J. Phys. Chem. A **2006,** *110,* 8451−8456

Electron Attachment to Higher Fullerenes and to $Sc_3N@C_{80}$[†]

Sylwia Ptasińska,[‡] Olof Echt,*[,§,||] Stephan Denifl,[‡] Michal Stano,[‡] Philipp Sulzer,[‡] Fabio Zappa,[‡] Aleksandar Stamatovic,[‡,⊥] Paul Scheier,[‡] and Tilmann D. Märk*[,‡,#]

Institut für Ionenphysik, Leopold Franzens Universität Innsbruck, Technikerstrasse 25,
A-6020 Innsbruck, Austria, and Physics Department, University of New Hampshire,
Durham, New Hampshire 03824-3568

Received: January 17, 2006; In Final Form: February 21, 2006

We report on attachment of free electrons to fullerenes C_n ($n = 60$, 70, 76, 78, 80, 82, 84, 86) and to $Sc_3N@C_{80}$. The attachment cross sections exhibit a strong resonance at 0 eV for all species. The overall shape of the anion yield versus electron energy is quite similar for the higher fullerenes, with a minimum around 1 eV and a maximum which gradually shifts from 6 eV for C_{60} to ≈4 eV for large n. The endohedral $Sc_3N@C_{80}$ exhibits a particularly shallow minimum and a maximum below 4 eV. We model autoionization of the anions with due consideration of the internal energy distributions. The relatively low electron affinity of $Sc_3N@C_{80}$ is reflected in its reduced ion yield at higher attachment energies.

Introduction

The Langevin cross section for electron attachment to fullerenes is large at low energies because of the large polarizability of fullerenes. Early experiments on C_{60} confirmed the large cross section at low energy[1] although they suggested a threshold value around 0.2 eV below which free electrons could not be attached.[2−5] The threshold was attributed to the absence of s-wave capture.[6] However, transfer of electrons from atoms excited into Rydberg states[5,7−9] and subsequent electron attachment experiments[10−12] did not confirm the existence of a threshold.

Perhaps the most compelling experimental evidence for a resonance at 0 eV comes from depletion data of neutral fullerenes upon electron scattering; cross sections as large as 1000 Å^2 were obtained for the lowest electron energies, $E_e <$ 0.1 eV.[13] Gianturco and co-workers showed that scattering in the a_g symmetry dominates at energies below 0.03 eV due to a near-threshold virtual state in the s-wave scattering.[14]

As suggested in refs 9, 13, and 15 and elsewhere, formation of anions by capture of low-energy electrons may be viewed as a two-step process, (i) capture of the electron in the polarization field at a rate close to the Langevin rate followed by (ii) diving of the electron from a quasi-bound continuum state into a bound state by electron−phonon coupling. The electron scattering data suggest a probability for conversion from step 1 to step 2 of about 40% for energies up to 3 eV, except for a deep minimum around 0.4 eV.[13]

While the formation of C_{60} anions has been studied in considerable detail (for recent reviews see refs 15 and 16), little is known about larger fullerenes. For C_{70}, attachment thresholds have been reported in some of the early work[3,17] although, in contrast to C_{60}, the alleged absence of s-wave scattering does not follow from symmetry arguments. Later work showed strong 0-eV resonances for attachment of electrons to C_{70}[10,11] and transfer of electrons from Rydberg atoms.[8]

Concerning fullerenes larger than C_{70}, only one study has been devoted to the energy dependence of anion formation, namely for C_{76} and C_{84} by Abouaf and co-workers.[18] In contrast to C_{76}^-, C_{84}^- did not display a peak at 0 eV, although the authors could not rule out that a sharp peak at 0 eV was missed because they had to work with reduced electron energy resolution.

No electron attachment data have been reported so far for endohedral fullerenes. Even though the correlation between attachment spectra and the electronic structure of fullerenes is by no means obvious,[10,14,15,18,19] a direct comparison of spectra for empty and filled fullerenes is highly desirable. Apart from the effect due to transfer of six electrons from the caged Sc_3N unit to the fullerene and the concomitant change in single-particle excitations, the change of symmetry from D_2 or D_{5d} for C_{80} to I_h for $Sc_3N@C_{80}$[20] will affect collective excitations that may be relevant to the formation of anions.[19,21]

In this work we have measured spectra for empty fullerenes C_n with $n = 60$, 70, 76, 78, 80, 82, 84, and 86 and for $Sc_3N@C_{80}$. By and large the spectra are quite similar, but with increasing size a gradual red-shift of the maximum around 4−6 eV is observed; the shift is particularly strong for the endohedral $Sc_3N@C_{80}$.

Furthermore, we analyze autodetachment by modeling the falloff of the anion yield toward higher electron energies. The data provide information on the nature of the reaction (truly statistical or nonstatistical[22,23]), the detachment energy, and the energy dependence of the attachment cross section.[4,10,12,15,18] However, as pointed out by Andersen et al.,[16] previous conclusions drawn from experimental data are questionable because the finite width of the vibrational energy distributions of the fullerenes emerging from a thermal source was usually ignored in the data analysis.

[†] Part of the “Chava Lifshitz Memorial Issue”.

* Corresponding authors. E-mail: olof.echt@unh.edu (O.E.); Tilmann.Maerk@uibk.ac.at (T.D.M.).

[‡] Leopold Franzens Universität Innsbruck.

[§] University of New Hampshire.

[||] Also Guest Professor at the University of Innsbruck.

[⊥] Permanent address: Faculty of Physics, P.O. Box 368, Yo-11001 Beograd, Yugoslavia.

[#] Also Adjunct Professor at the Department of Plasma Physics, Comenius University, SK-84248 Bratislava, Slovak Republic.

10.1021/jp060324v CCC: $33.50

Experiment and Data Modeling

Experimental Details. The experiments were carried out with a crossed electron/molecular beam apparatus described in detail in ref 24. The electron beam was formed in a custom-designed hemispherical electron monochromator with a maximum resolution of 30 meV. For reasons of higher sensitivity the present measurements were performed with an electron energy resolution of about 120−150 meV close to 0 eV as determined from the full-width-at-half-maximum (fwhm) of the 0-eV resonance of Cl^- from CCl_4. The electron energy scale was calibrated using electron attachment to SF_6 which has a narrow resonance in the SF_6^- yield at 0 eV due to s-wave scattering.

Empty fullerenes (C_{60} (stated purity 99.9%), C_{70} (99%), and a mixture of higher fullerenes (stated content C_{76}, C_{78}, and C_{84} at 33% each) were obtained from MER Corp. $Sc_3N@C_{80}$ was obtained from Luna nanoWorks. The powder was, without further treatment, vaporized from an oven made of stainless steel. The oven is resistively heated by a tantalum wire which is isolated by ceramics and woven through bores in the stainless steel oven chamber. The design minimizes perturbing magnetic fields caused by the heating current. A copper capillary with a length of 8 cm and an inner diameter of 1 mm is screwed into the oven. Neutral fullerenes effuse from the end of the capillary directly into the collision chamber.

The negative ions formed in the reaction chamber were extracted by a weak electric field toward the entrance of the quadrupole mass spectrometer. The mass selected negative ions were detected by a channeltron detector and the pulses processed using a pulse counting technique and computer. The intensity of a mass selected negative ion was recorded as a function of the electron acceleration voltage.

Modeling Autoionization. The observed intensity of fullerene anions exhibits a gradual decline beyond a maximum located around 4−6 eV. As shown in earlier work on C_{60}, C_{70}, C_{76}, and C_{84} this falloff is, at least partly, caused by thermally activated electron detachment, or autoionization in short.[3,4,10−12,18,23,25,26] We follow the treatment by Andersen et al. (see section 8.2 in ref 16) to model the survival probability,

$$P_{\mathrm{surv}} = \exp(-kt) \qquad (1)$$

of the metastable anions. t is the instrumental time necessary for their detection, and the rate coefficient k is assumed to follow an Arrhenius relation,

$$k = A \exp\left(-\frac{E_{\mathrm{a}}}{k_{\mathrm{B}}T_{\mathrm{e}}}\right) \qquad (2)$$

where A is the Arrhenius factor and E_a the activation energy for electron emission which we take to be identical with the electron affinity E_{aff} (see Table 1) of the neutral fullerene.

T_e in eq 2 is the so-called emission temperature.[27] Most authors [3,4,10,11,18,23,25,26] have used the parent temperature instead, i.e., the microcanonical temperature T_p of the anion which is calculated from

$$E^*(T_{\mathrm{p}}) = E_{\mathrm{ov}}(T_{\mathrm{ov}}) + E_{\mathrm{aff}} + E_{\mathrm{e}} \qquad (3)$$

E^* is the total excitation energy of the metastable anion, $E_{\mathrm{ov}}(T_{\mathrm{ov}})$ the vibrational energy of the molecules emerging from the fullerene source at temperature T_{ov}, and E_e the electron energy. $E(T)$ denotes the dependence of the vibrational energy on the temperature which may be computed for C_{60} from its well-known vibrational frequencies.[28] From T_p one obtains $T_e \approx T_p - E_a/(2C)$ with C being the (vibrational) heat capacity. For fullerenes other than C_{60} we scale $E(T)$ and therefore C with the number of vibrational degrees of freedom, $3q - 6$ (q = number of atoms).

TABLE 1: Electron Energy $E_{1/2}$ Where the Survival Probability Drops to 1/2, Calculated from the Electron Affinities E_{aff} and Source Temperature T_{ov}

species	E_{aff} (eV)	T_{ov} (°C)	$E_{1/2}$ (eV)
C_{60}	2.666[a]	460	9.2
C_{70}	2.676[a]	520	10.0
C_{76}	2.89[b]	630	11.0
C_{78}	3.10[b]	570	14.1
C_{80}	3.17[b]	630	14.1
$Sc_3N@C_{80}$	2.81[c]	605	11.8
C_{82}	3.14[b]	630	14.2
C_{84}	3.14[b]	630	14.5
C_{86}	3.23[b]	630	15.7

[a] Reference 42. [b] Reference 43. [c] Reference 41.

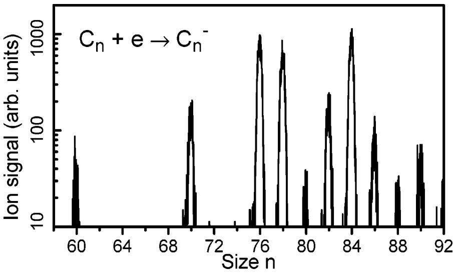

Figure 1. Mass spectrum of fullerene anions formed by electron attachment at 0 eV. The mix of higher fullerenes was vaporized at 630 °C.

Several groups have measured the time dependence of the survival probability of C_{60}^- as a function of the electron energy. Their data were analyzed as outlined above to deduce E_a and A.[3,4,10,11,18,23,25,26] However, as demonstrated in ref 16, a large systematic error arises when the distribution of vibrational energies in the canonical ensemble of C_{60} emerging from the hot oven is ignored. We avoid the error by numerically integrating eq 1 over the energy distribution which is, to a good approximation, Gaussian with a width (standard deviation) of $\sigma_{\mathrm{ov}} = T_{\mathrm{ov}}\sqrt{Ck_B}$. For example, for C_{60} at an oven temperature of 460 °C the width is 0.72 eV.

Furthermore, we distinguish between T_p and $T_e \approx T_p - E_a/(2C)$. For the A-factor of C_{60}^- we use $A = 3 \times 10^6\,(T_f/\mathrm{K})^2\ \mathrm{s}^{-1}$, which is based on an thermally averaged capture cross section of 60 Å^2 and takes into account the 6-fold electronic degeneracy of the anion.[16] $T_f \approx T_p - E_a/C$ is the temperature of the reaction product (C_{60}). The A factor of C_n^- is assumed to scale with the size n.

Results and Discussion

Mass Spectrum of Anions. Figure 1 displays a mass spectrum of anions obtained by electron attachment at 0 eV to a mix of higher fullerenes. The spectrum reflects the abundance of neutral fullerenes; no fragment ions are formed under these conditions. Dominant species are C_{76}, C_{78}, and C_{84} in agreement with the manufacturer's specification. The intensity of C_{80}, which is of particular interest for a direct comparison with $Sc_3N@C_{80}$, is, unfortunately, very low.

Attachment Spectra for C_{60}, C_{70}, C_{76}, and C_{84} and Comparison with Previous Work. There has been a considerable controversy over the electron attachment cross section for C_{60} and, to some degree, C_{70}. Only one published report was devoted to higher fullerenes, namely C_{76} and C_{84}.[18] Before presenting our data pertaining to other fullerenes, we compare our results with previously published work. There is a rich literature on attachment of free electrons to C_{60}[1,3,5,10−13,25,26,29] and some work on C_{70}.[1,3,10,11] Early experiments by Märk and co-workers,[3] Compton and co-workers,[5] and Vostrikov and co-workers[25] had indicated a barrier of ≈0.2 eV toward electron attachment to C_{60}. The results found further support in the temperature dependence of the attachment rate coefficient measured by the flowing-afterglow/Langmuir probe technique by Smith and Spanel.[17] Tosatti and Manini explained the findings as arising from the rotational barrier for p-wave scattering and the absence of s-wave scattering for the nearly spherical C_{60}.[6] However, according to recent computations employing more realistic interaction potentials, the threshold for p-wave scattering is much lower than calculated previously.[9,30]

Moreover, experiments by Compton and co-workers,[5] Finch et al.,[7] and Hotop and co-workers[8] showed that reaction rates for electron transfer from Rydberg atoms to C_{60} exhibit a dependence on the Rydberg quantum number *n* characteristic of strong s-wave capture. Subsequent measurements by Vasil'ev et al.,[11] Abouaf and co-workers,[10] Vostrikov et al.,[26] and Krishnakumar and co-workers[12] did indeed show resonances in the cross section for attachment of free electrons at the same energy as for SF_6, within the stated experimental energy resolution of <0.1 eV. Also noteworthy is the work by Kresin and co-workers that shows a strong low-energy resonance.[13] Their energy resolution was only 0.3 eV fwhm, and their energy scale was not calibrated by direct comparison with another molecule known to have a 0-eV resonance. However, they measured the depletion of a C_{60} beam rather than the formation of C_{60}^-, thereby avoiding the application of an ion extraction field and its possible distortion of the energy scale.

In Figure 2 we present our data for C_{60}, C_{70}, C_{76}, and C_{84} together with literature data for C_{60},[10,11,13] C_{70},[10] and C_{76} and C_{84}.[18] Other data reported for C_{60} and C_{70} will be included in the discussion.

For ease of comparison, all data in Figure 2 have been scaled to the same height at their maximum around 4−6 eV. In this representation, the strength of the 0 eV resonance differs widely among data sets. Such a variability is not surprising for a resonance that is narrower than the energy distribution of the electron beam. Furthermore, different methods have been applied to correct the ion yield for changes in electron current. In the present work, the electron current is constant within ±10% for $E_e \geq 0.3$ eV but it drops off strongly at lower energies. We have chosen not to correct our data for changes in electron current; therefore, the strength of the resonance at low energies is underestimated. In general, the amplitudes and shapes of the low-energy resonances reported by us and others have to be judged with a grain of salt.

With this caveat in mind we find that our C_{60} spectrum agrees closely with the spectrum reported by Vasil'ev et al.[11] A narrow maximum at 0 eV is followed by a deep minimum around 0.4 eV, a stepwise rise to 1 eV, and a broad maximum that levels off above 6 eV. A similarly deep minimum at 0.4 eV is also seen in the data by Kresin and co-workers,[13] but the large scatter makes it difficult to judge the spectral shape beyond that minimum.

In contrast, and despite their stated higher energy resolution (30 meV at 0 eV), Abouaf and co-workers[10] report a rather broad and weak resonance at 0 eV followed by a shallow minimum at 0.25 eV and a broad bump between 0.8 and 1.5 eV. For higher energies, their spectrum resembles ours. Their more rapid falloff toward higher energies could be caused by a higher C_{60} source temperature or a larger instrumental time required for detection of the anions as discussed further below.

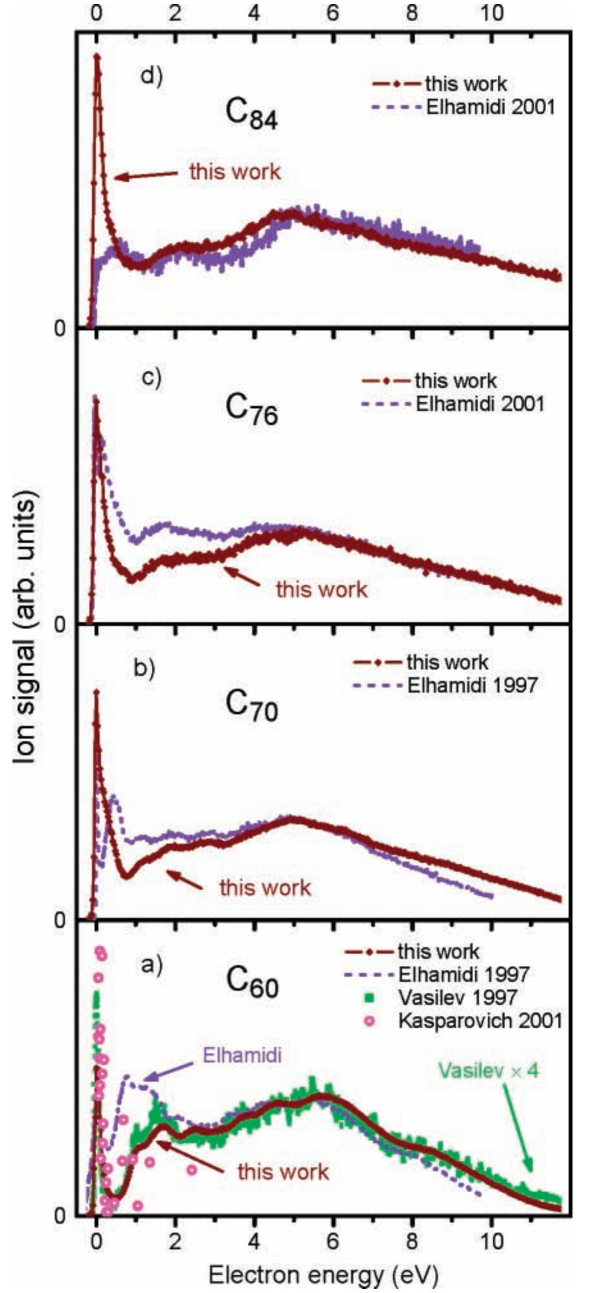

Figure 2. Our electron attachment spectra for C_{60}, C_{70}, C_{76}, and C_{84} shown together with published spectra.[10,11,13,18]

Our C_{60}^- spectrum shows a series of local maxima or distinct shoulders. By fitting a set of Gaussians, we determine their positions to be 1.0, 1.7, 2.5, 3.1, 3.7, 4.6, 5.8, and 8.4 eV, with uncertainties of ±0.1 to ±0.2 eV. The Abouaf spectrum shows a similar series of peaks which the authors place at 0.75, 1.20, 2.08, 2.74, 3.5, 4.27, and 5.35 eV. Another maximum (giving rise to a shoulder) is seen at ≈8 eV in their spectrum although the authors do not mention it. All these values are below our values; the average difference is 0.3 eV. In a recent publication Krishnakumar and co-workers[12] reported a C_{60}^- spectrum that was similar to Abouaf's except that their 0-eV resonance was much narrower and stronger, and their subsequent maxima were, like ours, located at slightly higher energies (≈0.2 eV) than in the Abouaf spectrum.

As for C_{70}, the only published spectrum of good statistical quality is the one by Abouaf and co-workers;[10] it is included in

Figure 2. Above 2 eV the agreement with our spectrum is reasonable. In particular, the positions of the maximum around 5 eV and some weaker features agree quite well. The faster falloff toward higher energies could, again, be caused by differences in source temperature or the instrumental time scale. However, there are serious deviations below 2 eV. Our spectrum shows a gradual decrease from the 0-eV resonance toward a minimum at 0.8 eV. The Abouaf spectrum shows no such minimum but a pronounced local maximum at 0.4 eV. In support of our results, a (rather noisy) C_{70} spectrum published by Vasil'ev et al.[11] (not shown) is quite similar to ours, except that their 0-eV resonance is narrower.

The only previously published work on higher fullerenes is for C_{76} and C_{84} by Abouaf and co-workers.[18] For C_{76} the overall agreement with our data is not bad. However, their intensity around 2 eV exceeds ours by a factor 2, and we do not observe the strong local maximum that Abouaf find at 0.2 eV (this maximum is difficult to discern from Figure 2; it is as large as the 0-eV resonance in Abouaf's data). Whereas the disagreement below 0.5 eV could possibly be attributed to different procedures used to correct for the energy dependence of the electron current, the disagreement at higher energies (up to 3 eV) is discomforting.

Our C_{84} spectra show a distinct 0-eV resonance, a shallow minimum around 1 eV, and two distinct maxima at 2.0 and 4.7 eV. The Abouaf spectrum resembles ours above 1 eV, except for a deeper minimum around 3.5 eV. However, their spectrum does not show a resonance at 0 eV. They admit that they had to record their C_{84} data with reduced energy resolution in order to make up for a low C_{84} intensity in the neutral beam and that they might have "missed a sharp peak at zero if it exists".[18]

In summarizing this section, above 2−3 eV, we find good to modest agreement between our C_{60}, C_{70}, C_{76}, and C_{84} spectra and those published in the literature. Some striking discrepancies exist below 2 eV. Also, an unexplained shift of 0.2−0.3 eV exists between our C_{60} spectrum and the one reported by Krishnakumar and co-workers [12] on one hand and the Abouaf spectrum[10] on the other hand.

Comparison of C_{60}, C_{70}, C_{76} C_{78}, C_{80}, $Sc_3N@C_{80}$, C_{82}, C_{84}, and C_{86}. Figure 3 displays our results. For ease of comparison we have included our spectra already shown in Figure 2. The spectra have been scaled to equal height at their maxima around 4−6 eV. The spectra are also displayed with reduced scales to reveal the relative height of the low-energy resonance. In general, the spectra are quite similar. They show a distinct peak at 0 eV, a minimum somewhere between 0.5 and 1 eV, a broad maximum around 4−6 eV, which is a factor 2−10 weaker than the 0-eV resonance, and a gradual decrease toward higher energies. This latter feature is partly caused by autoionization; it will be discussed in the following section together with the dashed curves which model the process. The temperatures at which the fullerenes were vaporized are listed in Table 1.

As explained earlier, the anion yield below ≈0.5 eV is affected by the strong energy dependence of the electron current which we did not correct for. For that reason, we do not assign any significance to the different relative strengths of the 0-eV resonances. However, for higher energies there are several differences that appear to be significant. We focus on the differences between C_{80} and $Sc_3N@C_{80}$ which are particularly prominent: (a) Some spectra show a maximum around 2 eV. It is strongest for C_{80} but not discernible in the $Sc_3N@C_{80}$ spectrum. (b) The minimum near 1 eV is quite distinct for C_{80} but essentially absent for $Sc_3N@C_{80}$. It is possibly masked by the unusually long tail of the 0-eV resonance. (c) The $Sc_3N@C_{80}$ spectrum shows a maximum at 3.5 eV, slightly less than for C_{80} (4 eV) and considerably less than for several other fullerenes. (d) The spectra level off at different rates. Among the higher fullerenes, $Sc_3N@C_{80}$ decays most rapidly. By this we mean that the anion yield in the normalized spectrum at, say, 12 eV is lower than in any other spectrum for $n > 70$.

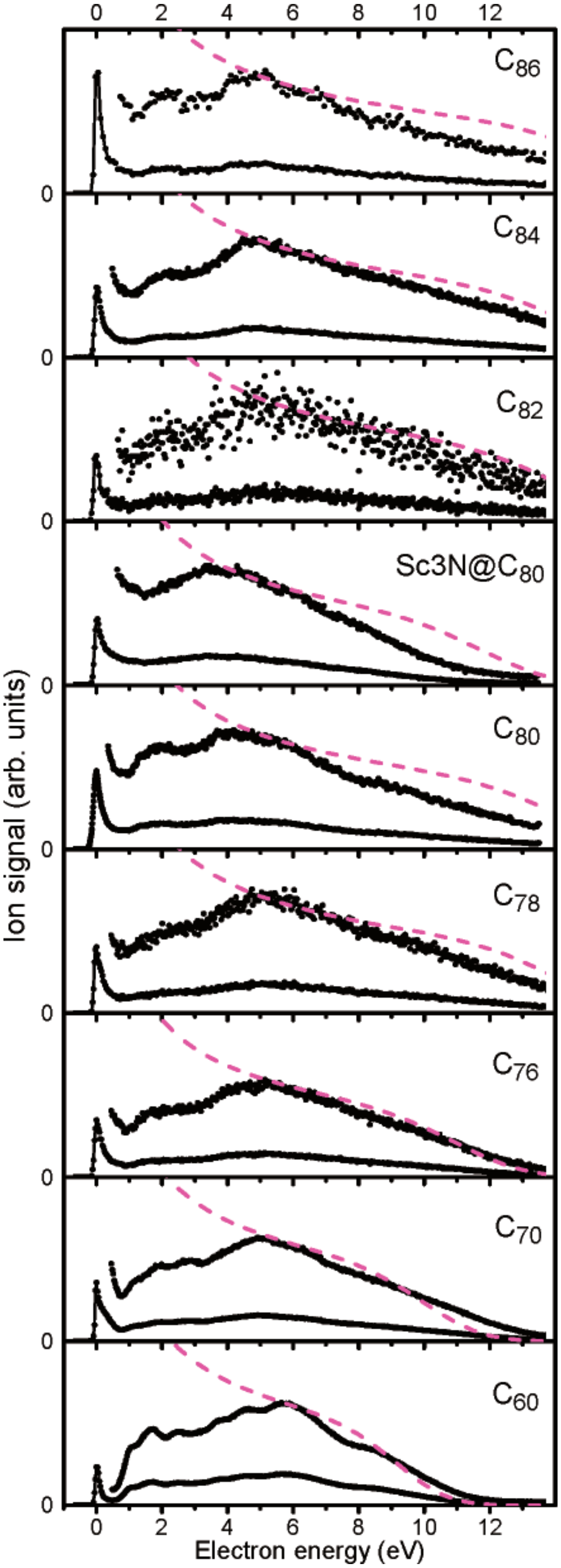

Figure 3. Electron attachment spectra recorded in this work. Each spectrum is displayed with two different intensity scales. Dashed lines model the probability of thermal electron detachment from the anions.

In the usual, admittedly simple two-step picture, the electron is attracted in the polarization field to form a temporary negative ion with the electron in a continuum state. In the second step the electronic energy is rapidly redistributed into internal degrees of freedom, and eventually a long-lived (metastable) anion is formed in which the excitation energy E^* is randomized. The energy exchange may excite the target molecule electronically or vibrationally, giving rise to so-called electronic and vibrational (or nuclear) Feshbach resonances, respectively. The observed anion yield $I(E_e)$ may then be written as the product of the initial capture cross section σ, the sticking probability P_{stick} which reflects the efficiency of energy redistribution between the electron and the target molecule, and the survival probability P_{surv},

$$I(E_e) \propto \sigma P_{stick} P_{surv} \quad (4)$$

The energy and size dependence of P_{surv} will be discussed in the following section; it is at least partly responsible for feature d listed above. The other features, a − c, are attributed to the energy and size dependence of σP_{stick}.

At low energies, a large capture cross section for s-wave electrons arises from the polarization potential $V(r) = -\alpha/(2r^4)$ (in cgs units, α is the polarizability of the fullerene). Antoniewicz et al.[31] were among the first to compute the energy of bound states in such a potential, suitably modified by a repulsive term for small r to mimic a dielectric sphere. For C_{60}, the polarization potential for s-electrons may be too weak to support bound states.[8,30]

Kresin and co-workers[13] have determined the sticking probability P_{stick} for electron attachment to C_{60}, defined as the ratio between the cross section for formation of long-lived C_{60}^- and the Langevin cross section. They find $P_{stick} \approx 0.4$ (with a large experimental scatter) below 0.3 V, followed by a deep, narrow minimum. In this context it is interesting to mention a recent electron attachment study for C_{60} in nonpolar solvents by Holroyd.[32] It was observed that the rates are very fast, comparable to the rates found for the most efficient acceptors such as SF_6. Only for solvents with very high electron mobility did the rate drop below the diffusion limit.

Several authors have attempted to interpret the structure in the attachment spectra at higher energies, above ≈1 eV. A common procedure,[3,10,11,18] although not very successful, has been a comparison with electron energy loss (EEL) spectra measured in the gas phase.[18,33] Lezius[15] has criticized such a comparison because EEL spectra reflect vibronic excitations in the neutral target molecule whereas resonance-like features in the attachment spectra refer to excitations in the anion. Furthermore, attachment spectra will be affected by the adiabatic electron affinity which becomes available to the system.

Lezius[15] has interpreted the C_{60} attachment spectrum in terms of bound−bound electronic transitions, obtained from the calculated density of states of the anion.[34] The agreement is good if 50 transition probabilities are fitted to the experimental spectrum.

Some authors have attempted to correlate the attachment spectra with calculated cross sections for elastic electron scattering. For example, Ekardt and co-workers find narrow resonances at 3.7 and 6.5 eV; the energies drop to 3.2 and 5.7 eV if higher harmonics in the core potential are included.[35] Gianturco and co-workers compute several resonances in this energy range which are, again, dependent on the details of the potential.[14] Furthermore, in the experiment the resonances will be broadened and shifted by vibrational coupling that is not taken into account in the calculations.[36]

Whereas most authors have interpreted the attachment spectra in terms of single-particle excitations,[15] some have considered collective excitations (also called plasmon- or multielectron-excited Feshbach resonances) to explain the maximum in the anion yield around 5 eV;[3,5,10,19] also see earlier theoretical work.[21] According to Tuktarov and co-workers,[19] plasmon excitations can quantitatively account for the yield of C_{60}^- and C_{70}^- above 2 eV, whereas the structure at lower energies is due to single-particle excitations. However, their computed excitation spectra fail to account for the resonances in the experimental attachment spectra below 5 eV (see Figure 2).

No compelling explanation has been offered for the minimum in the anion yield at low energies which is especially pronounced for C_{60}, at 0.4 eV. One interesting suggestion is in terms of the Ramsauer−Townsend minimum for s-wave scattering[37] because resonant features in the elastic scattering and electron capture cross sections often correlate. Experimental data for the elastic cross section do not extend below 1 eV,[38] but the computed Ramsauer−Townsend minimum for scattering in the t_{1u} symmetry is, indeed, located at 0.4 eV.[30] However, no such minimum is found in the computed total, integral cross section for elastic scattering.[36]

In summary, the observed resonances in the attachment spectra of C_{60} are still lacking a conclusive interpretation, despite the vast information that is available for this molecule. The electronic structure of higher fullerenes, including $Sc_3N@C_{80}$, has been the subject of much experimental and theoretical work (see ref 39 for recent reviews). The geometric and electronic structure has been characterized by high-level computations, visible-IR absorption and Raman spectroscopy, EPR, NMR, mass spectrometry, and other experimental techniques. Still, an interpretation of our attachment spectra with this published work would appear premature. Are the special features a−c of $Sc_3N@C_{80}$ listed above related to the transfer of six electrons from the caged Sc_3N complex and the unusually low band gap of 0.8 eV of this molecule?[40] How does the change of the cage symmetry from D_2 or D_{5d} for C_{80} to I_h for $Sc_3N@C_{80}$[20] affect the plasmon spectrum? Is the size dependence of the maximum anion yield caused by the shift of the plasmon peak which, according to Tuktarov et al., scales as $n^{-1/4}$, corresponding to a decrease by 8.6% from C_{60} to C_{86}? Further work is required before these and other questions can be answered.

Autodetachment. The decline of the C_{60}^- yield beyond the maximum at ≈6 eV is, at least partly, related to the energy dependence of the survival probability P_{surv} (see eqs 1 and 4). The decline of P_{surv} with increasing source temperature has been demonstrated unambiguously in refs 23 and 12. Several authors have attempted to determine P_{surv} by analyzing the time dependence of the anion yield. By extrapolating $I(E_e, t)$ to zero time, they extracted the inherent energy dependence of σP_{stick}.[3,4,10,11,18,26] They concluded that σP_{stick} diminishes with increasing electron energy or, in other words, that the decline of the observed ion yield above ≈6 eV is not solely due to autodetachment. Andersen et al. have questioned this conclusion.[16] In a reanalyzis of published data they showed that proper consideration of the energy distribution of the fullerenes emerging from a source at temperature T_{ov} yields values for σP_{stick} that do not markedly depend on E_e.

Instead of measuring the time dependence of the ion yield we invert the procedure by modeling P_{surv} and comparing the results with the measured ion yield. $P_{surv}(E_e)$ as defined in eq 1 is a smeared-out step function. In Table 1 we list the electron energies $E_{1/2}$ at which P_{surv} drops to 50%. The computed values depend on the electron affinity and source temperature (listed in Table 1) and the heat capacity (or number of vibrational degrees of freedom). The $E_{1/2}$ values correlate qualitatively with the experimental falloffs which occur at low energies for C_{60}, C_{70}, C_{76}, and $Sc_3N@C_{80}$ (in that order) and at particularly high energies for C_{84} and C_{86}. The unusually small value of $E_{1/2}$ for $Sc_3N@C_{80}$ is clearly related to its low electron affinity; see Table 1.

For a visual comparison of our model with the measured anion yield we multiply the computed $P_{\mathrm{surv}}(E_e)$ by the classical cross section for electron capture in the polarization field of a pointlike ion; this Langevin cross section scales as $1/\sqrt{E_e}$ (s-wave capture). The results, scaled to the experimental maxima, are shown in Figure 3 as dashed lines. Reasonable agreement with the experimental data is found for C_{76}, C_{78}, C_{82}, and C_{84}. The agreement is poor for $Sc_3N@C_{80}$. The disagreement implies that either the capture cross section deviates strongly from the classical capture cross section $1/\sqrt{E_e}$ or that the sticking probability P_{stick} strongly varies with E_e. Another, more remote, possibility is an error in the reported electron affinity.[41] The vibrational heat capacity may also deviate from the assumed scaling behavior because we treated the four caged atoms the same way as the 80 carbon atoms, but this approximation is not likely to introduce a significant error.

Conclusion

We have measured electron attachment spectra for several fullerenes including, for the first time, an endohedral fullerene. The overall shape of the spectra is similar but some features are noteworthy, in particular for $Sc_3N@C_{80}$. The anion yield reaches a second, broad maximum around 4−6 eV. The location of the maximum shifts to smaller energies with increasing size *n*, although not monotonically. The falloff past the maximum has been modeled by calculating the energy dependence of the survival probability P_{surv}. The agreement with the measured anion yield is reasonable for some, but not all, fullerenes. A qualitative correlation between the observed falloff and published electron affinities is observed.

Acknowledgment. We thank Luna Innovations, Inc. (www.lunainnovations.com), for supplying the $Sc_3N@C_{80}$ compound. This work was partially supported by the FWF, Wien, and the European Commission, Brussels. F.Z. gratefully acknowledges a post-doc grant from Brazilian agency CNPq.

References and Notes

(1) Lezius, M.; Scheier, P.; Märk, T. D. *Chem. Phys. Lett.* **1993**, *203*, 232.

(2) Smith, D.; Spanel, P.; Märk, T. D. *Chem. Phys. Lett.* **1993**, *213*, 202. Vostrikov, A. A.; Dubov, D. Y.; Agarkov, A. A. *Tech. Phys. Lett.* **1995**, *21*, 715.

(3) Jaffke, T.; Illenberger, E.; Lezius, M.; Matejcik, S.; Smith, D.; Märk, T. D. *Chem. Phys. Lett.* **1994**, *226*, 213.

(4) Matejcik, S.; Märk, T. D.; Spanel, P.; Smith, D.; Jaffke, T.; Illenberger, E. *J. Chem. Phys.* **1995**, *102*, 2516.

(5) Huang, J.; Carman, H. S.; Compton, R. N. *J. Phys. Chem.* **1995**, *99*, 1719.

(6) Tosatti, E.; Manini, N. *Chem. Phys. Lett.* **1994**, *223*, 61.

(7) Finch, C. D.; Popple, R. A.; Nordlander, P.; Dunning, F. B. *Chem. Phys. Lett.* **1995**, *244*, 345.

(8) Weber, J. M.; Ruf, M. W.; Hotop, H. *Z. Phys. D* **1996**, *37*, 351.

(9) Fabrikant, I. I.; Hotop, H. *Phys. Rev. A* **2001**, *63*, 022706.

(10) Elhamidi, O.; Pommier, J.; Abouaf, R. *J. Phys. B* **1997**, *30*, 4633.

(11) Vasil'ev, Y. V.; Tuktarov, R. F.; Mazunov, V. A. *Rapid Commun. Mass Spectrom.* **1997**, *11*, 757.

(12) Prabhudesai, V. S.; Nandi, D.; Krishnakumar, E. *Eur. Phys. J. D* **2005**, *35*, 261.

(13) Kasperovich, V.; Tikhonov, G.; Kresin, V. V. *Chem. Phys. Lett.* **2001**, *337*, 55.

(14) Gianturco, F. A.; Lucchese, R. R. *J. Chem. Phys.* **1999**, *111*, 6769.

(15) [15]Lezius, M. *Int. J. Mass Spectrom.* **2003**, *223*, 447.

(16) Andersen, J. U.; Bonderup, E.; Hansen, K. *J. Phys. B* **2002**, 35, R1.

(17) Smith, D.; Spanel, P. *J. Phys. B* **1996**, *29*, 5199.

(18) Elhamidi, O.; Pommier, J.; Abouaf, R. *Int. J. Mass Spectrom.* **2001**, *205*, 17.

(19) Tuktarov, R. F.; Akhmet'yanov, R. F.; E. S. Shikhovtseva; Lebedev, Y. A.; Mazunov, V. A. *JETP Lett.* **2005**, *81*, 171.

(20) Kobayashi, K.; Sano, Y.; Nagase, S. *J. Comput. Chem.* **2001**, *22*, 1353. Krause, M.; Kuzmany, H.; Georgi, P.; Dunsch, L.; Vietze, K.; Seifert, G. *J. Chem. Phys.* **2001**, *115*, 6596.

(21) Bertsch, G. F.; Bulgac, A.; Tomanek, D.; Wang, Y. *Phys. Rev. Lett.* **1991**, *67*, 2690. Bulgac, A.; Ju, N. *Phys. Rev. B* **1992**, *46*, 4297.

(22) Yeretzian, C.; Hansen, K.; Whetten, R. L. *Science* **1993**, *260*, 652.

(23) Bekkerman, A.; Tsipinyuk, B.; Kolodney, E. *Int. J. Mass Spectrom.* **1999**, *187*, 773.

(24) Muigg, D.; Denifl, G.; Stamatovic, A.; Echt, O.; Märk, T. D. *Chem. Phys.* **1998**, *239*, 409.

(25) Vostrikov, A. A.; Dubov, D. Y.; Agarkov, A. A. *Tech. Phys. Lett.* **1995**, *21*, 517.

(26) Vostrikov, A. A.; Dubnov, D. Y.; Agarkov, A. A. *High Temp.* **2001**, *39*, 22.

(27) Andersen, J. U.; Bonderup, E.; Hansen, K. *J. Chem. Phys.* **2001**, *114*, 6518.

(28) Schettino, V.; Pagliai, M.; Ciabini, L.; Cardini, G. *J. Phys. Chem. A* **2001**, *105*, 11192.

(29) Lezius, M.; Scheier, P.; Foltin, M.; Dünser, B.; Rauth, T.; Akimov, V. M.; Krätschmer, W.; Märk, T. D. *Int. J. Mass Spectrom. Ion Process.* **1993**, *129*, 49.

(30) Lucchese, R. R.; Gianturco, F. A.; Sanna, N. *Chem. Phys. Lett.* **1999**, *305*, 413.

(31) Antoniewicz, P. R.; Bennett, G. T.; Thompson, J. C. *J. Chem. Phys.* **1982**, *77*, 4573.

(32) Holroyd, R. A. *Radiat. Phys. Chem.* **2005**, *72*, 79.

(33) Burose, A. W.; Dresch, T.; Ding, A. M. G. *Z. Phys. D* **1993**, *26*, Supplement, S294. Abouaf, R.; Pommier, J.; Cvejanovic, S. *Chem. Phys. Lett.* **1993**, *213*, 503. Abouaf, R.; Pommier, J.; Asal, A. *Chem. Phys. Lett.* **1995**, *242*, 184.

(34) Wästberg, B.; Rosen, A. *Phys. Scr.* **1991**, *44*, 276.

(35) Ipatov, A. N.; Ivanov, V. K.; Pacheco, J. M.; Ekardt, W. *J. Phys. B* **1998**, *31*, L 511.

(36) Gianturco, F. A.; Lucchese, R. R.; Sanna, N. *J. Phys. B: At. Mol. Opt. Phys.* **1999**, *32*, 2181.

(37) Field, D. Personal communication.

(38) Tanaka, H.; Boesten, L.; Onda, K.; Ohashi, O. *J. Phys. Soc. Jpn.* **1994**, *63*, 485.

(39) Kobayashi, K.; Nagase, S. In *Endofullerenes: A New Family of Carbon Clusters*; Akasaka, T., Nagase, S., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 2002; p 99. Orlandi, G.; Negri, F. *Photochem. Photobiol. Sci.* **2002**, *1*, 289. Guha, S.; Nakamoto, K. *Coord. Chem. Rev.* **2005**, *249*, 1111.

(40) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; et al. *Nature* **1999**, *401*, 55.

(41) Sidorov, L. N. *Phys. Solid State* **2002**, *44*, 413.

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

(43) Boltalina, O. V.; Dashkova, E. V.; Sidorov, L. N. *Chem. Phys. Lett.* **1996**, *256*, 253. Boltalina, O. V.; Ioffe, I. N.; Sidorov, L. N.; Seifert, G.; Vietze, K. *J. Am. Chem. Soc.* **2000**, *122*, 9745.

(44) Krishnakumar, E. Personal communication.