

Ionization Energy of Fullerenes

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Abstract: Ionization energies of the higher fullerenes C_n ($n = 70–106$) were measured by means of the ion-molecular equilibria–Knudsen cell mass spectrometry method. The obtained values were found to decrease with the size, going from $IE(C_{70}) = 7.36$ eV down to $IE(C_{106}) = 6.92$ eV, with unexpectedly low $IE(C_{74}) = 7.13$ eV. A good correlation of the experimental results with the theoretical values is demonstrated. A simple model describing the ionization properties dependence from the fullerene size is proposed.

Introduction

In the past 10 years remarkable progress has been made in the studies of the fundamental properties of fullerenes. It was shown that, unlike most organic molecules, fullerenes can be both good electron donors and electron acceptors. The ionization energy (IE) of C_{60} is 7.54–7.61 eV according to the photoionization (PI) and photoelectron spectroscopy (PES) data^{1–5} and IE for C_{70} was found to be slightly lower, 7.48 eV, as determined by the PI method,⁵ or 7.47 eV, as obtained from PES data.⁶ Fullerenes can easily accept one electron in the gas phase, with $EA(C_{60}) = 2.67$ eV and $EA(C_{70}) = 2.68$ eV as obtained by the electron photodetachment method.⁷

Moreover, even multiply charged fullerenes were found to be relatively stable. For example, in the solution, [60]fullerene was shown to undergo six reversible reductions, and one irreversible oxidation.⁸ In contrast, in the gas phase, fullerenes were found to form only mono- and dianions,^{9,10} whereas cations with the charge from +1 to +5 can be readily observed.¹¹ This dual nature of the fullerenes is one of the major factors that determine the wealth of the fullerene chemistry.

In recent years, attention of researchers, both theorists and experimentalists, was focused mainly on the most abundant molecules of [60]- and [70]fullerenes, whereas properties of the higher fullerenes ($C_{n>70}$) were studied to a much lesser extent. Isolated larger fullerenes are still not available in sufficient

quantities for extensive experimental work. As for theoretical studies, the number of possible isomers of the fullerene molecules increases greatly with cage size and most of them possess rather low symmetries. This makes ab initio calculations of the large fullerene molecules structures and energetics very costly. As a consequence, even data on the fundamental characteristics of the higher fullerenes such as ionization energies and electron affinities are relatively scarce. In most studies, considerations are usually limited to [76]-, [78]-, and [84]fullerenes that are known to be easily extractable from the fullerene soot. The ionization energies for the latter determined by the PI method are 7.10 ± 0.10 , 7.05 ± 0.10 , and 7.15 ± 0.10 eV, respectively.⁵ Meanwhile, the tendency of the ionization energy to decrease with the cage size was suggested for the fullerenes theoretically^{12–14} and experimentally in the PI studies in solution.¹⁵

In our previous papers¹⁶ we reported on the experimental EAs of the fullerenes C_n ($n = 70–106$) obtained by means of Knudsen cell mass spectrometry. We found an overall tendency of an increase in the electron-withdrawing ability of fullerenes with the cage size. This tendency was also observed in EA calculations for a sequence of fullerene molecules: C_{60} , C_{70} , C_{76} , C_{82} , and C_{84} .^{12,13} Also, a remarkably high stability of the [74]fullerene anion in the gas phase was discovered.¹⁶ The latter observation was later confirmed both theoretically¹⁷ and experimentally.¹⁸ Reducing electrochemically fullerene soot prior to the extraction with solvent, Diener and Alford¹⁸ were first able to isolate [74]fullerene, though structural characterization is yet to be done.

In this paper, we present the first experimental determination of the IEs for the large series of the fullerenes from C_{70} to C_{106} . Trends in the ionization characteristics, both electron affinities and IE, as a function of fullerene size are discussed and comparison with the calculated values is made.

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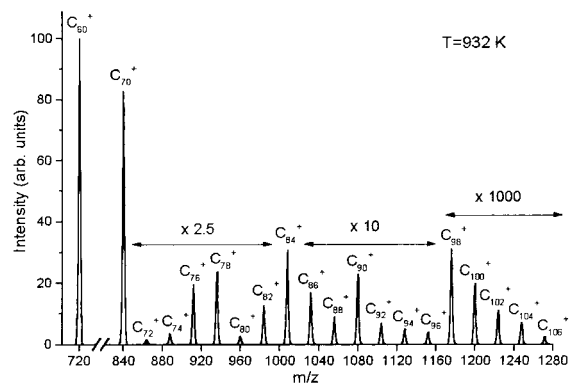


Figure 1. Typical EI mass spectrum of the higher fullerene sample.

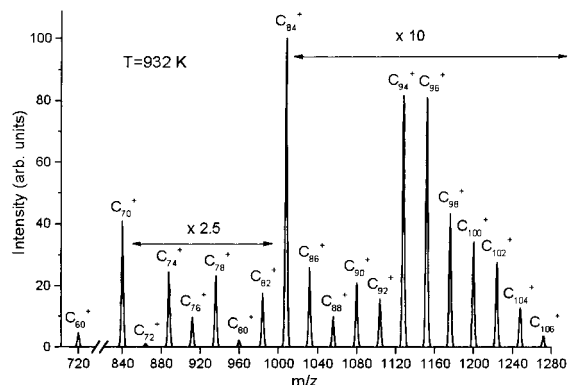


Figure 2. Typical TI mass spectrum of the higher fullerene sample.

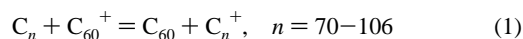
Experimental Section

1. Equilibrium Constants Measurements. The experimental method applied in this work (Knudsen cell mass spectrometry (KCMS) modified for ion/molecule reaction studies, IME-KCMS) provides direct measurements of the equilibrium constants of the gas-phase ion-molecular reactions.

Following the procedure described elsewhere in detail,¹⁹ a sample of the fullerene mixture was placed in the Ni (or Pt) effusion cell and then loaded in the ion source of the mass spectrometer. The MI-1201 60° magnetic sector mass spectrometer (Sumy, Ukraine) with the incorporated combined ion source was used. The latter enables partial pressure determinations of the neutral gas-phase species via detection of the positive ions produced by electron impact (EI) (75 eV electron energy) and thermal ions formed at elevated temperatures due to the surface thermal ionization (TI) inside the cell. Heating a higher fullerene sample up to about 800–1000 K yields typical mass spectra of the fullerene mixture in the EI (Figure 1) and TI modes (Figure 2).

To achieve sufficient thermal cation intensities, a few milligrams of transition metal fluoride, namely FeF₃, was added into the effusion cell. The latter was chosen because it does not react with the fullerene mixture as was found in our preliminary experiments. The obtained intensities of the C₆₀⁺ and C₇₀⁺ thermal cations were comparable to the intensities of the corresponding ions produced by electron impact. We are not able to estimate precisely the effect of the iron trifluoride addition. However, using the Saha–Langmuir equation²⁰ and employing an assumption that the EI ionization efficiency is ca. 0.01–0.001%, we may roughly estimate the work function of the effusion cell in our experiment to be 6.0–6.5 eV.

We studied the following gas-phase electron exchange reactions:



To ensure that equilibrium was attained in the reactions under study, we have carried out measurements of the equilibrium constants using two samples with significantly different content of the higher fullerenes. Following the difference in the relative abundance of the vapor species,

(20) See, for example: Fujii, T. *Eur. Mass Spectrom.* **1996**, 2, 91.

Table 1. Gibbs Energies of the Reactions $C_n + C_{60}^+ = C_{60} + C_n^+$, $n = 70-106$

C_n	temp range, K	no. of points	$\overline{\Delta_r G_T^0}$
C ₇₀	886–983	9	−20.0 ± 1.0
C ₇₂	886–983	9	−24.1 ± 1.9
C ₇₄	886–983	9	−42.0 ± 2.0
C ₇₆	886–983	9	−22.6 ± 3.2
C ₇₈	886–983	9	−29.6 ± 1.8
C ₈₀	886–983	9	−26.2 ± 2.2
C ₈₂	886–983	9	−30.8 ± 0.9
C ₈₄	886–983	9	−38.5 ± 1.8
C ₈₆	886–983	9	−39.1 ± 2.0
C ₈₈	886–983	9	−45.8 ± 1.2
C ₉₀	886–983	9	−45.7 ± 1.3
C ₉₂	886–983	9	−51.7 ± 2.2
C ₉₄	886–983	9	−58.6 ± 1.6
C ₉₆	886–983	9	−62.5 ± 2.2
C ₉₈	886–983	7	−59.7 ± 3.2
C ₁₀₀	886–932	3	−60.0 ± 1.1
C ₁₀₂	886–932	3	−65.4 ± 6.1
C ₁₀₄	886–932	3	−58.8 ± 4.4
C ₁₀₆	886–932	3	−62.6 ± 7.1

the ratios of the partial pressures of the reacting species varied by a factor of 10–100, in the majority of cases not less than 30. At the same time, the equilibrium constant values remained virtually unchanged (within the experimental error bars). It therefore allowed us to apply the mass action law for the verification of equilibrium in the studied systems.

In Table 1 we present the results of the Gibbs energy determination for reactions 1. Equilibrium constants of reactions 1 were calculated from eq 2

$$K_p(1) = \frac{I_{\text{EI}}(C_{60}^+) \sigma(C_n)}{I_{\text{EI}}(C_n^+) \sigma(C_{60})} \frac{I_{\text{TI}}(C_n^+) \sqrt{M(C_n^+)}}{I_{\text{TI}}(C_{60}^+) \sqrt{M(C_{60}^+)}} \quad (2)$$

where I_{EI} denotes the currents of the positive ions formed from the neutral molecules by the electron impact, σ_{IE} denotes the ionization cross-sections of the reacting molecules, I_{TI} denotes the ion currents of the thermal cations, and M denotes the masses of the thermal cations. The relative ionization cross-sections of the fullerene molecules were estimated as the number of carbon atoms in a molecule, according to the additivity rule.²¹ We considered the intensities of the C₂-loss fragment ions produced by the electron ionization of the higher fullerene molecules to be similar to those observed in the case of fragmentation of C₆₀ and C₇₀ (ca. 1% of the intensity of the molecular ion) and thus we assumed the contribution of the fragment ions to the observed spectrum to be insignificant. In the thermal ionization mode no fragmentation of C₆₀ and C₇₀ was observed.

The Gibbs energies were derived from the equilibrium constants using eq 3

$$\Delta G_T^0 = -RT \ln K_p \quad (3)$$

2. Theoretical Calculations of Ionization Energies. We have applied a density-functional-based tight-binding scheme (DF-TB) for the IE calculations. This method has been extensively described elsewhere.²² Briefly, we note that this scheme employs a nonorthogonal tight-binding (LCAO) model to determine the electronic states, the total energy, and the forces for a given atomic configuration. In contrast to other tight-binding schemes, the Hamiltonian and overlap matrix elements are calculated from first principles (“ab initio”). This method has already been successfully tested^{22,23} and applied to fullerenes, see

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e.g. refs 14, 24, and 25. It was especially shown to give reliable results for ionization energies of neutral fullerenes¹⁴ and their anions.²⁵ The initial structures of the fullerenes, from C₃₂ to C₈₄, were taken from ref 26 and were optimized using efficient conjugate gradient algorithms. Since a systematic investigation of all possible cage structures, as performed for C₂₀, C₂₂,²⁶ or C₄₀,²⁴ is unfeasible for the whole series of fullerenes, we have considered only the structures of those proposed by Fowler and Manolopoulos.²⁷

Results and Discussion

The ionization energy of the molecule is defined as the standard enthalpy of ionization at zero temperature. The Gibbs energy consists of two contributions according to

$$\Delta G_T^0 = \Delta H_0^0 - T\Delta\Phi_T^0 \quad (4)$$

In case of isomolecular reactions, when the thermodynamic functions of the species are not available, the default assumption is $\Delta\Phi = 0$. We have previously investigated the possible error arising due to the uncertainty in the thermodynamic functions of fullerenes and their singly charged anions while studying electron exchange reactions.¹⁶ Estimations of the entropy contribution ($T^*\Delta S^0$), which were obtained from the second-law treatment, showed an overall uncertainty to be less than ± 10 kJ/mol. More recently, evaluation of the entropy change has been done theoretically (PM3 method) for reactions of electron exchange between neutral fullerenes (C₆₀ and C₇₀) and their doubly charged cations and anions giving the values of -3 and 10 kJ/mol, respectively.²⁸ The above data permitted us to neglect the entropy contribution in the present calculations of enthalpy of reaction 1, assuming

$$-RT \ln K_p = \overline{\Delta G_T^0} = \Delta H_0^0 = \text{IE}(C_n) - \text{IE}(C_{60}) \quad (5)$$

We should mention that the IE values obtained for a C_n compound correspond not to the most abundant isomer but to the mixture of the isomers formed in the synthetic procedure. Unfortunately, the isomeric composition of the fullerenes beyond C₈₄ is not yet well established. As for the smaller fullerenes, such as C₇₈ and C₈₄, the theoretical¹² and experimental¹⁵ IE values for the distinct experimentally observed isomers do not differ by more than 0.1 eV.

To derive the absolute values of ionization energies of the fullerenes we anchored our experimental relative IEs to the value of ionization energy of [60]fullerene taken from ref 4. The IEs thus calculated are listed in Table 2.

We should note that IE values presented in Table 2 for C₇₆ and C₇₈ are ~ 0.2 eV higher than those determined in ref 5 (see Introduction) while our IE value for C₇₀ is ~ 0.1 eV lower than those from refs 5 and 6. Those differences may be due to a number of factors. First, the IE values for C₇₆ and C₇₈ from ref 5 correspond to the vibrationally excited molecules from the molecular beam obtained by heating the effusive source to 500 °C and thus may be underestimated. Second, our values, being adiabatic, may differ from the vertical values measured in the photoionization experiments.

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Table 2. Ionization Energies of the Fullerenes Relative to C₆₀

molecule	ionization energy, eV	molecule	ionization energy, eV
C ₆₀	7.57 ± 0.01 [4]	C ₈₈	7.09 ± 0.02
C ₇₀	7.36 ± 0.01	C ₉₀	7.09 ± 0.02
C ₇₂	7.32 ± 0.02	C ₉₂	7.03 ± 0.03
C ₇₄	7.13 ± 0.02	C ₉₄	6.96 ± 0.02
C ₇₆	7.34 ± 0.03	C ₉₆	6.92 ± 0.02
C ₇₈	7.26 ± 0.02	C ₉₈	6.95 ± 0.03
C ₈₀	7.30 ± 0.03	C ₁₀₀	6.95 ± 0.01
C ₈₂	7.25 ± 0.01	C ₁₀₂	6.89 ± 0.06
C ₈₄	7.17 ± 0.02	C ₁₀₄	6.96 ± 0.05
C ₈₆	7.16 ± 0.02	C ₁₀₆	6.92 ± 0.07

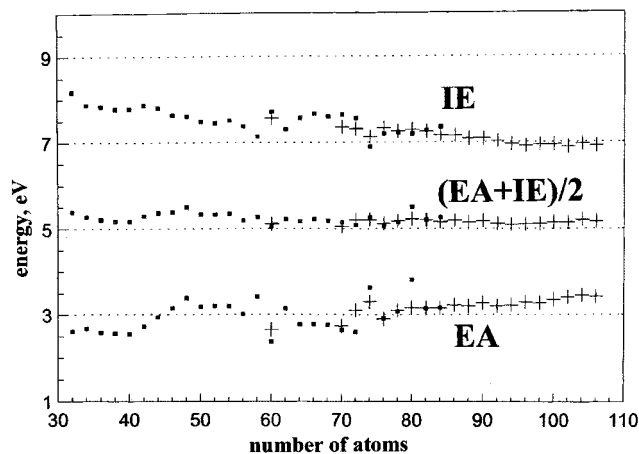


Figure 3. Experimental (crosses) and calculated (dots) ionization energy (IE), electron affinity (EA), and Mulliken electronegativity values $(EA + IE)/2$ of the carbon clusters.

The measured ($n = 60\text{--}106$) and calculated ($n = 32\text{--}84$) ionization energies (IE, upper curve), electron affinities (EA, lower curve), and the average of both $(IE + EA)/2$, middle curve) for fullerenes C_n are presented in Figure 3. There is generally a good agreement between the experimental and calculated values (for $n = 60$, $n = 70\text{--}84$). The only two considerable differences can be seen for the affinities of C₇₂ and C₈₀, which may originate from yet unclear isomerism of these molecules. The calculated data shown in Figure 3 for C₈₀ are those of the most stable isomer of the seven isomers given in ref 27. However, from our calculations it follows that there are three other isomers within an energy range of less than 8 kJ/mol. The other three isomers are less stable by only 17 kJ/mol than the most stable one. Hence, it cannot be excluded that the electron affinities and ionization energies of other isomers than the most stable ones have been measured. Considering the four most stable isomers, the ionization energies vary between 7.19 (for the most stable isomer, as shown in Figure 3) and 6.85 eV (for the third stable isomer). The electron affinities correspondingly vary between 3.81 (for the most stable isomer, as shown in Figure 3) and 3.22 eV (for the fourth stable isomer). Therefore, the presence of isomers could explain the deviation between theory and experiment as well as account for the “irregular” behavior in the electron affinity of C₈₀. In the case of C₇₂ there is only one isomer given in ref 27, but there are some theoretical suggestions that C₇₂ which is present in the fullerene soot does not satisfy the isolated pentagon rule.²⁹

The ionization energies tend to slightly decrease with increasing size of the fullerene, ranging from about 8 eV for small fullerenes down to about 7 eV for the large fullerenes. Superimposed on this tendency are fluctuations which can be

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attributed to structural (electronic) effects. Relatively high ionization energy of C_{60} and, in contrast to this, low ionization energy of C_{74} represent the most prominent deviations. The observed trend in electron affinities appears to mirror that of the ionization energy curve, i.e., the electron affinities increase with increasing size of the fullerene from about 2.5 eV for the small fullerenes up to nearly 3.5 eV for the larger ones. Also, the above-mentioned deviations are mirrored to a large extent. So the large ionization energy of C_{60} is countered by the low electron affinity of C_{60} , whereas the low ionization energy of C_{74} is countered by the large affinity of C_{74} . This mirror behavior of IE and EA leads to a nearly constant average $(IE + EA)/2$ at about 5.2 ± 0.2 eV. This average is nothing else than the Mulliken electronegativity³⁰ of the fullerene molecules, or their chemical potential, whereas the difference of $IE - EA$ may be viewed as the hardness of the systems.³¹ It is also a measure for the HOMO-LUMO gap, and this gap is closely related to the experimentally observed stability of a cluster.²⁷ This is nicely illustrated by the large $IE - EA$ (i.e. HOMO-LUMO gap) and high stability of C_{60} . It also indicates rather low stability for C_{74} with its relatively small gap.¹⁸ The overall tendencies—decreasing IE, increasing EA, and (nearly) constant average of IE and EA—can be understood considering the rather simple physical model for the fullerenes. The calculations show that the additional charges on the fullerene cages in the cationic and anionic states are nearly completely delocalized.¹⁴ This allows one to consider the fullerene anions or cations as singly charged hollow spheres to a good approximation. As already discussed for the multiple ionization of C_{60} ,²⁵ ionization energy trend in fullerenes¹⁴ and widely used for the explanation of the size dependence of ionization energies of alkali metal clusters^{32–35} one can then describe the size dependence of ionization energies by the simple model of a charged (hollow) sphere. This leads to simple electrostatic formulas for the ionization energy (IE):

$$IE = IE_{\infty} + \frac{1}{2}R^{-1}(2Q - 1) \quad (6)$$

and for the electron affinity:

$$EA = EA_{\infty} - \frac{1}{2}R^{-1}(2Q - 1) \quad (7)$$

where Q is the absolute value of the final charge ($Q = 1$ for a single ionization), R is the radius of the sphere, and IE_{∞} and EA_{∞} are the ionization energy and the electron affinity for $R \rightarrow \infty$, respectively.¹⁴ Since the corresponding infinite system for the fullerenes is a planar graphite monolayer, which has a zero electronic gap, hence IE_{∞} equals EA_{∞} becoming the work function (φ_{∞}) of a graphite monolayer. Using further the number of atoms (N) versus R^2 proportionality, which means simply a homogeneous, size-independent distribution of the carbon atoms on a sphere (fullerene cage), $(IE - IE_{\infty})$ and $(EA_{\infty} - EA)$ are proportional to $N^{-1/2}$. The measured and calculated data for IE, EA, and the average are drawn in Figure 4 in a $N^{-1/2}$ representation together with the $\pm \frac{1}{2}R^{-1}$ lines and the horizontal line at φ_{∞} , calculated for a graphite monolayer with the DFTB method (5.13 eV). The proportionality factor between R^{-1} and $N^{-1/2}$ was calculated using the radius of C_{60} (3.57 Å). It is clearly

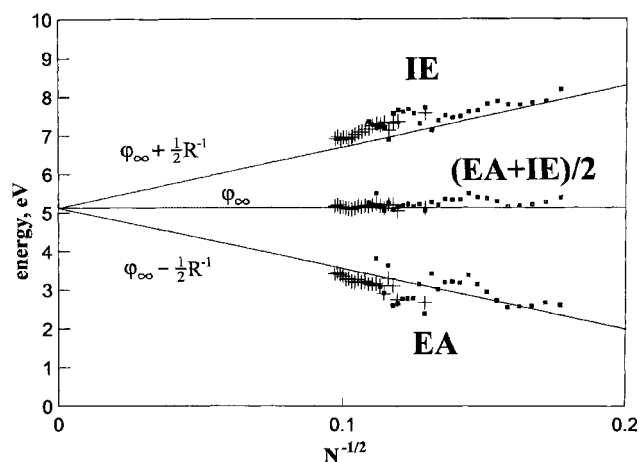


Figure 4. Experimental (crosses) and calculated (dots) ionization energy (IE), electron affinity (EA), and Mulliken electronegativity $(EA + IE)/2$ values of the molecules studied versus number of carbon atoms in a degree of $-1/2$.

seen that the data for the fullerenes, especially for the species beyond C_{60} , show a behavior that is close to a simple charged sphere behavior. Furthermore, the chemical potential of these fullerenes is nearly independent of size and close to the value expected for the corresponding infinite reference system (graphite monolayer). Interestingly, this asymptotic value is also close to the chemical potential of the carbon atom, calculated within the same DFT-LDA approximation, which is equal to 5.37 eV.

From the curve in Figure 4 one can also easily predict the ionization energies and electron affinities for larger fullerenes. Vanishing of the gap with increasing size of the fullerenes can also be deduced from this figure. Very recent STM investigations for large carbon clusters (diameters up to 1000 Å) have confirmed this result.³⁶

It is also interesting to compare this size dependence with the corresponding size dependencies of alkali metal clusters, where a R^{-1} dependence of the ionization energies was found previously.^{32–35}

There has been a long debate in the literature about the correct theoretical proportionality factor in this size dependence. Originally, Wood³⁷ argued that the correct proportionality factor should be $3/8$ instead of $1/2$, as noted above. The factor $3/8$ fits also the experimental data for alkali metal cluster better than $1/2$.^{32–35} However, it seems clear now that the arguments of Wood³⁷ were wrong, and the deviation from the $1/2R^{-1}$ dependence for the alkali metal clusters can be explained by quantum mechanical effects, mainly the “spill-off” of the electronic wave functions beyond the cluster edge.^{34,35,38} The fact that the data for fullerenes fit quite well to a proportionality factor close to $1/2$ may be interpreted that the “spill-off” of the electronic charge density in fullerenes is clearly smaller than that in the case of alkali metal clusters. This is not a surprising result, considering that the wave functions of alkaline metal atoms are much more long ranging than those of carbon atoms.

Conclusions

We have measured the ionization energies (IE) for a series of higher fullerenes from C_{70} to C_{106} and performed the IE calculations for a wide range of model carbon clusters (C_{32} , C_{34} , C_{38} – C_{58} , C_{62} – C_{68}) and experimentally observed fullerenes

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(C₆₀, C₇₀–C₈₄). The experimental results are in good agreement with theoretical predictions except for C₇₂ and C₈₀, possibly due to the calculated isomer not being the experimentally observed isomer, as discussed above. Our ionization energy and previously determined electron affinity values are found to be in accordance with the predictions of a charged hollow sphere model providing evidence for the almost homogeneous charge delocalization over the carbon cage in the fullerene ions. We

also observed an unexpectedly low IE value for C₇₄ for which the unexpectedly high electron affinity is also known.

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