

Absorption-Mode Fourier Transform Mass Spectrometry: Advantages for Protein and Petroleum Spectra

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Overview

In FT-ICR, the absorption-mode spectrum is systematically found to be superior than the magnitude-mode for the following reasons:

- 1.7 to 2-fold in mass resolving power (R)
- 1.4-fold in signal-to-noise ratio (S/N)
- a substantial improvement (10%-100%) in mass accuracy

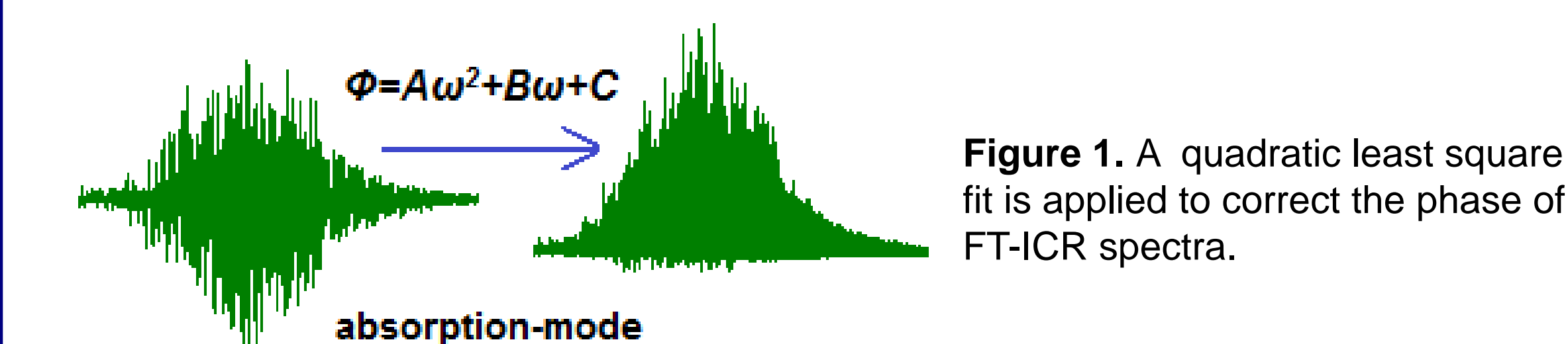


Figure 1. A quadratic least square fit is applied to correct the phase of FT-ICR spectra.

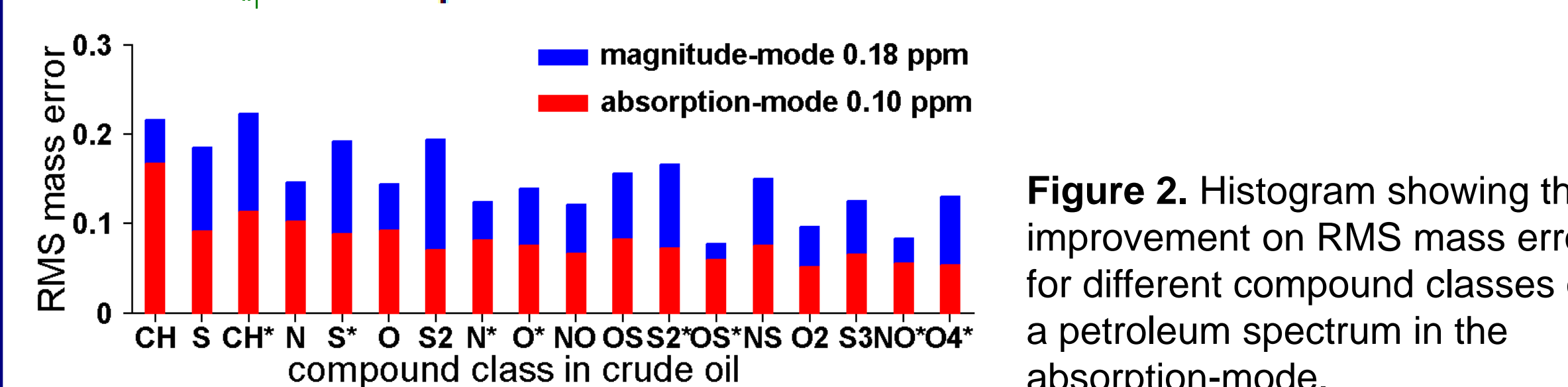


Figure 2. Histogram showing the improvement on RMS mass error for different compound classes of a petroleum spectrum in the absorption-mode.

Introduction

Phase correction, routinely done in FT-NMR, is still not used in FT-ICR due to the complexity of the phase function. This topic has been recently resurrected by two publications, first by F. Xian et al. [1], using a detailed model of the excitation pulse from the experiment, and second by Y. Qi [2], using a quadratic least square fit and iteration. The advantage of this method is that the user doesn't need to know anything about the experimental pulse sequence. Here, we demonstrate the advantages of the absorption-mode in crude oil and top-down protein spectra.

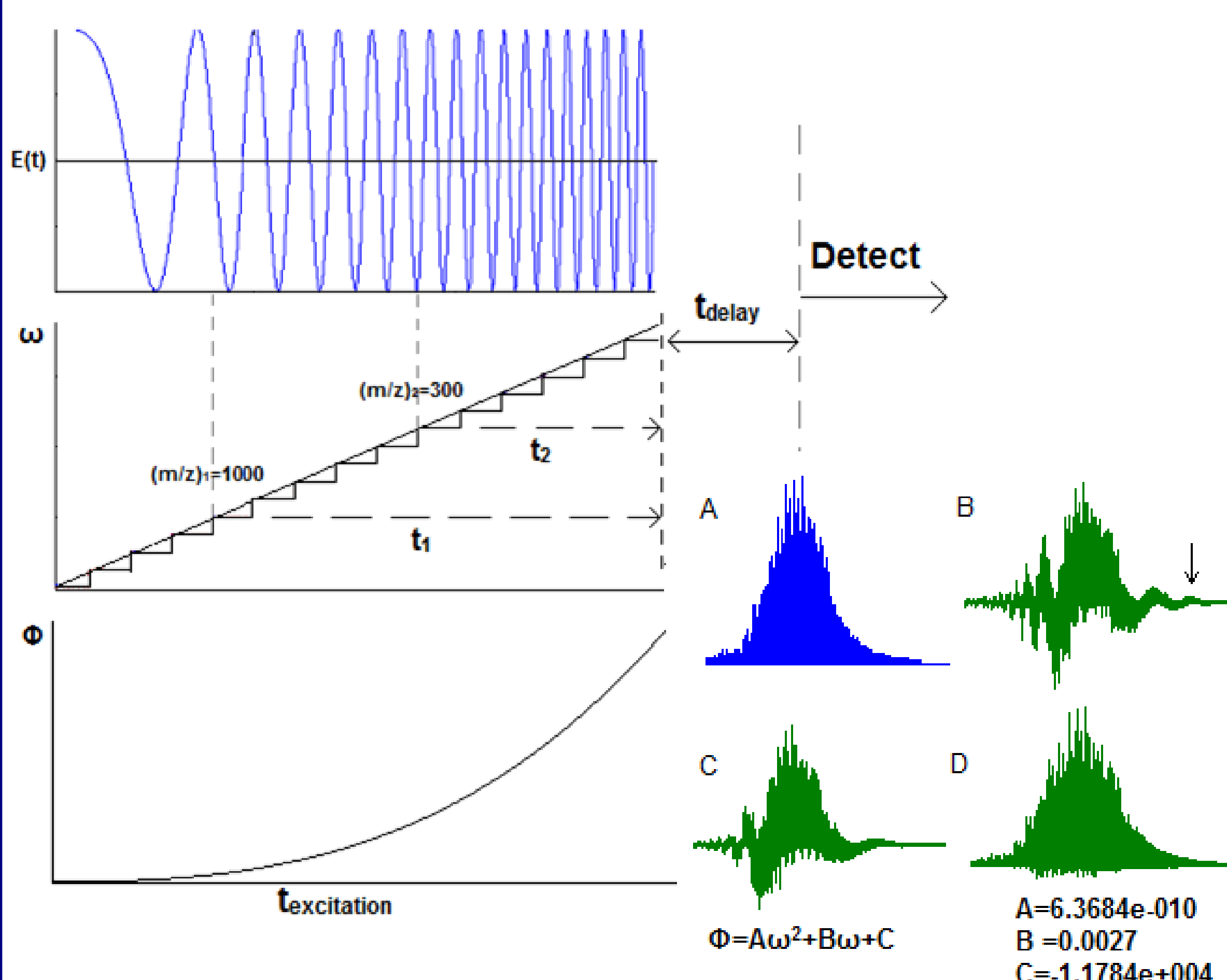
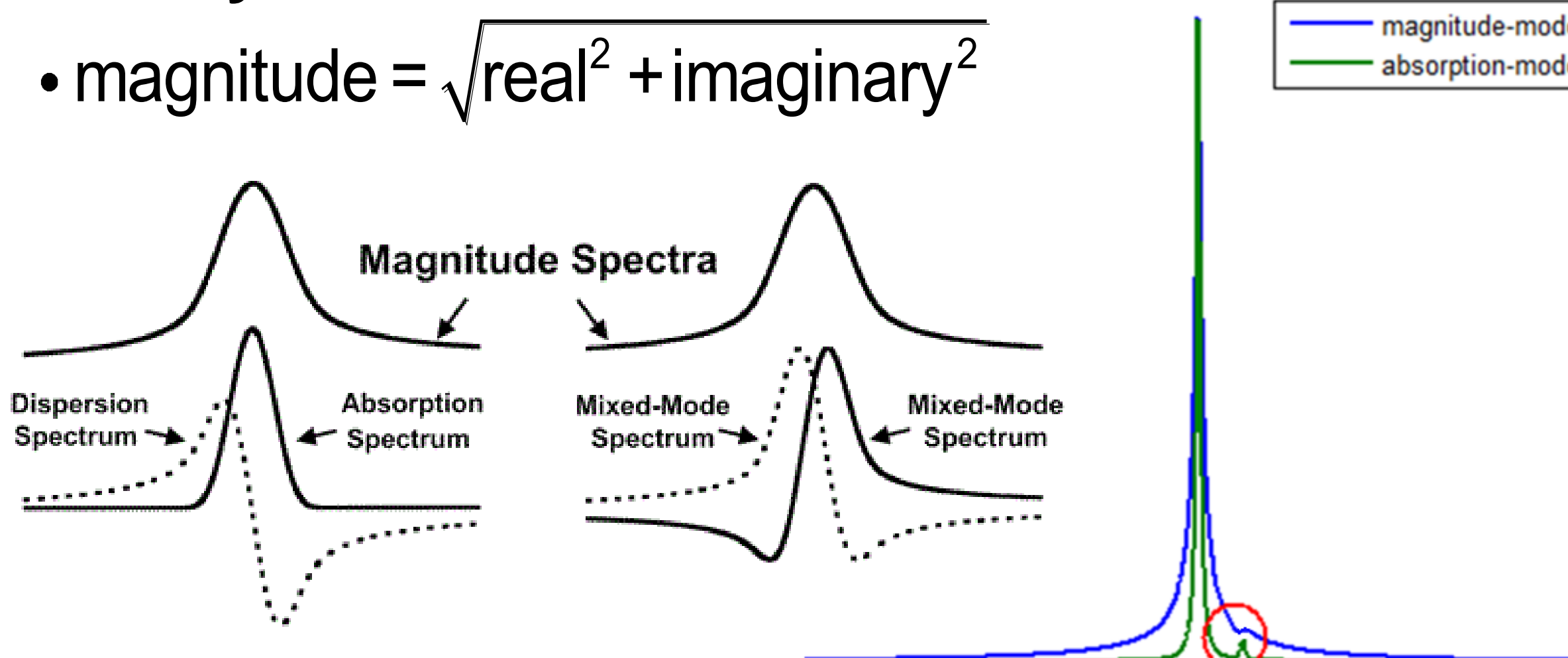
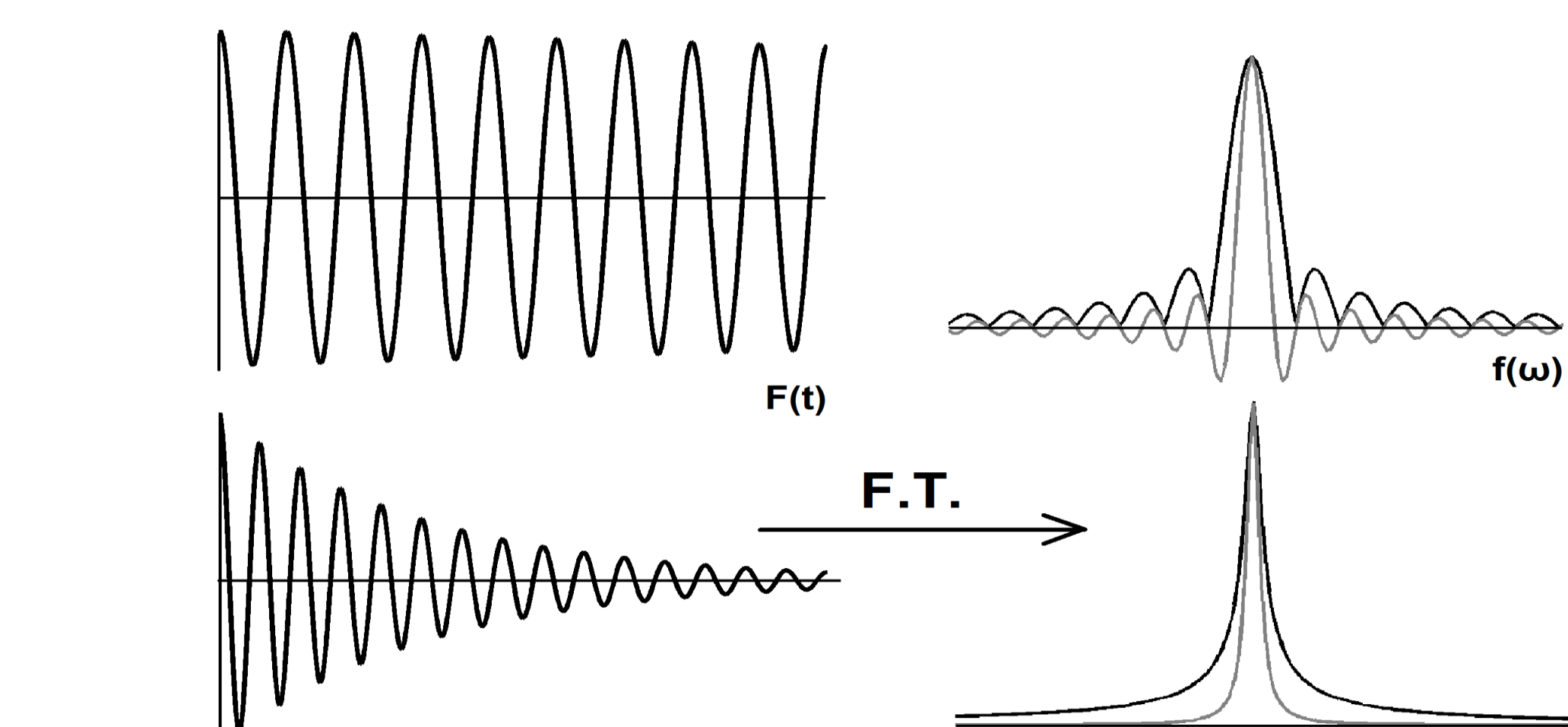


Figure 2. Left: time-domain profiles for frequency sweep excitation, frequency of the chirp and ions' quadratic phase accumulation. Right: a petroleum spectrum to show the phase correction by least square fit and iteration [2].

Theory



• 1.7-2-fold in mass resolving power



• 1.4-fold in S/N

$$A(\omega)_{noise} = \sqrt{\frac{a_1^2 + a_2^2 + \dots + a_n^2}{n}}$$

$$M(\omega)_{noise} = \sqrt{\frac{(a_1^2 + a_2^2 + \dots + a_n^2) + (b_1^2 + b_2^2 + \dots + b_n^2)}{n}} \cong \sqrt{2} \times A(\omega)_{noise}$$

Petroleum

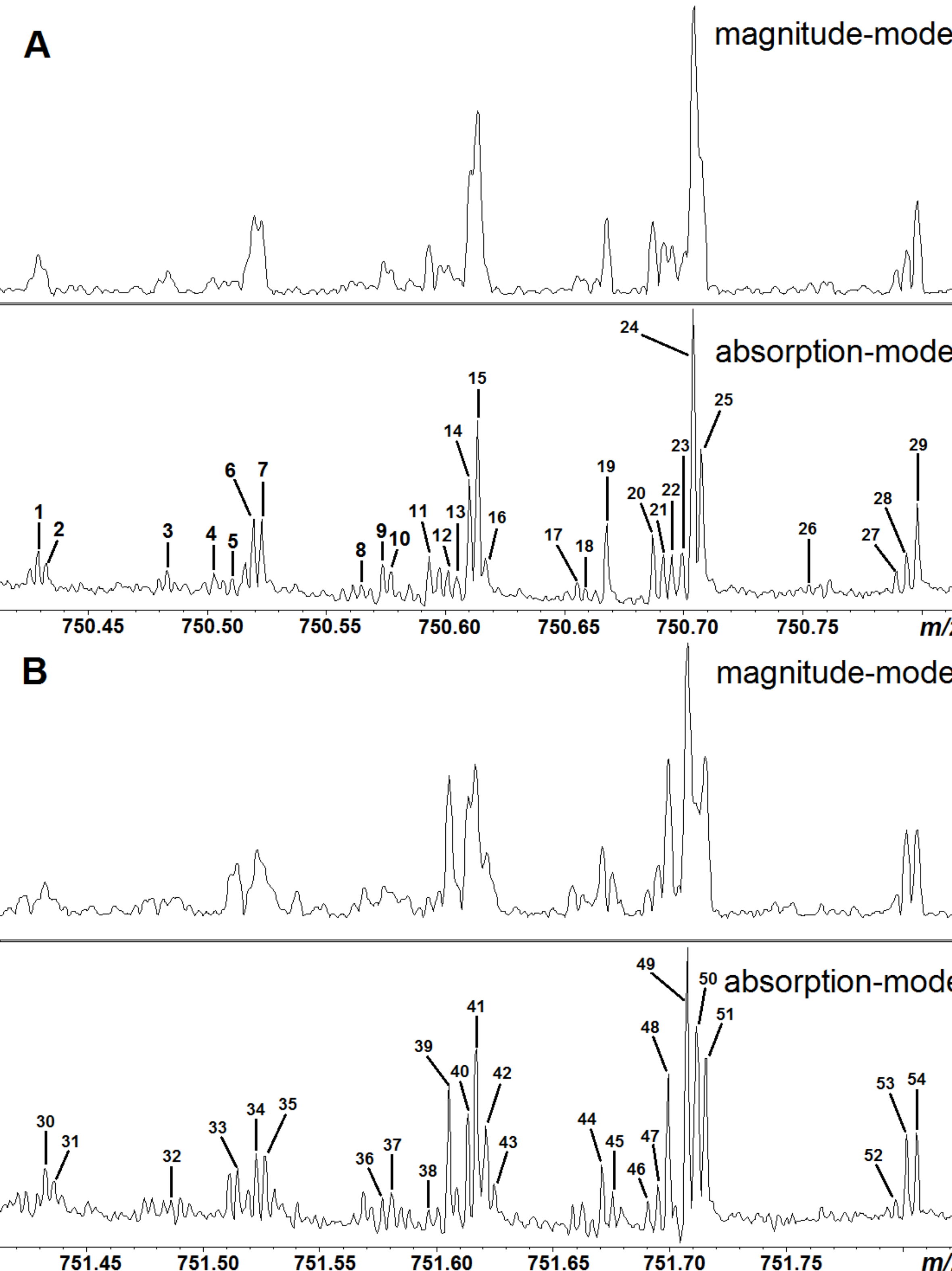


Figure 2. Close-up of two narrow m/z windows in the petroleum spectrum (SRM, 2721, purchase from NIST) spectrum, in both magnitude and absorption-mode [4].

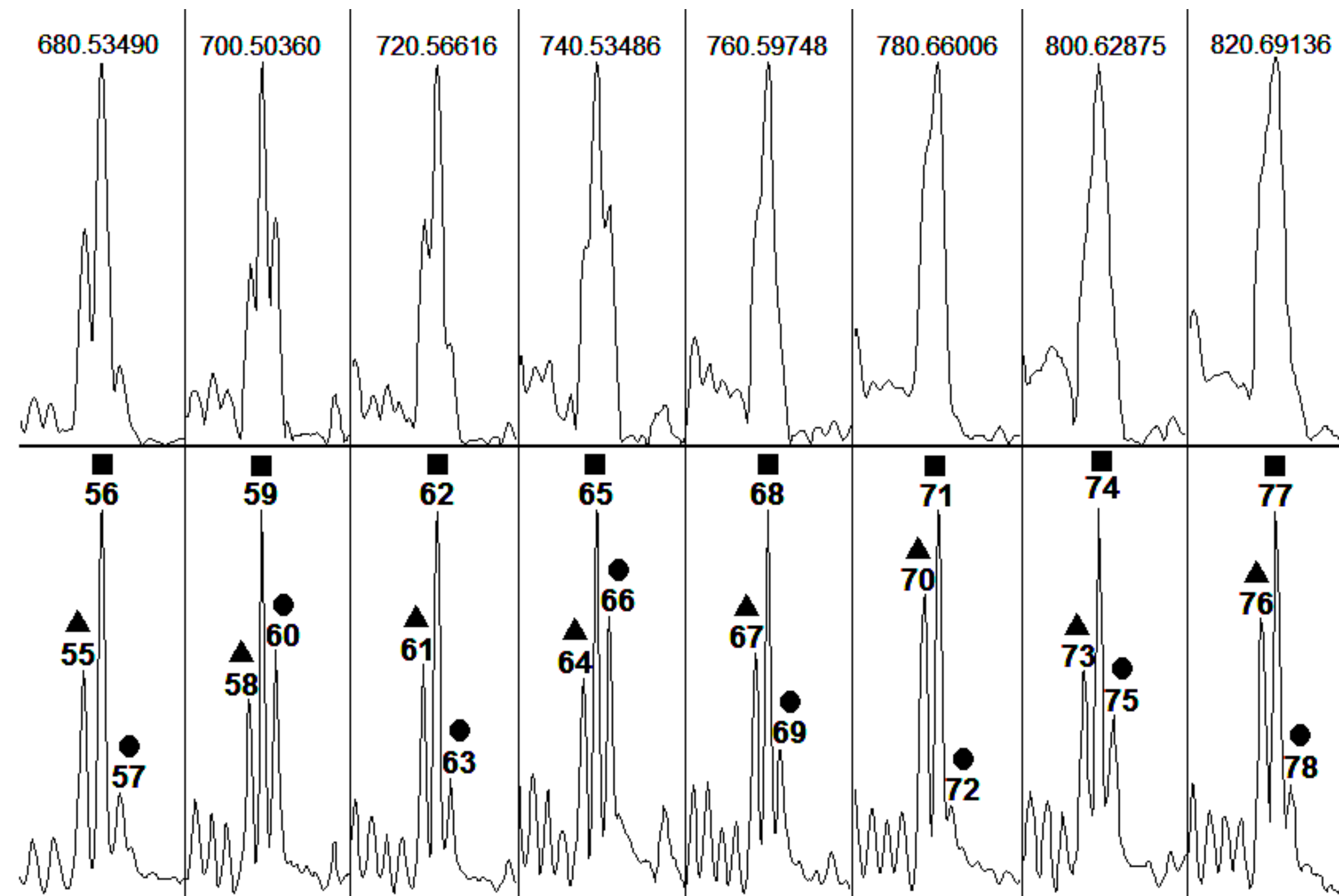


Figure 3. Zoom in of three adjacent classes: CH (▲), S (■), and S₂ (●) of the petroleum spectrum in both magnitude (top) and absorption-mode (bottom) of different m/z range.

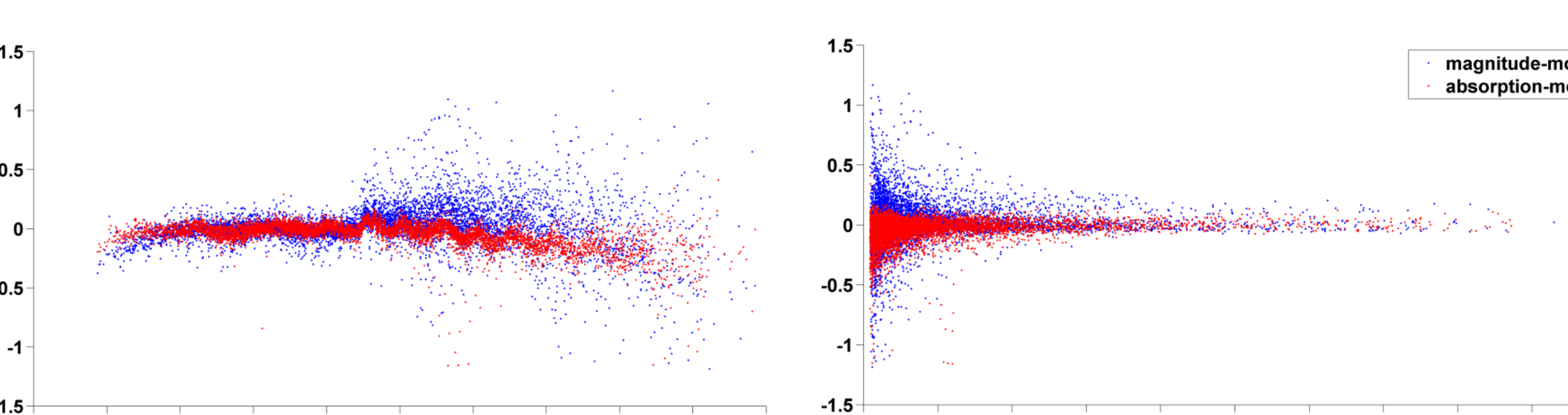


Figure 4. Mass error distribution (ppm) of the crude oil spectrum versus m/z (left) and S/N (right) domain for both magnitude and absorption-mode.

Top-down Protein

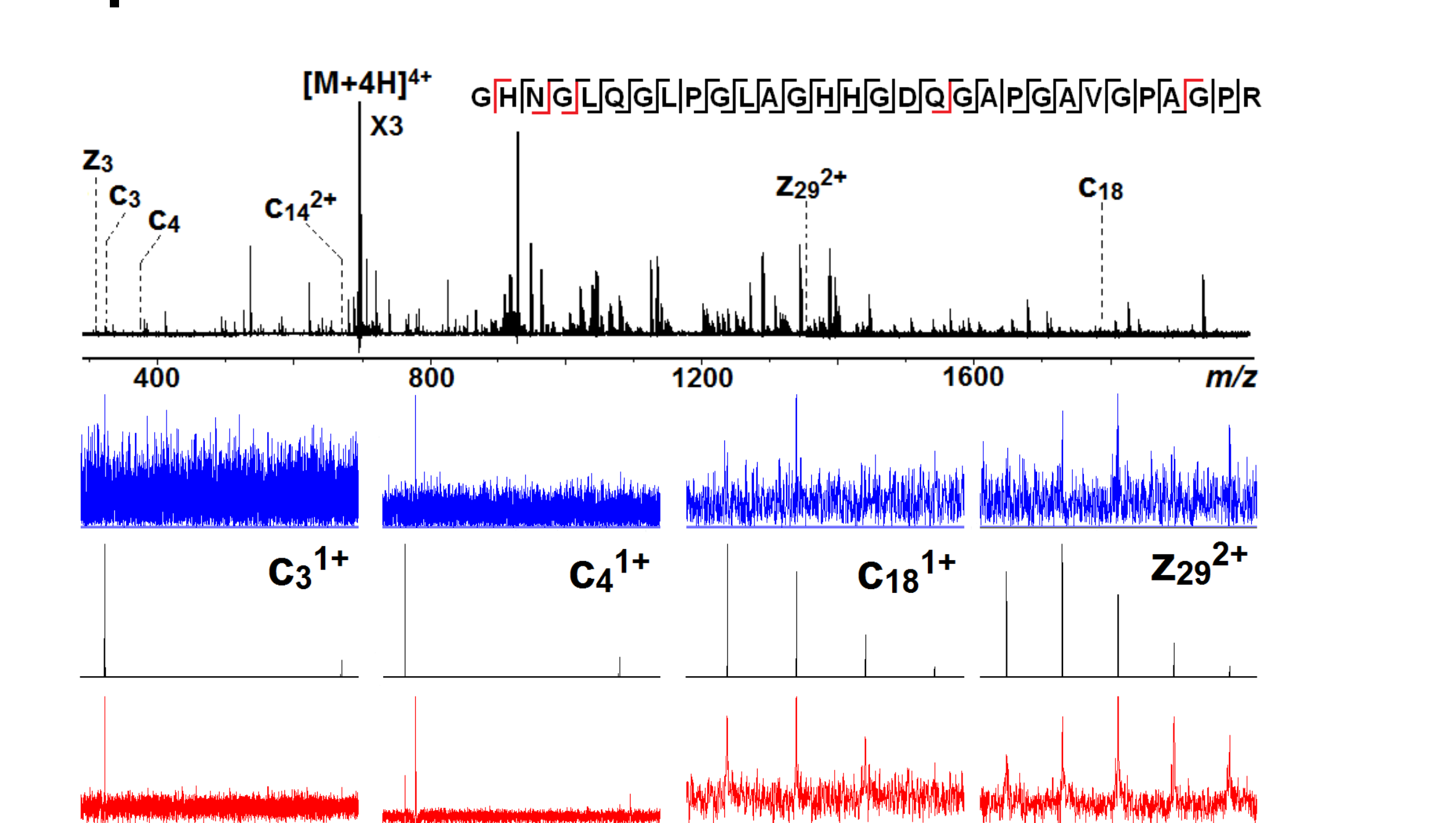


Figure 5. ECD spectrum of collagen with cleavage map, the absorption-mode (red) reveals more isotope peaks than the magnitude-mode (blue).

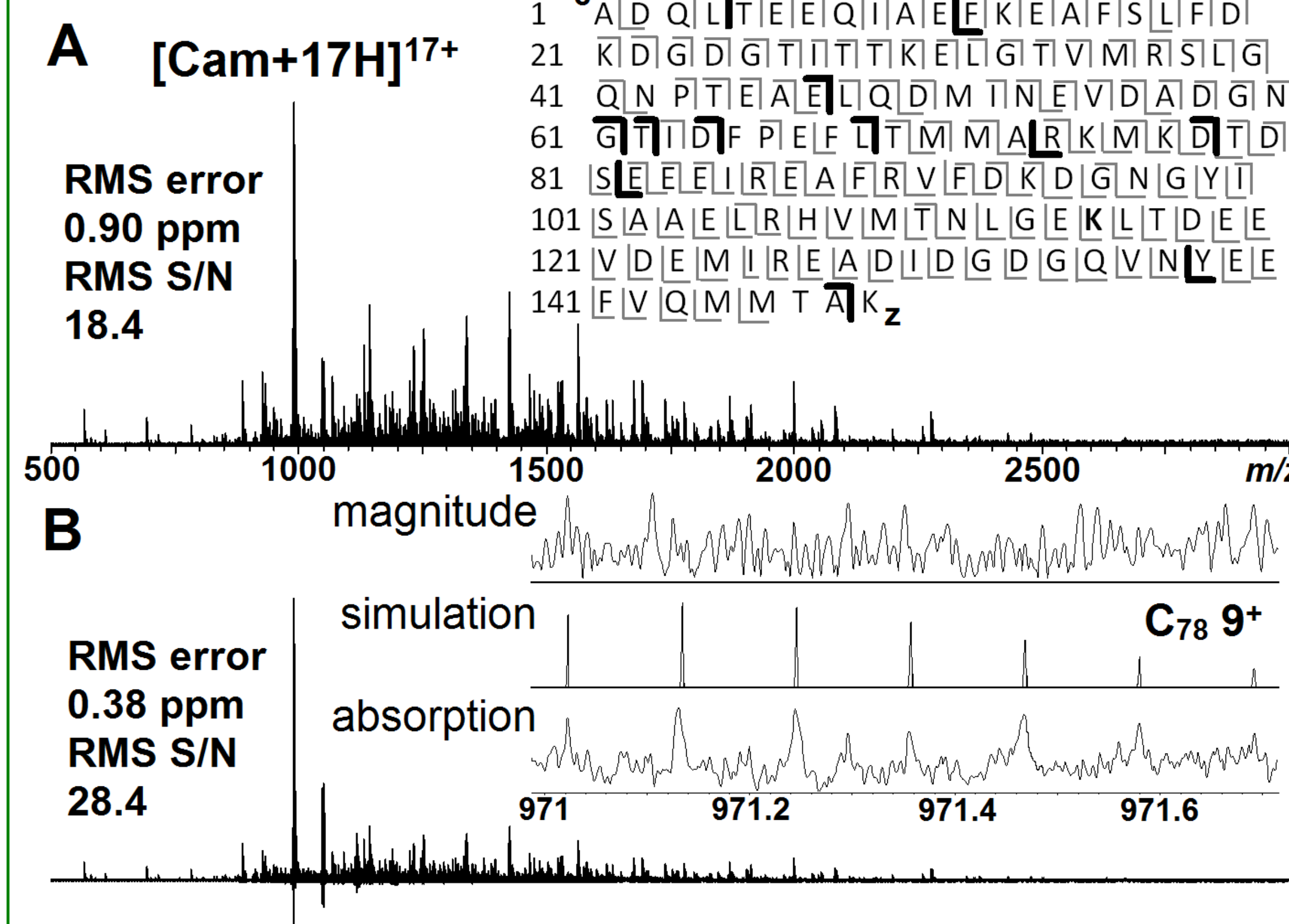


Figure 6. A: ECD spectrum of camodulin [Cam+17H]¹⁷⁺ in magnitude-mode with the RMS mass error and S/N labeled; inset: cleavage map (fragments observed in magnitude-mode are labeled in grey, new fragments in absorption-mode are in black). B: Spectrum in absorption-mode, inset: the C₇₈⁹⁺ fragment in magnitude (top), absorption-mode (bottom) and its isotope simulation (middle) [4].

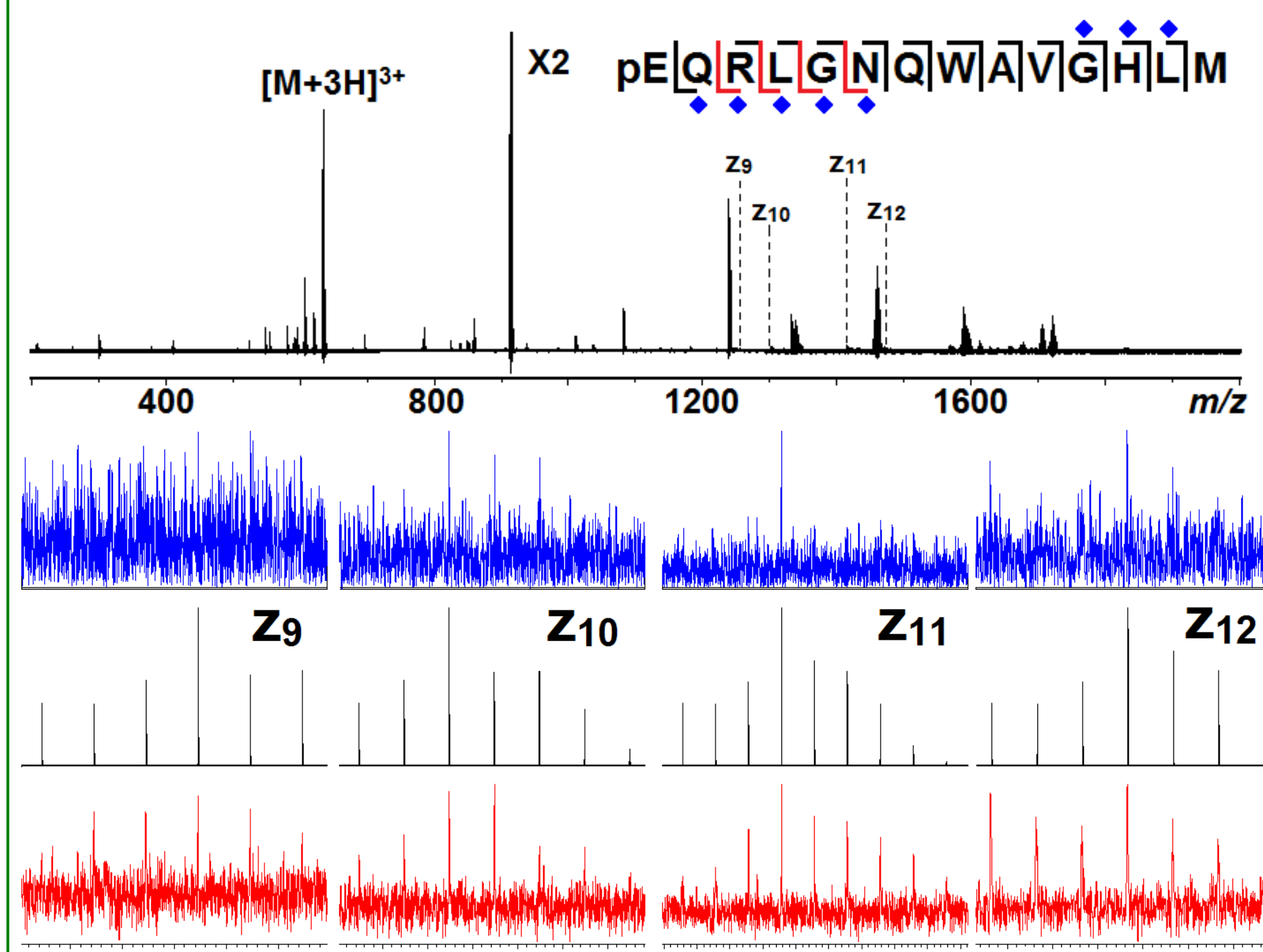


Figure 6. ECD spectrum of bombesin binding with AH078 (a ruthenium ligand), the absorption-mode (red) shows better isotope peaks of ruthenium than the magnitude (blue).

Conclusion

Ultra-high resolving power is the key feature which distinguishes the FT-ICR from all other mass analyzers because the measurement of the mass for a peak is only confident, and mass accuracy can only be truly defined, when the peak is fully resolved. The importance of resolving power is best recognized in complex spectra (eg. crude oil, top down protein), which is why these samples are generally best analyzed using FT-ICR. In this work, the superior performance of absorption-mode spectrum was successfully applied to petroleum and top-down protein spectra, and are found to be superior to the conventional magnitude-mode.

Acknowledgement

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Reference

- [1] Xian, F.; Hendrickson, C. L.; Blakney, G. T.; Beu, S. C.; Marshall, A. G. *Anal. Chem.* **2010**, *82*, 8807.
- [2] Qi, Y.; Thompson, C.; Van Orden, S.; O'Connor, P. *Journal of The American Society for Mass Spectrometry* **2011**, *22*, 138.
- [3] Qi, Y.; Barrow, M. P.; Van Orden, S. L.; Thompson, C. J.; Li, H.; Perez-Hurtado, P.; O'Connor, P. B., Variation of the Fourier Transform Mass Spectra Phase Function with Experimental Parameters. *Anal. Chem.* **2011**, *83* (22), 8477-8483.
- [4] Qi, Y.; Barrow, M. P.; Meier, J. E.; Li, H.; Van Orden, S. L.; Thompson, C. J.; O'Connor, P. B., Absorption-mode: The Next Generation of Fourier Transform Mass Spectra. *Anal. Chem.* **2012**, online. DOI: 10.1021/ac3000122.

