Liquid Injection Field Desorption/Ionization–Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: Optimized RF–Hexapole Trapping Avoids Fragmentation of Labile Molecular Ions

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LIFDI: How Does It Work? What Is It Good for?

Field desorption mass spectrometry (FD-MS) is applicable to nonpolar, polar, and ionic compounds [1,2]. We have devised a liquid injection field desorption/ionization (LIFDI) [3] and electrospray ionization (ESI) combination (LIFDI-ESI) ion source for a hybrid quadrupole Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer [4,5]. The unique LIFDI-ESI source unites two complementary ionization methods on one instrument.

The softness of LIFDI can only be exploited if the intact molecular ions, M⁺, are transferred from the field emitter through the matrix analyzer, i.e., ion-activating events like collisions need to be suppressed. However, in hybrid quadrupole FT-ICR mass spectrometers, multiple ion-guiding and ion-trapping events occur prior to mass analysis. Here, we present refined ion trapping conditions that even allow to preserve alkane molecular ions. In addition to the replacement of argon in the accumulation hexapole by helium, a hexapole DC bias is required.

Key to Success: Trapping Conditions

The experiments were performed on a Bruker Apex-Qe FT-ICR mass spectrometer equipped with our custom-built LIFDI-ESI combination ion source and a 9.4 T superconducting magnet [4,5]. It was operated to obtain LIFDI spectra of 4-tritylaniline, sewing machine oil, and docosane. The abundance of molecular ions, M⁺, was optimized, in particular by variation of the trapping conditions inside the instrument's accumulation RF-hexapole trap (h2, below).

To preserve molecular ions, the standard gas argon, admitted for ion cooling as well as for CID, had earlier been replaced with helium [5]. Thus, the loss of molecular ions by dissociation during transfer from the LIFDI source into the ICR cell was significantly reduced [5]. Furthermore, trapping potentials and DC bias of the RF-hexapole rods were of outmost importance for the LIFDI spectra.

Example 1: 4-Tritylaniline

LIFDI spectra of 4-(triphenylmethyl)-aniline (4-tertritylaniline), C₃₃H₂₈N, the molecular ion increases by a noteworthy degree as soon as aromatic groups are part of the analyte molecule. Here, the best spectrum is obtained at no DC offset, which in turn corresponds to most effective trapping in h2.

An earlier observed fragment ion at m/z 225 by phenyl loss from M⁺ is fully absent now. The insert shows the expanded M⁺ signal and suggested formulas that are in very good agreement with monoisotopic and first carbon isotopes of tritylaniline.

Example 2: Sewing Machine Oil

Different from tritylaniline, LIFDI spectra of a sewing machine oil sample is strongly dependent on the hexapole offset potential. With no offset, almost all molecular ions undergo fragmentation. The optimum is reached at an offset of about 8 V (bottom left). Higher offset, e.g., 11 V (upper left), would mean even softer trapping. However, the trapping well then appears too shallow to keep ions stored inside h2.

The list of suggested formulas (below) shows compositions corresponding to 1 to 3 double bond equivalents (dbd), i.e., to cycloalkanes, alkenes, alkanedienes and the like.

Example 3: Docosane

Alkane molecular ions are by far the most delicate species to be measured by LIFDI–FT-ICR–MS. This may appear astonishing as alkane analysis paved the road to organic MS.

Nonetheless, the life-time requirements for FT-ICR–MS are in the order of seconds rather than microseconds in magnetic sector and time-of-flight instruments. This poses severe limitations on alkane analysis by LIFDI–FT-ICR–MS.

In fact, we were able to obtain reasonable LIFDI spectra of docosane, C₂₂H₄₄, only in very limited range of trapping potentials and hexapole DC offsets. Even the 21 V setting for trapping prevents detection of M⁺ ions, m/z 310. The narrow range of optimum settings for docosane was found at trapping potentials of 18 V combined with a RF hexapole DC bias of 1 V.

Even under optimum conditions, there is some H₂ loss observed at m/z 230. H₂ losses from alkane molecular ions can be field-induced but these also occur by fragmentation of these ions upon CID.

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References