The Smallest Stable Fullerene, M@C_{28} (M=Ti, Zr, U): Stabilization and Growth From Carbon Vapor

P. W. Dunk (FSU, Chemistry), N. K. Kaiser (NHMFL, Chemistry), M. Mulet-Gas (Universitat Rovira i Virgil, Physical & Inorganic Chemistry), A. Rodríguez-Fortea (Universitat Rovira i Virgil, Physical & Inorganic Chemistry), J. M. Poblet (Universitat Rovira i Virgil, Physical & Inorganic Chemistry), H. Shinohara (Nagoya U., Chemistry), C. L. Hendrickson (FSU, NHMFL, Chemistry), A. G. Marshall (FSU, NHMFL, Chemistry) and H. W. Kroto (FSU, Chemistry)

Results and Discussion

The smallest fullerene to form in condensing carbon vapor has received considerable interest since the discovery of Buckminsterfullerene, C_{60}. Smaller fullerenes remain a largely unexplored class of all carbon molecules that are predicted to exhibit fascinating properties due to the large degree of curvature and resulting highly pyramidalized carbon atoms in their structures. However, that curvature also renders the smallest fullerenes highly reactive, making them difficult to detect experimentally. Gas-phase attempts to investigate the smallest fullerene by stabilization through cage encapsulation of a metal have been hindered by the complexity of mass spectra that result from vaporization experiments, including non-fullerene clusters, empty cages, and metallofullerenes. Here, we employ high resolution FT-ICR mass spectrometry to overcome that problem and investigate formation of the smallest fullerene by use of a pulsed laser vaporization cluster source. We find that the C_{28} fullerene stabilized by encapsulation with an appropriate metal atom forms directly from carbon vapor as the smallest fullerene under our conditions. Note the need for high mass resolution to distinguish ^{48}Ti from $^{12}C_4$ (see **Figure 1**). We show that M@C_{28} is formed by a bottom-up growth mechanism and is a precursor to larger metallofullerenes. In fact, it appears that the encapsulating metal species may catalyze or nucleate endohedral fullerene formation.[1]

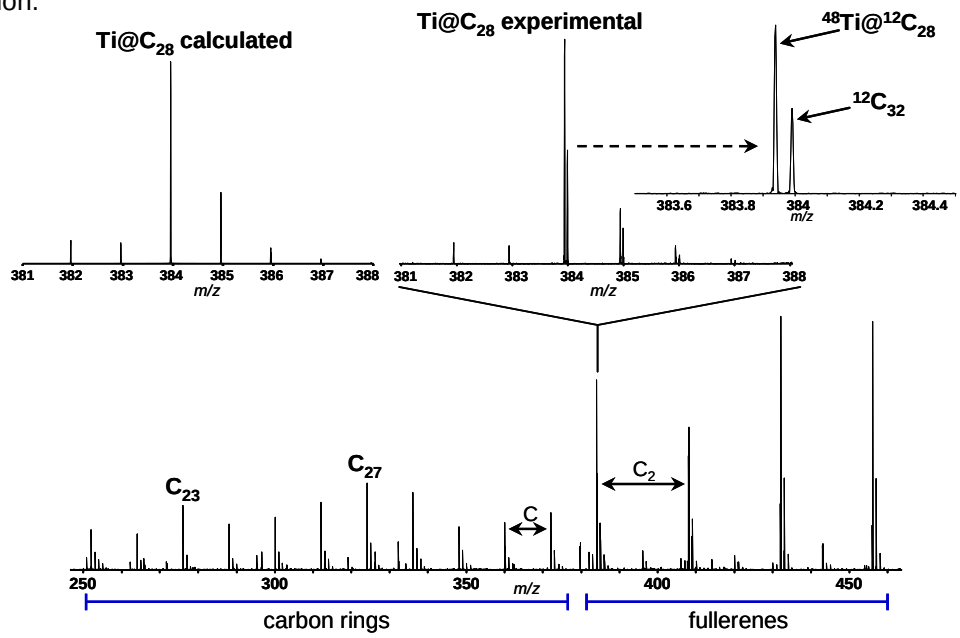

Figure 1. FT-ICR positive ion mass spectrum resulting from laser vaporization of a titanium-containing graphite target under conditions that probe the ring-to-fullerene transition. Ti@C_{28} forms as the smallest fullerene. The approximate 52 mDa mass difference between the smallest empty cage (C_{32}) and Ti@C_{28} is clearly resolved.

Acknowledgements

We thank M. A. Duncan for critical information regarding cluster source design, G. T. Blakney for modular ICR data system work, D. McIntosh for machining of custom ion source parts, and V. V. Lobodin for discussion. C.P.E thanks A. Zobelli for discussions. This work was funded by NSF Division of Materials Research through DMR-06-54118 and the Florida State University Research Foundation.

References

[1] Dunk, P. W., *et al.*, J. Am. Chem. Soc., **134**, 9380-9389 (2012).