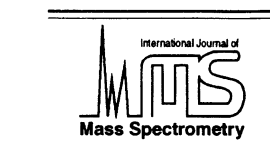




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Some new diatomic molecule containing endohedral fullerenes

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Abstract

Several new diatomic molecule-containing endohedral fullerenes were prepared by heating C₆₀ or C₇₀ under high pressures of the corresponding gases. The species prepared are N₂@C₆₀, N₂@C₇₀, ¹³CO@C₆₀, and ³He²²Ne@C₇₀. Their existence was demonstrated through high sensitivity, wide dynamic range mass spectrometry. Out of two thousand C₆₀ molecules about one is observed to incorporate N₂. The nitrogen molecule containing endohedral molecules are stable and the mass spectrometric signal is not lost even after several hours heating at 500 K. The corresponding endohedral ions undergo the Rice shrink-wrap mechanism; a mass-analyzed ion kinetic energy spectrum demonstrates the loss of a C₂ unit from the cage. The observation of ¹³CO@C₆₀ by mass spectrometry opens up the possibility for future NMR studies of this molecule. The observation of ³He²²Ne@C₇₀ is in accordance with the “promoter” mechanism of Thiel and co-worker [J. Am. Chem. Soc. 118 (1996) 7164; Helv. Chim. Acta 80 (1997) 495], whereby the singly and doubly occupied fullerenes are in equilibrium but the empty and filled fullerenes are not. (Int J Mass Spectrom 210/211 (2001) 241–247) © 2001 Elsevier Science B.V.

Keywords: Endohedral fullerenes; High-temperature high-pressure incorporation; MIKEs

1. Introduction

Buckminsterfullerene, C₆₀ was discovered through the observation of an intense peak at a mass to charge ratio $m/z=720$, in the mass spectra of carbon clusters [1]. Mass spectrometry has thus played a decisive role in the field of fullerenes. One of the fascinating properties of fullerenes is their ability to trap atoms and small molecules inside the cage. The first evidence for endohedral metallofullerenes was reported

soon after the discovery of C₆₀ in 1985 [2]. However, only in 1991 could endohedral metallofullerenes be isolated in macroscopic amounts. This was achieved by using laser- or arc-vaporization [3] of graphite-metal composites in helium. Endohedral metallofullerene compounds are stable by virtue of the transfer of electrons from the metal to the carbon cage. Schwarz and co-workers in high-energy ion beam collision experiments [4,5] have first observed endohedral fullerenes with a noble gas atom inside the fullerene cage. Saunders and co-workers have shown that neutral noble gas compounds can be prepared by heating fullerenes under high pressure of a noble gas [6,7]. Endohedral fullerenes of the noble gases were

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Dedicated to Professor Nico Nibbering an excellent scientist and a good friend

prepared using this method. In the latter compounds the endohedral atoms are trapped inside because the holes in the cage are too small for them to escape. Typical yields of incorporation in the early experiments were around 0.1% for helium, neon, argon, and krypton and around 0.03% for xenon. Recent experiments have been more successful and a considerably higher degree of xenon incorporation (0.25%) has been achieved [8]. Repetitive labeling of the same material increases the yields.

Mass spectrometry was instrumental in demonstrating the existence of endohedral noble gas fullerenes. We have recently demonstrated using mass spectrometric techniques, the existence of artificial noble gas molecules inside neutral fullerenes, first for Ne_2 [9] and later for He_2 [10]. The species were ionized by electron impact. A wide dynamic range was required in order to observe them mass spectrometrically. The He_2 “molecule” could also be observed by ^3He NMR.¹⁰ High-temperature and high-pressure labeling of C_{70} with ^{22}Ne or ^3He led to a ratio of empty C_{70} to mono-occupied to di-occupied of 1000:1:0.02, for Ne and 37:1:0.05, for He, respectively. Putting a pair of noble gas atoms inside a fullerene cage effectively creates an artificial molecule. The atoms are forced into contact by the cage and vibrate and rotate within the cage in the same manner as a diatomic molecule. The group of Schwarz and co-worker [11] had observed earlier in pioneering work the sequential insertion of ^3He and ^4He into C_{60}^+ . However these doubly occupied species were observed on the short time scale (μs) of an ion beam/collision chamber experiment. The neutral species observed more recently [9,10] have long shelf lives.

This research is still ongoing. We have now been able to detect and study several new endohedral compounds. We have reported recently on the mass spectrometry of N@C_{60} and N@C_{70} made by the ion implantation technique [12]. The present study is dedicated to $\text{N}_2@\text{C}_{60}$, $^{13}\text{CO@C}_{60}$, and HeNe@C_{70} . The long range purpose of these studies is to be able to produce endohedral compounds which can be analyzed by NMR (e.g. $^{13}\text{CO@C}_{60}$) or by electron paramagnetic resonance (EPR) (as has already been

demonstrated for e.g. N@C_{70} [13–15]), in addition to mass spectrometry, even though the degree of incorporation of the endohedral species is small.

In addition to reporting on the electron impact induced mass spectra of the endohedral compounds we will concentrate briefly on their gas phase ion chemistry, specifically, the unimolecular fragmentations obtained through mass-analyzed ion kinetic energy (MIKE) spectrometry. Fullerenes, endohedral fullerenes, and their respective cations are generally known to undergo consecutive C_2 eliminations in what used to be called the Rice shrink-wrap mechanism [16,17]. Using the technique of MIKE spectrometry it is possible to deduce kinetic energy release distributions (KERDs) for unimolecular decompositions. Modeling of these KERDs allows extraction of valuable information on the energetics and dynamics of the reactions involved. The C_2 binding energies of the empty fullerenes, endohedral metallofullerenes, and noble gas endohedral fullerenes have been deduced from such experiments [18–20].

2. Experimental

2.1. Mass spectrometry and MIKEs

Measurements were performed on a high-resolution double-focusing mass spectrometer of reversed geometry, the VG-ZAB-2F [21,22] running mass spectra at a very high-dynamic range as well as using the technique of MIKE spectrometry. The endohedral fullerene cations were obtained by ionization of the corresponding neutral samples.

The samples were introduced into the mass spectrometer using the direct insertion probe and evaporated at $\leq 400^\circ\text{C}$. The electron-impact conditions were as follows: electron ionizing energy, 70 eV; emission current, 5 mA; ion source temperature, 400°C ; resolution, 1100 (10% valley definition). Metastable ion peak shapes were determined by scanning the electrostatic analyzer and using single-ion counting. Ion counting was achieved by a combination of an electron multiplier, amplifier/discriminator, and multichannel analyzer [23]. The experiments

were performed at 8 kV acceleration voltage and a main beam width of 5 V.

2.2. Preparation of endohedral fullerenes

The neutral samples were prepared by methods described in detail previously [6,7]. NeHe@C₇₀ was prepared as follows: about 100 mg of 96% pure C₇₀ (MER Corporation) were placed inside a 4-in. annealed oxygen-free copper tube sealed at one end with a custom-made crimping tool. The open end was attached to a vacuum line using a glass adapter. The tube was evacuated and left under vacuum for approximately 5 min. Neon enriched in ²²Ne(70%) and ³He gases were introduced. In order to assure even mixing of the gases, the length of the mercury in the manometer was divided into equal portions each of one inch. Each gas was introduced sequentially in 1 in. portions beginning with ³He. The tube was then cooled in liquid nitrogen and sealed to give an ampoule. The mixture was subjected to high-temperature (650 °C) and pressure (3000 atm) treatments in a steel vessel over 8 h. The tube, now flattened, was retrieved and cut to remove the solid. A yield of around 70% was obtained after Soxhlett extraction using CS₂ as a solvent and drying of the solid. The process was repeated two more times on material extracted from each run. This was done to increase yields of the diatomic species. The ¹³CO@C₆₀ and N₂@C₆₀ (or N₂@C₇₀) were prepared by heating the corresponding fullerene at 650 °C and 3500 atm in the presence of the desired gas. After 8 h, the sample was cooled, extracted with CS₂ and dried. Attempts at preparation of H₂O@C₆₀ and H₂O@C₇₀ samples were carried out as follows: in two separate copper tubes, 100 mg of solid C₆₀ and C₇₀ were deposited and treated in the same way as described previously. Some water vapor was distilled into each of the tubes. The exact volume of water in each of the tubes was, however, not determinable. The sealed ampoules were subjected to the same high-temperature and pressure treatments. Extraction of the material gave a yield of about 80% in C₆₀, and slightly less in the C₇₀ case.

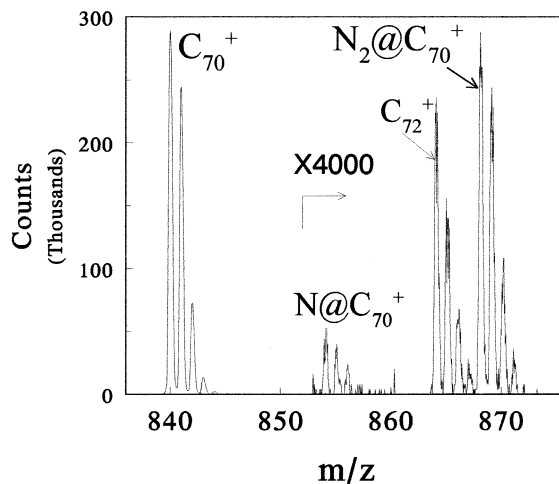


Fig. 1. Mass spectrum for a C₇₀ sample containing N₂@C₇₀ (and C₇₂ and possibly N@C₇₀). The spectrum was run on the ZAB-2F using electron impact ionization at 70 eV. The multiplet at C₇₀ is due to ¹³C isotopes as is the one for the nitrogen endohedral compound. The *m/z* scale gives the mass to charge ratio. Note the amplification factor of ×4000 for the intensity of ions at *m/z* > 853. The N₂@C₇₀ compound was prepared by the high-pressure high-temperature incorporation technique.

3. Results and discussion

3.1. Mass spectra of N₂@C₆₀ and N₂@C₇₀

The combination of the ZAB-2F mass spectrometer with ion counting and with the multichannel analyzer allowed the detection of even very low degrees of incorporation into the fullerene cage, because of the very wide dynamic range achieved. Fig. 1 demonstrates this for N₂@C₇₀. Beginning at a mass to charge ratio *m/z* 868, Fig. 1 shows the presence of a series of small peaks that is the unique signature of N₂@C₇₀⁺, whose relative intensities can be fit knowing the isotopic abundance of ¹³C. The ratio of the filled to the empty fullerene is seen to be about 1:4000 for N₂@C₇₀. In addition, one observes the isotopic multiplet of C₇₂⁺ and a small but discernible signal of N@C₇₀⁺. The latter ion has been observed with much greater abundance before [12] in ion beam implantation experiments. Fig. 2 presents the results for N₂@C₆₀. The isotopic multiplet of N₂@C₆₀⁺ is clearly observed beginning at *m/z* 748.

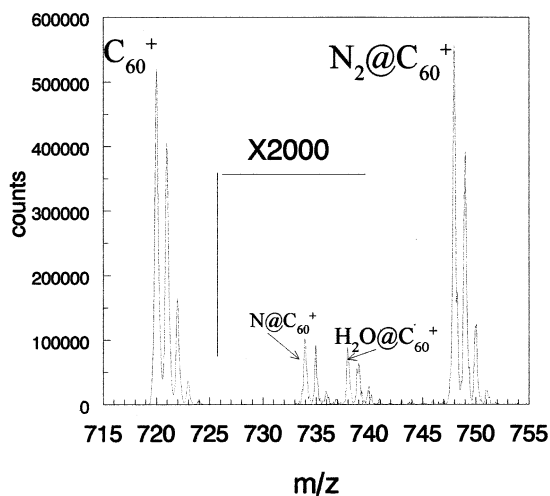


Fig. 2. Mass spectrum for a C_{60} sample containing $N_2@C_{60}$ (and possibly $N@C_{60}$ and $H_2O@C_{60}$). Note the amplification factor of $\times 2000$ for the intensity of ions at $m/z > 725$.

The ratio of filled to empty fullerene is about 1:2000 in this experiment. A small series of peaks is also observed for $N@C_{60}^+$. This species has been observed before upon ion beam implantation [12]. Since the N^+ beam was made from molecular nitrogen there was a small signal of $N_2@C_{60}^+$, the ratio of filled to empty fullerene being 1:21 000 for $N_2@C_{60}$ for that specific sample [12]. The ratio $N@C_{60}^+ : N_2@C_{60}^+$ is reversed in favor of the molecular nitrogen containing endohedral species in the present experiment when the synthesis involves high-temperature, high-pressure incorporation of molecular nitrogen (compare the present Fig. 2 with Fig. 1 of [12]).

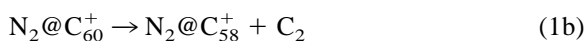
$N@C_{60}$ is stable at room temperature at ambient conditions and no loss of the EPR signal intensity is observed after storage for several months in the dark. Above 500 K, however, the EPR and the mass spectrometric signal intensities start to decrease on a time scale of minutes [8,12]. We were interested to find out whether the mass spectrometric signal of $N_2@C_{60}$ is also lost following a heating period. An experiment was done by accurately dividing a sample in half; one half was heated at 230 °C for 4 h whereas the other half was used as a control. The two samples were subjected to mass spectrometric studies. Whereas the $N_2@C_{60} : C_{60}$ ratio was unaffected by

heating, the ratio $N@C_{60} : N_2@C_{60}$ was observed to decrease as expected from the thermal instability of atomic nitrogen inside the fullerene cage.

The mechanism of production of $N@C_{60}$ and of $N@C_{70}$ in the present series of experiments is not quite clear. An additional interesting series of peaks observed beginning at m/z 738 has been tentatively ascribed to $H_2O@C_{60}^+$ (Fig. 2). All of the three species observed, namely $N_2@C_{60}$, $N@C_{60}$, and $H_2O@C_{60}$ may be formed by the so-called promoter mechanism [9,24] where the promoter is a foreign substance (free radical?) that forms an intermediate by adding to the fullerene cage. The observation of the series of peaks beginning at m/z 738 has led to an unsuccessful synthetic effort to produce $H_2O@C_{60}$ on its own. When nitrogen was not present in the synthesis, the series of peaks beginning at m/z 738 was not observed.

3.2. Unimolecular decomposition of $N_2@C_{60}^+$

The present data are the first efforts we are aware of in the direction of mass spectrometry of the nitrogen molecule-containing endohedral fullerenes. It is particularly interesting to study the unimolecular reactions of $N_2@C_{60}^+$. We have demonstrated [12] that, contrary to endohedral metallofullerenes and noble gas-containing endohedral fullerenes, $N@C_{60}^+$ does not demonstrate loss of C_2 but undergoes a unique nitrogen atom loss reaction. In principle there should be competition among the unimolecular reactions of endohedral fullerenes between the elimination of the endohedral species and the loss of a C_2 unit from the cage. For example in the case of $N_2@C_{60}^+$, there are two possible channels:



MIKE spectrometry is a powerful technique for determining which channel the endohedral fullerenes follow in their unimolecular reactions. Fig. 3 represents the metastable ion peak shape for the dissociation taking place in the second field free region of the ZAB-2F. The position of the maximum of the meta-

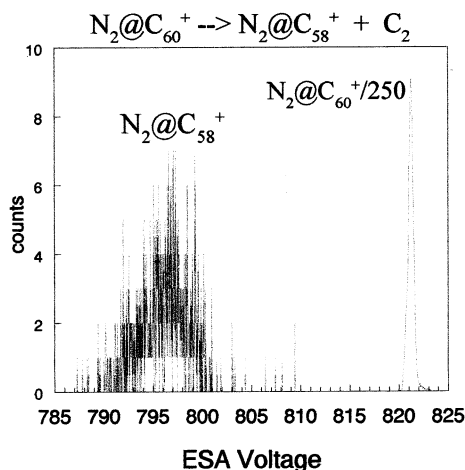


Fig. 3. Metastable ion peak shape for the indicated reaction of loss of C_2 from $N_2@C_{60}^+$ taking place in the second field free region of the VG-ZAB-2F obtained through a MIKE scan of the electrostatic analyzer (ESA) voltage. The precursor parent ion peak is given on a reduced (1/250) intensity scale. The metastable peak maximum is shifted slightly upwards from its calculated ESA voltage position (794.6 V). This is entirely due to the very low signal (4–6 ion counts at the maximum). The N_2 loss peak if it existed should have appeared at 790.3 V.

stable ion peak clearly indicates that $N_2@C_{60}^+$ undergoes the Rice shrink-wrap mechanism [16,17], that is the C_2 elimination, reaction (1b). Contrary to the atomic nitrogen containing endohedral fullerene that loses the nitrogen atom from the cage [12], molecular nitrogen is retained in the cage of internally excited $N_2@C_{60}^+$ and the cage loses a C_2 unit instead. Reaction (1a) does not occur. The increased stability of $N_2@C_{60}^+$ compared to $N@C_{60}^+$ toward loss of the endohedral species in the field free region of the ZAB-2F mass spectrometer correlates with the increased thermal stability of the corresponding neutral noted earlier. It has been demonstrated computationally [25] that the nitrogen atom escapes the cage via formation of intermediates that are covalently bound adducts with endohedral aza bridges. An autocatalytic bond breakage ensues that requires less energy than the considerable cage distortion needed for penetration by molecular nitrogen. In a recent review paper [26] of the current status of the C_2 binding energy in C_{60}^+ we have come to the conclusion that the evaporation energy (or binding energy) $\Delta E_{\text{vap}}(C_{60}^+) \geq 9.5$ eV.

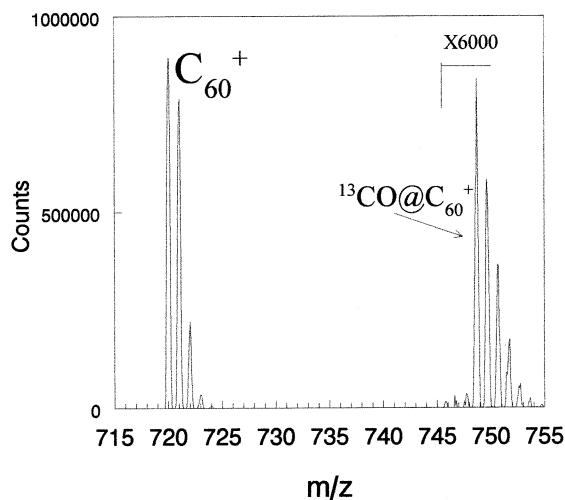


Fig. 4. Mass spectrum for a C_{60} sample containing $^{13}CO@C_{60}$. Note the amplification factor of $\times 6000$ for the intensity of ions at $m/z > 745$.

Since N_2 evaporation from $N_2@C_{60}^+$, reaction (1a), does not compete with reaction (1b), it must be concluded that the evaporation energy of the nitrogen molecule from $N_2@C_{60}^+$ [i.e. the activation energy for reaction (1a)] is higher than that for the C_2 evaporation, reaction (1b). The C_2 elimination reaction undergone by $N_2@C_{60}^+$ is totally analogous to the usual behavior of endohedral metallofullerenes and noble gas containing endohedral fullerenes, which do not lose the endohedral atom before they reach a critical size.

3.3. Mass Spectra of $^{13}CO@C_{60}$

Fig. 4 presents the results for $^{13}CO@C_{60}$. The isotopic multiplet of $^{13}CO@C_{60}^+$ is clearly observed beginning at m/z 749. The ratio of filled to empty fullerene is about 1:6000 in this experiment. Some interesting NMR experiments on ^{13}CO intercalated in C_{60} were carried out recently [27]. The present mass spectrometric observation of the endohedral ^{13}CO species is promising for future NMR experiments although considerably higher degrees of incorporation in C_{60} will be necessary in order to observe NMR spectra.

Attempts at obtaining MIKE spectra for $^{13}CO@C_{60}^+$ failed because of interference from artifact peaks in the spectrum.

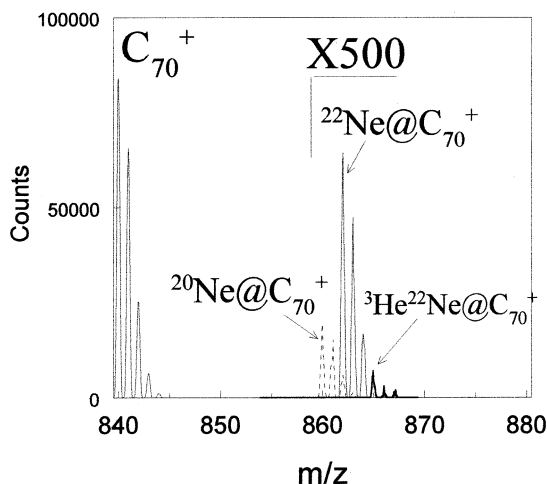


Fig. 5. Mass spectrum of a C_{70} sample containing $Ne@C_{70}$ [enriched in $^{22}Ne(70\%)$] and $^3HeNe@C_{70}$. Note the amplification factor of $\times 500$ for the intensity of ions at $m/z \geq 860$. $^{20}Ne@C_{70}^+$ (dashed line); $^{22}Ne@C_{70}^+$ (solid line); $^3He^{22}Ne@C_{70}^+$ (bold line).

3.4. Mass Spectra of $^3He^{22}Ne@C_{70}$

We found a new artificial noble gas molecule inside C_{70} , namely $HeNe@C_{70}$. As in the previous cases of $Ne_2@C_{70}$ [9] and $He_2@C_{70}$ [10], the work required careful fitting of calculated and experimental isotopic contributions to the mass spectra. Typical mass spectra are reproduced in Figs. 5 and 6. In view of the very low abundance of isotopic $HeNe@C_{70}$

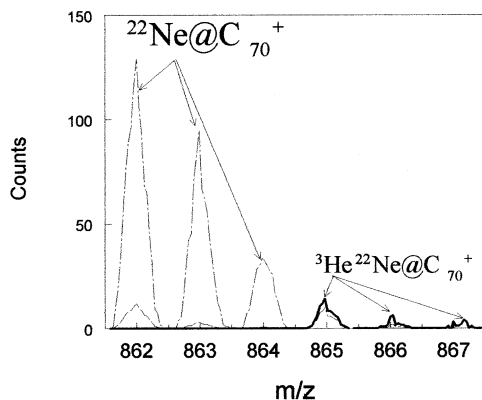


Fig. 6. Mass spectrum of a C_{70} sample containing $Ne@C_{70}$ [enriched in $^{22}Ne(70\%)$] and $^3HeNe@C_{70}$; part of Fig. 5 on an expanded scale. $^{20}Ne@C_{70}^+$ (dashed line); $^{22}Ne@C_{70}^+$ (long and short dashed line); $^3He^{22}Ne@C_{70}^+$ (solid line).

Table 1
Neon and helium inside C_{70}

Experiment No.	$^{20}Ne@C_{70}^+$ $^{22}Ne@C_{70}^+ : C_{70}$	$^3He@C_{70} : C_{70}$	$^3He^{22}Ne@C_{70}^+ : ^{22}Ne@C_{70}^+$
1	19.9:10 000	4.7:1000	7.8:100
2	18.8:10 000	5.0:1000	5.7:100
3	22.9:10 000	4.2:1000	4.2:100
4	21.8:10 000	6.0:1000	6.9:100
5	22.8:10 000	4.7:1000	4.7:100
6	25.4:10 000	5.0:1000	7.3:100
7	22.7:10 000	6.4:1000	6.6:100
Average	2.2(± 0.2):1000	5.1(± 0.8):1000	6.2(± 1.3):100

peaks, the final results summarized in Table 1, were obtained by averaging seven experiments, each of which was the result of many repetitive MCA scans.

Approximately 2% of the neon-labeled C_{70} contain two neon atoms [9] whereas 5% of the helium-labeled C_{70} contain two helium atoms [10]. These ratios are close to equilibration. The new artificial noble gas molecule detected demonstrates a similar degree of double occupancy (Table 1) of $\sim 6.2\%$.

The observation of ratios of double occupancy to single occupancy, which are close to the ones expected at equilibrium, is in agreement with the promoter mechanism of Thiel and co-worker [24] for noble gas labeling of fullerenes. Empty and filled fullerenes are not in equilibrium under the experimental conditions of high-pressure and high-temperature incorporation of the noble gases. However, once a window opens up in the C_{70} cage to allow the entrance of one noble gas atom, a second atom requires very little additional energy to enter. The window then closes, trapping the gas atoms inside and the singly occupied and doubly occupied species are at equilibrium.

High-pressure and high-temperature incorporation of Ne and He led to the additional observation of an isotopic multiplet beginning at m/z 858 (Fig. 7) that can be tentatively ascribed to an $H_2O@C_{70}$ endohedral species. However, as noted earlier, a well-planned synthesis of water containing endohedral species of C_{60} and C_{70} failed to detect these species in the corresponding mass spectra.

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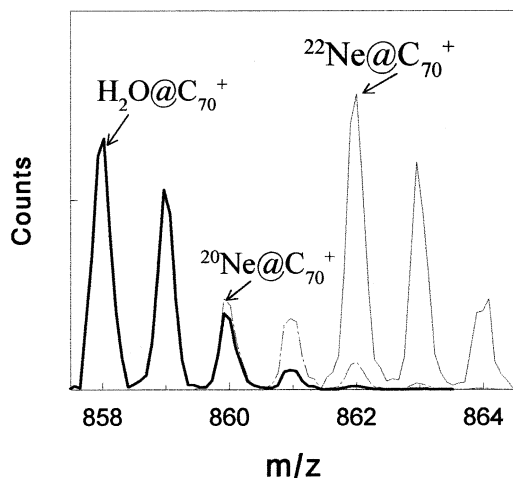


Fig. 7. Partial mass spectrum of a C_{70} sample containing $Ne@C_{70}$ [enriched in ^{22}Ne (70%)] and possibly $H_2O@C_{70}$. $H_2O@C_{70}^+$ (solid bold line); $^{20}Ne@C_{70}^+$ (long and short dashed line); $^{22}Ne@C_{70}^+$ (solid line).

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