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International Journal of Mass Spectrometry 243 (2005) 223–230

International Journal of Mass Spectrometry

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Mass spectrometry, photoelectron spectroscopy, and quantum chemical studies of fluorofullerene dianions

I.N. Ioffe[a,*], S.M. Avdoshenko[a], O.V. Boltalina[a], L.N. Sidorov[a], K. Berndt[b], J.M. Weber[b,*]

[a] Moscow State University, Chemistry Department, Moscow 119992, Russia
[b] Institut für Physikalische Chemie, Kaiserstraße 12, 76128 Karlsruhe, Germany

Received 4 February 2005; accepted 16 March 2005
Available online 15 April 2005

Abstract

Singly and doubly charged anions of fluorofullerenes were produced by means of electrospray ionization from acetonitrile/dichlorobenzene solutions of $C_{60}F_{36}$ and $C_{60}F_{48}$ doped with organic electron donors. These anions can be formally viewed as products of mono- and bis-substitution of fluorine atoms by electrons. Photoelectron spectra of $C_{60}F_{34}^{2-}$ and $C_{60}F_{46}^{2-}$ allow estimating the second electron affinity of the corresponding neutral species to be 2.4 (1) and 3.2 (1) eV, respectively. Quantum chemical calculations at the DFT level of theory suggest that the observed dianions form due to fluorine rearrangements on the carbon shell, which is governed by their high relative stability.

Keywords: Electrospray mass spectrometry; Photoelectron spectroscopy; Dianions; Fluorinated fullerenes

1. Introduction

The electronic structure of multiply charged anions has attracted much attention in the past few years [1–3]. The strong mutual repulsion of their excess charges generates an interesting electron-molecule potential dominated by a repulsive Coulomb barrier (RCB), interfacing the attractive short-range interaction between an excess electron and the charged molecular "core" with the long-range Coulomb repulsion. This potential gives rise to electronic resonances, which are unstable with respect to autodetachment by tunneling through the RCB, but have lifetimes up to several hundred seconds [4]. Moreover, the presence of the RCB affects the rules for photodetachment from multiply charged anions, since the photon energy required to detach an electron from a given state has to be greater than the sum of its binding energy and the height of the RCB, if tunneling can be neglected on the experimental time scale.

Fullerenes, which are known as good electron acceptors, represent very interesting objects for the studies of anionic properties. Unlike many strong acceptors, fullerenes are stable closed-shell molecules, and their electron-withdrawing properties are due to the presence of three-dimensional π-systems regarded as special cases of spherical aromaticity [5,6], which allow for efficient charge delocalization. Among other techniques, negative ion electrospray (ESI) mass spectrometry can be used to generate fullerene dianions [7,8]. Furthermore, subsequent photo- and autodetachment studies demonstrated that the second electron affinity (EA) of higher fullerenes is positive [8–11]. In this context, fluorinated fullerenes represent very attractive objects for such studies, since they exhibit much stronger electron-accepting properties than the parent fullerenes due to the high content of electronegative fluorine atoms. For example, the EA value for C_{60} is 2.67 eV [12], whereas EA estimates for $C_{60}F_{36}$ and $C_{60}F_{44–48}$ yield 3.5 eV [13] and 4.1 eV [14], respectively. The observation of $C_{60}F_{46}^{2-}$ in the ESI mass spectrometric studies of $C_{60}F_{48}$ in a decamethylferrocene-doped solution [15] demonstrated the suitability of this ionization method for the production of doubly charged anions of highly fluorinated fullerenes. Similarly, electron capture and collisional

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* Corresponding authors. Tel.: +7 95 939 1240 (I.N. Ioffe)/+49 721 608 7232 (J.M. Weber).
E-mail addresses: ioffe@phys.chem.msu.ru (I.N. Ioffe), jmathias.weber@chemie.uni-karlsruhe.de (J.M. Weber).

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doi:10.1016/j.ijms.2005.03.005

electron transfer techniques were successfully applied to the production of fullerene fluoride dianions [14,16,17]. More recently, direct observation of fluorofullerene dianions by ESI MS, which did not involve ion pre-formation in solution, was reported [18]. In the present work, we performed ESI mass spectrometry and the first photoelectron (PE) spectroscopy studies of $C_{60}F_{34}{}^{2-}$ and $C_{60}F_{46}{}^{2-}$ dianions obtained from $C_{60}F_{36}$ and $C_{60}F_{48}$, respectively.

2. Experimental and theoretical methods

$C_{60}F_{36}$ and $C_{60}F_{48}$ were synthesized by means of a solid-phase metal-fluoride (MnF_3) fluorination technique or fluorination with elemental fluorine, respectively, as described elsewhere [19]. Both samples were analysed by electron impact ionization mass spectrometry, ^{19}F NMR and IR spectroscopy, which showed 90+% compositional purity. Organic donor compounds, such as tetramethylphenylenediamine (TMPD) and tetrakis(dimethyamino)ethylene (TDAE), and HPLC grade solvents (*o*-dichlorobenzene (DCB) and acetonitrile) were purchased from commercial vendors and used without further purification. 10^{-3} M stock solutions of fluorofullerenes in *o*-dichlorobenzene (DCB) were diluted (1:20) by a mixture of acetonitrile and DCB (4:1), and doped by an excess of organic donors dissolved in acetonitrile. For $C_{60}F_{36}$, a mixture of TMPD and TDAE was used in a ∼20:1 ratio, while only TMPD was employed for $C_{60}F_{48}$. In order to prevent degradation of target compounds via fluorination of donor molecules, the quantity of a donor added was empirically adjusted so that the color of the resulting solution due to formation of charge-transfer complexes was not too saturated. Besides, only freshly diluted and doped solutions were used. We note that polar protic solvents could not be used because of the instability of fullerene fluorides with respect to hydrolysis.

Analogous to previous studies involving higher fullerenes [10,11], ions were produced in a commercial micro-ESI source (Analytica of Branford) with nitrogen as a drying and nebulizing gas (drying gas temperature 300 °C). Subsequently, ions were accumulated for 1/30 s in a hexapole ion trap in order to increase signal-to-noise ratio. The ions of interest were mass-selected using a reflectron time-of-flight MS (mass resolution ∼ 1200) and entered the detachment zone of a “magnetic bottle” type time-of-flight PE spectrometer [20] where they interacted with the third or fourth harmonic of a pulsed Nd:YAG (laser pulse duration 5–6 ns, typical fluence 30 and 15 mJ/cm^2 at 3.49 and 4.66 eV photon energy, respectively). Prior to photodetachment, the ions were decelerated by a high voltage pulse in order to suppress the kinematic Doppler effect inherent in this spectrometer type. The energy resolution of the instrument was around $\Delta E/E = 5\%$ at 1 eV electron kinetic energy. In order to subtract background electron signals, every second laser shot was fired in the absence of the ion beam. The spectra were accumulated and averaged over several 10^5 laser shots. They were calibrated using the known PE spectra of I^- at the same photon energies, which were produced by ESI from a 1 mM solution of CsI in a methanol/water mixture (9:1).

Ground states of multiply charged anions can display strong correlation effects between valence electrons, since the excess electrons are largely unscreened from each other. Presently, density functional theory (DFT) is the only feasible approach to the routine treatment of large objects, such as fullerene derivatives. DFT calculations of the electron affinities and relative stabilities of the neutral and anionic species as well as time-dependent DFT (TDDFT) computations of excited states were carried out with the use of the PRIRODA DFT package [21] employing a computationally inexpensive implementation of the resolution-of-identity (RI) approach [22]. The PBE exchange-correlation functional [23] and an original basis set of TZ2P quality [21] were used. Semiempirical AM1 calculations used as a starting point for further DFT treatment were performed with the use of the PC-GAMESS package [24].

3. Results and discussion

3.1. ESI mass spectra

Fig. 1 shows typical negative ion ESI mass spectra of the $C_{60}F_{36}$ and $C_{60}F_{48}$ solutions in acetonitrile/DCB doped with TMPD and/or TDAE. The spectrum of the former compound

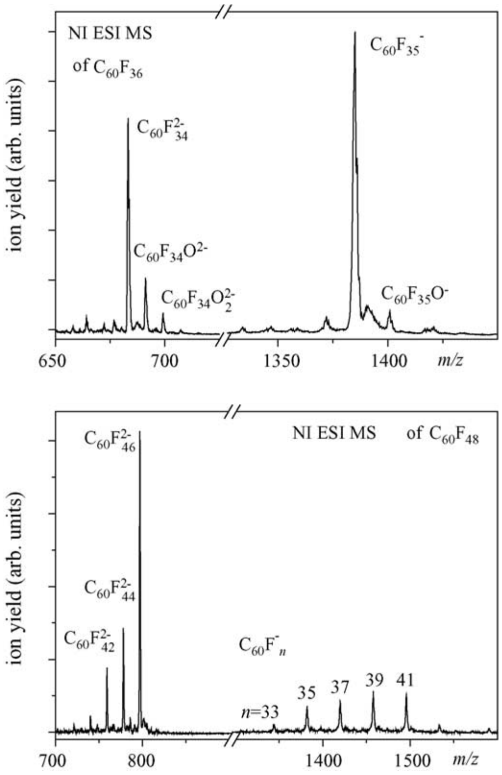


Fig. 1. Negative ion ESI mass spectra of $C_{60}F_{36}$ (top) and $C_{60}F_{48}$ (bottom) solutions in acetonitrile/DCB doped with TMPD and TDAE.

consists of fewer species, the most abundant correspond to the $C_{60}F_{35}^{-}$ monoanion and the $C_{60}F_{34}^{2-}$ dianion. Some oxygenated derivatives of these species can be seen as well, originating from reactions of fluorofullerenes with traces of water or oxygen in the solvent. The mass spectrum of $C_{60}F_{48}$ is dominated by the $C_{60}F_{46}^{2-}$ dianion. A series of $C_{60}F_{35}^{-}$ to $C_{60}F_{41}^{-}$ monoanions with odd F numbers can also be observed, which originate from partial degradation/fragmentation. Interestingly, the monoanionic part of the mass spectrum shows more extensive fragmentation than the dianionic part. Both fluorofullerenes produce monoanions with closed electronic shells, which can be formally regarded as products of the stepwise substitution of F atoms by electrons accompanied by a certain degree of defluorination in the case of $C_{60}F_{48}$. Similar fluorine loss upon charging was observed in the ESI mass spectrometry studies of $C_{60}F_{48}$ [15] and $C_{60}F_{18}$ [25] in the presence of electron donors, and in the MALDI studies of various fluorofullerenes [26], where F abstraction was even more pronounced. In contrast, ESI MS in the absence of electron donor molecules is known to produce either molecular anions of fluorinated fullerenes almost without F abstraction [27] or in the case of pure $C_{60}F_{48}$, monoanions of both $C_{60}F_{48}$ and $C_{60}F_{47}$, the latter being more abundant, and dianions of $C_{60}F_{47}$ [18]. Hence, charge-transfer complexes with donor molecules should play an important role in the mechanism of the fluorofullerene anion formation process. On the basis of voltammetric studies of the reduction behavior of $C_{60}F_{48}$, Zhou et al. [15] suggested a scheme involving sequential charge transfer from donor molecules to form $C_{60}F_{48}^{2-}$ followed by F^{-} abstraction from the dianionic state forming $C_{60}F_{47}^{-}$. This ion then undergoes a similar charging process up to the triply charged state, followed again by fluoride release and formation of $C_{60}F_{46}^{2-}$. Using the assumption that in the absence of donor molecules, formation of the highly charged states is less likely, this model appears to agree well with the experimental data obtained in the present work and other ESI studies mentioned above. However, F atom or ion loss from fluorofullerene molecules could also be a result of fluorination of donor molecules in a concerted process involving F atom and electron transfer. This hypothesis is supported by our observations of the partial or even complete defluorination of fullerene fluorides upon the increase of the donor concentration. The lower strength of C–F bonds in fluorofullerenes relative to sterically unstrained organic compounds (the average C–F bond energy in $C_{60}F_{2n}$ does not exceed 300 kJ/mol and decreases from $C_{60}F_{36}$ to $C_{60}F_{48}$) [28,29] and higher stability of the closed-shell anionic species can serve as additional driving forces for the processes of F atom loss and charging. On one hand, such defluorination processes that accompany ESI MS of fluorofullerenes can be regarded as a drawback of the ESI-based method of anion production as compared to the gas-phase electron-capture techniques, since it is more difficult to generate molecular ions or doubly charged anions of the parent molecules. On the other hand, as we argue below, ESI ionization of fluorofullerenes can lead to the formation of unexpected and interesting structures, which are significantly different from the parent species.

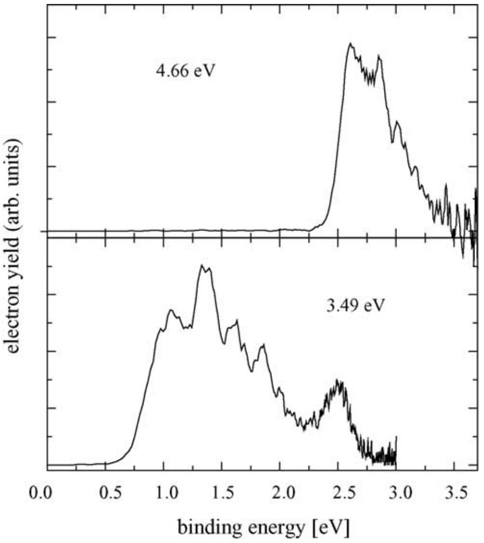


Fig. 2. Laser PE spectra of the $C_{60}F_{34}^{2-}$ dianion acquired at 4.66 eV (top) and 3.49 eV photon energies (bottom).

3.2. Photoelectron spectra

Fig. 2 shows the PE spectra of $C_{60}F_{34}^{2-}$ at photon energies of 4.66 and 3.49 eV, respectively. The 4.66 eV spectrum contains several unresolved bands with a threshold at 2.4 eV, while the 3.49 eV spectrum consists of several strong bands between 0.7 and 2.2 eV and a weaker feature at 2.5 eV, which coincides in position with the first band in the 4.66 eV spectrum. At lower laser fluence, the relative intensities of the low binding energy bands in the 3.49 eV spectrum with respect to the 2.5 eV band are reduced substantially indicating that the low-energy bands are due to two-photon processes.

From the 4.66 eV PE spectrum, we are able to derive an estimated second adiabatic electron affinity for $C_{60}F_{34}$ (2.4 ± 0.1 eV) using the onset of the first band. The vertical detachment energy of the $C_{60}F_{34}^{2-}$ dianion (2.6 ± 0.1 eV) is determined from the position of the first maximum. These values are remarkably high compared to the values for unfluorinated fullerenes, estimated to be negative for C_{60}, and measured to be below 0.5 eV for C_{76}, C_{78}, and C_{84} [10,11]. The cutoff of the PE spectra at high binding energies allows a rough estimate of the RCB height in $C_{60}F_{34}^{2-}$ (1.0 ± 0.2 eV) similar to the RCB height of C_{84}^{2-} [10].

Fig. 3 shows the 4.66 eV PE spectrum of $C_{60}F_{46}$, which consists of a single band, possibly consisting of several highly congested structures. The spectrum allows estimation of the second adiabatic electron affinity of $C_{60}F_{46}$ (3.2 ± 0.1 eV), which appears to be even higher than that of $C_{60}F_{34}$, whereas the RCB value of 1.0 ± 0.2 eV is roughly the same as for $C_{60}F_{34}^{2-}$ (the RCB height is estimated from the half-maximum energy on the high binding energy slope of the single broad peak in the PE spectrum in Fig. 3). Unlike

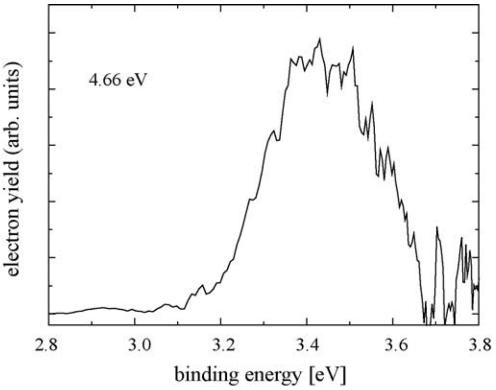


Fig. 3. Laser PE spectrum of the $C_{60}F_{46}{}^{2-}$ dianion acquired at 4.66 eV photon energy.

the case of $C_{60}F_{34}{}^{2-}$, no photoelectrons were observed after irradiation of $C_{60}F_{46}{}^{2-}$ at 3.49 eV photon energy.

Attempts to acquire PE spectra of fluorofullerene monoanions both at 3.49 and 4.66 eV were unsuccessful despite substantial ion signals, which indicates that the first electron affinity must be of the order or higher than 4.66 eV. This agrees with the results of the DFT estimates of the EA values for closed-shell highly fluorinated fullerenes containing an even number of F atoms and odd-F-atom radical species: the latter species have 0.8–1.0 eV higher EAs than the former ones. Taking into account a 3.5 eV estimate for EA ($C_{60}F_{36}$) [13] and a 4.1 eV value for $C_{60}F_{48}$ [14], one can conclude that even if photodetachment of $C_{60}F_{35}{}^{-}$ (the least fluorinated monoanion observed in this study) was possible with the 266 nm wavelength (4.66 eV), one would expect the onset for photodetachment from $C_{60}F_{35}{}^{-}$ at the very edge of the available photon energies.

3.3. Structural considerations

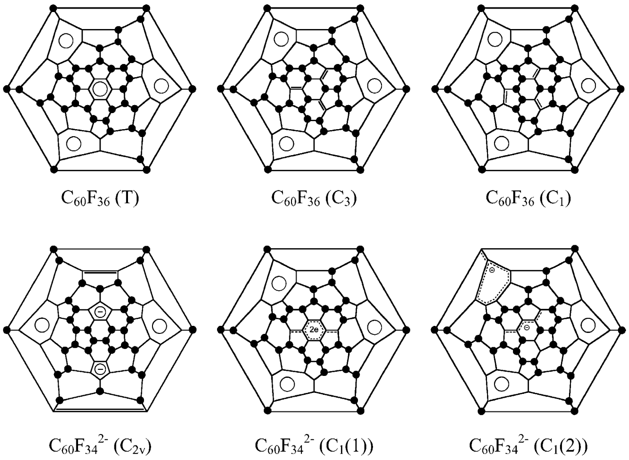
Our experimental second EAs for both fluorofullerene dianions appear unexpectedly high, when compared with the values obtained in our DFT calculations performed for several stable closed-shell isomers of $C_{60}F_{34}$ and $C_{60}F_{46}$ (the DFT-derived second EAs do not exceed 1.5 eV). Such a considerable discrepancy may indicate that isomers with an open-shell neutral ground state could be responsible for the observed PE spectra. At this point, it is necessary to take into account a well-known feature in the chemistry of fullerene fluorides—their ability to isomerize at elevated temperatures via rearrangements of F atoms towards the formation of the most thermodynamically stable products [30]. The C_1 isomer of $C_{60}F_{36}$ can isomerize into a more stable C_3 structure even at room temperature in solution [31]. We, therefore, may expect that ESI performed at the elevated drying-gas temperatures is likely to facilitate isomerization processes leading to the formation of highly stable isomers of the dianions, which should possess different structures than the most stable neutral species.

The search for relevant structures of $C_{60}F_{34}{}^{2-}$ was restricted to two major families of isomers. The first one consists of the structures connected to the major $C_{60}F_{36}$ isomers via removal of two F atoms. The high relative stability of $C_{60}F_{34}{}^{2-}$ isomers from this family is based on their close structural relations to the parent $C_{60}F_{36}$. In addition, they constitute the most likely kinetic products of F-atom abstraction reactions. The second family includes structures that are expected to possess high first and second electron affinities, based on their high relative stability in a doubly charged state. The π-systems of these isomers incorporate two highly electron-withdrawing cyclopentadienyl fragments, whereas the rest of the sp^2 carbon atoms form isolated double bonds and benzenoid six-membered rings. For several dozens of isomers from both families, full geometry optimization of the dianionic state at the AM1 level of theory was performed. The structures within 150 kJ/mol from the most stable species were then reoptimized at the DFT level of theory without symmetry constrains applied. It was shown in [32] that for a test set of $C_{60}F_{36}$ isomers the discrepancies between the AM1 and DFT results do not exceed 140 kJ/mol. The differences are mainly due to the systematic underestimation of the stabilizing effect of the benzenoid rings by the semiempirical method. As will be shown below, the most stable structures contain sufficient number of aromatic fragments to be rather under than overestimated by AM1. Several structures that proved to be the most stable at the DFT level of theory were fully optimized in the neutral and monoanionic states in order to calculate their first and second adiabatic electron affinity.

To our experience, the first EA values obtained with the functional employed here typically overestimate the EA values of the fullerene-based systems by about 10%, while the second EA values overestimate the experimental values for higher fullerenes [10,11] by about 0.4 eV. We apply corresponding corrections to estimate first and second EA values based on our calculations. We note that the true overestimation of the second EA values for fullerene fluorides should probably be even higher due to the lower magnitude of the correlation effects in these larger systems with excess electrons delocalized over a higher number of atoms. Fig. 4 shows Schlegel diagrams for two most abundant isomers of $C_{60}F_{36}$ and three most stable isomers of $C_{60}F_{34}{}^{2-}$. Estimated relative stabilities, and first and second electron affinities for these isomers are given in Table 1.

Table 1
Estimated first and second electron affinities of $C_{60}F_{34}$ isomers corresponding to the most stable $C_{60}F_{34}{}^{2-}$ dianions (see Fig. 4)

	Isomer		
	C_{2v}	C_1 (1)	C_1 (2)
Relative stability in dianionic state (kJ/mol)	0.0	16.3	21.7
EA_2 (eV)	2.6	1.8	1.7
EA_1 (eV)	5.6	4.5	4.5



$C_{60}F_{36}$ (T) $C_{60}F_{36}$ (C_3) $C_{60}F_{36}$ (C_1)

$C_{60}F_{34}^{2-}$ (C_{2v}) $C_{60}F_{34}^{2-}$ ($C_1(1)$) $C_{60}F_{34}^{2-}$ ($C_1(2)$)

Fig. 4. Schlegel diagrams of the three most abundant isomers of $C_{60}F_{36}$ and three most stable isomers of $C_{60}F_{34}^{2-}$ dianions.

Two of the three most stable $C_{60}F_{34}^{2-}$ isomers belong to the $C_{60}F_{36}$-structurally related family, whereas the third one belongs to the cyclopentadienyl family, its formation requiring multiple F-atom migration steps. However, our calculations imply that only the cyclopentadienyl isomer can be responsible for the observed PE spectra, since $C_{60}F_{36}$-related structures are characterized by the significantly lower second EA values. Moreover, our DFT calculations of the second EA for a number of less stable isomers demonstrate that this characteristic is rather family-specific than isomer-specific. Consequently, the 2.4 eV threshold in the 4.66 eV PE spectrum points to the formation of a cyclopentadienyl isomer, for which the proposed C_{2v} structure is depicted in Fig. 4. This suggests that the conditions of the ESI experiment at elevated drying-gas temperatures allow migration of F atoms over the carbon cage, which results in their rearrangement. This is compatible with the fact that the high-temperature fluorination conditions described in Ref. [19] enable abundant formation of the most thermodynamically stable isomers of fluorofullerenes.

Unlike the case of $C_{60}F_{34}^{2-}$, an analogous structural survey of possible $C_{60}F_{46}^{2-}$ isomers provided inconclusive results. The parent $C_{60}F_{48}$ molecule is known to incorporate six isolated double bonds [30], their rather uniform distribution over the carbon cage probably being responsible for relaxation of this highly strained structure. As shown in an extensive computational survey of higher fluorides of C_{60} [33], the isomers of $C_{60}F_{48}$ with less uniformly distributed double bonds appear to be significantly less stable than the experimentally observed ones. Moreover, unlike the case of $C_{60}F_{36}$, the most stable isomers of $C_{60}F_{48}$ with three or six fluorine atoms attached endohedrally are kinetically inaccessible structures. Therefore, one can expect that the major role in stability of the $C_{60}F_{48}$-related anions is played by steric effects rather than by effects of electron affinity. Hence, regarding $C_{60}F_{46}^{2-}$, compact assembly of sp^2 carbon atoms into large conjugated fragments, such as cyclopentadienyl rings, is unlikely. Indeed, DFT calculations suggest that the most stable $C_{60}F_{46}^{2-}$ isomers are those containing two allylic anionic fragments; several isomers of this kind, being coupled to $C_{60}F_{48}$ via simple detachment of two fluorine atoms adjacent to different double bonds, are the most kinetically accessible structures as well. Among the isomers containing two cyclopentadienyl fragments, the most stable ones are 90 kJ/mol higher in energy, and other types of isomers including mixed allylic-cyclopentadienyl structures were predicted to be even less stable. Therefore, it may be suggested that the experimentally observed isomer (or isomers) of $C_{60}F_{46}^{2-}$ contain two allylic anionic fragments. However, such a conclusion appears to be incompatible with the results of our calculations regarding the second EA values. We found that no isomer of $C_{60}F_{46}$ exhibited the second EA higher than 2.5 eV, except for cyclopentadienyl structures, which were calculated to possess the second EA comparable to the experimentally measured value of 3.2 eV. One might argue that this disagreement may be solved by taking into account the above-mentioned isomers containing endohedrally attached fluorine atoms. The higher degree of steric relaxation in such structures may be more favorable than effects of electron affinity regarding the stability of their anions. However, there are no indications that such isomers can form without a high-energy impact, and we, therefore, cannot give a stability- or kinetics-consistent interpretation of the high second EA of $C_{60}F_{46}^{2-}$.

We attempted to model PE spectra of various $C_{60}F_{34}^{2-}$ and $C_{60}F_{46}^{2-}$ isomers mentioned above by calculating excitation spectra of the corresponding monoanionic products of photoionization by means of TDDFT. As in previous work [10,11], PE spectra were simulated by placing the monoanion ground state to the vertical detachment energy and superimposing the lowest doublet states of monoanions considered with Gauss functions. It was shown in [10] that the errors in the excitation energies thus obtained do not exceed 0.2–0.3 eV. TDDFT calculations predict a major difference between the PE spectra of cyclopentadienyl and non-cyclopentadienyl structures within 1 eV from the threshold energy. In the case of $C_{60}F_{34}^{2-}$, a common feature for the majority of isomers from the $C_{60}F_{36}$-related family is a two-band shape of the simulated spectra, whereas four bands are common for all isomers containing two cyclopentadienyl fragments, corresponding to the symmetrized products of four typical Hückel-type HOMOs of five-membered cycles. HOMOs for the particular case of the C_{2v} isomer are presented on Fig. 5. Similar distinctions between the spectra of allylic isomers (two bands) and cyclopentadienyl isomers (four bands) can be predicted for $C_{60}F_{46}^{2-}$. Unfortunately, the experimental PE spectrum of the latter covers a range of only 0.5 eV, and does not allow isomer identification. This, however, does not apply to the 4.66 eV PE spectrum of $C_{60}F_{34}^{2-}$, which covers a much wider energy range. In Fig. 6, we present a comparison of the experimental 4.66 eV PE spectrum and simulated spectra of the most stable $C_{60}F_{34}^{2-}$ isomers. Although from the formal point of view, two-band spectra of the $C_{60}F_{36}$-related

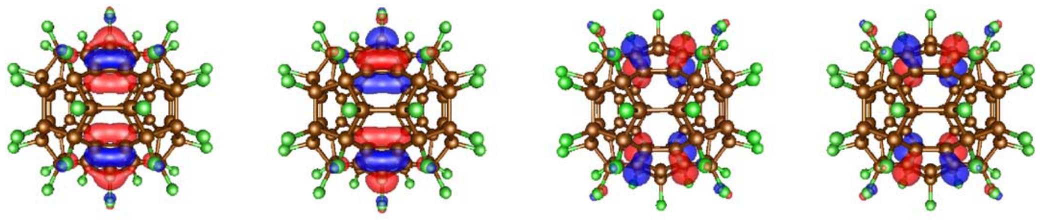

HOMO-3 (a1) HOMO-2 (b1) HOMO-1 (b2) HOMO (a2)

Fig. 5. Four HOMOs of the C_{2v} isomer of $C_{60}F_{34}{}^{2-}$.

isomers seem to simulate the experimental data somewhat better, the 4.66 eV spectrum apparently contains no fewer than three partially resolved bands, which is in better agreement with the TDDFT results for cyclopentadienyl isomers. Unfortunately, the presence of the RCB leads to a cutoff on the high-energy slope of the spectrum and precludes a more definitive judgment. However, we stress that the formation of the isomers that belong to the $C_{60}F_{36}$-related family seems unlikely on the basis of our electron affinity calculations.

3.4. Repulsive Coulomb barriers

The estimated RCB heights of 1.0 ± 0.2 eV are somewhat lower than that derived by Compton and co-workers for $C_{60}F_{48}{}^{2-}$ (1.5 eV) from the charged-sphere model [14]. However, the equation used in [14], which contains a conducting sphere potential corrected for a finite dielectric constant, is not exact. Similarly, a formula used for RCB estimation by Hartig et al. [34], introducing a polarization term similar to the homogeneous external field case, overestimates the experimentally determined RCB in C_{84} dianion (0.80 (10)–1.05 (10) eV [5]) by about 0.7 eV. We use an alternative description for the interaction potential between a charged dielectric sphere and a point charge given in [35]:

$$E(r) = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r} - \frac{b}{2r^2}\sum_{k=1}^{\infty}\left[\left(\frac{b}{r}\right)^{2k}\frac{k(\varepsilon-1)}{k(\varepsilon+1)+1}\right]\right), \quad (1)$$

where b stands for the radius of the sphere, ε_0 is the vacuum dielectric constant and ε denotes its dielectric constant. The power series used to express the polarization term converge rather rapidly; for example, 15 terms allow to reproduce the barrier shape with 0.01 eV accuracy for $b > 5$ Å and $r > 1.2b$, irrespective of ε. In the limit of a high dielectric constant, the series converges into the exact formula describing the interaction between the conducting sphere and a point charge, whereas for low values of ε, the attractive term becomes more short-range and the Coulomb barrier position shifts towards the sphere, its height approaching $e^2/4\pi\varepsilon_0 b$.

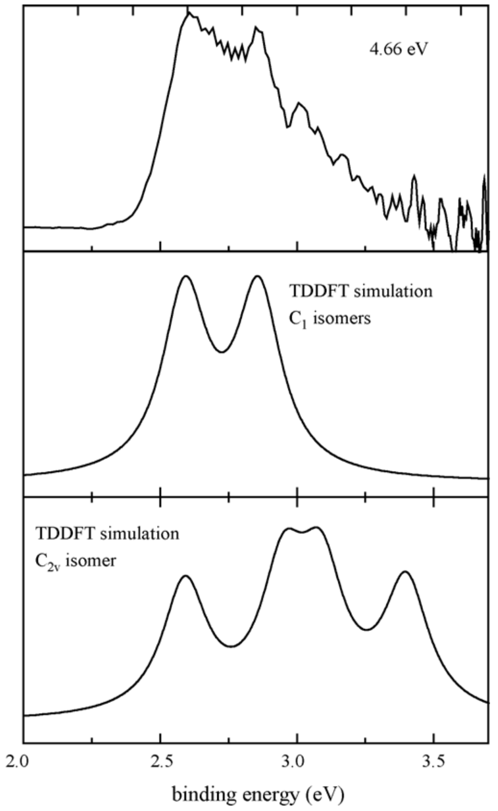


Fig. 6. Experimental 4.66 eV PE spectrum of $C_{60}F_{34}{}^{2-}$ (above) compared with TDDFT simulations (see text) for three most stable isomers of this dianion. The simulated spectra of the two C_1 isomers proved to be virtually equivalent.

First, an appropriate value for b needs to be found. In an attempt to estimate the dielectric constant of C_{60} we derive

$$\alpha = \frac{\varepsilon - 1}{\varepsilon + 2} b^3 \quad (2)$$

from the Clausius–Mosotti relation and the experimentally determined gas-phase polarizability value of 76.5 ± 8.0 Å^3 [36], we found that the result is meaningless for $b < 4.25$ Å, whereas center-to-nuclei distance in C_{60} is only 3.57 Å. This observation, which can be accounted for by the protrusion of π-electron clouds far beyond the nuclei, brings up the question of the correct choice of the sphere radius. Since the major contribution to the polarizability comes from the valence electrons, the most natural option would be an average radius of the molecular van-der-Waals surface.

Following the approach described above, the effective radius of C_{60} can be found as a half the distance between the centers of adjacent molecules in the closely packed C_{60} solid. Using the value of 5 Å thus obtained [37] and the polarizability value presented above, one can estimate the dielectric constant of C_{60} to be 6.0 ± 1.3. Our further considerations for the case of fluorofullerene dianions will be based on the C_{2v} isomer of $C_{60}F_{34}{}^{2-}$. We believe that the result should not significantly depend on the molecular structure and should not be much affected by the attachment of 12 more fluorine atoms. The effective radius of $C_{60}F_{34}{}^{2-}$ was taken as 6.6 Å, which includes the average F atoms displacement from the molecular center of mass and the van-der-Waals radius of F (ca. 1.35 Å [38]). DFT calculation of the dipole polarizability of $C_{60}F_{34}{}^{-}$ via analytical computation of the second derivatives of the total energy with respect to the electric field yields a 97.4 $Å^3$ value of its isotropic component; this gives a value of 2.5 for its dielectric constant. As one could expect, this value is considerably lower than that of C_{60} due to replacement of the easily polarizable π-system of the latter by the F shell.

Using Eq. (1), we obtain an estimate of the RCB height in $C_{60}F_{34}{}^{2-}$, which amounts to 1.35 eV and corresponds to a 9-Å distance from the center of mass (or 2.4 Å from the boundary of the van-der-Waals surface). Similar treatment of C_{84} (estimated radius 5.7 Å, dielectric constant taken equal to that of C_{60}) results in a pronounced decrease of the predicted RCB down to 1.4 eV. Although both RCB heights thus obtained still overestimate the experimental values, the agreement between classical model predictions and experimental data is somewhat improved. One of the possible reasons for the remaining discrepancy between the classical model and the experiment in the case of $C_{60}F_{34}{}^{2-}$ is the observable anisotropy in the charge and valence orbital density distribution. Indeed, as shown in Fig. 5, the highest occupied molecular orbitals of the C_{2v} isomer of $C_{60}F_{34}{}^{2-}$ are localized on the cyclopentadienyl fragments, whereas the calculated Hirshfeld atomic charges [39] in the monoanionic state range from −0.08 to −0.11 for F atoms but do not exceed −0.05 even for those carbon atoms, which belong to cyclopentadienyl fragments. As a result, formally computed dipole and higher-order moments appear to be nonzero, which will result in an anisotropic potential. However, we have to bear in mind that effects, such as correlation, cannot be included in these simple classical models, and we, therefore, expect that the accuracy of classical models will be limited.

4. Conclusions

We have shown that $C_{60}F_{34}$ and $C_{60}F_{46}$ possess high positive second electron affinities, which highlights the dramatic influence of F atoms on the properties of the fullerene electronic system. The isomers responsible for the high second electron affinities observed in our experiment are likely to be brought about by a rather high mobility of F atoms on the carbon shell of the negatively charged fluorofullerene species. The mechanism of the F-atom migration and related catalytic effects of the surrounding medium remain interesting problems to be pursued in future studies. Further systematic studies of multiply charged anions of fullerene derivatives could provide important fundamental information related to electron delocalization and properties of the repulsive Coulomb barriers.

Acknowledgments

The MSU team acknowledges the Volkswagen-Stiftung (I-77/855) for partial financial support, Dr. I.V. Goldt for preparation of $C_{60}F_{36}$ sample, and Dr. V.I. Pupyshev for helpful discussion. I.N.I. is thankful to INTAS (YS grant 2004-83-3316) and Russian President's grant MK-2734.2004.3. Partial support from the Humboldt Foundation (through the F. Bessel award to OVB) is appreciated. The Karlsruhe team acknowledges the Deutsche Forschungsgemeinschaft for financial support, and Professor Dr. Manfred M. Kappes for generous support and helpful discussions.

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