General phase modulation method for stored waveform inverse Fourier transform excitation for Fourier transform ion cyclotron resonance mass spectrometry

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A general phase modulation algorithm has been developed for the stored waveform inverse Fourier transform (SWIFT) excitation method used in Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR or FTMS). The algorithm, based on the time shifting theorem and the uncertainty principle, shows that the quadratic phase modulation is the theoretically optimal method for square magnitude spectral profiles. For more complicated magnitude spectral profiles, the corresponding phase functions can be generated through the algorithm by using a nonlinear grid on the frequency domain. The degree of dynamic range reduction can be estimated from a simple equation.

I. INTRODUCTION

Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry has become one of the most powerful techniques for mass analysis and for the study of ion-molecule reactions. The principles and applications of FT-ICR mass spectrometry have been reviewed.[1] One of the most attractive features of the FT-ICR technique is its ability to manipulate trapped ions.[2] Ions can be excited or ejected selectively in routine FT-ICR experiments. The development of FT-ICR ion-excitation methods has provided new power for the technique.[3] High quality excitation methods without mass discrimination are required for high resolution quantitative mass analysis and isotope ratio determinations as well as for ion manipulation. The first FT-ICR excitation method is the rectangular-pulse technique[4(a)] which has very limited bandwidth. The bandwidth limit of the single pulse excitation technique was overcome by introduction of the "frequency sweeping" or "chirp" technique which becomes the most widely used FT-ICR excitation method.[4(b)] However, the magnitude spectra obtained by frequency sweeping excitation are nonuniform over the frequency range to be examined. Furthermore, the broad roll off in excitation magnitude at the low- and high-frequency limits of the frequency sweeping method restricts it from high resolution applications. The frequency sweeping has to be carried out stepwise in order to obtain the desired magnitude spectral profile for selective excitation experiments. Recently, the single pulsed excitation has regained its position in FT-ICR mass spectrometry.[5] The single pulse excitation, so-called "impulse excitation" or "burst excitation," gives flat amplitude response from zero to a few MHz in the sample magnitude spectrum. This is important for accurate determination of the relative intensities of ions. However, the technique completely lacks the ability to excite ions selectively.

High mass selectivity and uniform excitation magnitude spectra can be obtained by the stored waveform inverse Fourier transform (SWIFT) excitation method introduced by Marshall *et al.*[6] In the SWIFT method, a desired excitation magnitude spectral profile and the corresponding phase function are specified. They are then subjected to inverse Fourier transform to give the time-domain excitation waveform. The waveform is converted into an analog signal which is amplified and applied to the transmitter plates differentially. Although the phase excitation is important for two-dimensional (2D) FT-ICR experiments[7] and for the "ion-partitioning" experiments,[8] in most FT-ICR applications, the phase function is considered to be without physical or chemical significance. However, the selection of a proper phase function is quite important for practical reasons. For broadband excitation, the power of the excitation signal is concentrated in a short time duration if a constant or linear phase function is used because of the phase coherence of all the frequency components. This results in a sharp peak (wave packet) with very high amplitude in the time-domain waveform. The high amplitude of the sharp peak requires not only large word length in the digital hardware for storing, transferring, and processing the time-domain data (especially for digital to analog converters), but high dynamic range of the transmitting analog circuitry as well.[9] In order to reduce the dynamic range, the phase coherence must be destroyed. The simplest way to break the phase coherence is to scramble the phase in a random manner.[6] By the "random phase scrambling" technique, a reduction of one order of magnitude in the dynamic range is achieved. However, phase scrambling also causes phase discontinuity which may be responsible for the nonuniform excitation power between the inverse Fourier transform frequency intervals. Although some effort has been put into a search for optimal phase functions,[10] none has been found, at least in a theoretical point of view, even for the simplest excitation profile: a square magnitude spectrum. In this work, an algorithm is proposed for the phase modulation problem. The algorithm is based on the time shifting theorem and the uncertainty principle of Fourier-analysis. The algorithm is then used to show that the quadratic phase modulation, which was found by trial-and-error to be superior to other methods,[10] is indeed the theoretically optimal phase modulation for a square magnitude spectrum.

II. GENERAL ALGORITHM

The inverse Fourier transformation of a broad-band magnitude spectrum $F(\omega)$ (within $[\omega_I,\omega_F]$) with a con-

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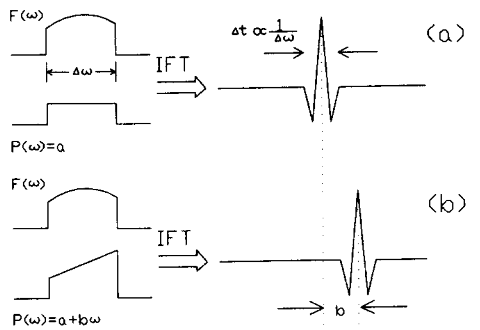

FIG. 1. (a) The effect of the uncertainty principle is illustrated for magnitude spectra $F(\omega)$ with constant phase $P(\omega)$ and its corresponding wave packet. (b) The effect of the time shifting theorem with phase $P(\omega) = (a + b\omega)$ shows the wave-packet time shifted with a linear phase function. Here a and b in the phase function are constants. "IFT" denotes inverse Fourier transformation and the right-hand plots show the real part of the corresponding time domain $f(t)$.

stant phase function $P(\omega)$ gives a wave packet (within Δt) in the time domain at $t = 0$ (see Fig. 1). According to the uncertainty principle of Fourier analysis,[11] the product of $\Delta\omega$ (where $\Delta\omega = \omega_F - \omega_I$) and Δt is a constant (Δt is the time interval in which the highest power of the wave packet is concentrated). If the phase is a linear function of frequency, the time shifting theorem of Fourier analysis[12] states that the wave packet shifts in the time dimension. The shifting distance is determined by the slope of phase function.

The algorithm starts by dividing the broadband magnitude spectrum into n segments (see Fig. 2). Each segment has the same area under the spectrum profile. Notice the intervals ($\Delta\omega_i$) of the segments generally are not equal. According to the analysis above, each of the segments generates a small wave packet at $t = 0$ and the whole time domain is the superposition of all the wave packets if the phase is constant for all the segments. If the wave packets are distributed in such a way so that they do not overlap in the time limits (between $t = 0$ and $t = T$), a reduction of about n times in the dynamic range of the magnitude spectrum can be achieved. The segment number n cannot be infinitely large since when segments become small their wave packet width increases and the overlap becomes inevitable.

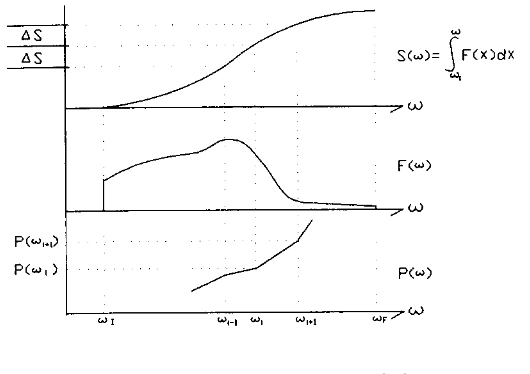

FIG. 2. The division of the frequency domain into segments with equal area is illustrated where $F(\omega)$ is the magnitude spectrum, $P(\omega)$ is the phase function, and $S(\omega)$ is the integral of $F(\omega)$.

For a square magnitude spectrum, the maximum value of number n can be determined as shown in the following. Since equal area spacing implies equal length spacing for a constant profile, we can simply divide the magnitude spectrum from ω_I to ω_F with equally spaced grid elements (ω_1, $\omega_2,\ldots,\omega_n = \omega_F$, where $\omega_{i+1} - \omega_i = \Delta\omega$, and $n\Delta\omega = \omega_F - \omega_I$) into n equally spaced segments. By assuming that the width of the wave packet $\Delta t = a/\Delta\omega$ ($\Delta\omega$ is the length of magnitude spectrum segment i and a is a proportionality constant) and all the wave packets completely cover the entire time limits ($T = n\Delta t$), the number n can be derived as

$$n = (T(\omega_F - \omega_I)/a)^{1/2}. \tag{1}$$

Before Eq. (1) can be used to estimate the degree of reduction of the dynamic range, the parameter a has to be chosen so that highest power of a wave packet is confined to the time interval Δt. If $a = 8\pi$, the amplitude of a wave packet of a square magnitude spectrum outside Δt ($a/\Delta\omega$) drops to about 14 times below its maximum. For a waveform of a square magnitude spectrum with a 1 MHz bandwidth to be transmitted in a time duration of 2 ms, a dynamic range reduction of approximately 22 times can be achieved [from the estimation provided by Eq. (1)].

In general cases in which magnitude spectra are not square profiles, Eq. (1) gives the upper limit for the dynamic range reduction since the maximum reduction in dynamic range is expected for square magnitude spectra. For practical applications, the number n should be chosen to be less than the value calculated from Eq. (1). Once n and $\Delta\omega_i$ ($i = 1,2,\ldots,n$) are determined, the parameter a can be calculated from $a = T/(\Sigma_{i=1}^{n} 1/\Delta\omega_i)$. By using $\Delta t_i = a/\Delta\omega_i$ ($i = 1,2,\ldots,n$), the time interval T between $t = 0$ and $t = T$ is divided into n intervals by t_k ($t_k = \Sigma_{i=1}^{k}\Delta t_i$, $k = 1,2,\ldots,n$). Now, the task is to move the wave packet of the magnitude spectrum segment k (in $\Delta\omega_k$) into the corresponding time interval Δt_k. This can be done according to the time shifting theorem by choosing the slope of phase in the segment to be equal to the time distance of shifting, t_k:

$$t_k = \sum_{i=1}^{k} \Delta t_i = \frac{P_k(\omega) - P_k(\omega_k)}{\omega - \omega_k}. \tag{2}$$

Another consideration that should be taken is to assure phase continuity at the boundaries of segments, that is where $P_{k-1}(\omega_k) = P_k(\omega_k)$. Therefore, the phase function in the segment k can be expressed as

$$P_k(\omega) = P_{k-1}(\omega_k) + t_k(\omega - \omega_k). \tag{3}$$

Here $P_{k-1}(\omega_k)$ is the upper-limit value of phase function from the segment $k - 1$. The upper-limit value $P_k(\omega_{k+1})$ of this segment (k) can be calculated from Eq. (3). In this way the whole phase function can be constructed by the line segments if the initial phase $P_1(\omega_I)$ is specified.

III. QUADRATIC PHASE MODULATION

Now the above general algorithm can be applied to a square magnitude spectrum which is the excitation profile most commonly used in FT-ICR experiments. As discussed above, the square magnitude spectrum from ω_I to ω_F can be divided with an equally spaced grid ($\omega_1, \omega_2, ..., \omega_n = \omega_F$, where $\omega_{k+1} - \omega_k = \Delta\omega$) into n equally spaced segments and the time distance T can be divided into equally spaced (Δt) intervals. Here n can be calculated from Eq. (1). Applying Eq. (3) to the upper-limit point ω_{k+1} of the kth segment gives the following recurrence equation:

$$P(\omega_{k+1}) = P(\omega_k) + k\,\Delta\,t\,\Delta\omega. \tag{4}$$

If $P(\omega_I)$ is set to zero, we have

$$P(\omega_k) = \Delta\omega\,\Delta t \sum_{i=1}^{k} i \approx \Delta t\,\Delta\omega\,k^2/2.$$

Using $\omega_k = \omega_k + k\,\Delta\omega$, $n\,\Delta\omega = \omega_F - \omega_I$ and $n\Delta t = T$ and dropping the subscript in ω_k, the phase function at the grid points is obtained:

$$P(\omega) = (\omega - \omega_I)^2 T/2(\omega_F - \omega_I). \tag{5}$$

Although the equation is about the phase function at the grid points, the conclusion can be expanded to all the points in the frequency interval (from ω_I to ω_F) without introducing non-negligible error if the grid becomes sufficiently dense. Notice that the phase function does not depend on the number n.

VI. CONCLUSIONS

We have developed a general algorithm to solve the phase modulation problem in FT-ICR stored waveform inverse Fourier transform excitation. The algorithm, in general, can be programed to generate phase functions for complex magnitude excitation profiles. The degree of dynamic range reduction can be easily estimated by Eq. (1). Application of the algorithm to square magnitude excitation shows that quadratic phase modulation is the theoretically optimal modulation method.

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