Abstract. The first experimental results on photoionization of mass-selected endohedral
Sc$_3$N@C$_{80}^+$ and Ce@C$_{82}^+$ fullerene ions are reported. The merged-beams technique was employed
to measure photo-ion yield spectra as well as absolute cross sections. Comparing the results
of endohedral fullerenes with those obtained using "empty" C$_{80}^+$ and C$_{82}^+$ ions provides insight
into the mutual influence of the fullerene cage and the encapsulated atom or molecule on one
another in photoabsorption processes.

1. Introduction
Within days of the discovery of C$_{60}$ by Kroto et al [1] the same team found evidence for
the existence of LaC$_{60}$ structures and hypothesized a metal atom within a soccer-ball shaped
cage [2]. During the subsequent two decades such endohedral metallofullerenes, characterized
by a metal atom encapsulated within a cage of carbon atoms, have received increasing interest,
partly because of their intriguing structures but also because they provide new possibilities
of applications in nanostructure science and technology [3]. In order to make use of such
applications detailed knowledge about the production, the handling and the structure of
endohedral fullerenes is required. Most importantly, ways of understanding and manipulating
the encaged atom’s or molecule’s properties have to be investigated.

Numerous theoretical studies have explored the response of atoms encapsulated in fullerene
cages to ionizing electromagnetic radiation. Interesting questions address the effect of the
surrounding fullerene cage on the properties of the caged atom or molecule, and vice versa.
In particular, resonance phenomena have been theoretically studied in a rapidly increasing
number of papers [4, 5]. Mutual influences on resonances in the photoabsorption by the caged
atoms and the surrounding carbon shell in endohedral fullerenes are presently a hot topic in
theory. Intriguing predictions have been published for photoionization of Xe@C$_{60}$ giving rise to
splitting of resonances through the coupling of collective plasmon excitations in the C$_{60}$ cage
and the giant dipole resonance in the encapsulated xenon atom [6, 4]. While the spectra of
endohedral fullerenes are a topical subject of theory, experimental results are extremely sparse.
Clearly, this is a consequence of the difficulty to produce sufficient amounts of purified endohedral
fullerenes for gas phase experiments. The only photoionization measurements available so far

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were published by Mitsuke and collaborators [7] who carried out time-of-flight measurements analyzing the charged products of photoabsorption in neutral metallofullerene vapors such as Ce@C$_{82}$. The data obtained have big absolute uncertainties due to difficulties in measuring and controlling the vapor density. In addition, the measured relative photo-ion yields have large statistical uncertainties resulting from the low target densities.

It is obvious that definitive experiments with mass and charge selected clusters in general, and with endohedral fullerenes in particular, are urgently needed at this time to test the available theoretical methods and to stimulate their further development.

2. Experiment

For the present experiments, endohedral Sc$_3$N@C$_{80}$ and Ce@C$_{82}$ fullerenes were synthesized in milligram quantities by using a new production process based on the reactive gas atmosphere technique [3]. In a time consuming process the $I_h$ isomer of Sc$_3$N@C$_{80}$ was separated to an estimated 99% degree of purification. In search of an optimized supply for pure ion beams of endohedral fullerenes, a mixture of higher order fullerenes with an estimated fraction of 20% of Ce@C$_{82}$, but a higher absolute content of the desired species in the sample, was also investigated.

Beams of the endohedral Sc$_3$N@C$_{80}^+$ and Ce@C$_{82}^+$ fullere ions were produced by evaporating the sample powder at low pressure ($\sim$10$^{-6}$ hPa) into the discharge of a permanent-magnet 10-GHz electron-cyclotron-resonance (ECR) ion source operated at a rf power level of only a few mW to minimize fragmentation. C$_{80}^+$ and C$_{82}^+$ ions were produced under almost identical conditions by gently evaporating mixed-fullerene powder into the ion source plasma. After acceleration by 4 kV, the ion beam was mass/charge selected by using a 60$^\circ$ magnetic-dipole mass spectrometer with a resolution of 1%. The Sc$_3$N@C$_{80}$-based ion-beam mass spectrum measured under the conditions of this experiment is shown in Fig. 1. It is evident that these endohedral molecular ions are robust in the discharge of the ion source, surviving ionization and up to five stages of fragmentation and reorganization of the C$_{80}$ cage due to ejection of C$_2$ fragments.
Beams of monochromatized synchrotron radiation from an undulator on Beamline 10.0.1.2 at the Advanced Light Source (ALS) were merged with the accelerated and mass/charge selected fullerene ion beam, and the yield of doubly charged product ions was measured as the photon energy was stepped. The typical endohedral fullerene ion beam current in the merged-beams apparatus during the photoionization measurements was of the order of one pA, which corresponds to less than 100 molecular ions in the photon-ion interaction region at one time. The $C_{80}^+$ and $C_{82}^+$ currents for the reference measurements were of the order of 10 pA. Cross sections were measured for single photoionization of the fullerene ions in the photon energy range 17–75 eV. Descriptions of the ALS merged-beams endstation [8] and its application to absolute photoionization measurements with fullerene ions [9] have been reported previously. Estimated total uncertainties of absolute cross sections at this stage of the experiments are of the order of ±30 to ±50% for the fullerene ions.

3. Results

First results from the present research project are available for $\text{Sc}_3\text{N}@\text{C}_{80}$ and $\text{Ce}@\text{C}_{82}$ fullerene materials. Examples are discussed below. It is interesting to note that the materials encaged inside a fullerene sphere typically carry an electrical charge. Such information can be deduced, for example, from characteristic features of the enclosed atoms in photoabsorption experiments. For the purpose of characterizing the available $\text{Sc}_3\text{N}@\text{C}_{80}$ sample, a near-edge x-ray atomic fine-structure (NEXAFS) spectrum was recorded on the Scanning Transmission X-ray Microscope [11] at ALS Beamline 5.3.2 using a µm-sized crystal structure obtained from the solid $\text{Sc}_3\text{N}@\text{C}_{80}$ I$_h$ isomer sample available for the present study. The measurement in the region of the scandium L-edge is presented in Fig. 2. Obviously, the encapsulated scandium atoms are responsible for a very distinct additional absorption feature of the endohedral fullerene.

The relative absorption coefficient resulting from the experiment was normalized at high photon energies to the photoabsorption cross section constructed by employing the method of Henke et al [10]. This method is based on the approximation that the photoabsorption...
coefficients of compound materials can be estimated from the coefficients of their individual atoms. It is expected to provide useful data for photon energies beyond 30 eV and far away from absorption edges. The interactions between the individual atoms in the material are neglected. Accordingly, the absorption cross section of a molecule can be approximated by \[ \sigma_a = \sum_i x_i \sigma_{a,i} \]

where \( x_i \) is the number of atoms of element \( i \) in the molecule and \( \sigma_{a,i} \) is the absorption cross section for an individual atom of type \( i \). The element-specific cross sections \( \sigma_{a,i} \) follow from scattering factors calculated and tabulated by Henke et al. [10].

The resulting cross section \( \sigma_a \) for the \( \text{Sc}_3\text{N@C}_{80} \) fullerene is shown as a dotted line in Fig. 2. It reproduces the gross features of the measured absorption spectrum far away from the present L-edge (not shown) but deviates in the details, especially in the energy range shown in Fig. 2. Different from the prediction of a simple scandium L-edge, strong resonances are observed at about 401.5 eV and 405.7 eV that are associated with excitation from the \( L_3 \) (2p\(3/2\)) and the \( L_2 \) (2p\(1/2\)) sub-shells of Sc to the lowest unoccupied molecular orbitals of the endohedral fullerene. The energies of these resonances in the measured NEXAFS spectrum in comparison with those of neutral Sc are related to the valency of the encapsulated Sc atoms. On the basis of similar absorption measurements and with the help of atomic multiplet calculations Alvarez et al. [12] concluded that the scandium atoms bound in the \( \text{Sc}_3\text{N@C}_{80} \) fullerene donate 2 electrons each to the carbon cage while the nitrogen atom on the average attracts \( 3 \times 0.4 \) elementary charges leaving each scandium atom with a fractional charge \( q = 2.4e \) (where \( e \) is the elementary charge), i.e., in the effective charge state \( \text{Sc}^{2+/3+} \). Similarly it has been found that the effective charge state of the Ce atom inside \( \text{Ce@C}_{80} \) is \( \text{Ce}^{3/+} \) [13].

3.1. Photoionization of \( \text{Sc}_3\text{N@C}_{80}^+ \)

The upper panel of Fig. 3 compares cross-section measurements for single photoionization of \( \text{C}_{80}^+ \) and \( \text{Sc}_3\text{N@C}_{80}^+ \). The relative experimental data obtained for \( \text{Sc}_3\text{N@C}_{80}^+ \) have been normalized to absolute measurements for \( \text{C}_{80}^+ \) at the maximum of the cross section near 21 eV. In the energy range of Fig. 3 an enhancement of the cross section for the endohedral \( \text{Sc}_3\text{N@C}_{80}^+ \) relative to the empty \( \text{C}_{80}^+ \) fullerene ion is evident in the measurements.

As noted above, each scandium atom carries a positive charge \( q = 2.4e \). This is reasonably close to \( q = 2e \) for which case, i.e., for \( \text{Sc}^{2/+} \) ions, absolute cross-section measurements for single photoionization have been reported by Schippers et al. [15, 14]. Strong resonances were observed in the 35-40 eV energy range, as illustrated in the lower panel of Fig. 3. However, such distinct structure is absent in the measurements for the \( \text{Sc}_3\text{N@C}_{80}^+ \) ion.

To ascertain whether the cross-section enhancement in the endohedral molecule may be accounted for quantitatively by photoionization of the caged \( \text{Sc}_3\text{N} \) cluster, a simple model was employed. Consideration was given to the possibility that the molecular bonding and the presence of the fullerene cage could cause significant broadening of any atomic resonance features in photoionization. The \( \text{Sc}^{2/+} \) cross section was therefore arbitrarily convoluted with a Gaussian of 6 eV full width at half maximum. Additionally, it was shifted on the energy axis by +1.5 eV. This shift may account for the increased electronic binding energy of the Sc charge state of 2.4+ instead of 2+. The smooth experimental cross section of Samson and Angel [16] for photoionization of atomic nitrogen which does not show any resonance features in this photon energy range was additionally considered. Comparison of the model with the present measurements is provided in Fig. 3. The simulated cross section consisting of three times the energy-convoluted and shifted photoionization cross section for \( \text{Sc}^{2/+} \) added to that for the N atom, i.e., the model cross section for the \( \text{Sc}_3\text{N} \) cluster was added to the fitted cross section for the \( \text{C}_{80}^+ \) cage producing the dashed line in the upper panel of Fig. 3. This is in very good agreement with the measurement on the endohedral \( \text{Sc}_3\text{N@C}_{80}^+ \) fullerene ion indicating that the total resonance strength of the isolated constituents of \( \text{Sc}_3\text{N} \) in the present energy range is conserved even when they form a cluster and are encapsulated in a fullerene cage.
Figure 3. The upper panel displays measured cross sections for photoionization of $\text{Sc}_3\text{N}@\text{C}_{80}^\text{+}$ (full circles) and $\text{C}_{80}^\text{+}$ (open circles). The inset in the upper panel provides an overview of these cross sections over the full experimental range of 17–75 eV. The area between the curves fitted to these cross sections indicates the excess cross section obtained with the endohedral $\text{Sc}_3\text{N}@\text{C}_{80}^\text{+}$ fullerene relative to the empty $\text{C}_{80}^\text{+}$ cage. The error bars are statistical only. The dashed curve is the sum of the fit for the empty $\text{C}_{80}^\text{+}$ cage and the model cross section (see text) for the encaged $\text{Sc}_3\text{N}$ cluster. The lower panel shows the cross section for photoionization of $\text{Sc}^{2+}$ ions [14]. This cross section is dominated by excitation of a 3p electron in $\text{Sc}^{2+}$ to autoionizing states as indicated.
3.2. Photoionization of Ce@C$_{82}^+$

Figure 4. Measured relative cross sections for photoionization of Ce@C$_{82}^+$ (black circles) and C$_{82}^+$ (gray circles). The data for C$_{82}^+$ were normalized to the results for Ce@C$_{82}^+$ in the energy region around 80 eV.

Preliminary data were available at the time of ICPEAC XXV for endohedral Ce@C$_{82}^+$ and C$_{82}^+$ ions. Fig. 4 shows cross sections for single ionization of Ce@C$_{82}^+$ ions by incident VUV photons. Evidence for the resonance feature in the 115–140 eV photon energy range was already obtained in the previous experiments by Mitsuke et al. [7] employing neutral Ce@C$_{82}$ vapor. The resonance is due to the 4d excitation of the encaged cerium atom. For Xe@C$_{60}$, it was hypothesized that there are oscillations on the 4d giant dipole resonance due to reflection of the photoelectron from the fullerene cage [6, 4]. While the previous experiment left ambiguity about whether such oscillations occur in Ce@C$_{82}$, the present experiment appears to exclude such a phenomenon in the metallofullerene studied. The reason for the missing structures in the 4d $\rightarrow$ 4f excitation of an encapsulated cerium atom (Z=58) in comparison to xenon (Z=54) may be that the 4f subshell has already collapsed in the heavier atom and, hence, does no longer give rise to a giant resonance phenomenon.

In summary, the present paper reports on the first photoionization experiments with endohedral fullerene ions. In particular, ion beams could be produced from miniscule amounts of endohedral fullerenes by very gently evaporating the synthesized materials into a highly efficient low-power ion source. Working with ions at defined energies, magnetic mass selection and therefore chemical purification of the endohedral species became possible. Such measurements are needed at this time to test and to guide theoretical efforts trying to clarify the mutual influence of the encaged atoms and the surrounding carbon shell on one another. By the techniques that have been developed in the context of this work, a new class of photoionization experiments not only with mass-selected endohedral fullerenes, but also clusters and nanoparticles in general, is now becoming accessible.
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