy}.$$

Substituting the above to Eq. (1) gives

$$t = \frac{t_1 - t_0}{\int_{\omega_0}^{\omega_1} G(y)dy} \int_{\omega_0}^{\omega} G(y)dy + t_0.$$

Using the time shifting theorem [Eq.(2) in Ref. 7], the differential equation for the optimal phase function is obtained

$$\frac{dP(\omega)}{d\omega} = t = \frac{t_1 - t_0}{\int_{\omega_0}^{\omega_1} G(y)dy} \int_{\omega_0}^{\omega} G(y)dy + t_0. \tag{2}$$

Integration of the above equation gives the phase function

$$P(\omega) = \left\{ \frac{t_1 - t_0}{\int_{\omega_0}^{\omega_1} G(y)dy} \int_{\omega_0}^{\omega} \int_{\omega_0}^{y} G(x)dxdy \right\} + t_0(\omega - \omega_0) + P_0. \tag{3}$$

The phase function contains three terms having different orders with respect to ω. The first term, which is second order in ω, is responsible for spreading the excitation power over a time period $(t_1 - t_0)$. The second term, which is first order in ω, time shifts the wave form to the time location between t_0 and t_1. The third term is the initial phase P_0, and it does not change the structure of the wave form. In the following, we can simply choose it to be zero.

III. COMPARISON OF SWIFT AND CHIRP EXCITATION

In this section, we establish the relation between SWIFT excitation and frequency sweeping (or chirp) excitation. We first consider how to synthesize a time domain wave form with a square magnitude spectrum [$F(\omega)$] from frequency 0 to Ω

$$F(\omega) = \begin{cases} F_0, & 0 \leqslant \omega \leqslant \Omega, \\ 0, & \text{otherwise}. \end{cases}$$

The power of the wave form is uniformly distributed over a time period $\alpha\Omega$ (or from t_0 to $t_1 = t_0 + \alpha\Omega$). Using Eq.(3) developed in last section, the optimal phase function can be written as

$$P(\omega) = \alpha\omega^2/2 + t_0\omega_0 + P_0.$$

The time-domain excitation wave form $f(t)$ can be expressed as the Fourier transformation of the square magnitude spectrum and above phase function:

$$f(t) = (1/2\pi)F_0 \int_0^{\Omega} e^{[j(\alpha\omega^2/2 + t_0\omega + P_0)]} e^{[j\omega(t - t_0)]} d\omega. \tag{4}$$

The above equation can be rewritten as

$$f(t) = F_0/[2\sqrt{(\pi\alpha)}]\phi(t) \int_{-\gamma}^{\beta - \gamma} e^{[j\pi u^2/2]} du = F_0/[2\sqrt{(\pi\alpha)}]\phi(t)E(\beta,\gamma). \tag{5}$$

Here $\phi(t) = e^{[j(P_0 - t^2/2\alpha)]}$, $\beta = \alpha\Omega/\sqrt{(\pi\alpha)}$, and $\gamma = t/\sqrt{(\pi\alpha)}$. The properties of the function $E(\beta,\gamma)$ have been studied in detail.[9]

We can show that the above equation has the same structure as Eq. (1) in Ref. 9, which has been shown to be the frequency domain of a frequency sweeping wave form (different in a constant factor). The similarity is not a coincidence because a frequency sweeping or chirp wave form has a square profile and a quadratic phase which

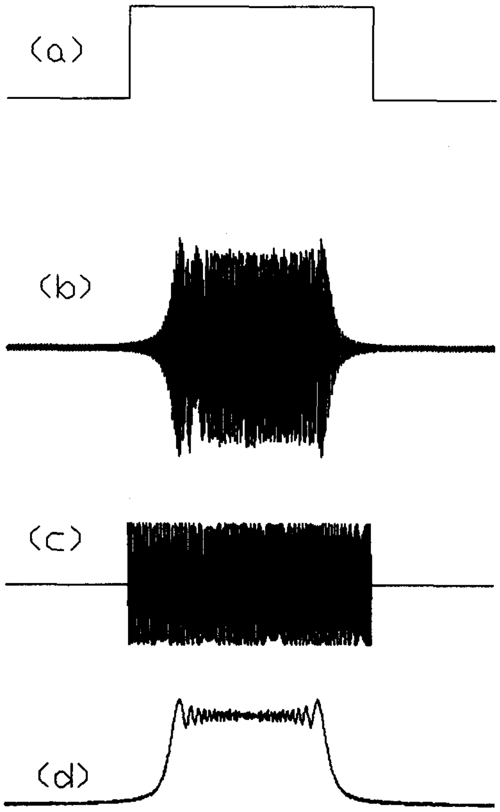

FIG. 1. The relation between frequency sweeping or "chirp" excitation and SWIFT excitation. A rectangular SWIFT magnitude spectrum (a) with a quadratic phase produces a time-domain wave form (b) which has the same profile as the magnitude spectrum (d) of a frequency sweeping signal or chirp (c). Notice the frequency sweeping wave form has a rectangular profile.

compares with the frequency domain of a square magnitude spectrum and a quadratic phase in the SWIFT excitation (see Fig. 1). This allows us to use the analysis on frequency sweeping excitation to the SWIFT technique with careful handling.

Since the function $\phi(t)$ in Eq. (5) is a phase factor, the profile of the wave form is described by the function $E(\beta,\gamma)$. This statement can be expanded to more general cases where the frequency range spans from ω_i to $\omega_i+\Omega$ instead of from 0 to Ω. The frequency shifting only contributes a phase factor to $\phi(t)$ and leaves $E(\beta,\gamma)$ unchanged. Now we can use some of the properties to estimate the dynamic range reduction.

IV. DYNAMIC RANGE REDUCTION

The phase shifting algorithm developed in the previous sections distributes the excitation power uniformly over the time period of the excitation wave form. This is important because it reduces the dynamic range required by the analog and digital hardware that are used to generate the excitation wave form.[3] In this section we present a method for estimating the dynamic range reduction.

If there is no phase modulation or $\alpha = 0$, function (4) reduces to the following expression:

$$f(t)=F_0/2\pi \int_0^{\Omega} e^{[j\omega t]}\, d\omega \quad (P_0=0),$$

which is a sinc function. The maximum of this function is

$$DR_{\text{no modulation}}=F_0\Omega/2\pi$$

where $DR_{\text{no modulation}}$, the dynamic range with no phase modulation, is evaluated at $t=0$.

In the case of large phase modulation or $\beta\rightarrow\infty$, $|E(\beta,\gamma)| \rightarrow \sqrt{2}$ for $\gamma = \beta/2$ (center of the wave form). The maximum of $E(\beta,\gamma)$, located near $\gamma = 1$, is about 17% above the value at the center of the wave form. Therefore, the dynamic range of the large modulated wave form is given by

$$DR_{\text{large modulation}}=1.17F_0/(2\pi\alpha)^{1/2}.$$

We define a number n, the dynamic range reduction, as the ratio of these two limiting cases

$$n=DR_{\text{no modulation}}/DR_{\text{large modulation}} = (\Omega\alpha\Omega/2\pi)^{1/2}/1.17.$$

Since Ω is the frequency range or bandwidth and $\alpha\Omega$ is the time period in which the excitation power is distributed, we can rewrite the above equation as

$$n=[(\omega_F-\omega_I)T/2\pi]^{1/2}/1.17. \tag{6}$$

Here $T = \alpha\Omega$ and $\omega_F - \omega_I = \Omega$.

Compared with the result from the previous work, Eq. (6) gives a more accurate estimate for the dynamic range reduction. In the previous work, interference between wave-packets was not taken any consideration. In other words, the wave-packets were considered to be independent, and this results in an underestimation of the dynamic range reduction. Since Eq. (6) is derived from a square magnitude spectral profile, it gives an estimation of maximum dynamic range reduction for arbitrary magnitude spectral profiles.

V. ALGORITHM FOR GENERATING OPTIMAL WAVE FORMS

Before a time-domain excitation wave form can be synthesized, the desired excitation magnitude spectrum and additional parameters have to be specified. These parameters include the desired excitation resolution and the required dynamic range (DR_{req}). We first discuss the dynamic range problem. Once the excitation spectrum is given, the maximum amplitude (dynamic range) of the unmodulated wave form can be determined by integration of the magnitude spectrum $F(\omega)$ (all the frequency components are added at $t=0$):

$$DR_{\text{no modulation}}=1/2\pi \int_{\omega_I}^{\omega_F} F(\omega)d\omega. \tag{7}$$

If the required dynamic range is DR_{req}, the minimum time length T for distributing the excitation power can be estimated from Eq. (6):

$$DR_{\text{no}}/DR_{\text{req}}=n=[(\omega_F-\omega_I)T/2\pi]^{1/2}/1.17. \tag{8}$$

In practical applications, T should be larger than the value estimated from the above equation.

The second problem, excitation resolution, results from the fact that excitation wave forms used in FT-ICR experiments are essentially band-limit signals. According to the uncertainty principle of Fourier analysis, these wave forms have to be transmitted in infinitely long time periods. Most commonly used FT-ICR excitation profiles consist of rectangular functions. Ideally, the transitions at the edges of the "boxes" are vertical (or infinitely high resolution). However, the excitation spectrum of the corresponding wave form always contains Gibb's oscillations near the discontinuity points if the wave form is transmitted in a time-limit period. In actual experiments, however, the wave form must be terminated after a finite transmission period. Now the basic question is how to generate a time-limit wave form having a magnitude spectrum that best approximates the desired excitation profile. Although the time shifting effect can be used to concentrate most of the excitation power, a fraction of the excitation power still leaks outside of the time period for distributing the excitation power. With optimal phase modulation, the power leakage decreases rapidly beyond the limits of the duration (T), and the rate of the decrease in amplitude of the wave form outside the time period (T) depends on the sharpness of the transitions in the magnitude spectrum.

In real applications, the frequency resolution cannot be infinitely high and the specified magnitude spectral profile should reflect this fact. Since it is convenient to specify the magnitude spectrum as a collection of square waves, additional data processing steps are required to smooth the sharp edges of the square boxes. There are many ways to smooth the sharp transitions; here we propose a very simple method. The original magnitude spectrum $F(\omega)$ is transformed to a new magnitude spectrum $F_1(\omega)$ by the relation

$$F_1(\omega)=\frac{1}{\Delta\omega}\int_{\omega-\Delta\omega/2}^{\omega+\Delta\omega/2} F(y)dy. \tag{9}$$

As shown in Fig. 2, this procedure removes the vertical jumps in $F(\omega)$ and produces continuous transitions in $F_1(\omega)$ over an interval $\Delta\omega$ (the filter bandwidth). The smoothing filter can be run many times to achieve the desired degree of smoothness in the specified magnitude spectrum. We should point out that this procedure may not be an optimal one, although it is effective and very easy to use. In fact, the algorithm proposed by Goodman[8] is another smoothing procedure (IFT-window-FFT) in which a low-pass filter is used for a specified magnitude spectrum. Magnitude spectra can also be smoothed by FFT-window-IFT procedures.

Once the resolution requirement is specified, the finite time length of the wave form can be estimated. In the algorithm proposed by Goodman,[8] the wave form is truncated by a window within a time length T. Compensation for the power leakage is provided by adding expanded windows. However, these processes are not necessary since a larger window, which includes the time duration T, can be used initially. The time length of the "larger window" (denoted T_1, the real length of the wave form) can be determined by the resolution requirement. A detailed study has shown that if the smooth filter [Eq. (9)] is run m times the amplitude of the wave form decreases as $1/[(\Delta\omega/2)^m \times t^{m+1}]$ outside the power distribution period (t denotes the time distance from the limits of the excitation power distribution period). For simplicity, we place the time period T in the central region of T_1. If the smoothing filter bandwidth is $\Delta\omega$ and the wave form is truncated when its amplitude drops η times below its maximum, the time distance, $(T_1-T)/2$ (between the time limit of the wave form to the boundaryof T) can be determined by using the following relation:

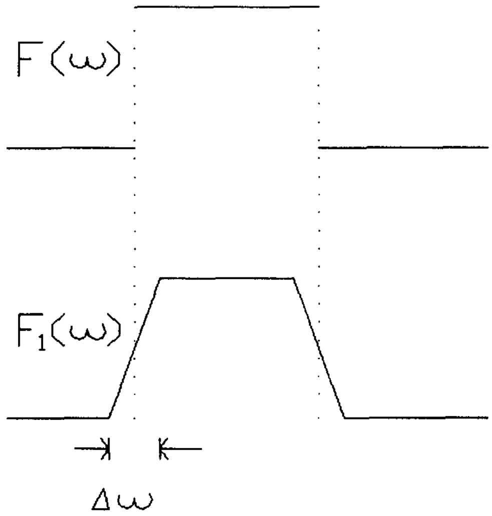

FIG. 2. The effect of the smoothing procedure on discontinuity points in a magnitude spectral profile. $\Delta\omega$ is the filter bandwidth.

$$(T_1-T)/2 \geqslant \left\{\frac{\eta T^{1/2}}{1.17\times[2\pi(\omega_F-\omega_I)]^{1/2}(\Delta\omega/2)^m}\right\}^{1/(m+1)}. \tag{10}$$

Here $\omega_F - \omega_I$ is the frequency range, T is the time period in which the excitation power is distributed, and m is the number of the smoothing procedures performed. T_1 can thus be estimated from Eq. (10). If the parameter η is sufficiently large, the time durations $(T_1 - T)/2$ at each end-point of T_1 provide sufficient space to accommodate most power leakage from the distributing time limits (end points of T).

After T, T_1, and $F(\omega)$ are determined, the optimal phase function can be calculated by using Eq. (3), and FFT procedures can be used to synthesize the time domain wave form from the specified magnitude spectrum and the optimal phase function. The resulting wave form has nearly uniform excitation power in a time period T in the central region of wave form time duration T_1. Outside of the period T the profile of the wave form drops monotonically. At the time limits of the wave form, the amplitude of the wave form is almost zero. The Gibb's oscillation in the actual excitation spectrum is greatly suppressed by the smoothing procedure. Therefore, no apodization of the time-domain wave form is required since the wave form already has very small amplitude at the time limits. This signal processing algorithm produces excitation wave forms with specified dynamic range and frequency resolution.

VI. AN EXAMPLE

To illustrate the algorithm developed above, we shall synthesize a SWIFT excitation signal by following the steps of the algorithm. The specified magnitude spectral profile is shown in Fig. 3(a). The dynamic range of the unmodulated wave form can be calculated by using Eq.(7) and the parameters specified in Fig.3. This gives

$$DR_{\rm no}=360({\rm V}).$$

If the required dynamic range is 30 V, the minimum time duration (T) for distributing the excitation power can be calculated from Eq.(8):

$$T=(1.17n)^2 2\pi/(\omega_4-\omega_1)=0.39 \ ({\rm ms})$$

Here, $n = 360/30$ and $\omega_4 - \omega_1 = 2\pi\times 512$ kHz. For convenience, the value of T is chosen to be 0.5 ms (larger than calculated).

The specified magnitude spectrum is subjected to the smoothing procedure *twice* ($m = 2$) [Eq.(9)]. The bandwidth of the filter is chosen to be 5 kHz ($\Delta\omega = 2\pi\times 5$ kHz). The smoothed magnitude spectrum is shown in Fig. 3(b). Substituting $\Delta\omega$ ($2\pi\times 5$ kHz), m (2), and $\omega_4-\omega_1$ ($2\pi\times 512$ kHz) into Eq.(10) gives T_1 equal to 0.91 ms if η is chosen to be 500. Since this is the minimum value, we choose T_1 to be 1 ms. Now the task is to synthesize the wave form that starts at $t = 0$ and ends at $t = T_1$ and has most of its power confined in the range from $t_0 = (T_1 - T)/2$ to $t_1 = T_1 - t_0$. The optimal phase function can be calculated from Eq.(3). Notice that the power spectrum is used to generate the optimal phase function. The phase function is shown in Fig. 3(c).

Inverse Fourier transformation (IFT) of the magnitude spectrum and the optimal phase function gives the wave form with a duration of 1 ms (T_1), as shown in Fig. 3(d). The time-domain wave form synthesized has a dynamic range of 31.4 V (base to peak). The "actual" magnitude spectrum [Fig. 3(e)] of the wave form is obtained by a forward FFT with one zero fill. Notice that this is essentially the same as the smoothed magnitude spectrum [Fig. 3(b)] and that the Gibb's oscillations are absent.

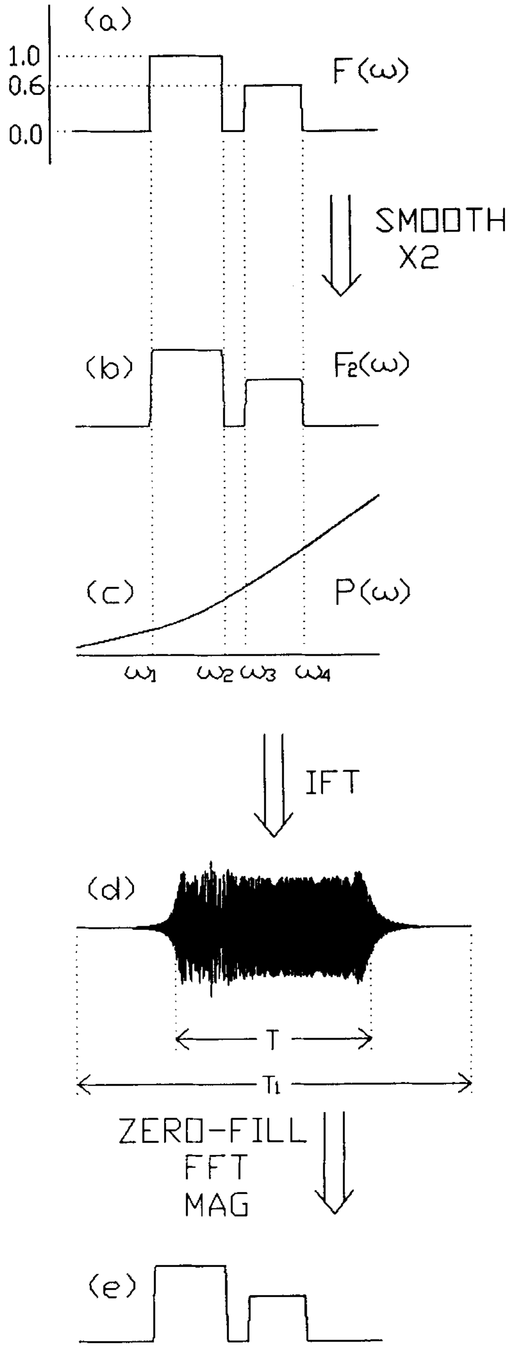

FIG. 3. Illustration of the new method for generating an optimal excitation wave form from a desired magnitude spectrum and additional requirements of dynamic range and frequency resolution. The frequencies in the figure are $\omega_1 = 2\pi\times 256$ kHz, $\omega_2 = 2\pi\times 500$ kHz, $\omega_3 = 2\pi\times 575$ kHz, and $\omega_4 = 2\pi\times 768$ kHz. The excitation magnitude spectrum (voltage density) has a unit of mV/radian.

VII. CONCLUSON

We have developed a comprehensive method for generating optimal excitation wave forms for Fourier transform mass spectrometry. The method involves fewer data processing steps than the algorithm proposed previously by Goodman. The dynamic range reduction can be estimated more accurately. The intrinsic relations between SWIFT and chirp excitation have been studied, and it has been shown that the profiles for SWIFT wave forms with square magnitude spectra and quadratic phases have the same functional structure as the frequency domain of chirp signals. This means that they are counterparts of the Fourier transformation. The well-known properties of chirp excitation can be used for the analysis of the SWIFT technique.

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