Charge Reversal Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

V. V. Lobodin (NHMFL, Chemistry), J. J. Savory (NHMFL, Chemistry), N.K. Kaiser (NHMFL, Chemistry), P. W. Dunk (FSU, Chemistry), and A. G. Marshall (FSU, NHMFL, Chemistry)

Results and Discussion

We report the first charge reversal experiments performed by tandem-in-time rather than tandem-in-space MS/MS. Precursor odd-electron anions from fullerene C_{60}, and even-electron ions from 2,7-di-*tert*-butylfluorene-9-carboxylic acid and 3,3'-bicarbazole were converted into positive product ions ($^{-}CR^{+}$) inside the magnet of a Fourier transform ion cyclotron resonance mass spectrometer. Charge reversal was activated by irradiating precursor ions with high energy electrons or UV photons: the first reported use of those activation methods for charge reversal. We suggest that high energy electrons achieve charge reversal in one step as double electron transfer, whereas UV-activated $^{-}CR^{+}$ takes place stepwise through two single electron transfers and formally corresponds to a neutralization-reionization ($^{-}NR^{+}$) experiment.

Compounds ionized by "soft" non-destructive ionization techniques (e.g., electrospray ionization, matrix-assisted laser desorption ionization, etc.) typically require additional activation to produce structurally informative fragment ions. Negative ions from many compounds do not give informative CID mass spectra. $^{-}CR^{+}$ can potentially produce structurally informative fragment ions not readily generated by other dissociation techniques (see Figure 1). In addition, $^{-}CR^{+}$ can also generate unusual positive ions not accessible by conventional ionization methods.

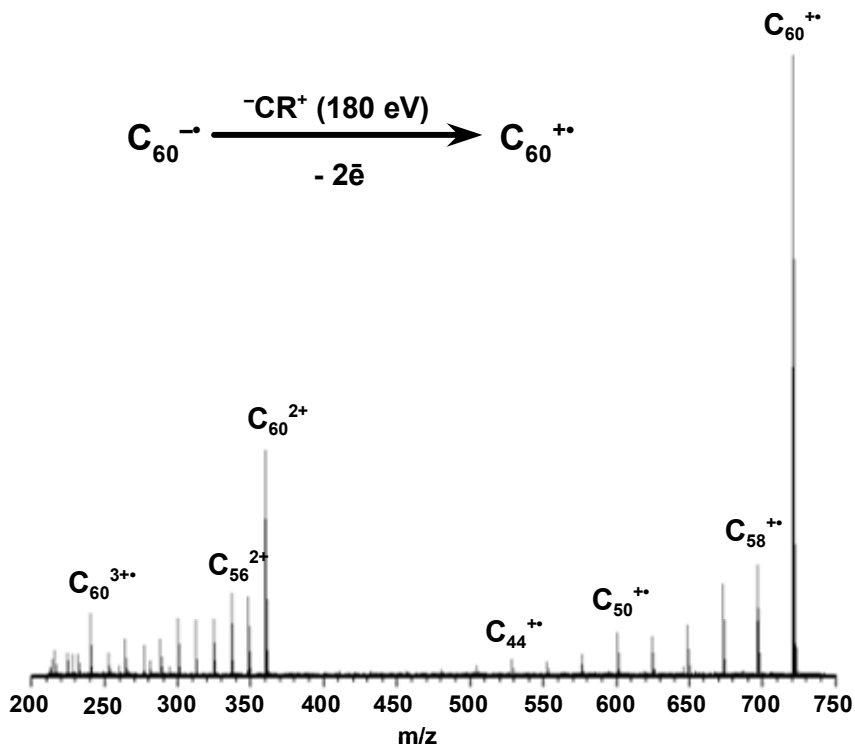

Figure 1.. $^{-}CR^{+}$ FT-ICR mass spectrum produced by irradiation of $C_{60}^{-\bullet}$ with 180 eV electrons. The $^{-}CR^{+}$ process yields $C_{60}^{+\bullet}$, C_{60}^{2+}, and C_{60}^{3+}, as well as a wealth of fragment ions not produced by positive electrospray ionization.

Acknowledgments

This work was supported by NSF DMR-06-54118 and the State of Florida. The authors thank Christopher L. Hendrickson and Ryan P. Rodgers for helpful discussions. We also acknowledge John P. Quinn for help with Figures design, and thank the Florida State University Shared High-Performance Computing Facility and staff for their generous allowance of supercomputer time.

References

[1] Lobodin, V. V., *et al.*, J. Am. Soc. Mass Spectrom., **24**, 213-221 (2013).