EVALUATION AND OPTIMIZATION OF ELECTRON CAPTURE DISSOCIATION EFFICIENCY IN FT-ICR MASS SPECTROMETRY

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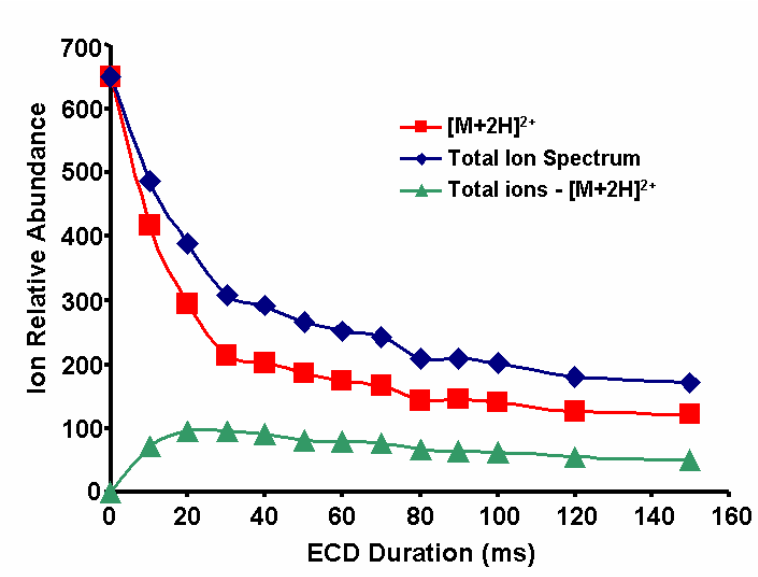
Results and Discussion

Electron capture dissociation (ECD) efficiency has typically been lower than for other dissociation techniques. Here we characterize experimental factors that limit ECD and seek to improve its efficiency. ESI FT-ICR ECD mass spectra were acquired with NHMFL's homebuilt 9.4 T FT-ICR instrument in Tallahassee, FL. Efficiency of precursor to product ion conversion was measured for a range of peptide (~15 % efficiency) and protein (~33 % efficiency) ions of differing sizes and charge states. Conversion of precursor ions to products depends on electron irradiation period and maximizes at ~5-30 ms (see Figure). The optimal irradiation period scales inversely with charge state. We demonstrate that reflection of electrons through the ICR cell is more efficient and robust than a single pass, because electrons can cool to the optimal energy for capture, which allows for a wide range of initial electron energy. Further, efficient ECD with reflected electrons requires only a short (~500 µs) irradiation period followed by an appropriate delay for cooling and interaction. Reflection of the electron beam results in electrons trapped in or near the ICR cell, and thus requires a brief (~50 µs) purge for successful mass spectral acquisition. Further electron irradiation of refractory precursor ions did not result in further dissociation. Possibly the ion cloud and electron beam are misaligned radially, or the electron beam diameter may be smaller than that of the ion cloud such that remaining precursor ions do not overlap with the electron beam. Several ion manipulation techniques and use of a large, movable dispenser cathode reduce the possibility that misalignment of the ion and electron beams limits ECD efficiency.



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References

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