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## INVITED ARTICLE

## Large fullerenes in mass spectra

Paul W. Dunk<sup>a,b</sup>, Hiroyuki Niwa<sup>c</sup>, Hisanori Shinohara<sup>c</sup>, Alan G. Marshall<sup>a,b</sup> and Harold W. Kroto<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL, USA; <sup>b</sup>Ion Cyclotron Resonance Program, National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL, USA; <sup>c</sup>Department of Chemistry and Institute for Advanced Research, Nagoya University, Nagoya, Japan

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Fullerenes have been studied for nearly three decades and enormous advances have been made. Mass spectrometry is commonly used for investigations on the distribution of fullerenes formed from evaporated graphite targets, and soot produced from such targets. We report distributions of fullerenes formed by graphite evaporation by use of a pulsed supersonic cluster source and compare them to certain distributions synthesised by other techniques, such as arc discharge and combustion methods. We highlight the fact that physical processes can occur during the mass spectral analysis of fullerenes under certain conditions that may skew the observed distribution of cage sizes present in a sample. In some cases, an analysis of fullerene-containing soot can greatly exaggerate the relative abundance of large fullerenes compared to C<sub>60</sub> and medium-sized fullerenes, depending on the particular experimental setup.

**Keywords:** fullerenes; mass spectrometry

## 1. Introduction

It is well-known in the field that the magnitudes of mass spectrometric peaks require great care when interpreting the relative abundances of the parent neutrals in a sample. There may be a wide range of complicated reasons for this and a key issue is, among other things, the ionisation mechanism. Here, we draw attention to the fact that such phenomena can cause significant errors in an interpretation of the relative abundances of smaller (C<sub>2n</sub> < C<sub>60</sub>–C<sub>70</sub>) with respect to medium (~C<sub>80</sub>–C<sub>100</sub>) and in particular the much larger fullerene cages (C<sub>2n</sub> > C<sub>100</sub>–C<sub>500</sub>) from fullerene-containing soot or extracted samples. Although fullerenes originally detected were produced by the laser ablation of graphite [1], commercial samples are now typically generated by a carbon arc discharge in an inert atmosphere, such as helium [2] or by the combustion of methane and other hydrocarbons [3]. Figure 1(a) shows the cluster cations directly produced by laser vaporisation [4] of graphite in a pulsed supersonic cluster source. In that experimental setup, fullerenes remain in the gas phase until they are detected by the mass spectrometry. When the arc discharge method is used, the fullerenes produced in the gas phase are generally solvent-extracted from the carbon soot also produced by the process. Solvent extraction with toluene and similar solvents, for example, is a common way to extract popular fullerenes from the bulk soot. Figure 1(b) shows the fullerene distribution from an o-xylene extract of soot produced by an arc discharge of graphite. C<sub>72</sub>, C<sub>68</sub>–C<sub>62</sub>, and all fullerenes smaller than C<sub>60</sub>, however, are not detected

in the fullerene-containing soot because they are insoluble or ‘react away’ (i.e., unstable) in the solid state. In fact, a large number of fullerene species – especially large ones – appear to be insoluble in common solvents [5] and thus the comparison of all small-, medium-, and large-sized cages in a given extract is not an accurate reflection of the fullerene cage size distribution actually produced by the vapourisation of graphite.

## 2. Fullerenes from soot and extracts

Analysis of raw soot produced by the evaporation of graphite by the use of the arc discharge, or combustion methods with other carbon starting materials, therefore, will be a more accurate reflection of the fullerene distribution than solvent extracted samples. However, fullerenes that exhibit significant curvature (i.e., smaller fullerenes and non-isolated pentagon rule species) tend to react with other fullerenes or other carbon species in the soot [6]. Consequently, smaller pristine fullerenes generally cannot be detected in arc discharge extracts or soot. Subsequent analysis of the remaining medium- to large-sized cages, which form weaker bonds to other carbon species in soot than the smallest fullerenes, can be analysed by laser desorption mass spectrometry (LD-MS). Mass spectrometric investigation of samples by means of LD-MS, however, still must proceed with caution because fullerene coalescence and/or fragmentation can occur. Fullerene coalescence is a process in which at least

\*Corresponding author. Email: [kroto@chem.fsu.edu](mailto:kroto@chem.fsu.edu)

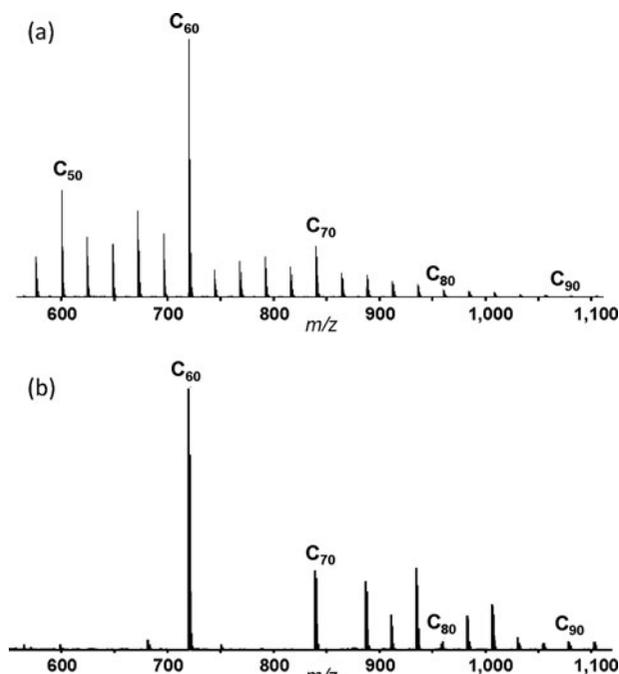


Figure 1. Fullerenes formed by the vaporisation of graphite: (a) Fourier transform ion cyclotron resonance (FT-ICR) mass spectrum of the medium sized to the larger fullerene region for  $C_{2n}$  positive ions observed directly from the vaporisation of graphite by the use of a pulsed laser vaporisation cluster source, (b) mass spectrum of fullerenes produced by the arc discharge method from an *o*-xylene extracted fullerene-containing soot.

two highly thermally excited fullerenes, such as  $C_{60}$  may merge together to form a series of larger fullerene cages that contain  $\sim 120$  carbon atoms [7]. The process can skew the fullerene distribution, making larger cages apparently more abundant than they were in the original sample. Fullerene coalescence occurs when the laser fluence and the gas-phase fullerene density are sufficiently high. As another example, the Nd:YAG laser desorption followed by electron ionisation yields  $C_{60}^+$  (99%) and  $C_{70}^+$  from a thin ( $0.5 \mu\text{g}$  fullerene/ $\text{cm}^2$ ) yellow film of chromatographically purified  $C_{60}$  in benzene applied to a stainless steel probe tip, whereas the same treatment of a thick ( $>5 \text{ pg}$  fullerene/ $\text{cm}^2$ ) black deposit yields not only  $C_{60}^+$  but a broad distribution of giant fullerenes extending from  $C_{200}^+$  to more than  $C_{400}^+$  [8]. Fragmentation of carbon cages can occur at a high laser fluence yielding smaller cage products, which would also produce an observed distribution different from the ‘actual’ distribution. It is emphasised that pure fullerene cages  $C_{2n}$  ( $C_{2n} = 62\text{--}68$ ) as well as all fullerenes with  $C_{2n} < C_{60}$  have not been isolated from the soot in pristine form, a result rationalised on the basis that they cannot conform to the isolated pentagon rule [6]. Furthermore, empty cage  $C_{72}$  has also never been isolated, probably because it is unstable relative to  $C_{70}$ . These observations suggest that when the laser fluence is too high, at least some significant compo-

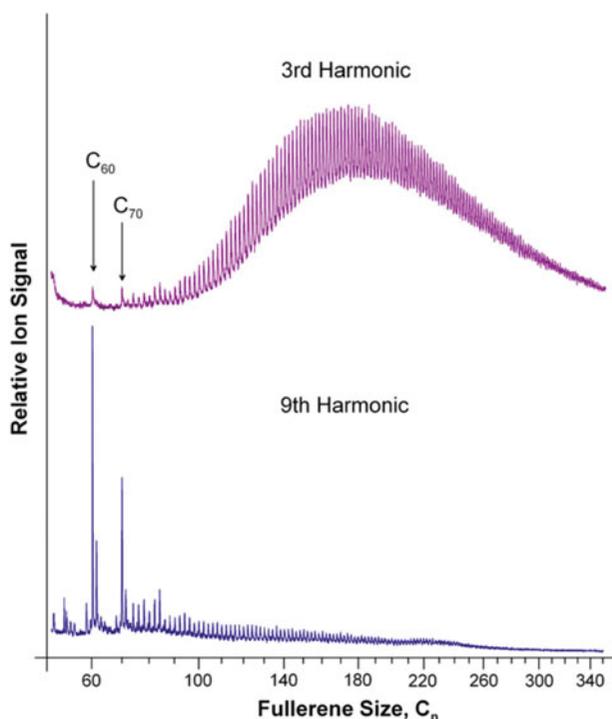


Figure 2. Third harmonic (top) and ninth harmonic (bottom) laser ionisation mass positive ion spectra produced from the same fullerene-containing sample. The relative abundance of the large fullerenes to the medium fullerenes is greatly exaggerated in the top spectrum, whereas the bottom spectrum more accurately reflects the abundance of neutral species. Adapted from Ref. [10], used with permission.

nent of the fullerenes detected in such mass spectra may have been produced during the sampling process. Thus, in such a scenario, the observed mass spectrum may not be a reliable indication of the fullerenes actually produced in the target sample [9]. Moreover, the relative abundances of the unstable fullerenes relative to those of  $C_{60}$  and  $C_{70}$  from the fullerene-containing soot in such mass spectra may indicate that the fullerene distribution is a result of fragmentation or an early stage gas-phase carbon aggregation process.

Another factor that may play a key role is the ionisation energy, particularly for LD-MS investigations that use laser radiation to directly ionise neutral cages for a mass spectroscopic detection. The upper spectrum in Figure 2 (labelled third harmonic) is the positive ion  $m/z$  distribution when (1) the third harmonic of an Nd:YAG laser is used to sublime the products and (2) also ionise them [10]. The lower spectrum in Figure 2 (labelled ninth harmonic) is the mass spectrum produced when processes (1) and (2) take place, but also another process occurs in which (3) the remaining neutrals are ionised by the ninth harmonic of the Nd:YAG laser. When the results of the two experiments are compared to each other (and to Figure 1), there is a major difference in overall fullerene abundance contours. In particular, the relative intensity of  $C_{60}$  to the summed intensities to all

of the larger species has increased by approximately two orders of magnitude from the third harmonic to the ninth harmonic data. Raebiger *et al.* rationalise that observation on the basis of, among other things, the difference in ionisation energies for what they term large gap fullerenes (LGF) and small gap fullerenes (SGF) [10,11]. The SGF fullerenes (cage sizes of  $\sim C_{80}$  to larger than  $C_{100}$ ) require only one third harmonic photon to ionise them, whereas LGF fullerenes (such as  $C_{60}$ ) require two or more. However, both subsets can be ionised by a single ninth harmonic photon. Raebiger *et al.* write 'This (effect) dramatically skews the relative signal intensity of Nd:YAG 3<sup>rd</sup> harmonic mass spectra toward extreme exaggeration of small band gap fullerene abundance', in which the large cage ( $> 100$  carbon atoms) intensity is clearly distorted. They also took great care to eliminate, as much as possible, the significant problems caused by variation in solubility during the extraction of their fullerene samples from soot. These results seem to be in line with the amount of isolated  $C_{60}$  or  $C_{70}$  product relative to higher fullerenes ( $C_{76}$ ,  $C_{78}$ ,  $C_{84}$ , etc.) from the fullerene-containing soot [12]. In addition, another possible process that may skew the observed relative abundance to larger cages in a mass spectrum could be 'ion levelling', in which, for example, a collision between a neutral SGF and  $C_{60}^+$  results in  $C_{60}$  and  $SGF^+$ .

### 3. Conclusions

To sum up, great care should be taken when making conclusions regarding fullerene distributions from a matrix of soot or solvent-extracted samples that contain a diverse range of cage sizes.

### Disclosure statement

No potential conflict of interest was reported by the authors.

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