

# New Developments in the Modeling of Ion Fragmentation by MS Interpreter Software

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## Introduction

For over 20 years, MS Interpreter has been a freely available software tool for quickly examining the possible origin of EI mass spectra for GC/MS and more recently ESI-Tandem Spectra for LC/MS. After input of a structure and a spectrum, it assigns peaks to plausible molecular substructures based on a set of thermochemical estimates and fragmentation mechanisms based on a proposed chemical structure. A calculated rate for every bond dissociation shows its reactivity with values from 0 to 120.

## Fragmentor Rates and Reactions

Rule development and optimization were derived from computer analysis of NIST libraries. An example is shown in Fig 1a which shows the relation between the fastest rate and the fraction of EI spectra with no molecular ion peak and Figure 1b showing the distribution of rates. These provide a guide to developing a robust set of rates – where the ultimate target is a uniformly increasing curve in Fig 1 and a smoother curve in Fig 2. A wide range of reactions were developed to explain the major peaks. The most significant reactions for EI, ESI Positive and ESI Negative are shown in Figs 3-5 based on assignments of most abundant fragment ion in each spectrum. Dissociation accounts for over half of the base peaks in EI, 35% in Negative ESI while H-displacement accounts for nearly half of base peaks in Positive ESI. Many other less significant reactions derived from observations and the literatures are not shown. Examples for the most common reactions are shown in the Figs. 6a-d.

## User Interface

Fig. 7 shows a range of new features in MS Interpreter to aid the interpretation of mass spectra on the basis of chemical structure. Spectrum handling, such as zoom in and out and sliding the mass spectrum have been added along with facile calculation of m/z differences between selected peaks. Fragmentation unreliable mechanisms are shown in yellow. These reactions often involve complex rearrangements, but possible origins of the peak are shown to aid interpretation. These reactions are denoted using the reaction type suffix UF (unfiltered), which are shown in yellow using a button at the top. When no interpretation at all can be made, peaks appear in white. Unfiltered possible fragments have a tic mark above the peak and show an ion/neutral pair in the Structure window. Other new features are: marking low confidence mechanisms (shown by red arrows); restricting the number of assignments per peak (shown by green arrow); set rate threshold to restrict black peaks to those with the most reliable assignments (blue arrow); slide spectrum with mouse with left CTRL pressed; zoom spectrum near mouse using wheel with left CTRL pressed; saving mass spectrum with molecule structure as SDF format file; display improvements for high res display.

## Summary

Fragmentation reactions and their rates from MS Interpreter were significantly enhanced over the past year using spectra in NIST MS Libraries. At the same time, major improvements were made in the MS Interpreter user interface, enabling more efficient interpretation and validation of mass spectra. The software, with a direct connection to NIST library software may be freely downloaded from <https://chemdata.nist.gov>.

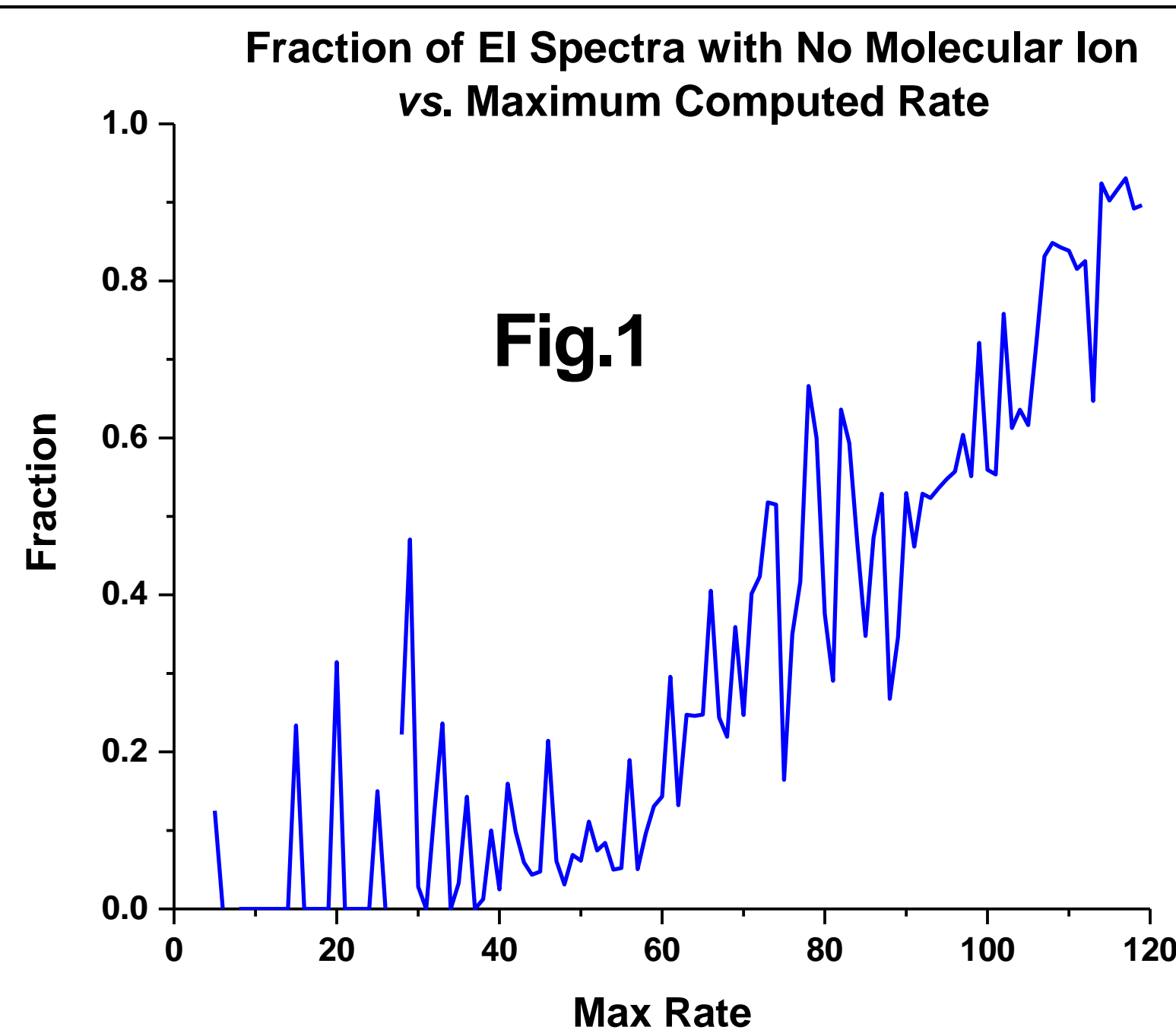


Fig.1

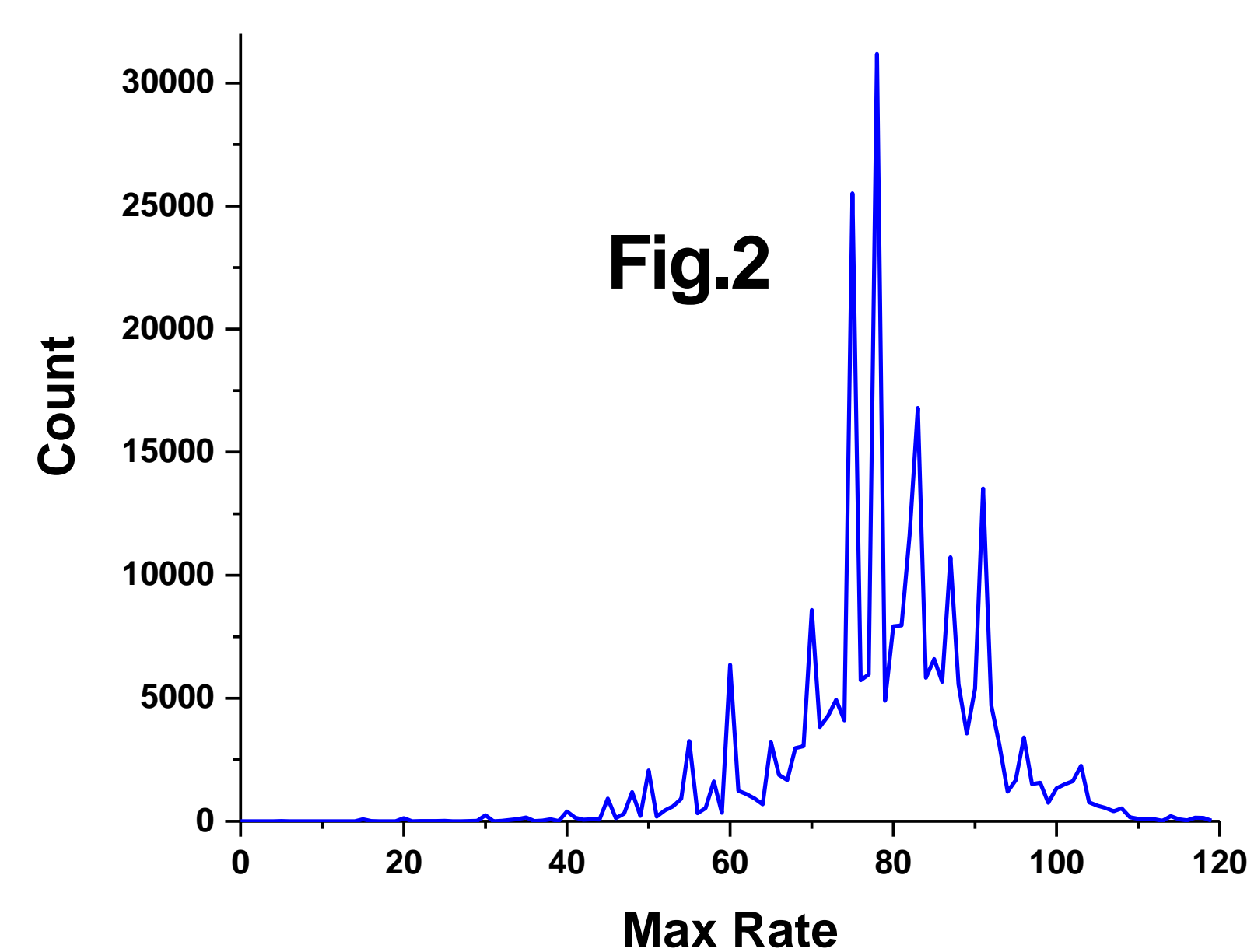


Fig.2

20 Most Common Origins of Largest EI Fragment Ion

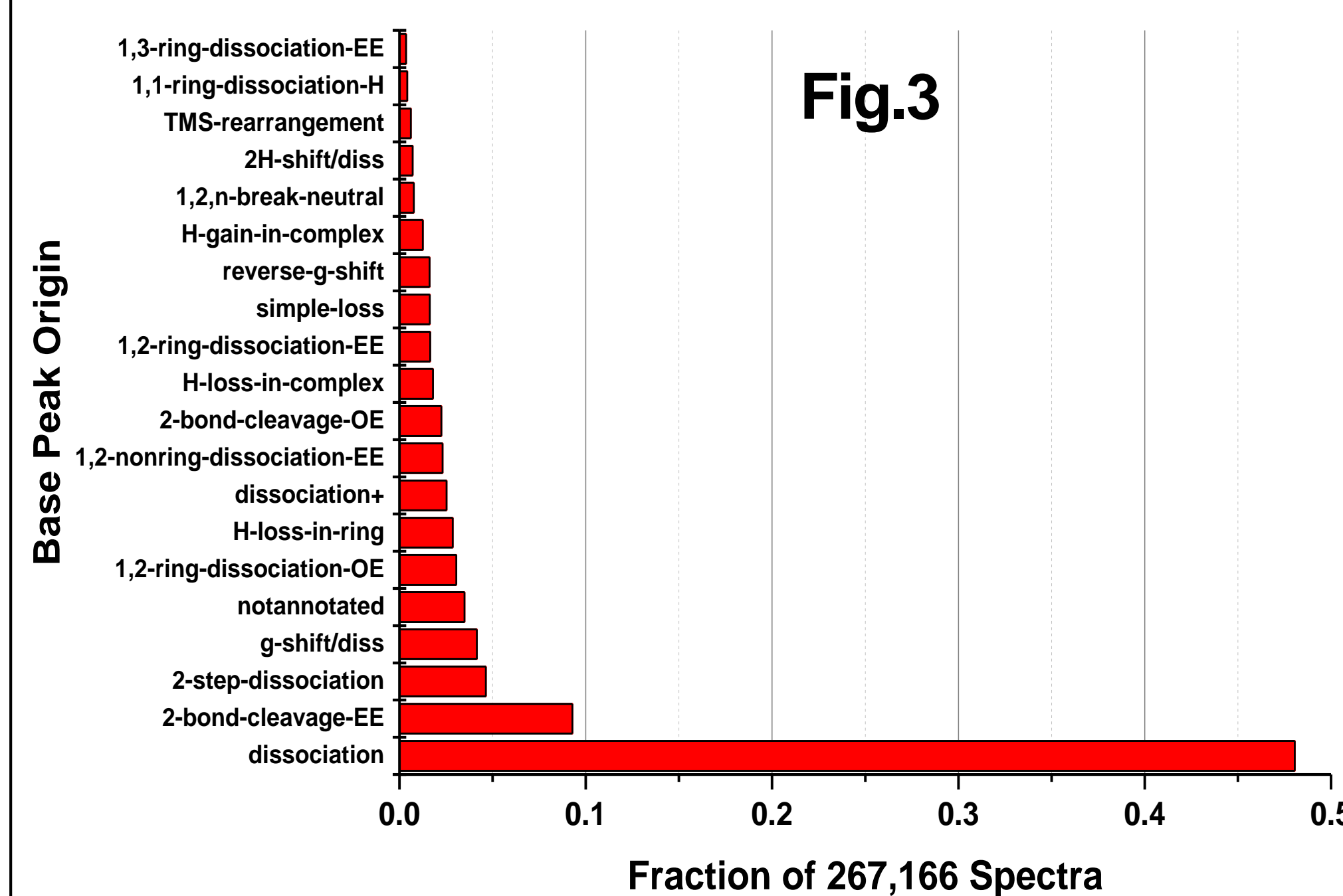


Fig.3

ESI Ion Trap - Positive Mode  
10 Most Common Base Peak Origins

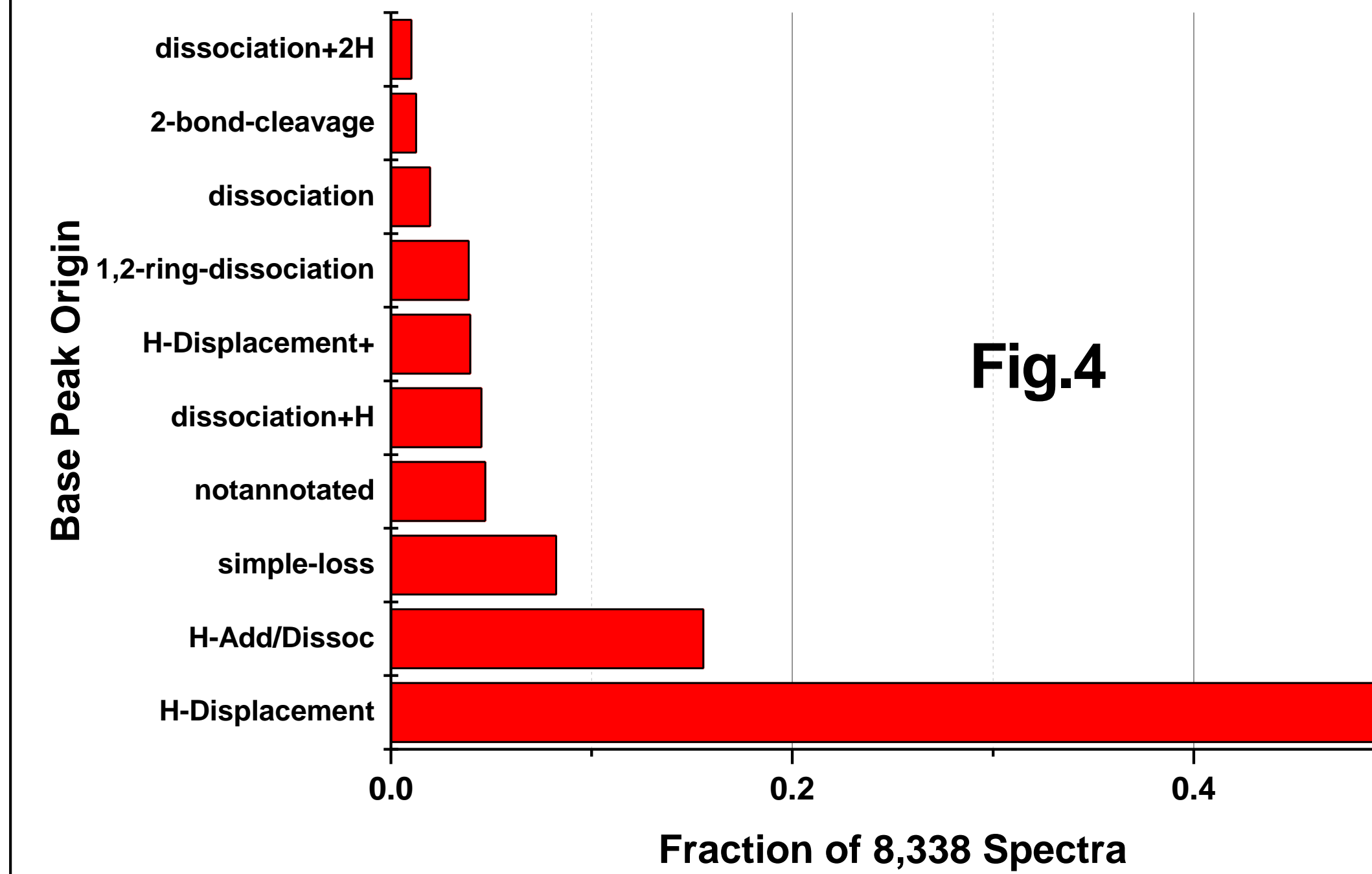


Fig.4

ESI Ion Trap - Negative Mode  
10 Most Common Base Peak Origins

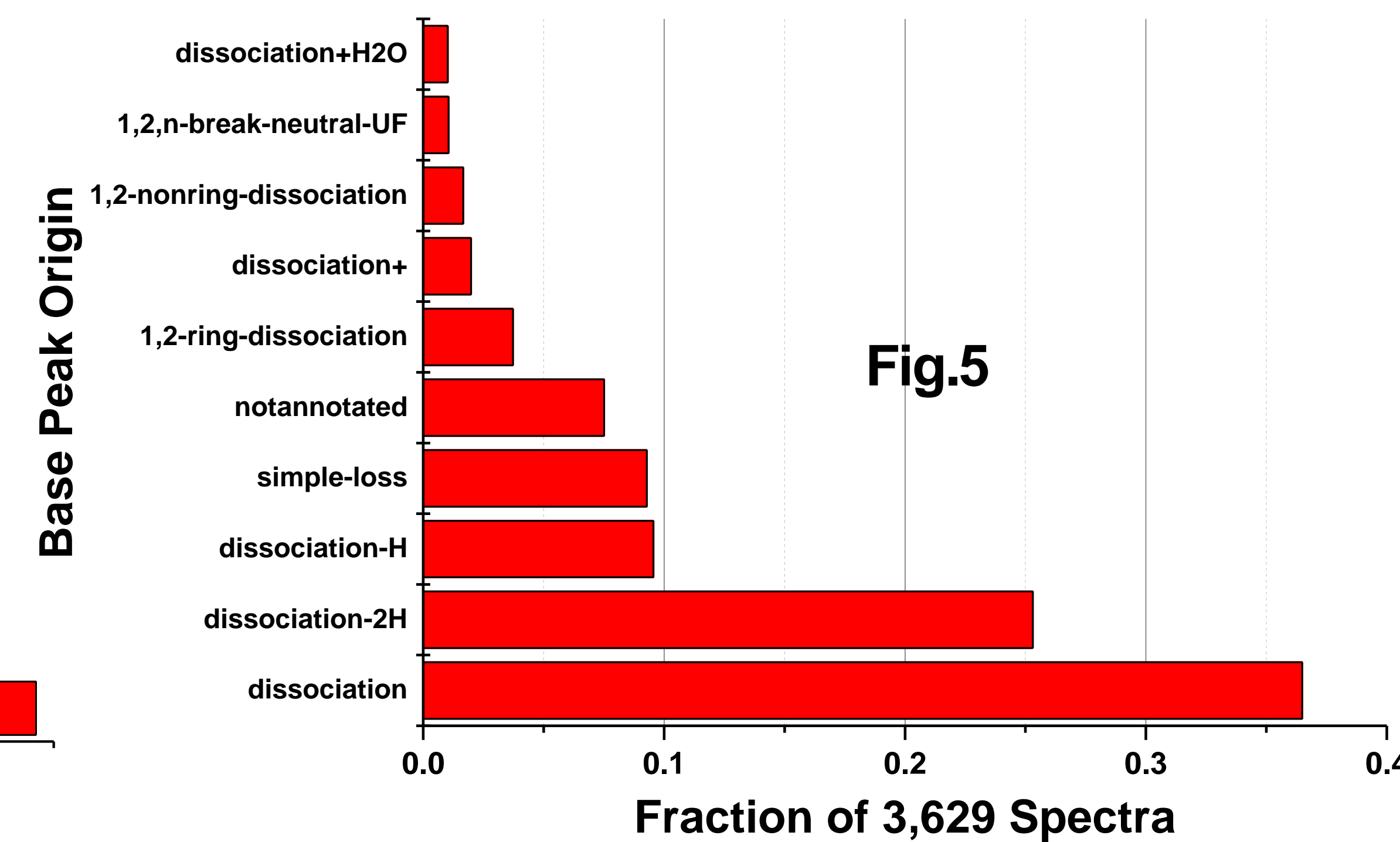


Fig.5

Fig.7 User Interface

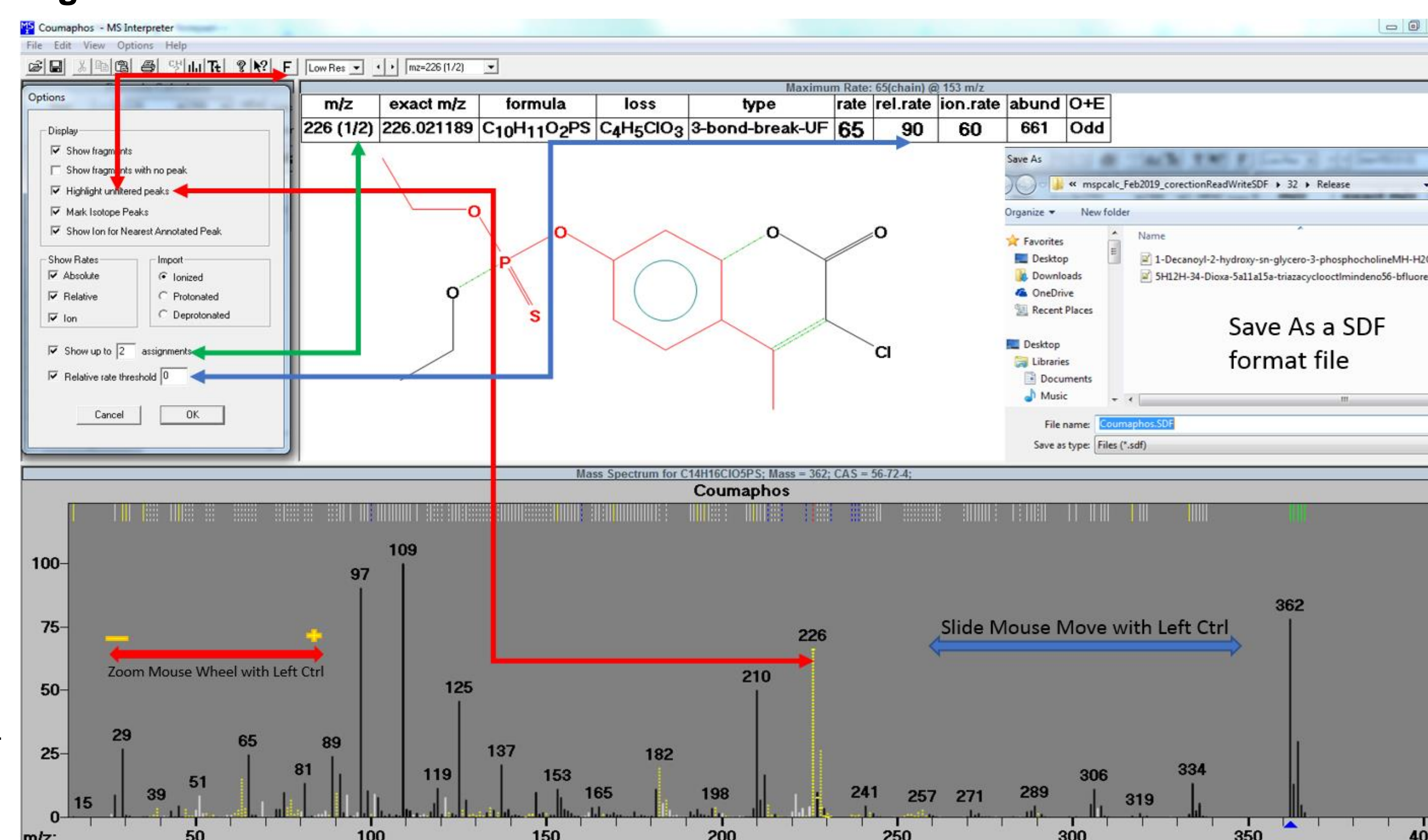


Fig.6a Dissociation+H peak 93.0571 m/z and H-displacement peak 92.0492 m/z of Diphenylamine

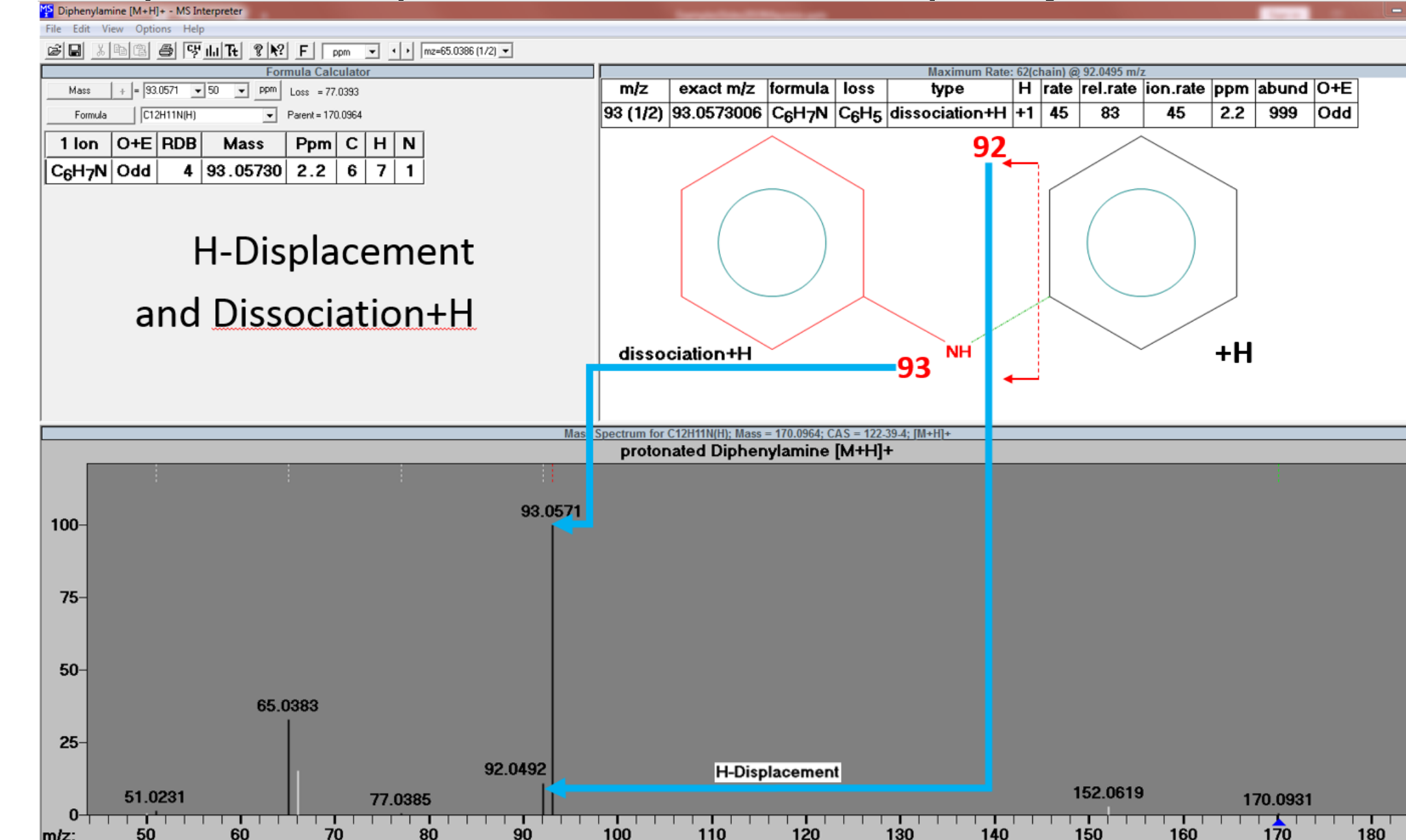


Fig.6b H-Add/Dissoc peak 184.0522 m/z of Bupropion

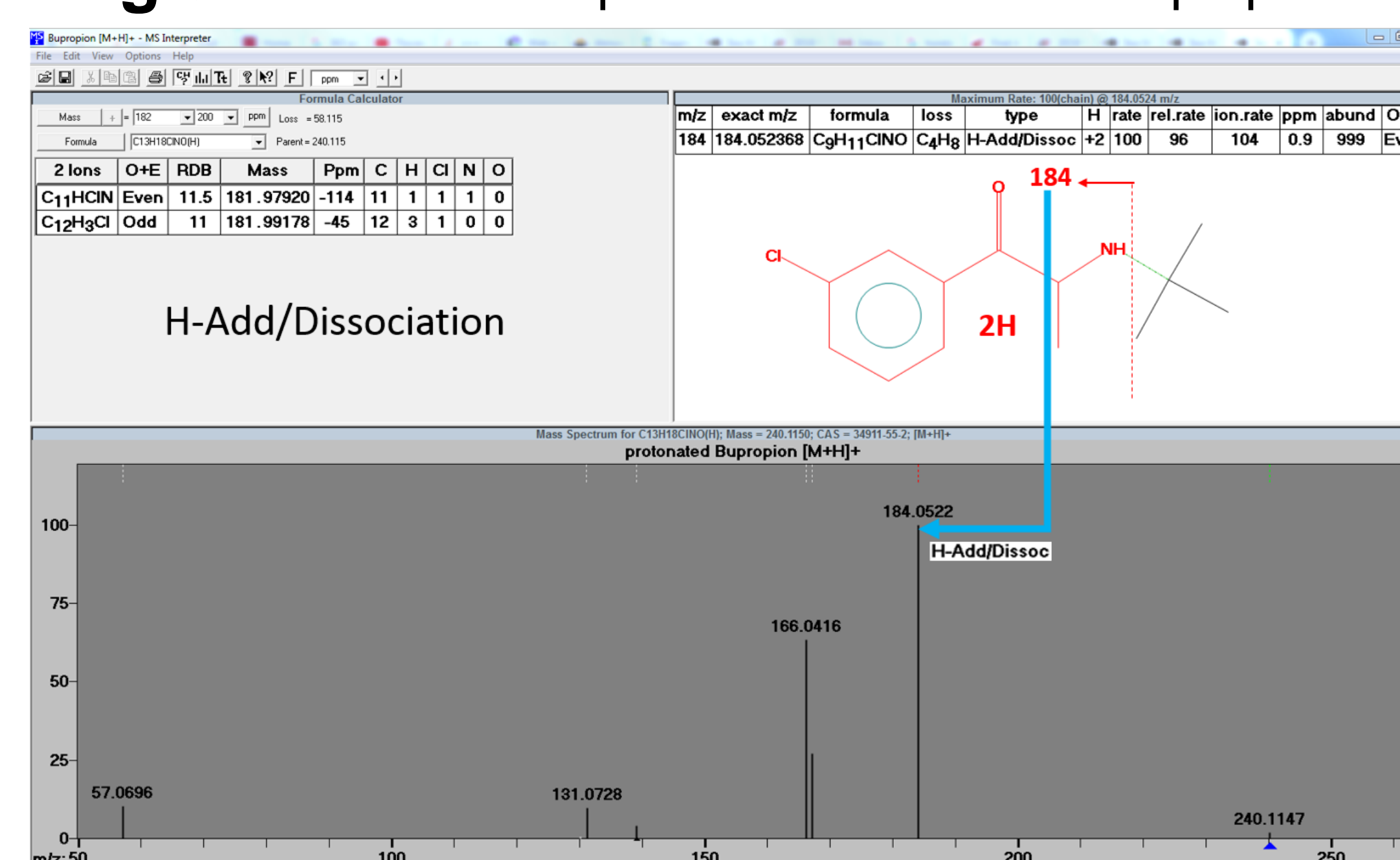


Fig.6c 2-bond-cleavage peak 107 m/z, Dissociation 149 m/z and g-shift/diss 186 m/z of 3-Acetoxybenzyl bromide

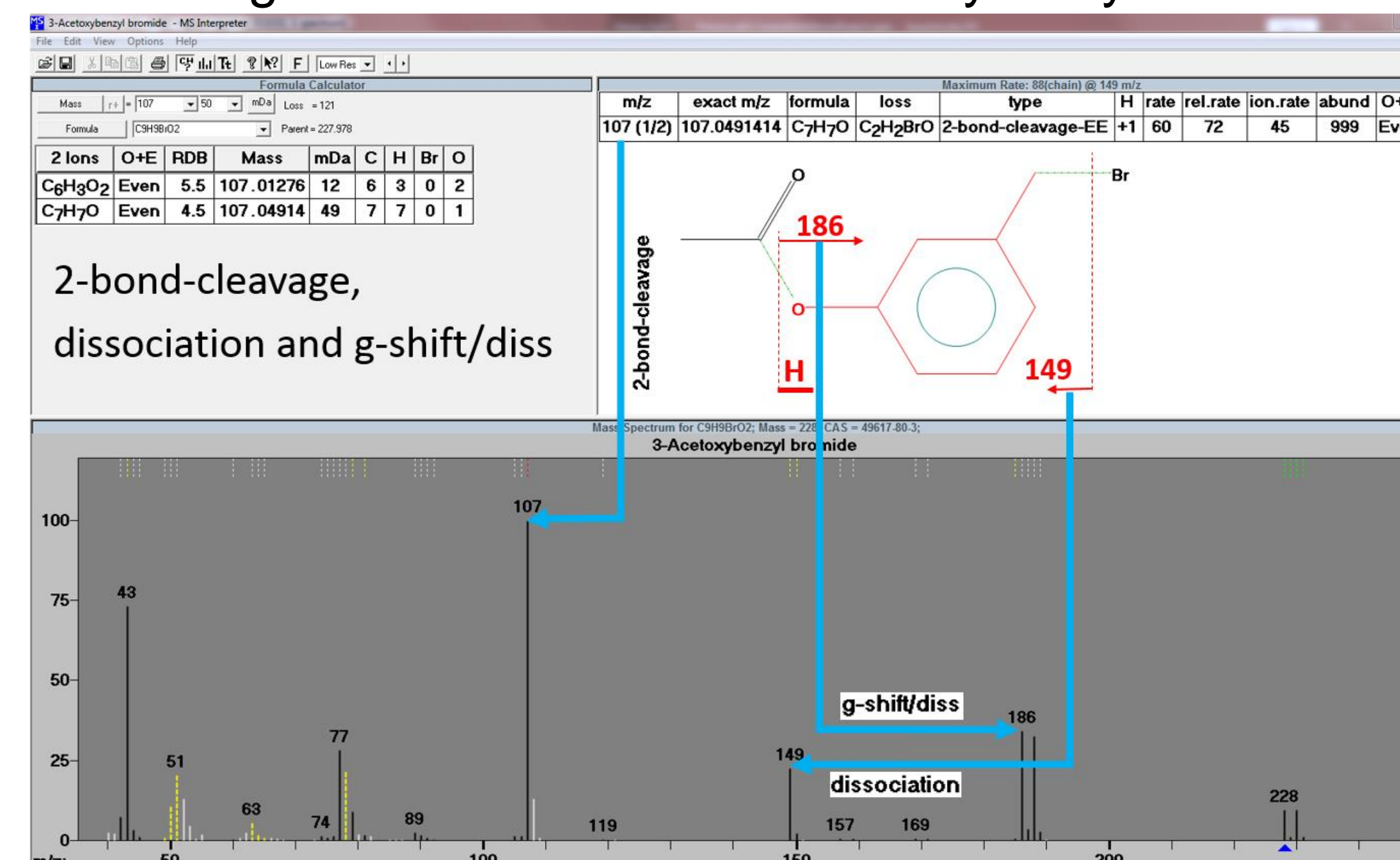


Fig.6d Dissociation-2H peak 142.0511 m/z of N-Acetyl-L-methionine

