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# The stability of singly and multiply charged $La@C_{80}$ and $La@C_{82}$ ions determined from kinetic energy release measurements

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**Abstract**

We have measured the kinetic energy release distributions for unimolecular $C_2$ loss from singly and multiply charged endohedral $La@C_{80}{}^{z+}$ and $La@C_{80}{}^{z+}$ ions for charge states $z = 1–3$. Using finite heat bath theory, we deduce the dissociation energies for loss of $C_2$. The charge state $z$ has no statistically significant effect on the dissociation energies. The dissociation energies of endohedral fullerene ions are larger than those of the corresponding empty fullerene ions by a few tenths of an electron volt, but the differences are barely statistically significant. The small differences also imply that the complexation energies of $La@C_n{}^{z+}$ and $La@C_{n-2}{}^{z+}$ are identical within the experimental errors, for $n = 80$ and 82 and all charge states.

*Keywords:* C-82; Lanthanum; Endohedral; Metastable reaction; Kinetic energy release distribution (KERD)

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## 1. Introduction

Two decades after the discovery of endohedral fullerenes [1], research into their fascinating properties continues unabated (for recent reviews, see [2–5]). For example, endohedral $H_2@C_{60}$ has been prepared by organic synthesis [6]. The quantized rotational motion of $C_2$ in the “fullerene quantum gyroscope” $C_2Sc_2@C_{84}$ has been spectroscopically resolved [7], as has the vibrational motion of the $La_2$ molecule caged in $La_2@C_{80}$ [8]. Trimetallic nitride clusters $M_3N@C_{80}$ have been isolated with surprisingly large yields for a variety of group 3 and rare-earth metals (see [9–12], and references therein).

$La@C_{82}$ is one of the prototypical metallofullerenes. It was among the first metallofullerenes to be isolated [13]; since then it has been characterized by a variety of physical methods (see [2–5,14] and references therein). It has also been subject of several investigations in the gas phase [15–24]. In several of these studies, decay channels for highly excited $La@C_{82}$ and $La@C_{82}{}^+$ were characterized, such as electron emission [19], fragmentation [16–21,23], and radiation [22]. However, in only one of these studies [24] it was attempted to determine the stability of $La@C_{82}{}^+$ in a quantitative way, by measuring the activation energy, or “dissociation energy” $D$ for the reaction:

$$M@C_n{}^+ \rightarrow M@C_{n-2}{}^+ + C_2 - D(M@C_n{}^+). \tag{1}$$

Surprisingly, the value for $D(La@C_{82}{}^+)$ was found to exceed the dissociation energy $D(C_{82}{}^+)$ of the empty fullerene,

$$C_n{}^+ \rightarrow C_{n-2}{}^+ + C_2 - D(C_n{}^+) \tag{2}$$

by 2.2 eV, or 26%. An even larger difference of 5.3 eV was obtained for $Tb@C_{82}{}^+$. These findings contrast with results for other metallofullerenes [24–26] according to which the dissociation energies of filled and empty fullerenes are iden-

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tical within the experimental uncertainties of, typically, 1 eV or less.

The values of the dissociation energies have implications for the complexation energy (also termed *stabilization* or *embedding energy*) which is defined as:

$$\mathrm{M}^+ + \mathrm{C}_n \rightarrow \mathrm{M@C}_n{}^+ - E_{\mathrm{cmplx}}(\mathrm{M@C}_n{}^+). \tag{3}$$

$E_{\mathrm{cmplx}}$ will be negative if reaction (3) is exothermic. From a thermodynamic cycle, one has [26]:

$$\begin{aligned} & D(\mathrm{M@C}_n{}^+) - D(\mathrm{C}_n{}^+) \\ & \quad = -E_{\mathrm{cmplx}}(\mathrm{M@C}_n{}^+) + E_{\mathrm{cmplx}}(\mathrm{M@C}_{n-2}{}^+) \\ & \quad = -\Delta E_{\mathrm{cmplx}}(\mathrm{M@C}_n{}^+) \end{aligned} \tag{4}$$

Thus, a measurement of dissociation energies provides the *differential* complexation energy, $\Delta E_{\mathrm{cmplx}}$. A large positive value for $D(\mathrm{La@C_{82}}^+) - D(\mathrm{C_{82}}^+)$ would imply that a caged La atom stabilizes $\mathrm{C_{82}}^+$ much more strongly than $\mathrm{C_{80}}^+$.

A potential problem in the mass spectrometric studies, which rely on an accurate determination of the kinetic energy released in reactions (1) or (2), is the occurrence of isotopomers. Although a high resolution double-focusing mass spectrometer can easily resolve stable isotopomers of different nominal mass, a mass-analyzed ion kinetic energy (MIKE) scan may be affected by contributions from parent ions of adjacent masses. Even if this problem were avoided, the metastable fragment ion peak may contain contributions from different isotopomers, especially if the kinetic energy release is large. This would lead to an overestimate of the kinetic energy release (KER), and thus of the dissociation energy.

As illustrated in recent publications [26–30], the problems can be avoided if the double-focusing mass spectrometer is combined with a second electrostatic analyzer. In the present work, we use such an instrument to measure MIKE spectra of singly and multiply charged $\mathrm{La@C_{80}}^{z+}$ and $\mathrm{La@C_{82}}^{z+}$ for $z = 1$–3. From these data, we determine the dissociation energies for $\mathrm{C_2}$ loss. In agreement with earlier work, we find that the charge state $z$ has no statistically significant effect on the dissociation energies. The difference in dissociation energies between filled and empty fullerenes is, in all cases, less than 1 eV. For $\mathrm{La@C_{82}}^+$, in particular, it is only $0.5 \pm 0.6$ eV.

## 2. Experiment and data analysis

### 2.1. Sample preparation

The production and rough separation of La-metallofullerenes have been published previously [31,32]. Briefly, the soot containing the metallofullerenes was generated by DC arc discharge method. A composite graphite rod (La/C atomic ratio: 0.8%; Ø 4.6 mm × 130 mm, Tokyo Tenso Co.) was vaporized under 150 Torr flowing He atmosphere. The mixture of metallofullerenes and empty fullerenes was extracted from the soot by 1,2,4-trichlorobenzene (TCB) under reflux with protection of Ar for overnight. After removal of the solvent TCB, a controlled-potential bulk reduction of the extract was carried out in *o*-dichlorobenzene (*o*-DCB) solution in the presence of *n*-$\mathrm{BuNClO_4}$ ($3.0 \times 10^{-2}$ M) for selective reduction of metallofullerenes into their anions, which left the empty fullerenes in the neutral state. The metallofullerene anions were then selectively extracted by a mixture of acetone/$\mathrm{CS_2}$ (volume ratio ∼4:1) and oxidized by a moderate oxidant $\mathrm{CHCl_2COOH}$ into their neutral state that precipitated from the solvent. Mass spectroscopic and high performance liquid chromatography (HPLC) analyses on the precipitate of metallofullerenes thus separated indicate that most of the abundant empty fullerenes have been removed from the sample. The mixture of metallofullerenes was dissolved in toluene for HPLC separation. A PYE column (Ø 20 mm × 250 mm, eluant-toluene, room temperature, flow rate 10 mL/min) was employed for the separation of our target $\mathrm{La@C_{82}}$. As confirmed by HPLC and mass spectroscopic analyses the $\mathrm{La@C_{82}}$ sample thus obtained is almost free of larger monometallofullerenes $\mathrm{La@C}_n$ ($n \geq 84$).

### 2.2. Mass spectra and MIKE scans

The apparatus consists of a high resolution double-focusing mass spectrometer (Varian MAT CH5-DF) of reversed Nier-Johnson type BE1 geometry combined with a second electrostatic analyzer E2 [27,33]. The fullerene sample was, without further treatment, evaporated into a vacuum of about $10^{-7}$ Torr from a temperature-controlled oven operating at 680 °C. The effusive beam is intersected by an electron beam. An electron energy of 120 eV and a current of 1 mA were used in experiments involving cations. Anions were formed by electron attachment at 7 eV. The resulting ions are extracted perpendicular to the fullerene and electron beams and accelerated into the mass spectrometer with $U_{\mathrm{acc}} = 3$ kV. Ions passing through the first field-free region are momentum-analyzed by a magnetic sector field B, enter a second field-free region (ff2), pass through a 90° electric sector field (E1), enter a third field-free region (ff3, length 92 cm), pass through another electrostatic sector field (E2), and are detected by an electron multiplier. Referenced to the time of their formation, $\mathrm{C_{60}}^+$ parent ions traverse ff3 during the time interval $75\ \mu\mathrm{s} \leq t \leq 91\ \mu\mathrm{s}$. The corresponding times for other ions of mass $m$ (in atomic units) and charge state $z$ are obtained by multiplying with $\sqrt{m/720z}$.

Mass-analyzed ion kinetic energy (MIKE) spectra of ions that undergo spontaneous decay in ff3 are analyzed by tuning the magnet and first electric sector field to transmit the parent ion (mass $m_{\mathrm{p}}$), and scanning the sector field voltage of E2. In this mode, B and E1 constitute a double-focusing high resolution mass spectrometer, and E2 will transmit fragment ions (mass $m_{\mathrm{f}}$) formed in ff3 if the sector field voltage $U_{\mathrm{f}}$ is set to:

$$U_{\mathrm{f}} = \frac{m_{\mathrm{f}}}{m_{\mathrm{p}}} U_{\mathrm{p}} \tag{5}$$

This relation also holds for multiply charged parent ions provided the charge state $z$ of the fragment ions equals that of the parent ions. The MIKE spectra, together with scans of the parent ions around voltage $U_{\mathrm{p}}$, provide the experimental raw data from which the kinetic energy release, and the dissociation energies, are derived.

### 2.3. Data analysis

The MIKE spectra reveal the distribution of the kinetic energy released in the reaction. Whereas a parameter-free determination of the distribution is rather involved [28,34], data analysis is greatly simplified if the MIKE peaks are Gaussians. This is the case in the present study. The average KER ($\bar{\varepsilon}$) is computed from $\Delta U$, the full-width-at-half-maximum (FWHM) of a Gaussian fitted to the MIKE peak after correction for the scaled width of the parent ion, from the relation [35]

$$\bar{\varepsilon} = 2.16 \frac{z m_{\mathrm{p}}^2 U_{\mathrm{acc}}}{16 m_{\mathrm{f}}(m_{\mathrm{p}} - m_{\mathrm{f}})} \left( \frac{\Delta U}{U_{\mathrm{p}}} \right)^2 . \quad (6)$$

The transition state temperature $T^{\dagger}$ of the dissociating complex follows from:

$$1.5 k_{\mathrm{B}} T^{\dagger} = \bar{\varepsilon} \quad (7)$$

According to Klots's finite-heat-bath theory [36], one derives from $T^{\dagger}$ the isokinetic temperature $T_{\mathrm{b}}$ of a canonical ensemble that would have the same rate $k$ as the evaporative ensemble,

$$T_{\mathrm{b}} = T^{\dagger} \frac{\exp[\gamma/(C-1)] - 1}{\gamma/(C-1)} \quad (8)$$

where $k_{\mathrm{B}}C$ is the vibrational heat capacity of the parent ion. We assume the value given by the equipartition theorem, $C = 3p - 6$ where $p$ is the number of atoms in the cluster. $\gamma$ is the Gspann factor defined as [37]

$$\gamma = \ln \frac{A}{k} = \frac{D}{k_{\mathrm{B}} T_{\mathrm{b}}} \quad (9)$$

where $D$ is the activation energy of the reaction and $A$ is the pre-exponential in the Arrhenius relation that is assumed here for $k(T_{\mathrm{b}})$. If an evaporative ensemble of cluster ions is sampled at time $t$ after excitation and if competing cooling channels can be neglected, then the most likely decay rate will be characterized by [38,39]:

$$k = \frac{1}{t} \quad (10)$$

In the present work, we use $A = 2 \times 10^{19}\ \mathrm{s}^{-1}$ for all ions. This value is identical to, or very close to, the value used in several other recent studies of unimolecular dissociation of fullerene ions [25,40–45].

For a comparison of the present results with previously published data [18,24], we re-analyze those data and apply a scaling factor to bring the $C_{60}{}^{+}$ dissociation energy into agreement with our most recent value of 10.25 ± 0.08 eV [26]. The quoted uncertainty merely reflects the uncertainty of the average KER (394 ± 3 meV [26]), but the agreement with other recently reported dissociation energies is excellent [41,46].

Finally, in our analysis, we have ignored the effect of radiative cooling. As discussed elsewhere [47], this will result in dissociation energies that are too low by about 4% for the fullerene sizes discussed here. For multiply charged clusters, the difference will be even smaller because their time-of-flight is shorter.

## 3. Results

The first few mass spectra of the sample were dominated by a long sequence of intense ion peaks. These peaks were identified as $C_{60}(CS_2)_n$ cations with $n$ extending beyond $n = 20$. However, spectra free of any traces of solvent molecules were observed after outgassing the sample in vacuum at $T_{\mathrm{ov}} = 350\,^{\circ}\mathrm{C}$ for several hours.

We have recorded anion mass spectra by electron attachment at an energy of 7 eV (Fig. 1, top), and cation mass spectra at an electron energy of 120 eV (Fig. 1, middle and bottom panels). The sample temperature was $T_{\mathrm{ov}} = 680\,^{\circ}\mathrm{C}$. Whereas cation spectra recorded at elevated electron energies can possibly be distorted by dissociative ionization, electron attachment to fullerenes below 10 eV safely avoids fragmentation [48]. The excellent agreement between the anion and cation spectra seen in Fig. 1 (top two panels) suggests that the dominant ion peaks are not a result of fragmentation. Therefore, the most prominent neutral species in the sample are identified as La@$C_{82}$,

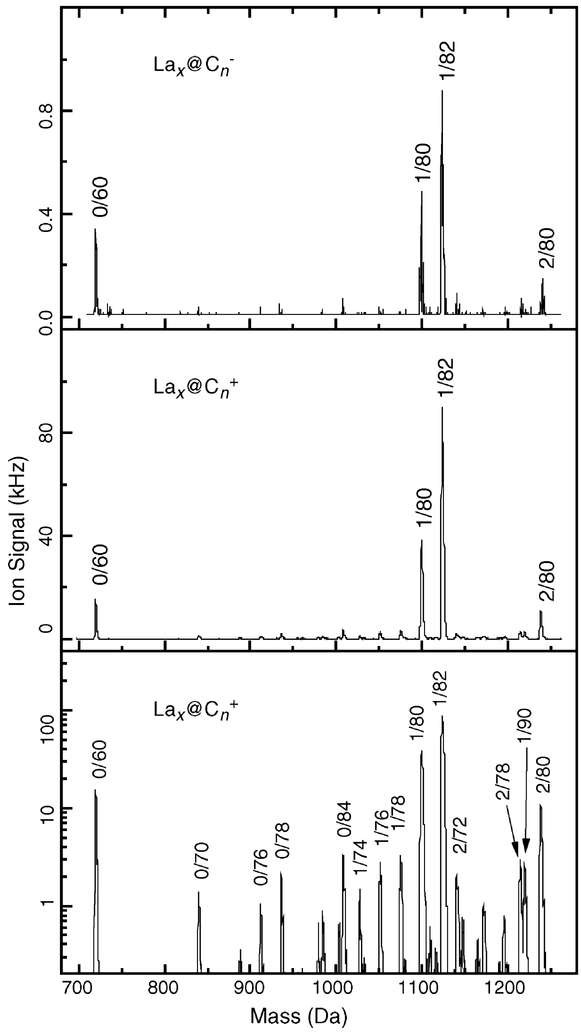

Fig. 1. Mass spectra of the metallofullerene sample. *Upper panel:* Anions formed by electron attachment. *Middle and lower panels:* Cations formed by electron impact, plotted with linear and logarithmic ordinate, respectively. Prominent peaks are labeled by the number of lanthanum and carbon atoms.

La@$C_{80}$, $La_2$@$C_{80}$, and $C_{60}$. For elements M from group 3 and the rare earths, M@$C_{82}$ and the dimetallofullerene $M_2$@$C_{80}$ are efficiently synthesized by standard techniques [2,4], but the appearance of La@$C_{80}$ ions is somewhat of a surprise. The first successful isolation of M@$C_{80}$ was by Sun et al. [49] who synthesized Eu@$C_{80}$. Lassesson et al. [21] observed La@$C_{80}{}^+$ and La@$C_{80}{}^-$ ions in laser-desorption mass spectra of La@$C_{82}$ samples, but only if the samples exposed to air for extended periods of time. In the present study, the samples were kept under anaerobic conditions except for the very brief transfer from a quartz ampoule to the mass spectrometer. Our mass spectra show no evidence for oxides. Preliminary laser-desorption time-of-flight mass spectra of samples separated by different HPLC columns suggest that, indeed, La@$C_{80}$ exists in the sample.

Several other ion species are seen in the cation spectrum that is plotted with a logarithmic scale (Fig. 1, bottom panel). In particular, $La_2$@$C_n{}^+$ is also identified for $n = 72$ and 78. However, it is not possible to exclude formation by dissociative ionization for these less abundant species, and it was not possible to record their MIKE spectra.

In Fig. 2, we display sections of a mass spectrum that reveal doubly and triply charged cations. The most prominent ion peaks are identical to the ones observed in Fig. 1, but the La@$C_n{}^{z+}$ sequence ($n \leq 78$) likely contains fragment ions.

We have recorded MIKE spectra for $C_2$ loss from parent ions La@$C_n{}^{z+}$ for $n = 80$ and 82, $z = 1$–3. In Fig. 3, we present an example, the MIKE scan of La@$C_{82}{}^{2+}$. Gaussian curves fitted to the data are displayed as solid lines. From the fitted width of the fragment ion peak, we obtain after correction for the width of the parent ion peak, the average kinetic energy release of the reaction. All experimental values are summarized in Table 1.

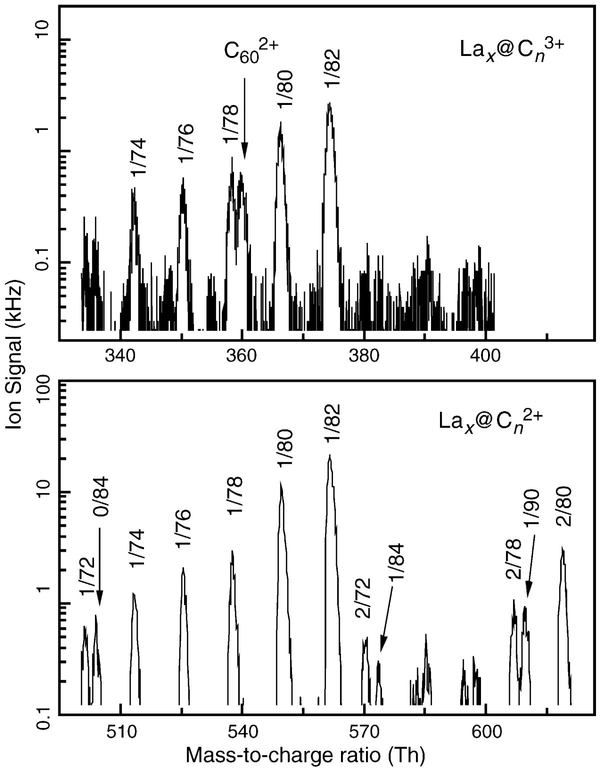

Fig. 2. Mass spectra of the metallofullerene sample showing the presence of doubly and triply charged cations.

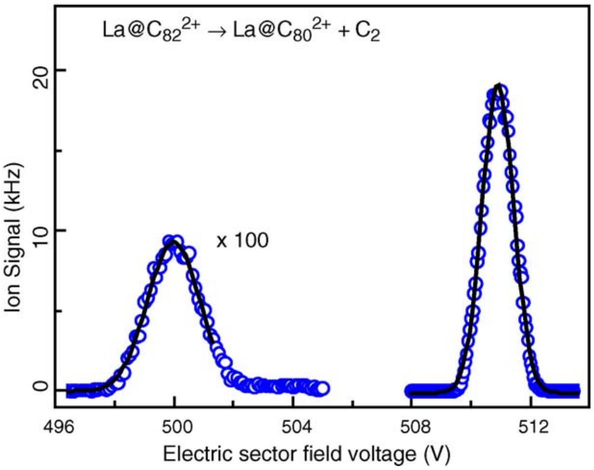

Fig. 3. Open dots: MIKE spectrum for unimolecular decay of La@$C_{82}{}^{2+}$ displaying the fragment ion peak La@$C_{80}{}^{2+}$ (left, multiplied by a factor 100), and the parent ion peak (right). Solid lines represent Gaussians fitted to the data.

Table 1
Average kinetic energy release ($\bar{\varepsilon}$) and activation energy ($D$) for $C_2$ loss calculated from $\bar{\varepsilon}$ using finite heat bath theory and an Arrhenius pre-exponential of $2 \times 10^{19}$ s$^{-1}$

| Parent ion | $\bar{\varepsilon}$ (meV)[a] | $D$ (eV)[a] | $D$ (eV)[b,c] |
|---|---|---|---|
| $C_{60}{}^+$ | | | 10.25 ± 0.08[b] |
| $C_{80}{}^+$ | | | 9.26 ± 0.38[b]<br>9.8 ± 0.7[c] |
| $C_{80}{}^{2+}$ | | | 9.30 ± 0.58[b] |
| $C_{80}{}^{3+}$ | | | 8.89 ± 0.37[b] |
| La@$C_{80}{}^+$ | 372 | 9.39 ± 0.47 | |
| La@$C_{80}{}^{2+}$ | 382 | 9.65 ± 0.48 | |
| La@$C_{80}{}^{3+}$ | 387 | 9.76 ± 0.49 | |
| $C_{82}{}^+$ | | | 8.4 ± 0.4[b]<br>8.7 ± 0.6[c] |
| La@$C_{82}{}^+$ | 352 | 8.85 ± 0.44 | 10.7 ± 0.7[c] |
| La@$C_{82}{}^{2+}$ | 352 | 8.87 ± 0.44 | |
| La@$C_{82}{}^{3+}$ | 368 | 9.28 ± 0.46 | |

Also listed are some relevant dissociation energies measured previously [24,26]. Data from [24] have been re-analyzed and scaled as explained in Section 2.3 and ref. [26].

[a] This work.

[b] Ref. [26].

[c] Ref. [24].

## 4. Discussion

We derive the activation energies $D_n$ for $C_2$ loss from the measured average kinetic energies, using finite heat bath theory and a pre-exponential factor $A = 2 \times 10^{19}$ s$^{-1}$. Results are listed in Table 1; they are plotted in Fig. 4 as solid squares. Also shown in Fig. 4, as triangle, circles and diamonds, are several previously published values for filled and empty fullerenes [24–26]; they are represented by filled and open symbols, respectively. Data from

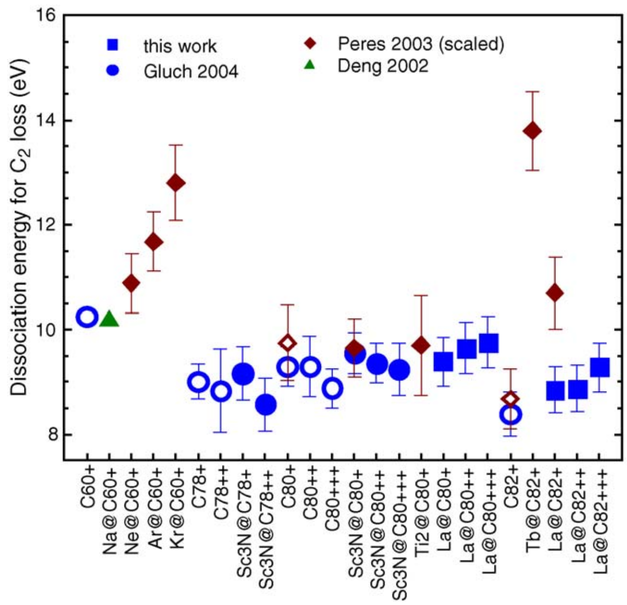

Fig. 4. Dissociation energies for $C_2$ loss from empty and filled fullerenes (empty and filled symbols, respectively). Values obtained in the present work for La@$C_{80}{}^{z+}$ and La@$C_{82}{}^{z+}$ ($z = 1$–3) are indicated by squares. Other data are from refs. [18,24–26].

[24] have been re-analyzed and scaled as explained in Section 2.3.

As seen from Fig. 4, the charge state $z$ has no statistically significant effect on the dissociation energies of La@$C_{80}{}^{z+}$ and La@$C_{82}{}^{z+}$. This observation agrees with our earlier findings concerning empty and filled fullerene ions of size $n = 78$ and 80 and $z \leq 3$ [26].

The average dissociation energies (averaged over $z = 1$–3) are $9.6 \pm 0.2$ and $9.0 \pm 0.2$ eV for La@$C_{80}{}^{z+}$ and La@$C_{82}{}^{z+}$, respectively, where the uncertainties are computed from the standard deviations of the two data sets. For comparison, the dissociation energies of $C_{80}{}^{z+}$ (averaged over $z = 1$–3) and $C_{82}{}^{+}$ are $9.2 \pm 0.2$ and $8.4 \pm 0.4$ eV, respectively, i.e., dissociation energies of the endohedrals are larger than those of empty fullerenes by $0.4 \pm 0.3$ and $0.6 \pm 0.5$ eV, respectively. These differences are hardly significant because the uncertainties specify the one-sigma errors.

Peres et al. [24] reported that the dissociation energy of $C_{82}{}^{+}$ increases by 26% (from 8.5 to 10.7 eV) upon caging of La. However, their value of $10.7 \pm 0.7$ eV for La@$C_{82}{}^{+}$ greatly exceeds our present value of $8.9 \pm 0.4$ eV. One possible reason for the difference is the presence of isotopomers in the ion beam. Lanthanum has only one isotope ($^{139}$La) of significant natural abundance, but the La@$C_{82}{}^{+}$ ion peak will contain one or more $^{13}$C isotopes with a probability of 60%. If decay of these isotopically mixed ions contributes to the fragment ion peak in the MIKE scan, then its width, and hence the kinetic energy release will be overestimated. In the present work, we have used a double-focusing mass spectrometer equipped with an additional electrostatic analyzer (BEE geometry), whereas in the previous study [24], an instrument with BE geometry was used. Although both instruments feature excellent mass resolution, during a MIKE scan the BE instrument will select parent ions only with the magnetic sector field, and "wrong" parent ions of slightly different mass may contribute to the MIKE spectrum. For an illustration of the related problems, and how they are solved if an instrument with BEE geometry is used, see ref. [26,29].

There may be an alternative explanation for the large difference of 1.8 eV between our current value for La@$C_{82}{}^{+}$, and the value reported by Peres et al. [24]. The sample analyzed in the latter work was a mixture of metallofullerenes including La@$C_{84}$, and the La@$C_{82}$ in that sample contained two isomers, say isomers I and II. In contrast, the sample investigated by us was almost free of La@$C_{84}$ and the La@$C_{82}$-II isomer. These differences between the two samples could possibly affect the measured KERD. On the other hand, the metastable ions undergoing dissociation are highly excited (their transition state temperatures are about 2800 K, see Eq. (7). Ions that overcome the large barrier for dissociation will probably also overcome the barrier separating different isomers.

The main result of the present study is the small difference in $D_n$ between filled and empty fullerenes. This has implications for our knowledge of the thermal emissivity $\varepsilon_{\text{th}}$ of metallofullerenes. Recent experiments by the Gothenborg group [22] show that the quantity $\varepsilon_{\text{th}} \times D_n^3$ is practically the same for La@$C_n{}^{+}$ and $C_n{}^{+}$, within the experimental uncertainty. A large difference between the dissociation energies of La@$C_{82}{}^{+}$ and $C_{82}{}^{+}$ by 26% [24] would therefore imply that the thermal emissivity of the metallofullerene is reduced by a factor of two. Our present results indicates that the difference, if any, is much smaller. The very large difference of 64% (see Fig. 4) between the reported dissociation energies [24] of Tb@$C_{82}{}^{+}$ and $C_{82}{}^{+}$, though, remains puzzling.

It may seem surprising that neither the charge state nor the presence of the endohedral metal atom have a large effect on the dissociation energies. Either way, the number of electrons in bonding or anti-bonding orbitals of the ion will be affected. However, in the absence of reverse activation barriers, dissociation energies indicate *differences* in the *total* energies of reactant and products. If reactant and product are stabilized (or destabilized) to the same degree by the caged atom, or by the removal of one or more valence electrons, then the dissociation energy is not likely to change significantly.

For a quantitative analysis, one also has to consider possible changes of the ionization energies; these are not well known for endohedral ions, especially for $z > 1$. Alternatively, it is possible [26] to deduce accurate information about the complexation energy of metallofullerenes by comparing the dissociation energy of M@$C_{n-2}{}^{z+}$ with that of M@$C_n{}^{z+}$, see Eqs. (3) and (4). From the values listed in Table 1, one obtains $\Delta E_{\text{cmplx}}(\text{La@C}_{80}{}^{z+}) = -0.1 \pm 0.6$, $-0.4 \pm 0.8$, and $-0.9 \pm 0.6$ eV for $z = 1$–3, respectively. Therefore, the complexation energies of La@$C_{78}{}^{z+}$ are nearly as large as those of La@$C_{80}{}^{z+}$.

For La@$C_{82}{}^{+}$, we find $\Delta E_{\text{cmplx}}(\text{La@C}_{82}{}^{+}) = -0.5 \pm 0.6$ eV. A similar analysis is not possible for the higher charge states because the values of $D(C_{82}{}^{2+})$ and $D(C_{82}{}^{3+})$ have not been determined, but in view of the small effects of the charge state on dissociation energies of other fullerenes, $\Delta E_{\text{cmplx}}(\text{La@C}_{82}{}^{z+})$ appears to be small, less than 1 eV, as well.

Unfortunately, we cannot determine absolute complexation energies. Theoretical values reported thus far mostly pertain to $C_{60}$ and $C_{70}$ (see refs. in [26]); only a few calculations are available for larger fullerenes. For $Sc_3N@C_{80}$ complexation energies of 10.72 [50] and 11.60 eV [51] have been calculated with density functional methods for the most stable endohedral isomer ($I_h$ symmetry, isomer 7). Several computational studies have been devoted to the classical fullerene $M@C_{82}$. Kobayashi and Nagase [52] obtained, at the B3LYP level of theory, complexation energies of 3.3, 4.6 and 5.0 eV for or M = Sc, Y and La, respectively, while >3.55 eV has been obtained for $Sc@C_{82}$ in an ab initio Hartree–Fock calculation [53]. Whaley and coworkers report 5.6 eV for $Gd@C_{82}$ [54]. Relative energies (relative to the most stable isomer) have been calculated for $Ca@C_{82}$ [55] and $La_2@C_{80}$ [8].

In conclusion, we have measured the average kinetic energy released upon metastable $C_2$ loss from endohedral $La@C_n{}^{z+}$ for $n = 1$ and 2, and $z = 1$–3. From these data, we have deduced the activation energies for the reaction, i.e., the dissociation energies $D_n$. They are larger than those of the corresponding empty fullerene ions by a few tenths of an electron volt, but the differences are barely statistically significant. The small differences also imply that the complexation energies of $La@C_{78}{}^{z+}$ are only slightly smaller than, or equal to, the complexation energies of $La@C_{80}{}^{z+}$, which in turn, is not much less than that of $La@C_{82}{}^{z+}$. The previously reported [24] large increase by 26% in the stability of $C_{82}{}^{+}$ upon caging of La could not be confirmed.

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## References

[1] J.R. Heath, S.C. O'Brien, Q. Zhang, Y. Liu, R.F. Curl, H.W. Kroto, F.K. Tittel, R.E. Smalley, J. Am. Chem. Soc. 107 (1985) 7779.
[2] H. Shinohara, Rep. Prog. Phys. 63 (2000) 843.
[3] S.Y. Liu, S.Q. Sun, J. Organomet. Chem. 599 (2000) 74.
[4] T. Akasaka, S. Nagase, Endofullerenes: A New Family of Carbon Clusters, Kluwer Academic, Dordrecht, 2002.
[5] S. Guha, K. Nakamoto, Coord. Chem. Rev. 249 (2005) 1111.
[6] K. Komatsu, M. Murata, Y. Murata, Science 307 (2005) 238.
[7] M. Krause, M. Hulman, H. Kuzmany, O. Dubay, G. Kresse, K. Vietze, G. Seifert, C. Wang, Phys. Rev. Lett. 93 (2004) 137403.
[8] H. Shimotani, T. Ito, Y. Iwasa, A. Taninaka, H. Shinohara, E. Nishibori, M. Takata, M. Sakata, J. Am. Chem. Soc. 126 (2004) 364.
[9] S. Stevenson, P.W. Fowler, T. Heine, J.C. Duchamp, G. Rice, T. Glass, K. Harich, E. Hajdu, R. Bible, H.C. Dorn, Nature 408 (2000) 427.
[10] H.C. Dorn, E.B. Iezzi, S. Stevenson, A.L. Balch, J.C. Dunchamp, in: T. Akasaka, S. Nagase (Eds.), Endofullerenes: A New Family of Carbon Clusters, Kluwer Academic, Dordrecht, 2002, p. 121.
[11] M.M. Olmstead, H.M. Lee, J.C. Duchamp, S. Stevenson, D. Marciu, H.C. Dorn, A.L. Balch, Angew. Chem. Int. Ed. 42 (2003) 900.
[12] M. Krause, J. Wong, L. Dunsch, Chem. Eur. J. 11 (2005) 706.
[13] K. Kikuchi, S. Suzuki, Y. Nakao, N. Nakahara, T. Wakabayashi, H. Shiromaru, K. Saito, I. Ikemoto, Y. Achiba, Chem. Phys. Lett. 216 (1993) 67.
[14] T. Akasaka, et al., J. Am. Chem. Soc. 122 (2000) 9316.
[15] J.H. Callahan, S.W. McElvany, M.M. Ross, Int. J. Mass Spectrom. Ion Process. 138 (1994) 221.
[16] R.D. Beck, P. Weis, J. Rockenberger, R. Michel, D. Fuchs, M. Benz, M.M. Kappes, Surf. Rev. Lett. 3 (1996) 881.
[17] T. Kimura, T. Sugai, H. Shinohara, Chem. Phys. Lett. 304 (1999) 211.
[18] J. Laskin, T. Peres, A. Khong, H.A. Jimenez-Vazquez, R.J. Cross, M. Saunders, D.S. Bethune, M.S. DeVries, C. Lifshitz, Int. J. Mass Spectrom. 185–187 (1999) 61.
[19] A. Lassesson, K. Mehlig, A. Gromov, A. Taninaka, H. Shinohara, E.E.B. Campbell, J. Chem. Phys. 117 (2002) 9811.
[20] A. Lassesson, A. Gromov, K. Mehlig, A. Taninaka, H. Shinohara, E.E.B. Campbell, J. Chem. Phys. 119 (2003) 5591.
[21] A. Lassesson, A. Gromov, M. Jonsson, A. Taninaka, H. Shinohara, E.E.B. Campbell, Int. J. Mass Spectrom. 228 (2003) 913.
[22] M. Hedén, K. Hansen, F. Jonsson, E. Rönnow, A. Gromow, E.E.B. Campbell, A. Taninaka, H. Shinohara, J. Chem. Phys. 123 (2005) 044310.
[23] D.C. Lorents, D.H. Yub, C. Brink, N. Jensen, P. Hvelplund, Chem. Phys. Lett. 236 (1995) 141.
[24] T. Peres, B.P. Cao, H. Shinohara, C. Lifshitz, Int. J. Mass Spectrom. 228 (2003) 181.
[25] R. Deng, O. Echt, Chem. Phys. Lett. 353 (2002) 11.
[26] K. Gluch, S. Matt-Leubner, O. Echt, P. Scheier, T.D. Märk, J. Phys. Chem. A 108 (2004) 6990.
[27] K. Gluch, J. Fedor, S. Matt-Leubner, O. Echt, A. Stamatovic, M. Probst, P. Scheier, T.D. Märk, J. Chem. Phys. 118 (2003) 3090.
[28] K. Gluch, S. Matt-Leubner, O. Echt, R. Deng, J.U. Andersen, P. Scheier, T.D. Märk, Chem. Phys. Lett. 385 (2004) 449.
[29] K. Gluch, S. Matt-Leubner, L. Michalak, O. Echt, A. Stamatovic, P. Scheier, T.D. Märk, J. Chem. Phys. 120 (2004) 2686.
[30] S. Matt-Leubner, S. Feil, K. Gluch, J. Fedor, A. Stamatovic, O. Echt, P. Scheier, K. Becker, T.D. Märk, Plasma Sources Sci. Technol. 14 (2005) S26.
[31] B. Cao, T. Wakahara, T. Tsuchiya, M. Kondo, Y. Maeda, G.M.A. Rahman, T. Akasaka, K. Kobayashi, T. Nagase, T. Yamamoto, J. Am. Chem. Soc. 126 (2004) 9164.
[32] T. Tsuchiya, T. Wakahara, S. Shirokura, Y. Maeda, T. Akasaka, K. Kobayashi, S. Nagase, T. Kato, K.M. Kadish, Chem. Mater. 16 (2004) 4343.
[33] S. Matt-Leubner, A. Stamatovic, R. Parajuli, P. Scheier, T.D. Märk, O. Echt, C. Lifshitz, Int. J. Mass Spectrom. 222 (2003) 213.
[34] S. Matt, O. Echt, R. David, A. Stamatovic, T.D. Märk, J. Chem. Phys. 113 (2000) 616.
[35] J.L. Holmes, A.D. Osborne, Int. J. Mass Spectrom. Ion Phys. 23 (1977) 189.
[36] C.E. Klots, Z. Phys. D 21 (1991) 335.
[37] C.E. Klots, J. Phys. Chem. 92 (1988) 5864.
[38] C.E. Klots, J. Chem. Phys. 98 (1993) 1110.
[39] K. Hansen, J.U. Andersen, P. Hvelplund, S.P. Möller, U.V. Pedersen, V.V. Petrunin, Phys. Rev. Lett. 87 (2001) 123401.
[40] S. Matt, M. Sonderegger, R. David, O. Echt, P. Scheier, J. Laskin, C. Lifshitz, T.D. Märk, Chem. Phys. Lett. 303 (1999) 379.
[41] S. Matt, O. Echt, P. Scheier, T.D. Märk, Chem. Phys. Lett. 348 (2001) 194.
[42] S. Matt, R. Parajuli, A. Stamatovic, P. Scheier, T.D. Märk, J. Laskin, C. Lifshitz, Eur. J. Mass Spectrom. 5 (1999) 477.
[43] C. Lifshitz, Int. J. Mass Spectrom. 198 (2000) 1.
[44] T. Peres, B.P. Cao, W.D. Cui, A. Khong, R.J. Cross, M. Saunders, C. Lifshitz, Int. J. Mass Spectrom. 210 (2001) 241.
[45] S. Tomita, J.U. Andersen, C. Gottrup, P. Hvelplund, U.V. Pedersen, Phys. Rev. Lett. 87 (2001) 073401.
[46] S. Tomita, J.U. Andersen, K. Hansen, P. Hvelplund, Chem. Phys. Lett. 382 (2003) 120.
[47] K. Gluch, S. Matt-Leubner, O. Echt, B. Concina, P. Scheier, T.D. Märk, J. Chem. Phys. 121 (2004) 2137.
[48] M. Lezius, P. Scheier, M. Foltin, B. Dünser, T. Rauth, V.M. Akimov, W. Krätschmer, T.D. Märk, Int. J. Mass Spectrom. Ion Process. 129 (1993) 49.
[49] B. Sun, T. Inoue, T. Shimada, T. Okazaki, T. Sugai, K. Suenaga, H. Shinohara, J. Phys. Chem. B 108 (2004) 9011.

[50] K. Kobayashi, Y. Sano, S. Nagase, J. Compd. Chem. 22 (2001) 1353.
[51] J.M. Campanera, C. Bo, M.M. Olmstead, A.L. Balch, J.M. Poblet, J. Phys. Chem. A 106 (2002) 12356.
[52] K. Kobayashi, S. Nagase, Chem. Phys. Lett. 282 (1998) 325.
[53] A. Gruss, M.C. Bohm, J. Schulte, K.P. Dinse, Z. Naturf. A 53 (1998) 801.
[54] L. Senapati, J. Schrier, K. Whaley, Nano Lett. 4 (2004) 2073.
[55] Z. Slanina, K. Kobayashi, S. Nagase, J. Chem. Phys. 120 (2004) 3397.