In-Plume Thermodynamics of the MALDI Generation of Fluorofullerene Anions

Alexey V. Streletskii,[†] Ilya N. Ioffe,[†] Sotirios G. Kotsiris,[‡] Mark P. Barrow,[‡]
Thomas Drewello,*,[‡] Steven H. Strauss,*,[§] and Olga V. Boltalina*,[†,§]

Chemistry Department, Moscow State University, Moscow 119992, Russia, Department of Chemistry,
Warwick University, Coventry CV4 7AL, United Kingdom, and Department of Chemistry,
Colorado State University, Fort Collins, Colorado 80523

Received: August 19, 2004; In Final Form: November 6, 2004

The mechanism of formation of fluorofullerene (FF) negative ions derived from the compounds $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$ was studied by matrix-assisted laser desorption/ionization (MALDI) time-of-flight (ToF) mass spectrometry (MS). A combined experimental/theoretical approach provides compelling evidence of nondissociative, thermodynamically controlled electron transfer from matrix-derived negative ions to the FF analyte as the main secondary-ionization process. Consistent with this thermochemical model, analyte parent molecular ion yield and degree of fragmentation for a particular MALDI experiment was found to depend on the nature of the matrix material (the five matrices investigated were sulfur, *trans*-2-[3-{4-*tert*-butylphenyl}-2-methyl-2-propenylidene]malononitrile, 9-nitroanthracene, 2,6-bis((furan-2-yl)methylene)cyclohexanone, and 2,6-bis((thiophen-2-yl)methylene)cyclohexanone). For mixtures of $C_{60}F_n$ compounds with different *n* values and therefore different electron affinitites, unwanted electron-transfer reactions, which can lead to the suppression of $C_{60}F_n^-$ ions with low *n* values, were successfully blocked for the first time by judicious choice of the matrix. Therefore, reliable qualitative MS analysis of FF mixtures with wide ranges of composition is now possible.

Introduction

Mass spectrometry (MS) is one of the most successful analytical methods for the characterization of fullerenes and their derivatives. However, the product analysis following halogenation, alkylation, or fluoroalkylation is challenging as these radical reactions normally yield a wide range of complex mixtures of polysubstituted compounds. The MS analysis of fluorinated fullerene (FF) derivatives[1−6] is often hampered by significant degradation/dissociation of FFs, thereby preventing adequate characterization of their molecular compositions. This is particularly true for methods based on desorption/ionization such as MALDI-MS. However, the high sensitivity of this method, which requires only minute amounts of sample, makes it desirable to develop MALDI protocols for decomposition-free analysis of these molecules. Progress toward improved applicability of MALDI-MS is connected with an improved understanding of the underlying mechanisms of essential processes such as desorption and ion formation. Recent MALDI studies of specific FFs and related halofullerenes provided a strong indication of the importance of electron-transfer processes in the formation of various charged species in the plume.[7,8] The present paper describes a comprehensive investigation, based on these initial reports, into one of the fundamental questions in MALDI: In general, is electron exchange between neutral analyte molecules and charged matrix species *the* major process that determines the final ion distribution?

Previous work detailed the importance of electron-transfer reactions in MALDI for the formation of *positive* ions.[9,10] It was suggested that charge-transfer reactions took place in the laser ablation plume, involving matrix ions formed in the primary ionization process and excited neutral species of the analyte, so that electron transfer was largely responsible for the generation of the intact parent molecular radical cations of the analyte. Importantly, the presence or absence of analyte ions could be predicted on the basis of the thermodynamics of the charge-transfer process. For this process to be thermodynamically feasible, the ionization energy (IE) of the analyte must be lower than the IE of the matrix, otherwise analyte species exceeding the IE of the matrix would not be detected.

In this work, a similar mechanistic approach is developed for molecular systems, in which the formation of *negative* ions is the preferred ionization process. A variety of individual FFs have become available in macroscopic amounts. The high electronegativity of the F-atom-bearing fullerene and the strong correlation between electron affinity (EA) and fluorine content provide a convenient and versatile model system for the mechanistic studies of in-plume ionization processes. Taking advantage of the ionic properties and energetics that were gathered for fluorine derivatives of C_{60} in recent years,[6,11−13] and applying a careful selection of matrix materials of varying ionization characteristics and molar absorbances, the study provides a rationale for the formation and relative distributions of negative FF ions in MALDI mass spectra and, in particular, allowed us to explain (and then predict) the presence or absence of parent molecular anions of the FF analytes.

Experimental Section

Materials. The samples of $C_{60}F_{18}$ and $C_{60}F_{36}$ were prepared in a solid-state reaction of C_{60} with K_2PtF_6 and MnF_3, respectively, as described elsewhere.[14,15] The former compound was purified by vacuum sublimation followed by HPLC; the

---

* To whom correspondence should be addressed. E-mail: OVB, ovbolt@lamar.colostate.edu; TD, t.drewello@warwick.ac.uk; SHS, steven.strauss@colostate.edu.

[†] Moscow State University.

[‡] Warwick University.

[§] Colorado State University.

10.1021/jp046243l CCC: $30.25

latter compound was purified by sublimation, and $C_{60}F_{48}$ was used as prepared. Direct fluorination of C_{60} was used to prepare $C_{60}F_{48}$,[16] the purity of which was estimated as 95 mol % by MS and NMR spectroscopy. IR spectra showed that all three compounds contained, at most, a negligible amount of unreacted C_{60} (i.e., C_{60} bands at 526, 577, 1182, and 1428 cm^{-1} were absent). The matrix materials *trans*-2-[3-{4-*tert*-butylphenyl}-2-methyl-2-propenylidene]malononitrile (DCTB; Fluka), 9-nitroanthracene (9-NA; Sigma-Aldrich), and sulfur (Sigma-Aldrich) were used as received. The matrix materials 2,6-bis((furan-2-yl)methylene)cyclohexanone (DFMC) and 2,6-bis((thiophen-2-yl)methylene)cyclohexanone (DTMC) were a gift from Professor N. V. Zyk of Moscow State University and were used as received.

Instrumentation. All mass spectrometric experiments were conducted with a Kompact MALDI IV (Kratos Analytical, Manchester, UK) reflectron time-of-flight mass spectrometer in the reflectron mode. A 337-nm N_2 laser was used for target activation. Each mass spectrum was the average of 50−100 laser shots. For measurements of ion abundance as a function of laser fluence, the laser fluence was varied from 70 to 180 arbitrary units, which for a pristine laser cartridge would correspond to a fluence of ca. 40 to 1140 mJ cm^{-2}. The actual fluences may have been lower than these values at the time of the experiments. While the succession of ion appearances with increasing laser fluence should remain unchanged, the actual value of the appearance threshold fluence may differ when different instrumentation is used. At each laser fluence increment, ions were accumulated for five laser shots to construct the ion-yield curve.

MALDI Sample Preparation. Fluorinated fullerenes and matrices (DCTB, sulfur, 9-NA, DFMC, DTMC) were dissolved separately in toluene. The matrix:analyte mole ratio was typically 100:1 unless otherwise noted. A droplet of the prepared solution was deposited on the stainless steel slide with use of a capillary under a strong cool air stream from an air-sprayer/brush to achieve uniformity of the sample surface.

Theoretical Methods. The computations were performed at the DFT level of theory with the program PRIRODA,[17] a TZ2P basis set specially optimized for DFT calculations, and the PBE exchange-correlation functional.[18] All of the computations were performed with full geometry optimization. Electron affinity values were obtained by using the Δ_{SCF} procedure.

Results and Discussion

Ionization Processes in Direct LDI Experiments. (*a*) *Fluorofullerene Negative Ions.* In earlier investigations involving laser ablation (i.e., direct LDI) of FFs, the samples were complex mixtures of FFs with a range of compositions.[4,5] This precluded an unambiguous assignment of the origin of some of the observed ions. The present work allowed, for the first time, an in-depth analysis of FF LDI-MS data because three compositionally pure FFs, $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$, were used. Negative ion LDI mass spectra of these three compounds are shown in Figure 1. In each case, the spectrum was recorded at or near the laser-fluence threshold; at higher laser fluences, more extensive fragmentation was observed. There are several interesting features that can be understood by using the experimental and theoretical thermodynamic data listed in Tables 1 and 2. These are (i) a smaller range of compositions of $C_{60}F_{n-m}^-$ ions for $n = 18$ than for $n = 36$ or 48, (ii) the absence of $C_{60}F_n^-$ parent molecular ions for $n = 36$ or 48, even at the lowest laser fluences used, (iii) the presence of a $C_{60}F_{n+1}^-$ ion, but only for $n = 18$, and (iv) the presence $C_{60}F_{n-m}^-$ ions with both odd and even $n - m$ values for $n = 18$ but with only odd $n - m$ values for $n = 36$ and 48.

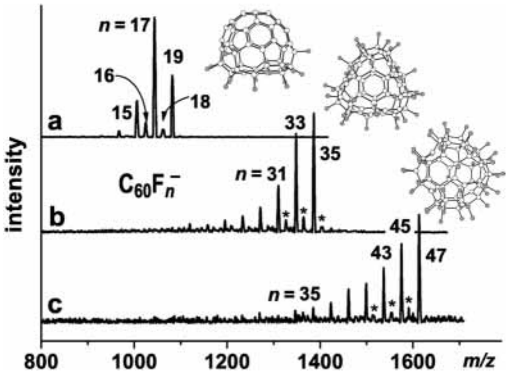


Figure 1. Negative ion LDI mass spectra of (a) $C_{60}F_{18}$, (b) $C_{60}F_{36}$, and (c) $C_{60}F_{48}$ recorded with similar 337-nm laser fluences. The peaks marked with asterisks are due to trace amounts of oxofluorofullerene ions such as $C_{60}F_{35}O^-$ in spectrum b and $C_{60}F_{45}O^-$ in spectrum c. Drawings of the X-ray structures of the three fluorofullerenes are shown above and to the right of each spectrum.

TABLE 1: Experimental Gas-Phase Electron Affinities, Ionization Energies, and Mean C−F Bond Dissociation Energies of $C_{60}F_n$ Derivatives ($n = 18, 36, 48$)[a]

compd	EA/eV	IE/eV	mean C−F BDE/eV
C_{60}	2.667(1)[21]	7.57(1)[22]	
$C_{60}F_{18}$	3.1 (est)[23]	8(1)[24]	3.2[b]
$C_{60}F_{36}$	3.5 (est)[25]	11.1(2)[6]	3.06(6)[12]
$C_{60}F_{48}$	4.1(3)[11]	12.1(2)[6,26]	2.98(4)[13]

[a] One estimated standard deviation in the least significant figure shown in parentheses; the mean C−F BDE is $1/n$ times the standard enthalpy change for the gas-phase reaction $C_{60}F_n \rightarrow C_{60} + nF$; est = estimated from electrochemical reduction potentials. [b] Calculated by DFT methods in ref 27.

TABLE 2: DFT Calculated Enthalpies of Fluorine Atom Loss from Selected Fluorofullerenes and Fluorofullerene Negative Ions

gas-phase reaction	$\Delta_rH°$/eV per F atom	$\Delta_rH°$/kJ mol^{-1} per F atom	ref
$C_{60}F_{48} \rightarrow C_{60} + 48F$	3.0 (2.98(4)[a])	290	27
$C_{60}F_{18} \rightarrow C_{60} + 18F$	3.2	310	27
$C_{60}F_{48}^- \rightarrow C_{60}F_{47}^- + F$	2.0	190	this work
$C_{60}F_{36}^- \rightarrow C_{60}F_{35}^- + F$	2.4	230	this work
$C_{60}F_{18}^- \rightarrow C_{60}F_{17}^- + F$	2.6	250	this work
$C_{60}F_{36} \rightarrow C_{60}F_{34} + 2F$	3.2	310	27
$C_{60}F_{18} \rightarrow C_{60}F_{16} + 2F$	3.4	331	27

[a] Experimental value from ref 13.

It has been shown that an important ionization process in LDI-MS is the capture of free electrons (i.e., electrons generated by photoelectric emission) by neutral analyte molecules.[19,20] Therefore, we will assume that reaction 1, followed by subsequent unimolecular fragmentations and/or collision-induced reactions of the highly energetic $C_{60}F_n^-$ ion or less energetic $C_{60}F_{n-m}^-$ ions, accounts for most of the observed FF negative ions in the LDI mass spectra shown in Figure 1 (EA = electron affinity):

$$C_{60}F_n + e^- \rightarrow C_{60}F_n^- \qquad \Delta_rH \approx -\mathrm{EA}(C_{60}F_n) \qquad (1)$$

Therefore, the internal energy of the $C_{60}F_n^-$ ion formed in reaction 1 increases monotonically from $n = 18$ to 48 (see Table 1). At the same time, Δ_rH for reaction 2 decreases monotonically from $n = 18$ to 48 (see Table 2):

$$C_{60}F_n^- \rightarrow C_{60}F_{n-1}^- + F \qquad (2)$$

The result of these two trends is (i) more extensive fragmentation for $n = 36$ and 48 than for $n = 18$ and (ii) complete loss of the parent $C_{60}F_{36}^-$ and $C_{60}F_{48}^-$ molecular ions, but not complete loss of the $C_{60}F_{18}^-$ ion, formed in reaction 1. Specifically, the enthalpy change for overall reaction 3 is ca. −2.1 eV for $n =$ 48, ca. −1.1 eV for $n = 36$, and ca. −0.5 eV for $n = 18$:

$$C_{60}F_n + e^- \rightarrow C_{60}F_{n-1}^- + F \qquad (3)$$

Plots of ion current vs laser fluence for all three samples are shown in Figure S-1 (Supporting Information). There is a minor difference in the laser-fluence threshold for $C_{60}F_{18}$ than for $C_{60}F_{36}$ or $C_{60}F_{48}$. We cannot rule out that the slightly lower laser fluence used to collect the $C_{60}F_{18}$ LDI mass spectrum in Figure 1 might be responsible, in part, for the smaller degree of fragmentation. However, we believe that this factor is far less important than the above-mentioned differences in C−F bond enthalpies and electron affinities.

Since the sample of $C_{60}F_{18}$ used in this work was an HPLC-purified sample that did not contain any trace of $C_{60}F_{20}$ or higher FFs, the most likely explanation for the strong signal due to the $C_{60}F_{19}^-$ ion in the LDI spectrum of $C_{60}F_{18}$ is that it is formed via exothermic reactions 4 or 5 (F^- ions have been shown to be abundant during LDI of FFs[28]):

$$C_{60}F_{18} + F^- \rightarrow C_{60}F_{19}^- \qquad (4)$$

$$C_{60}F_{18}^- + F \rightarrow C_{60}F_{19}^- \qquad (5)$$

It is sensible that $C_{60}F_{n+1}^-$ ions are not formed for $n = 36$ or 48 because of the extremely stable structures of the two major $C_{60}F_{36}$ isomers (each has four stabilizing benzenoid rings)[29,30] and because the six remaining C=C double bonds in both isomers of $C_{60}F_{48}$ are sterically inaccessible to external reagents.[31] There is little doubt that reactions 4 and 5 are more favorable, both thermodynamically and kinetically, than the corresponding reactions for $n = 36$ or 48 species. An entire hemisphere of $C_{60}F_{18}$ is sterically free and therefore accessible for facile addition reactions.[32]

We previously reported that LDI-MS could provide a reliable estimate of the highest degree of fluorination in FF mixtures,[8] and the high sensitivity of the method led to the detection of even minor impurities. This conclusion must now be tempered because of the presence of $C_{60}F_{19}^-$ in the LDI mass spectrum of $C_{60}F_{18}$: some fullerene derivatives with relatively few substituents can undergo in-plume association reactions that may lead to an erroneous prediction of the maximum number of substituents.

It has been shown that the difference in EA values for a consecutive pair of fluorofullerenes $C_{60}F_n$ and $C_{60}F_{n-1}$ varies from ca. 0.5 eV for $n = 18$ to ca. 1.0 eV for $n = 48$ (the species with the odd number of F atoms have the higher EA values).[27] Therefore, electron-exchange reaction 6 is more exothermic for higher than for lower values of $n - m$ ($n - m$ is a positive integer):

$$C_{60}F_{n-m}^- + C_{60}F_{n-m-1} \rightarrow C_{60}F_{n-m} + C_{60}F_{n-m-1}^- \qquad (6)$$

Hence, the probability for the simultaneous existence of consecutive $C_{60}F_{n-m}^-$ and $C_{60}F_{n-m-1}^-$ anions is greater for $n - m < 18$ than for $n - m$ values between 30 and 46, in agreement with the presence of $C_{60}F_{18}^-$ and $C_{60}F_{16}^-$ in the LDI spectrum of $C_{60}F_{18}$ but the absence of $C_{60}F_{n-m}^-$ ions with even $n - m$ values in the LDI spectra of $C_{60}F_{36}$ and $C_{60}F_{48}$. It is noteworthy that similar observations were reported when other methods of ionization were used, including negative ion chemical ionization and thermal ionization.[33]

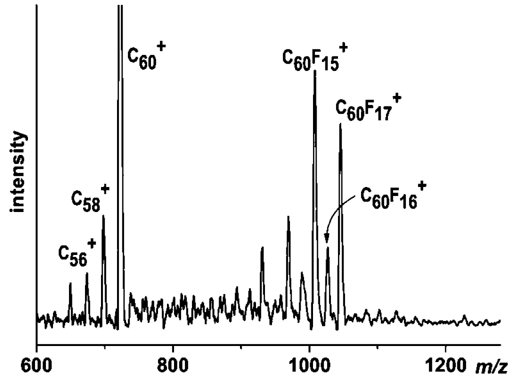


Figure 2. Positive ion LDI mass spectrum of $C_{60}F_{18}$. The intensity of the truncated C_{60}^+ signal is five times higher than that of $C_{60}F_{17}^+$.

(*b*) *Fluorofullerene Positive Ions.* The high ionization energies (IEs) in Table 1, especially for $C_{60}F_{36}$ and $C_{60}F_{48}$, lead to the expectation that the generation of FF positive ions under LDI conditions should be difficult. Indeed, the positive ion LDI mass spectra of $C_{60}F_{36}$ and $C_{60}F_{48}$ (not shown) exhibit a signal for C_{60}^+ but no signals for any FF positive ion. However, the corresponding spectrum for $C_{60}F_{18}$, shown in Figure 2, exhibits signals for the FF positive ions $C_{60}F_{n-m-1}^+$ ($n - m - 1 = 11-17$) in addition to a higher intensity signal due to C_{60}^+. This represents the first reported observation of FF positive ions with LDI-MS. Apparently, FF positive ions cannot be easily generated from FFs with 36 or more F atoms (i.e., with IEs ≥ 10 eV). Since these highly substituted FFs have, on average, weaker C−F bonds than, for example, $C_{60}F_{18}$, the accumulation of multiple photons may lead to complete defluorination (perhaps promoted by the metallic sample holder) before the ionization threshold of $C_{60}F_{36}$ and $C_{60}F_{48}$ is reached (note that even C_{60} must absorb at least three 337-nm photons for C_{60}^+ to be observed under similar LDI-MS conditions[34]).

Primary and Secondary Electron-Transfer Ionization Processes in MALDI Experiments. A notable recent review, primarily covering the generation of MALDI positive ions, highlighted the importance of in-plume reactions in MALDI-MS.[35] It was shown that, in most cases, the final distributions of positive ions in MALDI mass spectra could be understood on the basis of the thermodynamics of charge transfer (i.e., proton or electron-transfer reactions) between the various species present in the plume. Our results, discussed below, demonstrate that the thermodynamics of electron-transfer reactions is an important factor in determining the distribution of negative ions in FF MALDI mass spectra.

It is well-known that a significant number of free electrons are present in MALDI plumes along with various ions derived from the analyte and the matrix.[19,20] As in LDI-MS, free electrons play an essential role in the primary step of anion formation in MALDI-MS. The difference is that free electrons are only directly responsible for the generation of matrix-derived anions in the plume, and the observed analyte anions are primarily formed by secondary in-plume electron-transfer reactions between the matrix-derived anions and neutral analyte molecules. Therefore, it is essential to know the electron affinities of the matrix molecules used and relevant matrix-derived molecular fragments. With the exception of S_n fragments, experimental EA values have not been reported for the matrices used in this work. Instead, we calculated the necessary EA values at the DFT level of theory. The results are listed in Table 3.

TABLE 3: Electron Affinities and Laser-Fluence Thresholds for MALDI Matrix Compounds[a]

matrix	gas-phase matrix species	EA/eV of matrix species	laser-fluence threshold for matrix, arbitrary units (min−max: 0−180)
sulfur	S	2.077104(3)[b]	125−135
sulfur	S_2	1.57(5)[c]	
sulfur	S_3	2.3(1)[c]	
sulfur	S_4	2.22(3)[c]	
9-NA	9-NA	1.4	ca. 100
9-NA	ArO	2.2	
DCTB	DCTB	2.0	80−90
DFMC	DFMC	1.3	80−90
DTMC	DTMC	1.3	80−90

[a] All EA values calculated by DFT methods in this work unless otherwise indicated. Abbreviations: 9-NA, 9-nitroanthracene; ArO, 9-*O*-anthracenyl; DCTB, *trans*-2-[3-{4-*tert*-butylphenyl}-2-methyl-2-propenylidene]malononitrile; DFMC, 2,6-bis((furan-2-yl)methylene)cyclohexanone; DTMC, 2,6-bis((thiophen-2-yl)methylene)cyclohexanone. [b] Experimental value from ref 38. [c] Experimental value from ref 39.

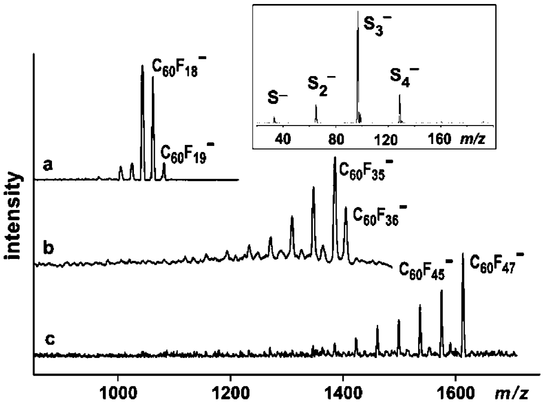


Figure 3. Negative ion S_8-MALDI mass spectra of (a) $C_{60}F_{18}$, (b) $C_{60}F_{36}$, and (c) $C_{60}F_{48}$ recorded with similar 337-nm laser fluences. The inset is the expanded region from *m/z* 30−200 in spectrum a, which shows the major matrix anions present in these experiments.

(*a*) *Sulfur as the MALDI Matrix.* Negative ion S_8-MALDI mass spectra of $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$ are shown in Figure 3. The matrix:analyte mole ratios spanned the narrow range from 50:1 to 100:1. Signals due to parent molecular anions are present in the $C_{60}F_{18}$ and $C_{60}F_{36}$ spectra but not in the spectrum of $C_{60}F_{48}$. Note that the intensity of the $C_{60}F_{18}^-$ signal in Figure 3a is nearly the same as the intensity of the $C_{60}F_{17}^-$ signal and that a small signal due to $C_{60}F_{19}^-$ is also present. However, except for $C_{60}F_{36}^-$, the signals in Figure 3b are due only to FF negative ions with an odd number of F atoms.

Sulfur has been used as a MALDI matrix for a wide variety of analytes, including porphyrins,[36] carotenoids,[36] fluorofullerenes,[8] and fullerenes with methano-bridged organic moieties.[36] Laser ablation of S_8 produces S_3^- and S_5^+ as the most abundant ions at low laser fluences in their respective ion modes.[37] The laser-fluence-dependent formation of these ions from S_8 suggested that the sequence $S_8 \rightarrow S_8^* \rightarrow S_3^- + S_5^+$ might be operative. The S_3^- and S_5^+ ions should therefore be considered as the principal charged protagonists for in-plume electron-transfer reactions, a conclusion that is consistent with our earlier results using S_8-MALDI to study $C_{60}F_{36}$.[8] The inset in Figure 3 demonstrates that S_2^- and S_4^-, which are also formed in our experiments, should be considered as potential, albeit minor, charged protagonists. The experimental electron affinities of gaseous S_n species ($n = 1−4$) are listed in Table 3.

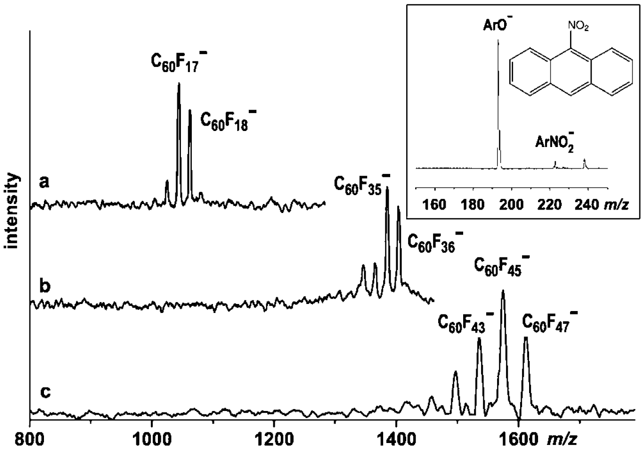


Figure 4. Negative ion 9-NA-MALDI mass spectra of $C_{60}F_{18}$ (a), $C_{60}F_{36}$ (b), and $C_{60}F_{48}$ (c) recorded with similar 337-nm laser fluences. The inset is the expanded region from *m/z* 160−240 in spectrum a, which shows the major matrix anions present in these experiments.

In-plume collision-induced electron transfers between S_3^- ions and neutral $C_{60}F_n$ molecules, shown in reaction 7, generate $C_{60}F_n^-$ parent molecular ions with lower internal energies than are produced in matrix-free LDI plumes:

$$S_x^- + C_{60}F_n \rightarrow S_x + C_{60}F_n^- \qquad \Delta_rH \approx \mathrm{EA}(S_x) - \mathrm{EA}(C_{60}F_n) \quad (7)$$

For all combinations of $x = 2$, 3, or 4 and $n = 18$ or 36, reaction 7 is less exothermic than −1.9 eV. Since the dissociation of an F atom from both $C_{60}F_{18}^-$ and $C_{60}F_{36}^-$ is more endothermic than 2.3 eV (see Tables 2 and 3), the appearance of significant signals for these parent molecular ions has a straightforward thermochemical basis. On the other hand, for Δ_rH values for reaction 7 involving $C_{60}F_{48}$, −2.4, −1.8, and −1.9 eV for $x =$ 2, 3, and 4, respectively, are similar in magnitude to the predicted value of 1.97 eV required to remove an F atom from $C_{60}F_{48}^-$. It was clear from these experiments that matrices with higher electron affinities than S_x moieties might lead to even less fragmentation in MALDI mass spectra. However, such matrix materials are rare. Alternatively, matrices with higher molar absorbances at 337 nm than S_8 would allow lower laser fluences to be used, and these were examined next.

(*b*) *9-NA and DCTB as MALDI Matrices.* The 9-NA- and DCTB-MALDI mass spectra of $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$ are shown in Figures 4 and 5, respectively. The parent molecular anions $C_{60}F_{18}^-$ and $C_{60}F_{36}^-$ were observed in both cases. In fact, these anions dominate over the fragment ions in the DCTB-MALDI experiments of these two FFs. As with the S_8-MALDI spectrum of $C_{60}F_{48}$, the $C_{60}F_{48}$ parent molecular anion was not observed with either 9-NA or DCTB as the matrix.

The insets in Figures 4 and 5 reveal the dominant matrix anions formed by the primary ionization processes, which are shown in reaction sequence 8 and reaction 9 (ArO = 9-O-anthracenyl; all species are in the gas phase):

$$\text{9-NA} + e^- \rightarrow \text{9-NA}^- \rightarrow \mathrm{ArO}^- + \text{other products} \quad (8)$$

$$\mathrm{DCTB} + e^- \rightarrow \mathrm{DCTB}^- \quad (9)$$

The DFT-calculated EA values for 9-NA, ArO, and DCTB, listed in Table 3, are close to the electron affinity of the gaseous S_3 molecular fragment. Therefore, the exothermicity of electron transfer from ArO^- or $DCTB^-$ to FF analytes should be virtually the same as that for reaction 7 when $x = 3$. In fact, the relative ion distributions are similar for all three analytes with either sulfur or 9-NA as the matrix. However, the DCTB-MALDI

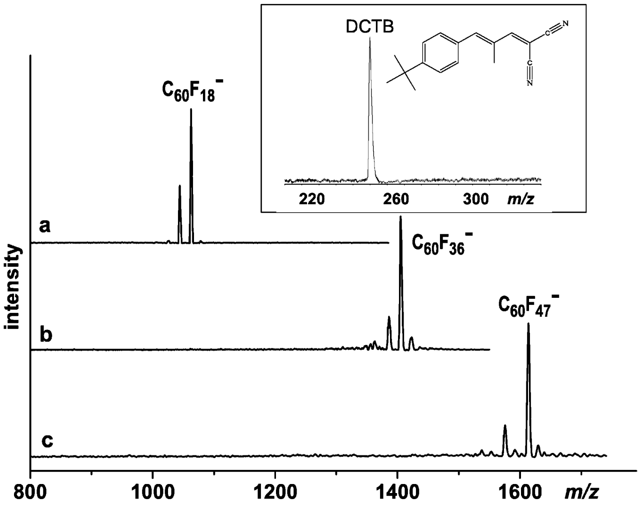


Figure 5. Negative ion DCTB-MALDI mass spectra of $C_{60}F_{18}$ (a), $C_{60}F_{36}$ (b), and $C_{60}F_{48}$ (c) recorded with similar 337-nm laser fluences. The inset is the expanded region from *m*/*z* 200−340 in spectrum a, which shows the matrix anion $DCTB^-$ that is present in these experiments.

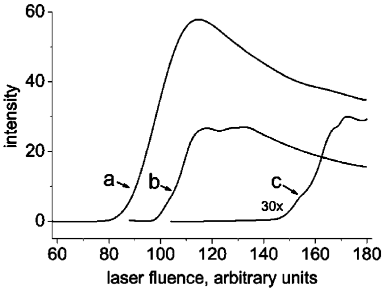
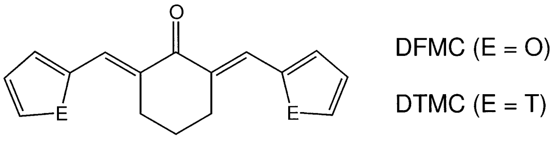


Figure 6. The dependence of ion intensity on laser fluence in mass spectra: (a) LDI-MS of DCTB (the $DCTB^-$ ion was monitored); (b) DCTB-MALDI-MS of $C_{60}F_{36}$ (the $C_{60}F_{35}^-$ ion was monitored); and (c) LDI-MS of $C_{60}F_{36}$ (the $C_{60}F_{35}^-$ ion was monitored; the vertical scale was expanded by 30×).

SCHEME 1



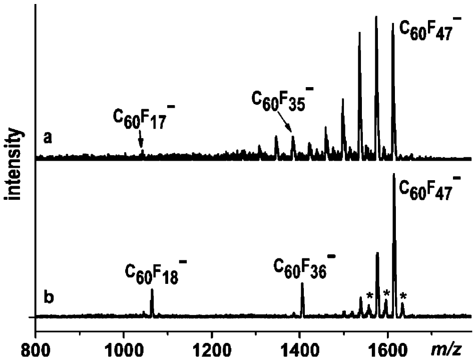


Figure 7. LDI (a) and DCTB-MALDI (b) mass spectra of an equimolar mixture of $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$. The peaks marked with asterisks in spectrum b are due to trace amounts of oxofluorofullerene ions such as $C_{60}F_{47}O^-$.

spectra showed the highest yield of parent molecular ions for $C_{60}F_{18}$ and $C_{60}F_{36}$ despite the slightly lower predicted EA for DCTB relative to ArO, S_3, or S_4. The reason for this is that a lower laser fluence is required for the DCTB-MALDI spectra than for the 9-NA-MALDI and S_8-MALDI spectra (see Table 3).

The dramatic suppression of fragmentation that occurs in MALDI-MS is, in part, associated with the decrease of laser fluence needed for the generation of charged analyte species, as is clearly shown in Figure 6. The laser-fluence threshold for the $C_{60}F_{35}^-$ signal in LDI mass spectra of $C_{60}F_{36}$ was considerably higher than the threshold for the $C_{60}F_{35}^-$ signal in DCTB-MALDI mass spectra of the same analyte (recall that the $C_{60}F_{36}^-$ parent molecular ion was absent in LDI mass spectra of $C_{60}F_{36}$). Similar observations were made with the $C_{60}F_{18}$ and $C_{60}F_{48}$ analytes.

(*c*) *DFMC and DTMC as MALDI Matrices.* These two matrices, shown in Scheme 1, were chosen for their high molar absorbance at 337 nm and because their laser-fluence thresholds are similar to DCTB. Their calculated EA values, 1.3 eV, are significantly lower than the 2.0 eV value for DCTB, and therefore the exothermicity of electron transfer between $DFMC^-$ or $DTMC^-$ and $C_{60}F_{36}$ is larger than that for the reaction of $DCTB^-$ and $C_{60}F_{36}$. The yields of the $C_{60}F_{36}^-$ parent molecular ion in DFMC- and DTMC-MALDI mass spectra of $C_{60}F_{36}$ were comparatively low, which further supports the conclusion that in-plume electron-transfer thermodynamics plays an important role in the final ion distribution in MALDI.

At present, DCTB and 9-NA can be referred to as the most effective matrices for the analysis of the organic fullerene derivatives, although "β-carboline matrices" have also been used successfully in some cases.[40] The application of DCTB and 9-NA for analysis of several different types of organic fullerene derivatives has recently been described.[41,42] Notably, the matrices perform well in both ion modes, ionization into positive ions also proceeding via electron transfer (the reverse process to the negative ion formation discussed here). Cationization of derivatized fullerenes has also been observed.[43,44] The present study provides further evidence that DCTB is the most universal and effective MALDI matrix for fullerenes, because the physicochemical properties of DCTB lie within the margins of the thermodynamic requirements of these experiments.

(*d*) *MALDI-MS as a Qualitative Analytical Tool for FF Mixtures.* An equimolar mixture of $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$ was examined by LDI- and DCTB-MALDI-MS. The spectra are shown in Figure 7. All three compounds were detected in the DCTB-MALDI spectrum. The parent molecular ions $C_{60}F_{18}^-$ and $C_{60}F_{36}^-$ had comparable intensities; the most abundant ion was $C_{60}F_{47}^-$. This is a sensible result, since $C_{60}F_{48}$ has the highest EA of the three analytes and it is known that the rate of electron-transfer reactions correlates with the exothermicity of the reactions.[45] More analytical work will be required to determine if suitable calibration curves can be constructed so that DCTB-MALDI-MS might serve as a quantitative analytical tool for FF mixtures. However, it is now clear that this technique is useful for the qualitative characterization of mixtures that contain species of considerably different electron affinities.

In contrast, signals due $C_{60}F_{18}$- and $C_{60}F_{36}$-derived ions were virtually completely absent in the LDI mass spectrum of the mixture, which resembled the LDI spectrum of pure $C_{60}F_{48}$ shown in Figure 1c. This represents a classic example of the analyte suppression effect, ASE,[35] in which species with high EAs prevent the formation of anions from species with lower EAs. This observation shows that direct LDI is of limited use for analytical purposes, especially when applied to mixtures containing compounds with varying degrees of derivatization and hence significantly different ionization properties.

Conclusions

The thermodynamic approach[9,10,35] has been applied here to the interpretation of a comprehensive set of LDI- and MALDI-MS data obtained for a series of pure fluorofullerenes with varying F-atom content. A general mechanism for the formation of FF anions was developed in which in-plume electron-transfer reactions between matrix-derived anions and neutral analyte molecules determine the outcome. In the case of LDI-MS, ionization proceeds by the capture of free electrons, presumably released from the metal support by photoemission. The high exothermicity of such processes results in undesired dissociations of F atoms from FFs. The application of matrices that possess high molar extinctions in the near-UV and relatively high electron affinities (2−3 eV) leads to significant suppression of fragmentation and the predominant formation of parent molecular anions from $C_{60}F_{18}$ and $C_{60}F_{36}$ and the anion $C_{60}F_{47}^-$ from $C_{60}F_{48}$. Among the matrices studied in this work, the best results (i.e., enhanced parent molecular ion yield, reduced fragmentation, and less discrimination against components in mixtures) were obtained with DCTB. The excellent performance of this matrix material can be understood within the thermodymanic framework of the MALDI process.

Acknowledgment. This work was supported by the Volkswagen Foundation (I-77/855), the RFBR (Project No. 02-03-33352), an INTAS Young Scientist Fellowship (No. 03-55-1811 to A.V.S.), a University of Warwick Fully-Funded Studentship (to S.G.K.), an AvH Foundation Friedrich Bessel Award (to O.V.B.), President of Russia Grant MK-2734.2004.03 (to I.N.I.), and the U.S. NSF (Grant No. CHE-9905482 to S.H.S.). We thank Prof. N. V. Zyk for samples of DFMC and DTMC.

Supporting Information Available: Figure S-1, showing laser-fluence thresholds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Abdul-Sada, A. K.; Boltalina, O. V.; Taylor, R. *Eur. Mass Spectrom.* **1997**, *3*, 461.

(2) Boltalina, O. V.; Galeva, N. A.; Markov, V. Y.; Borschevskii, A. Y.; Sorokin, I. D.; Sidorov, L. N.; Popovich, A.; Zigon, D. *Mendeleev Commun.* **1997**, 184.

(3) Barrow, M. P.; Feng, X.; Wallace, J. I.; Boltalina, O. V.; Taylor, R.; Derrick, P. J.; Drewello, T. *Chem. Phys. Lett.* **2000**, *330*, 267.

(4) Cozzolino, R.; Belgacem, O.; Drewello, T.; Kaseberg, L.; Herzschuh, R.; Suslov, S.; Boltalina, O. V. *Eur. Mass Spectrom.* **1997**, *3*, 407.

(5) Tuinman, A.; Mukherjee, P.; Hetich, R. L.; Compton, R. N. *J. Phys. Chem.* **1992**, *96*, 7584.

(6) Vasil'ev, Y. V.; Boltalina, O. V.; Tuktarov, R. F.; Mazunov, V. A.; Sidorov, L. N. *Int. J. Mass Spectrom. Ion Processes* **1998**, *173*, 113.

(7) Streletskiy, A. V.; Goldt, I. V.; Kuvycko, I. V.; Ioffe, I. N.; Sidorov, L. N.; Drewello, T.; Strauss, S. H.; Boltalina, O. V. *Rapid Commun. Mass Spectrom.* **2004**, *18*, 360.

(8) Streletskiy, A. V.; Kouvitchko, I. V.; Esipov, S. E.; Boltalina, O. V. *Rapid Commun. Mass Spectrom.* **2001**, *16*, 99.

(9) Macha, S. E. M., McCarley, T. D.; Limbach, P. A. *Anal. Chim. Acta* **1999**, *397*, 235.

(10) McCarley, T. D.; McCarley, R. L.; Limbach, P. A. *Anal. Chem.* **1998**, *70*, 4376.

(11) Jin, C.; Hettich, R. L.; Compton, R. N.; Tuinman, A. A.; Derecskei-Kovacs, A.; Marynik, D. S.; Dunlap, B. I. *Phys. Rev. Lett.* **1994**, *73*, 282.

(12) Papina, T. S.; Kolesov, V. P.; Lukyanova, V. A.; Boltalina, O. V.; Lukonin, A. Y.; Sidorov, L. N. *J. Phys. Chem. B* **2000**, *104*, 5403.

(13) Papina, T. S.; Kolesov, V. P.; Lukyanova, V. A.; Boltalina, O. V.; Galeva, N. A.; Sidorov, L. N. *J. Chem. Thermodyn.* **1999**, *31*, 1321.

(14) Goldt, I. V.; Boltalina, O. V.; Sidorov, L. N.; Kemnitz, E.; Troyanov, S. I. *Solid State Sci.* **2002**, *4*, 1395.

(15) Boltalina, O. V.; Borschevskii, A. Y.; Sidorov, L. N.; Street, J. M.; Taylor, R. *Chem. Commun.* **1996**, 529.

(16) Bagryantsev, V. F.; Zapol'skii, A. S.; Boltalina, O. V.; Galeva, N. A.; Sidorov, L. N. *Zh. Neorg. Khim. (Russian J. Inorg. Chem.)* **2000**, *45*, 1121.

(17) Laikov, D. N. *Chem. Phys. Lett.* **1997**, *281*, 151.

(18) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(19) Knochenmuss, R. *Anal. Chem.* **2004**, *76*, 3179.

(20) Frankevich, V. E.; Zhang, J.; Friess, S. D.; Dashtiev, M.; Zenobi, R. *Anal. Chem.* **2003**, *75*, 6063.

(21) Brink, C.; Andersen, L. H.; Hvelplund, P.; Mathur, D.; Volstad, J. D. *Chem. Phys. Lett.* **1995**, *233*, 52.

(22) Yoo, R. K.; Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1992**, *96*, 911.

(23) Ohkubo, K.; Taylor, R.; Boltalina, O. V.; Ogo, S.; Fukuzumi, S. *Chem. Commun.* **2002**, 1952.

(24) Gigli, G.; Cesaro, S. N.; Rau, J. V.; Goldt, I. y. V.; Markov, V. Y.; Goryunkov, A. A.; Popov, A. A.; Boltalina, O. V.; Sidorov, L. N. In *Proceedings—Electrochemical Society*; Vol. 13, Fullerenes and Nanotubes; Guldi, D. M., Ed.; Electrochemical Society: Pennington, NJ, 2003; p 453.

(25) Liu, N. M., Y.; Okino, F.; Boltalina, O. V.; Pavlovich, V. K. *Synth. Metals* **1997**, *86*, 2289.

(26) Steger, H. M., U.; Kamke, W.; Ding, A.; Fieber-Erdmann, M.; Drewello, T. *Chem. Phys. Lett.* **1997**, *276*, 39.

(27) Ioffe, I. N.; Goryunkov, A. A.; Boltalina, O. V.; Borschevsky, A. Y.; Sidorov, L. N. *Fullerenes, Nanotubes, Carbon Nanostruct.* **2004**, *12*, 169.

(28) Tuinman, A. A.; Lahamer, A. S.; Compton, R. N. *Int. J. Mass Spectrom.* **2001**, *205*, 309.

(29) Boltalina, O. V.; Street, J. M.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1998**, 649.

(30) Hitchcock, P. B.; Taylor, R. *Chem. Commun.* **2002**, 2078.

(31) Troyanov, S. I.; Troshin, P. A.; Boltalina, O. V.; Ioffe, I. N.; Sidorov, L. N.; Kemnitz, E. *Angew. Chem., Int. Ed.* **2001**, *40*, 2285.

(32) Neretin, I. S.; Lyssenko, K. A.; Antipin, M. Y.; Slovokhotov, Y. L.; Boltalina, O. V.; Troshin, P. A.; Lukonin, A. Y.; Sidorov, L. N.; Taylor, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 3273.

(33) Borshchevsky, A. Y.; Ponomarev, D. B.; Aleshina, V. E.; Boltalina, O. V.; Astakhov, A. V.; Alekseev, E. V.; Sidorov, L. N. In *Proceedings—Electrochemical Society*; Vol. 12, The Exciting World of Nanocages and Nanotubes; Guldi, D. M., Ed.; Electrochemical Society: Pennington, NJ, 2002; p 642.

(34) Clipston, N. L.; Brown, T.; Vasil'ev, Y. V.; Barrow, M. P.; Herzschuh, R.; Reuther, U.; Hirsch, A.; Drewello, T. *J. Phys. Chem.* **2000**, *104*, 9171.

(35) Knochenmuss, R.; Zenobi, R. *Chem. Rev.* **2003**, *103*, 441.

(36) Brune, D. *Rapid Commun. Mass Spectrom.* **1999**, *13*, 384.

(37) Hearley, A.; Johnson, B.; McIndoe, J.; Tuck, D. *Inorg. Chim. Acta* **2002**, *334*, 105.

(38) Blondel, C. *Phys. Scr.* **1995**, *58*, 31.

(39) Hunsicker, S.; Jones, R. O.; Gantefor, G. *J. Chem. Phys.* **1995**, *102*, 5917.

(40) Nonami, H.; Tanaka, K.; Fukuyama, Y.; Erra-Balsells, R. *Rapid Commun. Mass Spectrom.* **1998**, *12*, 285.

(41) Brown, T.; Clipston, N. L.; Simjee, N.; Luftmann, H.; Hungerbuhler, H.; Drewello, T. *Int. J. Mass Spectrom.* **2001**, *210*, 249.

(42) Ulmer, L.; Mattay, J.; Torres-Garcia, H. G.; Luftmann, H. *Chem. Phys. Lett.* **2000**, *6*, 49.

(43) Fati, D.; Leeman, V.; Vasil'ev, Y. V.; Leyh, B.; Hungerbuhler, H.; Drewello, T. *J. Am. Soc. Mass Spectrom.* **2002**, *13*, 1448.

(44) Fati, D.; Vasil'ev, Y. V.; Wachter, N. K.; Taylor, R.; Drewello, T. *Int. J. Mass Spectrom.* **2003**, *229*, 3.

(45) Knochenmuss, R. *Anal. Chem.* **2003**, *75*, 2199.