Overview

A discussion on the data processing to correct the phase of FTICR spectra biased (Fig.1) on mathematic theory and experimental data:

• Review the features of an absorption-mode signal.
• Parameterize the phase function with experimental conditions.
• Determine the extent of improvement in mass resolving power and accuracy.
• Apply the phase function from scan to scan in routine experimental work.

Figure 1: Left: phase correction of an absorption-mode spectrum using quadratic phase function. Right: quadratic phase correction of a crude oil spectrum which cannot be eliminated by apodization.

Figure 2: Left: time-domain profiles for frequency sweep excitation, the fringe of the chirp and tone-locked phase accumulation. Right: top: charge state spectra in absorption-mode frequency sweep (Fig.1, middle) and time accumulation (Fig.1, right), therefore, the position of peaks picked by centroiding is much narrower. When the accumulation time is the same, the intensity of a perfectly phased peak is identical to its corresponding magnitude mode.

Introduction

Phase correction, routinely done in FT-NMR, is not used in FT-ICR due to the complexity of the phase function. As is known for 40 years, the resolving power for FT-spectra can be enhanced by a factor up to two if the magnitude-mode spectrum is phase corrected into its corresponding aborption-mode. This topic has been recently resurrected by two publications, first by P. Xian et al., in using a detailed model of the excitation pulse from the experiment, and second by [4], using a quadratic least-squares fit and iteration. The resulting work demonstrates an improvement in resolving power of about 1.7 (Fig. 2). Additionally, the task commonly observed in traditional FT spectra, which exist in neighboring peaks and caving noise may decrease the resolving power. Thus, it is necessary to know anything about the experimental pulse sequence. Here, we continue the research by investigating the factors that determine and modify the phase function in order to optimize and automate the function from scan to scan.

Theory

• Reduce Ion Cyclotron Frequency

\[
\omega_{LC} = \frac{q}{m} V B
\]

• Variation of the Phase Function with Trapping Voltage

\[
\Phi(qB) = qB + \frac{q}{m} V B
\]

• Variation of the Phase Function with Total Ion Number

\[
\Phi(qB) = qB + \frac{q}{m} V B
\]

Method

The crude oil sample (SRM 2721) was purchased from NIST; ubiquitin was purchased from Sigma-Aldrich; samples were dissolved in 50:50:1 isopropanol: methanol: formic acid mixture. All spectra were recorded using a SolariX 12T FT-ICR mass spectrometer (Bruker, Bremen, Germany). Ions were excited using broadband frequency sweep (50-220 kHz) corresponding to a chirp factor of 2.8. The peak shift and width were determined using a sinc-20-limited ion current detection to yield 4 peaks over the time-domain data sets. The data sets were co-added (10 acquisitions at 1/1000 Hz) to increase the S/N, and the baseline was corrected using Fourier transformed without apodization, all data sets were then processed using MatLab. And a series of experiments were performed to test the variation of the phase function with particular experimental variables:

- Trapping voltage in the ICR cell from 0.1 to 10 volt (gated trapping).
- ion accumulation time in the accumulation cell (heparin) from 0.0001 to 10s.
- ion excitation power from 10 to 100 volts.

Figure 3: Left: a small segment from the absorption-mode crude oil spectrum, inset: zoom in for the labeled peak to show the negligible effect of a 'chin' function. Right: histogram showing the mass error of the oil with both magnitude-mode (top) and absorption-mode (bottom).

Results and Discussion

• Parameterize the phase function

The same instrument parameters of the oil spectrum were then applied to acquire ubiquitin charge state spectrum, which clearly shows that parameterizing the phase function must be done only when the pulse sequence is changed – as that is the vast majority of cases; it only has to be calculated once whenever instrument drift requires recalibration of the instrument. Subsequent experiments were performed to determine the phase function, and the existence of the phase function was applied to correct the phase of spectra using the predicted functions mentioned above.

1. Trapping Potential

Under the normal voltage (voltage), the phase shift is totally predictable, and as the magnetron expansion causes frequency shift is increased dramatically by the trapping potential, normal detection is performed with a trapping potential.

2. Number of Ion

As is pointed by Scharf et al.[3], the space-charge effect is linear with the ion population, moreover, the phase shift via ion accumulation time is independent of ions. The modified phase function remains stable for the entire time scale of accumulation time, even in the extreme space-charge condition which already shows the space-charge loss of coherence[6] in the transient (Fig. 3). However, in such extreme case, the peak shift and artifacts caused from the space-charge effect are much severer than the phase correction itself.

3. Excitation Radius

The shift of ion frequency was recorded which roughly follows a quadratic relation with the ion excitation potential. However, the data here was generated from the infinity cell, in which the trapping field is not ideal in any way. Thus, frequency does change slightly with the excitation Radius, and the resulting quadratic function varies for different type, thus not sufficiently accurate to much a reliable prediction for time-frequency behavior to be used for a proper evaluation of the phase function.

Figure 4: A: Ubiquitin charge state spectra in-accordance mode corrected by the phase function from crude oil spectrum (Fig. 3), using same instrument parameters; B: zoom in of the 1+ charge state peaks in A; C: correct the phase value of the start and end points, the entire spectrum is then perfectly phased; D: zoom in of the 1+ charge state peaks in C.

Conclusion

This project shows that the phase function can be applied directly from scan to scan and from sample to sample in cases where 1) the pulse sequence doesn’t change or 2) the pulse sequence change is limited to modest variation to trapping voltage or ion accumulation time. This broadband phase correction can be automated in routine work as is already done in NMR.

References


Acknowledgement

This work was supported by University of Warwick, Warwick Centre for Analytical Spectrometry (UWCRAS) funded, Propositional: ERR930410/7.