ELSEVIER International Journal of Mass Spectrometry 213 (2002) 183–189 www.elsevier.com/locate/ijms

Electron affinity of some trimetallic nitride and conventional metallofullerenes

I.N. Ioffe[a], A.S. Ievlev[a], O.V. Boltalina[a,]*, L.N. Sidorov[a], H.C. Dorn[b], S. Stevenson[b,c], G. Rice[b]

[a]Moscow State University, Chemistry Department, Moscow, 119899, Russia
[b]Virginia Polytechnic Institute of State University, Department of Chemistry, Blacksburg, VA 24061, USA
[c]Luna NanoMaterials, Blacksburg, VA 24060, USA

Received 19 June 2001; accepted 14 September 2001

Abstract

The electron affinity of a series of discandium endohedral fullerenes and new trimetallic nitride endohedral molecules $Sc_xEr_{3-x}N@C_{80}$ was determined by means of the Knudsen cell mass spectrometry—ion-molecular equilibria method. Some considerations were made concerning the influence of the charge transfer from the endohedral atoms to the carbon cage on the electron affinity of the endohedral molecule. (Int J Mass Spectrom 213 (2002) 183–189) © 2002 Elsevier Science B.V.

Keywords: Knudsen cell mass spectrometry; Ion-molecular equilibria; Electron affinity; Endohedral fullerenes

1. Introduction

Since the first synthesis and separation of endohedral lanthanofullerenes in macroquantities [1], a large group of fullerenes with entrapped lanthanide and other metal atoms have been successfully prepared and extensively studied by means of different experimental methods. Scandium endohedral compounds are known to be easily produced with high yields of di- and even triscandium fullerenes. Various $Sc_n@C_m$ compounds, such as $Sc@C_{82}$ [2,3], $Sc_2@C_{74}$ [3], $Sc_2@C_{82}$ [2,4,5], $Sc_2@C_{84}$[2,4], $Sc_2@C_{86}$[5], and $Sc_3@C_{82}$ [2,3] were isolated and studied. X-ray powder diffraction studies with data analysis by maximum entropy method applied to $Sc_2@C_{84}$ [6], $Sc@C_{82}$ [7] and $Sc_3@C_{82}$ [8] provided direct evidence for the location of the metal atom inside the fullerene cage (D_{2d} isomer of C_{84}, C_{2v} and C_{3v} isomers of C_{82}, correspondingly). The value of charge transfer from each scandium atom to the fullerene cage calculated from the electron density distribution was found to be 2.2—in good agreement with the theoretical predictions [9–11]. Some information about the symmetry of scandium endohedral fullerene molecules was also provided by magnetic resonance methods: a D_{2d} cage for $Sc_2@C_{84}$ was inferred by ^{13}C-NMR [12] and a C_{3v} cage was proposed for $Sc_3@C_{82}$ on the basis of the ESR hyperfine structure [13]. Erbium endohedral fullerenes were studied much less extensively than their scandium analogs. However, several compounds, namely $Er@C_{82}$ [14], $Er_2@C_{82}$ [14,15], $Er_2@C_{84}$ [14], and $Er@C_{60}$ [16] were isolated and characterized by means of UV-Vis-NIR absorption spectroscopy and mass spectrometry. The studies of the photoluminescence of the erbium

---

* Corresponding author. E-mail: ovb@thermo.chem.msu.ru

PII S1387-3806(01)00532-2

endohedral molecules [15,17] evidenced for the formal oxidation state +3 of the erbium ions entrapped. Recently, a new class of endohedral metallofullerenes containing a trimetallic nitride cluster $Sc_xEr_{3-x}N$, x=0–3 was discovered in the soot prepared by adding nitrogen into the helium synthetic atmosphere [18]. The isolated $Sc_3N@C_{80}$ was characterized by ^{13}C- and ^{45}Sc-NMR, which established I_h symmetry for the carbon cage and rapid reorientations for the entrapped Sc_3N cluster. This type of the cage is stabilized by addition of six electrons to its doubly occupied fourfold degenerate highest occupied molecular orbital level [19], as it was observed for $La_2@C_{80}$ molecule [20]. Thus, similarly to discandium metallofullerenes each scandium atom donates two electrons to the icosahedral carbon cage in $Sc_3N@C_{80}$. Presently, two trimetallic nitride compounds, namely $ErSc_2N@C_{80}$ [21], $Sc_3N@C_{78}$ [22], are structurally characterized by means of x-ray diffraction. Also, the successful isolation and spectroscopic characterization of nonconventional, isolated pentagon rule-violating, $Sc_3N@C_{68}$ [23] molecule was reported.

Notwithstanding the fundamental importance of the ionization characteristics of molecules, only few studies have been reported on the electron affinity (EA) of the endohedral fullerenes. The first EA determination for a metallofullerene was performed in 1992, and electron affinity of $Ca@C_{60}$ estimated from the threshold of the photoelectron spectrum was found to be about 3.0 eV, which is 0.3 eV higher than that for C_{60} [24]. Two experimental EA estimations were made for lanthanofullerenes. The first study was carried out by means of ion-molecular bracketing technique within the ion cyclotron resonance mass spectrometry, and electron affinity for the series of $La@C_n$ molecules (n=60, 70−84) was found to fall into the interval 2.7–3.3 eV [25]. Later, the estimation of the electron affinity of $La@C_{82}$ based on the correlation between EA and electrochemical reduction potential gave a value of 3.35 eV [26]. In our previous work we measured the electron affinity of gadolinium endohedral fullerenes ($Gd@C_{74}$-$Gd@C_{82}$) by means of Knudsen cell mass spectrometry using the ion-molecular equilibria technique [27]. The obtained electron affinity values for all the molecules appeared to be in the range of 3.2–3.3 eV—higher than for the parent hollow fullerenes. Notably, no considerable effect of the carbon cage type on the electron affinity was found, in contrast to what was observed for hollow fullerenes [28]. The EA values were in accordance with the theoretical predictions for a group of C_{82} monometalloderivatives, including scandium, yttrium, lanthanum etc. [29], though the electron affinity for the hollow C_{82} calculated in the same work was about 0.2 eV higher than the experimental value [28].

In this paper we report the electron affinity for a group of discandium fullerenes and a newly synthesized compounds mentioned above—$Sc_xEr_{3-x}N@C_{80}$, determined by the ion-molecular equilibria method.

2. Experimental

2.1. Sample preparation

A typical production protocol involves the core drilling of graphite rods (6.25 mm) and subsequent packing with Sc_2O_3/graphite (3%/97% w-w). This packed rod is then "burned" in a He atmosphere using a Kratschmer–Huffman type electric-arc generator. To enhance the production of trimetallic nitride template (TNT) endohedral metallofullerenes, the addition of small amounts of N_2 via the gas cylinder method greatly enhances the production of these TNT species [18]. The collected soot is then extracted with carbon disulfide to obtain a soluble scandium extract containing empty-cage fullerenes, conventional endohedral metallofullerenes (e.g. $Sc_2@C_{80}$, $Sc_2@C_{82}$, $Sc_2@C_{84}$), and TNT endohedral metallofullerenes.

The Sc TNT family consists of $Sc_3N@C_{68}$, $Sc_3N@C_{76}$, $Sc_3N@C_{78}$, and $Sc_3N@C_{80}$. The Sc raw extract was injected onto a PBB (pentabromobenzyl stationary phase, 250 mm×10 mm, CS_2 mobile phase, 2 mL/min, Phenomenex Co, Torrance CA, USA) column. This preliminary separation of the stock solution yielded a chromatographic fraction depleted in C_{60} and C_{70} and other empty-cages but enriched in $Sc_3N@C_{78}$ and $Sc_3N@C_{80}$. This TNT fraction also contains empty-cage fullerenes and conventional metallofullerenes which have similar retention times as $Sc_3N@C_{78}$ and $Sc_3N@C_{80}$.

The same production procedure followed by HPLC separation that was carried out with $Sc_2O_3+Er_2O_3$-containing graphite rods leads to the mixture of conventional Sc, Er, Sc+Er-containing metallofullerenes and a family of TNT compounds $Sc_xEr_{3-x}@C_n$, where x varies from 0 to 3.

LDI mass spectrometry was used for preliminary characterization of the samples, showing the presence of empty fullerenes in admixture or even trace quantities, depending on the degree of chromatographic purification.

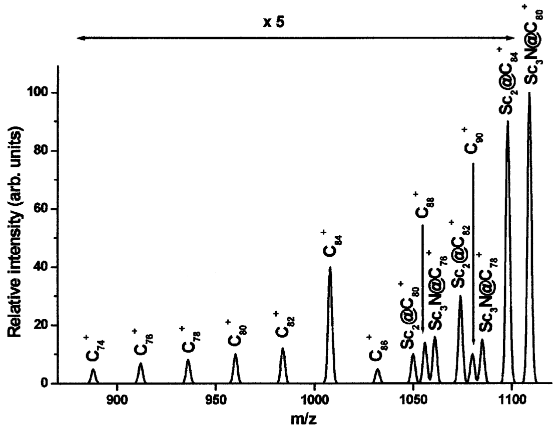

Fig. 1. Typical EI mass spectrum of the vapor over Sample 1 at T=916 K.

2.2. Mass spectrometric measurements

The samples were studied by means of Knudsen cell mass spectrometry (KCMS) using a magnetic sector mass spectrometer MI-1201V (Sumy, Ukraine) and a combined ion source with the incorporated nickel effusion cell. Such experimental setup, known as the ion-molecular equilibria technique, which is described in detail elsewhere [30], allows one to measure the partial pressures of both neutral and charged species that are present in the vapor inside the effusion cell and derive thermochemical data for the electron exchange reactions. The measurements were performed in the range of temperatures from 914 to 1020 K.

The pressures of the neutral components of the vapor were studied in the electron impact (EI) mode. The beam of 75 eV electrons was used to ionize the molecular beam leaving the effusion cell. We assumed that the fragmentation of both fullerenes and endohedral metallofullerenes under electron ionization is mainly a C_2- and C_4-loss process [31] with the yield of fragment ions similar to that for C_{60} or C_{70}, i.e. the fragment ion/molecular ion ratios were negligible. The thermal ionization (TI) mode was used to study negatively charged components of the saturated vapor. Negative ions were formed as a result of the surface ionization inside the effusion cell and extracted from the effusion cell by a weak electric field. To increase the anion concentrations we lowered the work function of cell surface by introducing potassium fluoride into the effusion cell.

3. Results and discussion

We have studied three samples of trimetallic nitride endohedral fullerenes with different degree of purity: Sample 1 (Sc) and Sample 2 (Sc+Er) contained considerable fractions of hollow fullerenes, whereas Sample 3 (Sc+Er) contained them only in trace amounts. Figs. 1 and 2 show typical EI and TI mass spectra of the vapor over Sample 1 in the mass range of 870–1120 amu. Both spectra contain the peaks of discandium derivatives of C_{80}, C_{82} and C_{84} and triscandium nitride endohedral fullerenes. Besides, the TI mass spectrum contains two peaks of unclear nature marked with “?” in Fig. 2. Since the relative intensities of the thermal ions are governed by their electron affinities, TI mass spectra may not reflect the composition of the sample and may contain signals, which originate from the trace amounts of high electron affinity species. Therefore, those unknown peaks can be tentatively referred to the $ScNC_{84}^-$ and $Sc_2NC_{82}^-$ species, but we are unable to assert this with confidence, since no corresponding neutral species were detected by LDI MS and KCMS. The mass spectra of Sample 2 were very complicated

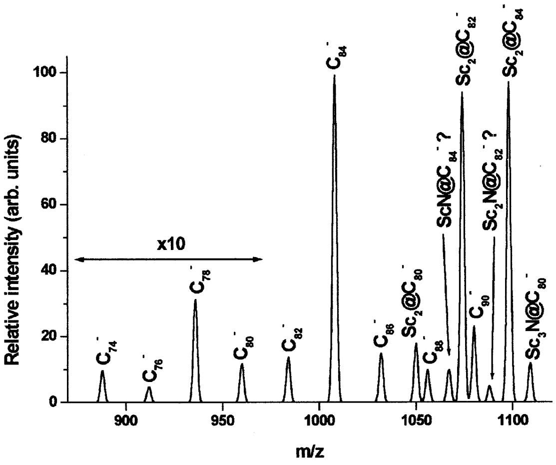

Fig. 2. Typical TI negative ion mass spectrum of the vapor over Sample 1 at T=916 K.

and we were able to perform the peak assignment only for some prominent empty fullerenes and $Sc_3N@C_{80}$.

We studied the equilibrium constants of

$$X@C_n + C_{84}^- = C_{84} + X@C_n^-, \quad X = Sc_2, \quad Sc_3N \tag{1}$$

The isomolecular reactions of this sort are easy to investigate due to mutual canceling out of the sensitivity constants and temperature coefficients, which connect the partial pressures with the measured intensities. Neglecting the fragmentation in the EI mass spectra, as mentioned in the Sec. 2, one can express the equilibrium constant by

$$K_p = \frac{I_{TI}\,(X@C_n^-) * I_{EI}\,(C_{84}^+)}{I_{EI}\,(X@C_n^+) * I_{TI}(C_{84}^-)} * \frac{\sigma\,(X@C_n)}{\sigma(C_{84})} * \sqrt{\frac{M\,(X@C_n^-)}{M\,(C_{84})}} \tag{2}$$

where $I_{EI/TI}$ denote the ion intensities in the electron impact or thermal ionization mass spectra, σ stands for the ionization cross-sections of the neutral molecules, and M stands for the masses of the negative ions. Since there is no experimental data on the ionization cross-sections of endohedral fullerenes, we approximated the cross-section ratio in Eq. (2) by n/84 according to the additivity rule. We did not take highly ionized entrapped atoms into account, not having relevant information about their role in the ionization process. We believe that the errors possibly arising from the cross-sections estimations are minor and should become negligible after the further logarithm taking.

Table 1
Experimental data for the reactions $X@C_n + C_{84}^- = C_{84} + X@C_n^-$ (1)

$X@C_n$		Temperature interval, K	Number of points	Mean Gibbs energy[a], kJ/mole
$Sc_3N@C_{80}$	Exp. 1	937–1016	4	32.2 ± 5.1
	Exp. 2	914–965	3	36.8 ± 2.7
	average	914–1016	7	33.7 ± 3.4
$Sc_2@C_{80}$		997–1020	4	−4.0 ± 1.5
$Sc_2@C_{82}$		997–1020	4	−5.2 ± 1.8
$Sc_2@C_{84}$		937–1020	5	5.8 ± 1.0
C_{76}		**937–1020**	**5**	**23.4 ± 2.4**
				25 ± 4 [28]

[a] Uncertainty is the standard deviation of the mean.

Applying the third-thermodynamics-law approach

$$\begin{aligned} RT * \ln K_p\,(1) &= -\,\Delta G_T^0\,(1) \\ &= -\,\Delta H_0^0\,(1) + T * \Delta\Phi_T^0\,(1) \end{aligned} \tag{3}$$

It is a generally reasonable assumption for isomolecular reactions that the temperature change of the thermodynamic functions of the reacting species and products may be compensated leading to $\Delta\Phi_T^0(1)=0$. The justification of this assumption was provided by our previous work on higher fullerenes [28]. In this case

$$\Delta G_T^0\,(1) = \Delta H_0^0\,(1) = EA\,(C_{84}) - EA\,(X@C_n) \tag{4}$$

and the electron affinity of the endohedral molecules under question may be easily obtained from the mean Gibbs energy of reaction (1) and the electron affinity of C_{84} which was determined in [28]. The Gibbs energies of reactions (1) are presented in Table 1. In order to verify that equilibrium was attained in the effusion cell, we also studied in the scope of the same experiment the charge transfer reaction between C_{76} and C_{84}, and the obtained Gibbs energy (printed in

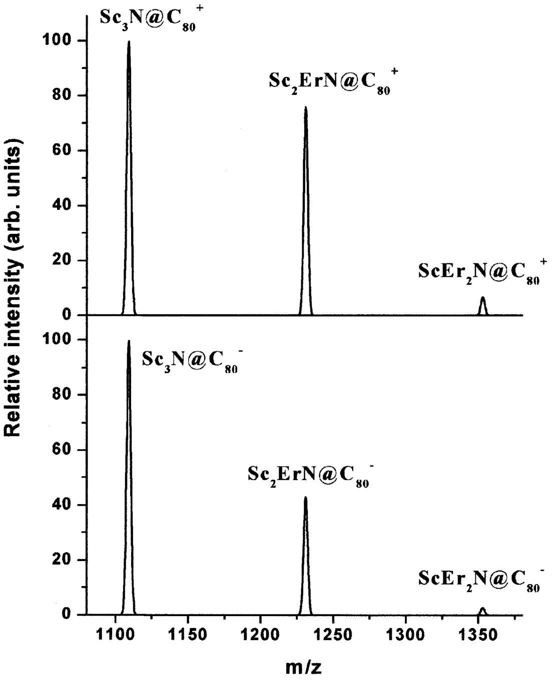

Fig. 3. Typical EI (above) and TI (below) mass spectra of the vapor over Sample 3 at T=1015 K.

bold in Table 1) was compared with our earlier work where the equilibrium conditions were proved [28].

The EI and TI mass spectra of Sample 3 presented on Fig. 3 contain only the peaks corresponding to $Sc_xEr_{3-x}N@C_{80}$ trimetallic nitride compounds. This allowed us to study the electron exchange

$$Sc_xEr_{3-x}N@C_{80} + Sc_3N@C_{80}^- = Sc_3N@C_{80} + Sc_xEr_{3-x}N@C_{80}^- \qquad (5)$$

Since the electron affinity of $Sc_3N@C_{80}$ was obtained in the experiments with Samples 1 and 2, we were able to derive the electron affinity of the other TNT compounds employing the procedure described above (Eqs. 2–4). The Gibbs energies of reaction (5) are given in Table 2.

Table 2
Experimental data for the reactions $Sc_xEr_{3-x}N@C_{80}$ + $Sc_3N@C_{80}^-$ = $Sc_3N@C_{80}$ + $Sc_xEr_{3-x}N@C_{80}^-$ (4)

$Sc_xEr_{3-x}N@C_{80}$	Temperature interval, K	Number of points	Mean Gibbs energy[a], kJ/mole
$Sc_2ErN@C_{80}$	886–1015	6	4.9 ± 2.0
$ScEr_2N@C_{80}$	886–1015	4	8.1 ± 3.7

[a] Uncertainty is the standard deviation of the mean

In Table 3 we present the electron affinity values of the endohedral molecules determined in our experiments, for comparison electron affinities of the corresponding hollow fullerenes from [28] are also presented. The effective charges on the fullerene cage and the symmetry of the molecules predicted by theoretical calculations [32,33] or established experimentally [6,18] are given in the parentheses.

As one can see, the electron affinity of the discandium fullerenes is very close to EA of the corresponding hollow fullerenes while EA ($Sc_3N@C_{80}$) is about 0.38 eV lower than EA (C_{80}). However, such comparison may be incorrect because of the different isomerism of the hollow fullerenes and corresponding endohedral compounds. We have, therefore, performed discrete Fourier transform (DFT) calculations [34] of the adiabatic electron affinity of C_{80} isomers with PBE exchange-correlation functional [35]. It was found that the electron affinity of the hollow I_h isomer of C_{80} may be even 0.4 eV greater than for the D_2 isomer. As for C_{84}, the EA values for D_{2d} and D_2 isomers are predicted to be almost equal [36]. If the above-mentioned predictions are true, we can con-

Table 3
Experimental electron affinities of some scandium endohedral fullerenes

Molecule	Electron affinity[a], eV	Effective charge on the cage
$Sc_3N@C_{80}$ ($\boldsymbol{I_h}$)	2.81 ± 0.05	−6
$Sc_2ErN@C_{80}$ ($\boldsymbol{I_h}$)	2.76 ± 0.05	−6
$ScEr_2N@C_{80}$ ($\boldsymbol{I_h}$)	2.73 ± 0.07	−6
$Sc_2@C_{80}$ ($\boldsymbol{D_{5h}}$)	3.20 ± 0.04	−4
C_{80} ($\boldsymbol{D_2}$)	3.19 ± 0.04	0
$Sc_2@C_{82}$(?)	3.21 ± 0.04	−4
C_{82}($\boldsymbol{C_2}$)	3.16 ± 0,04	0
$Sc_2@C_{84}$($\boldsymbol{D_{2d}}$)	3.10 ± 0.04	−4
C_{84}($\boldsymbol{D_{2d}}$, $\boldsymbol{D_2}$)	3.16 ± 0.04	0

[a] Uncertainty includes the standard deviation of the mean and error in the EA of C_{84} [28] and $Sc_3N@C_{80}$ (for TNT species).

clude that the decrease in the electron affinity values in going from discandium fullerenes to $Sc_3N@C_{80}$ and other triscandium molecules is governed by the increase in the charge transfer to the carbon cage. This suggestion is consistent with the EA data on monogadolinium fullerenes (see Sec. 1): being the molecules with lower charge on the carbon cage {-2 (DFT calculations, [9]) or -3 [ultraviolet photoelectron spectroscopy (UPS)], [37])} as compared with dimetallofullerenes, they reveal higher electron affinity than the latter ones. Another conclusion based on the results of both present work and results for monogadolinium fullerenes concerns the insignificance of the effects of carbon cage type on the EA of metallofullerenes in the series of molecules with the same number of atoms of the same metal. Surprisingly, within the TNT family, replacement of scandium by erbium have virtually no effect on the EA of the triscandium nitride molecules, whereas the difference in the first, second and third ionization potentials between scandium and erbium atoms equals to 0.4, 0.9, and 2.0 eV respectively [38]. One can suggest that localization of the lowest unoccupied molecular orbital (LUMO) of the TNT endohedral molecules occurs on the carbon cage rather than on the metal atom, thereby resulting in the observed negligible influence of the metal nature on the ionic properties of endohedral molecules. On the contrary, in the case of the conventional endohedral molecules where EA is found to depend on the entrapped metal, it is most likely that LUMO can be localized on the metal atom. This hypothesis however will have to be examined in more detail.

In summary, we suppose that there is a correlation between the electron affinity of an endohedral fullerene and the carbon cage charge: a smooth EA maximum is observed somewhere near 2 or 3 electron transfer which is followed by a considerable decrease beyond 4 electron transfer. We are currently performing further experiments involving various metallofullerenes, which will help to verify the hypothesis on the influence of the type of metal atoms, i.e. their electronic structure and ionization properties on the ionization properties of the endohedral molecules.

Acknowledgements

The authors thank the Russian Foundation of Basic Research (grant nos. 00- 03-32964, 99-15-96044, and 00-15-97346) and Program “Fullerenes and Atomic Clusters” (grant “Sphere”) for the partial financial support. I.N.I is grateful to Dr. D.N. Laikov (Organic Chemistry Institute, Zurich University) for his help in performing the computations.

References

[1] Y. Chai, T. Guo, C. Jin, R.E. Haufler, L.P.F. Chibante, J. Fure, L. Wang, J.M. Alford, R.E. Smalley, J. Phys. Chem. 95 (1991) 7564.
[2] H. Shinohara, H. Sato, M. Ohkohchi, Y. Ando, T. Kodama, T. Shida, T. Kato, Y. Saito, Nature 357 (1992) 52.
[3] C.S. Yannoni, M. Hoinkis, M.S. de Vries, D.S. Bethune, J.R. Salem, M.S. Crowder, R.D. Johnson, Science 256 (1992) 1191.
[4] H. Shinohara, H. Yamaguchi, N. Hayashi, H. Sato, M. Ohkohchi, Y. Ando, Y. Sayto, J. Phys. Chem. 97 (1993) 4259.
[5] C-R Wang, M. Inakuma, H. Shinohara, Chem. Phys. Lett. 300 (1999) 379.
[6] M. Takata, E. Nishibori, B. Umeda, M. Sakata, E. Yamamoto, H. Shinohara, Phys. Rev. Lett. 78 (1997) 3330.
[7] E. Nishibori, M. Takata, M. Sakata, M. Inakuma, H. Shinohara, Chem. Phys. Lett. 298 (1998) 79.
[8] M. Takata, E. Nishibori, M. Sakata, M. Inakuma, E. Yamamoto, H. Shinohara, Phys. Rev. Lett. 83 (1999) 2214.
[9] K. Kobayashi, S. Nagase, Chem. Phys. Lett. 282 (1998) 325.
[10] S. Nagase, K. Kobayashi, Chem. Phys. Lett. 276 (1997) 55.
[11] K. Kobayashi, S. Nagase, Chem. Phys. Lett. 313 (1999) 45.
[12] E. Yamamoto, M. Tansho, T. Tomoyama, H. Shinohara, H. Kawahara, Y. Kobayashi, J. Am. Chem. Soc. 118 (1996) 2293.
[13] T. Kato, S. Bandou, M. Inakuma, H. Shinohara, J. Phys. Chem. 99 (1995) 856.
[14] N. Tagmatarchis, E. Aslanis, H. Shinohara, K. Prassides, J. Phys. Chem. B 104 (2000) 11010.
[15] R.M. Macfarlane, G. Wittmann, P.H.M. van Loosdrecht, M. de Vries, D.S. Bethune, S. Stevenson, H.C. Dorn, Phys. Rev. Lett. 79 (1997) 1397.
[16] T. Ogawa, T. Sugai, H. Shinohara, J. Am. Chem. Soc. 122 (2000) 3538.
[17] K.R. Hoffman, B.J. Norris, R.B. Merle, M. Alford, Chem. Phys. Lett. 284 (1998) 171.
[18] S. Stevenson, G. Rice, T. Glass, K. Harich, F. Cromer, M.R. Jordan, J. Craft, E. Hadju, R. Bible, M.M. Olmstead, K. Maitra, A.J. Fischer, A.L. Balch, H.C. Dorn, Nature 401 (1999) 55.
[19] P.W. Fowler, F. Zebretto, Chem. Phys. Lett. 243 (1995) 36.
[20] T. Akasaka, S. Nagase, K. Kobayashi, M. Walchli, K.

Yamamoto, H. Funasaka, M. Kako, T. Hoshino, T. Erata, Angew. Chem. Int. Ed. Engl. 36 (1997) 1643.

[21] M.M. Olmstead, A. de Bettencourt-Dias, J.C. Duchamp, S. Stevenson, H.C. Dorn, A.L. Balch, J. Am. Chem. Soc. 122 (2000) 12220.

[22] M.M. Olmstead, A. de Bettencourt-Dias, J.C. Duchamp, S. Stevenson, D. Marciu, H.C. Dorn, A.L. Balch, Angew. Chem. Int. Ed. 40 (2001) 1223.

[23] S. Stvenson, P.W. Fowler, T. Heine, J.C. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible, H.C. Dorn, Nature 408 (2000) 427.

[24] L.S. Wang, J.M. Alford, Y. Chai, M. Diener, R.E. Smalley, Chem. Phys. Lett. 207 (1993) 354.

[25] R.L. Hettich, Z.C. Ying, R.N. Compton, Rec. Adv. Chem. Phys. Fullerenes Relat. Mater. 2 (1995) 1457.

[26] R.S. Ruoff, K.M. Kadish, P. Boulas, E.C.M. Chen, J. Phys. Chem. 99 (1995) 8843.

[27] O.V. Boltalina, I.N. Ioffe, I.D. Sorokin, L.N. Sidorov, J. Phys. Chem. A 101 (1997) 9561.

[28] O.V. Boltalina, E.V. Dashkova, L.N. Sidorov, Chem. Phys. Lett. 256 (1996) 253.

[29] S. Nagase, K. Kobayashi, J. Chem. Soc. Chem. Commun. (1994) 1837.

[30] L.N. Sidorov, L.V. Zhuravleva, I.D. Sorokin, Mass Spectrom. Rev. 5 (1986) 73.

[31] J. Laskin, T. Peres, A. Khong, H.A. Jimenez-Vazkuez, R.J. Cross, M. Saunders, D.S. Bethune, M.S. de Vries, C. Lifshitz, Int. J. Mass Spectrom. 185–187 (1999) 61.

[32] K. Kobayashi, S. Nagase, Chem. Phys. Lett. 262 (1996) 227.

[33] S. Nagase, K. Kobayashi, Chem. Phys. Lett. 231 (1994) 319.

[34] The "PRIRODA" program and a basis set of TZ2P quality specially optimized for DFT calculations were used. The more detailed information on the program can be obtained from D.N. Laikov, Chem. Phys. Lett. 281 (1997) 151 or personally from the developer, Dr. D.N. Laikov (laikov@oci.unizh.ch)

[35] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.

[36] R.N. Compton, A.A. Tuinman, C.E. Klots, M.R. Pederson, D.C. Patton, Phys. Rev. Lett. 78 (1997) 4367.

[37] S. Hino, K. Umishita, K. Iwasaki, T. Miyazaki, T. Miyamae, K. Kikuchi, Y. Achiba, Chem. Phys. Lett. 281 (1997) 115.

[38] CRC Handbook of Chemistry of Chemistry and Physics 77th Edition D.R. Lide, H.P.R. Frederikse (Eds.), CRC Press, Boca Raton, 1996, pp. 10-214–10-215.