SMALL ENDOHEDRAL METALLOFULLERENES: GROWTH MECHANISM IN THE TI@C_{2N} (2N=26-48) FAMILY

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The formation of the smallest fullerene C_{28} was reported recently using gas phase experiments combined with high-resolution FT-ICR mass spectrometry.[1] The tetravalent Ti^{4+} cation encapsulated by a series of non-IPR carbon cages between C_{28} and C_{50} has been demonstrated experimentally. However, less is known about the formation of endohedral fullerenes. Kroto *et al*. recently proposed the so-called Closed Network Growth (CNG) mechanism, which is based on a bottom-up formation process.[2] We show a detailed computational study for the formation of the Ti@C_{2n} (2n=26-48) family, linking the most stable C_{2n} isomers by a simple C_2 addition, and a few cases by a Stone-Wales (SW) transformation. Ingestion of a C_2 unit is an exergonic/exothermic cascade process and all the free energy barriers are attainable at temperature of fullerene formation (>1000 K).

In addition, the top-down mechanism reported by Irle and Morokuma[3] was also studied in our systems. We further verify that extrusion of C atoms from an already closed fullerene is much more energetically demanding than forming the fullerene in a bottom-up mechanism.

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