5. Endohedral Fullerene-Noble Gas Clusters Formed with High-Energy Bimolecular Reactions of C_x^{n+} ($x = 60, 70$; $n = 1, 2, 3$)

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Results are reported for high-energy beam experiments which establish the formation of endohedral carbon cluster-noble gas compounds by bimolecular reactions of C_x^{n+} ($x = 60, 70$; $n = 1, 2, 3$) with He and $C_{60}^{+\cdot}$ with Ne. The ions were accelerated up to 8 keV in a four-sector mass spectrometer and allowed to collide with the noble gas in a collision chamber at room temperature. Product ions were monitored with a B/E=constant linked scan. Within the sensivity of the experiments, no carbon cluster-gas compounds were observed in the reactions of $C_{60}^{+\cdot}$ with H_2, D_2, O_2, Ar, and SF_6, or of $C_{70}^{+\cdot}$ with O_2. The observed fall in the cross-section for carbon cluster-noble gas compounds with increasing size of the noble gas, the observation of unimolecular loss of C_2 from mass-selected $C_xHe^{+\cdot}$ ions, and the elimination of carbon fragments instead of He observed in the formation of the collision-induced C_xHe^{n+} product ions are taken as evidence for endohedral compound formation. Results of *ab initio* molecular-orbital calculations for the perpendicular penetration of the plane of ionized benzene with He, Ne, and Ar indicate that sufficient kinetic energy should be available in the collisions with $C_{60}^{+\cdot}$ to penetrate the $C_{60}^{+\cdot}$ cage at the collision energies of the experiments.

1. Introduction. – Of all the C_x carbon clusters (for a review, see [1]), the fullerene C_{60} (the 'third allotropic form of carbon') [2] is currently of greatest interest [3], largely because it can be produced in macroscopic quantities with the convenient method developed by *Krätschmer et al.* [4]. Sufficient experimental evidence now has been reported [1–4] to verify the visionary suggestion [3e] [5] that C_{60} is the celebrated icosahedron of the I_h point group.

One of the most intriguing aspects of C_{60} [1–5] is its $\sim$ 7-Å diameter cavity [6], which provides the possibility to generate endohedral fullerene compounds and so allow a new field of endohedral chemistry – chemistry proceeding *inside* a cage of (C) atoms[3]). For example, metal-containing cluster ions of the type $C_{60}M^+$ (with M = La, Ni, Na, K, Rb, and Cs) have been observed in the mass spectra produced in laser vaporization experiments on graphite doped with metal salts [8a, b, c] [9]. In the past, opinions differed, however, on the location of the metal atom: *Smalley* and coworkers [8a, b, c] indicated that the experimental results point to the formation of a spherically C_{60} cluster with the metal atoms inside; on the other hand, *Cox et al.* [9] were of the opinion that $C_{60}La$, for example, is an empty C_{60} cluster which has 'custody' of the metal on its outside surface.

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[3]) For theoretical studies on endohedral cluster carbon compounds, see [7].

Evidence for *externally* bound MC_{60}^+ clusters (M = Fe, Co, Ni, Cu, Rh, La, VO) in the gas phase was reported recently [10]: collision-induced dissociation of FeC_{60}^+, for example, required relatively little activation energy and resulted in the exclusive formation of C_{60}^+. This observation is consistent with both $IE(Fe) > IE(C_{60})$ and an externally bound Fe-atom. If the Fe or the other metal atoms were located inside the cage, these experimental findings would imply a *ready* inside $\rightleftarrows$ outside passage of the metal atom. This possibility is unlikely given the radius of Fe^+ of ~ 0.96 Å and that of Fe of ~ 1.24 Å as well as the MNDO results of *Bakowies* and *Thiel* [7e] for the Li migration out of the cage of $C_{60}Li^+$ for which they estimate a barrier > 6 eV. More recently, *Smalley* and coworkers demonstrated [8d] that the properties of C_xLa ($x = 60$, 70, 74, 82) generated by laser vaporization of doped graphite are very distinct from those of the *exohedral* complexes generated by low-energy bimolecular reactions of M^+ with C_{60} in the gas phase [10]. In addition, X-ray photoemission spectra showed [8e] that the La-atom of C_xLa complexes is in a charge state close to +3, and has been effectively protected from reaction with H_2O and O_2 by the enclosing fullerene cage. These findings are indeed compatible with an endohedral structure for which the symbol $M@C_x$ was suggested [8d].

In our laboratory, we recently were able to demonstrate that noble gases (He and Ne) can be injected into singly- and multiply-charged C_x^{n+} fullerene molecules ($x = 60$, 70; $n = 1$–3), and so provide the first evidence for the formation of endohedral carbon cluster-noble gas compounds by high-energy bimolecular reactions[4])[5]). Here, we present a full account of our experimental and theoretical studies.

2. Experimental. – The collision experiments were performed with a four-sector B(1)E(1)B(2)E(2) mass spectrometer (B stands for magnetic and E for electric sector)[6]). This is a modified *VG Instruments ZAB* mass spectrometer which has been built by *AMD Intectra*, W-2833 Harpstedt, Germany, by combining the BE part of a *ZAB-HF-3F* machine (MS I) with an *AMD 604* double-focussing mass spectrometer (MS II) by a system of 'einzel' lenses. C_x^{n+} ions ($x = 60$, 70; $n = 1$–3) were generated by electron-impact ionization at 100 eV of the vapor of C_{60} or C_{70} (the temp. of the solid-probe tip was *ca.* 550°) at a low pressure of 10^{-6} mbar and a source-block temp. of 270°. The ions were accelerated up to 8-keV maximum kinetic energy, mass-selected with B(1)E(1), and then allowed to collide with neutral gases N at r.t. in a collision chamber located in the field-free region between E(1) and B(2). In typical experiments, the primary ion beam was reduced by 60–70%. The resulting two-dimensional ion-current surface was explored with a B(2)/E(2)=constant linked scan (sampling all fragment ions arising from the same precursor ion) [14].

We will first discuss injection experiments accompanied with fragmentation of the encounter complexes, followed by a presentation of experiments in which the adduct formation occurs without decomposition. The results of *ab initio* MO calculations on appropriate model systems are used in order to get an upper limit of the energy necessary for the penetration of carbon hexagons of fullerene ions by noble gases as well as the binding energy of He.

3. Results and Discussion. – 3.1. *Injection Experiments of* C_x^{n+} ($x = 60$, 70; $n = 1$–3) *Accompanied with Fragmentation.* Earlier experiments in other laboratories have already shown [15] that highly accelerated C_x^+ ions ($x = 60$, 70) lose C_2 unimolecularly and even-numbered C_m units ($m = 2$, 4, 6, *etc.*) upon collisional activation. The detailed mechanism of carbon loss in the collision-induced dissociation of C_x^+ ions is unknown

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[4]) For short communications of our experiments, see [11].

[5]) Related high-energy experiments aimed at 'confirming our unexpected and unprecedented results' [12a] and to generate fullerene-noble gas clusters, were later reported by several groups as described in [12]. We are grateful to Prof. *S. L. Anderson*, Dr. *E. E. B. Campbell*, Prof. *M. L. Gross*, and Dr. *M. M. Ross* for having provided us with copies of their manuscripts prior to publication.

[6]) For a full description of the machine, see [13].

and is a matter of speculation [3b, i] [15a, d, h] [16]. With regard to the inclusion of the stationary gas N (*Eqn. 1*) in the collision experiments, no successful experiments were reported although the published data of *Luffer* and *Schram* [15b], though weak, show clearly recognizable features for $(C_{x-n})^+$ ions having 'shoulders' on the high-mass side of the peaks when He is used.

$$C_x^+ (8\text{ keV}) + N \rightarrow [C_{x-m} + N]^+ + C_m \quad (1)$$

$$x = 60, 70;\ m = 2, 4, 6, \ldots$$

In fact, in collision experiments with H_2, D_2, O_2, Ar, and SF_6, we also observe the exclusive production of fragment ions in which C_m has been split off. A typical example is shown in *Fig. 1* for collisions of C_{60}^+ (8 keV) with $N = D_2$, and the same processes were observed for the other gases. A general feature of the CA spectra is that with increasing center-of-mass-energy, E_{cm}, the maximum in the distribution of C_m losses shifts to the elimination of larger C_m units. This effect was demonstrated by either changing the mass of the collision gas N or the kinetic energy of the C_x^+ ions.

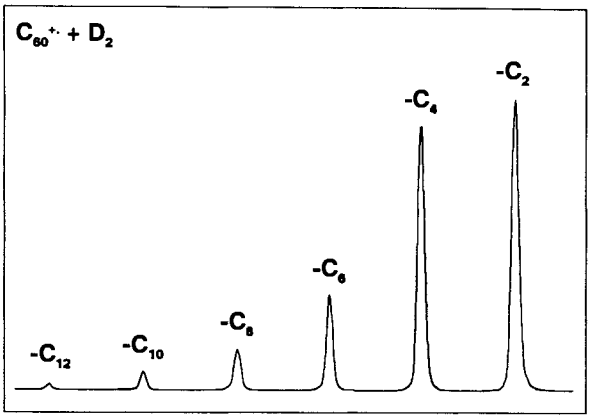

Fig. 1. *CA Mass spectrum of* C_{60}^+/D_2 ($E_{lab.}$ = 8 keV; linked scan with B/E = const.)

A fundamentally different, unexpected, and unprecedented result is obtained, when He is used as a collision gas (*Fig. 2*). In addition to the signals corresponding to losses of C_m, new signals appear at *higher* masses at all signals; the mass difference Δm is equal to 4 when ^{4}He is used (*Fig. 2a*) and 3 when ^{3}He is employed (*Fig. 2b*).

The differences which appear with D_2 and He cannot be accounted for by energetic effects since E_{cm} is identical for these two gases; rather, other factors (presumably size and shape of N) are responsible. Totally analogous results are obtained with C_{70}^+: While He is incorporated (appearance of $[C_{70-m}He]^+$, *Fig. 3*), the other collision partners only lead to collision-induced elimination of C_m. The observation that the $C_{60}He^+$ fragment arises from C_{70}^+ (*Fig. 3*; loss of formally C_{10}) is particularly noteworthy, as is the fact that the abundance of this signal does not conform to the monotonous decrease of signal intensities reported in *Fig. 2*. Obviously, $C_{60}He^+$ possesses a unique stability, and if *Smalley*'s

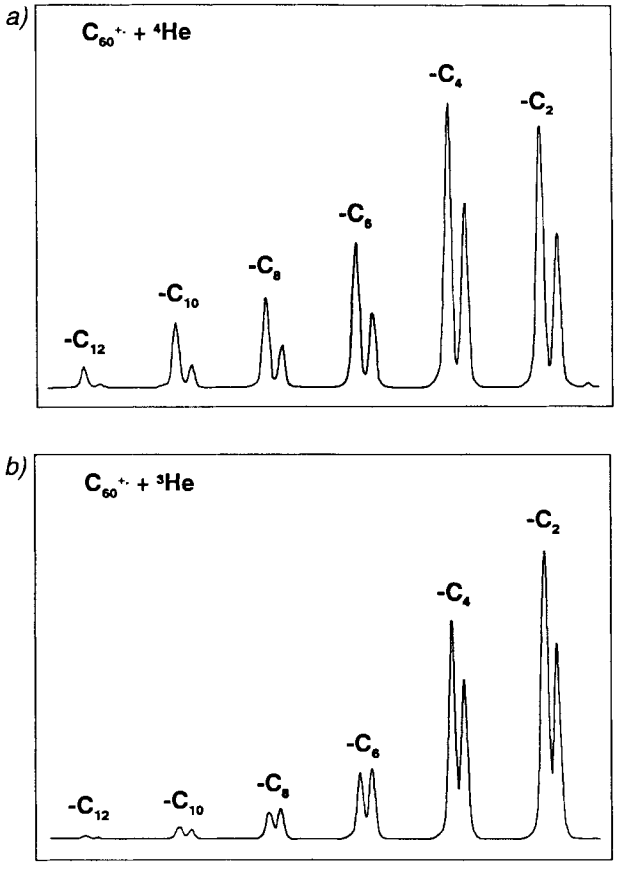

Fig. 2. *CA Mass spectra for* $C_{60}^{+\cdot}$ *with* ^{4}*He* (a) *and* ^{3}*He* (b) ($E_{lab.}$ = 8 keV; linked scan with B/E = const.)

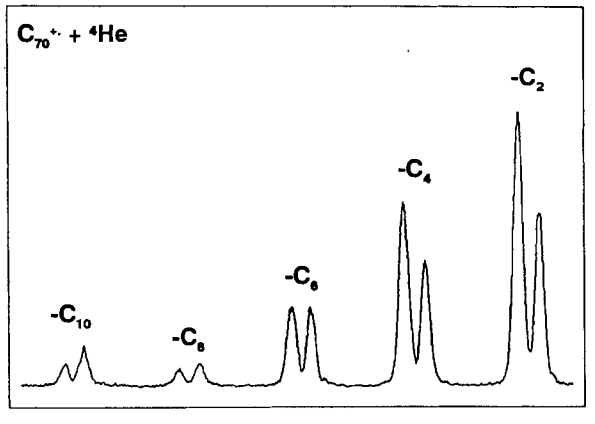

Fig. 3. *CA Mass spectrum of* $C_{70}^{+\cdot}$/^{4}*He* ($E_{lab.}$ = 8 keV; linked scan with B/E = const.)

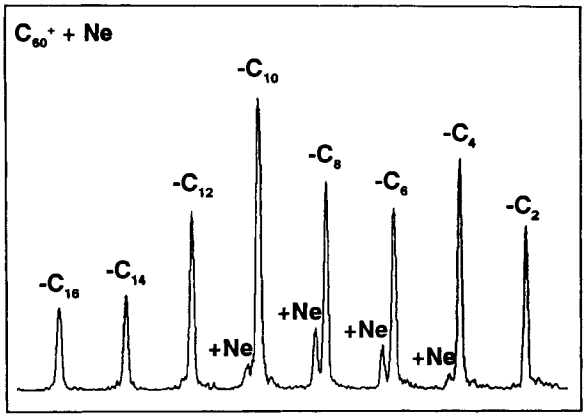

Fig. 4. *CA Mass spectra of* C_{60}^{+}/Ne ($E_{lab.}$ = 3 keV; linked scan with B/E = const.)

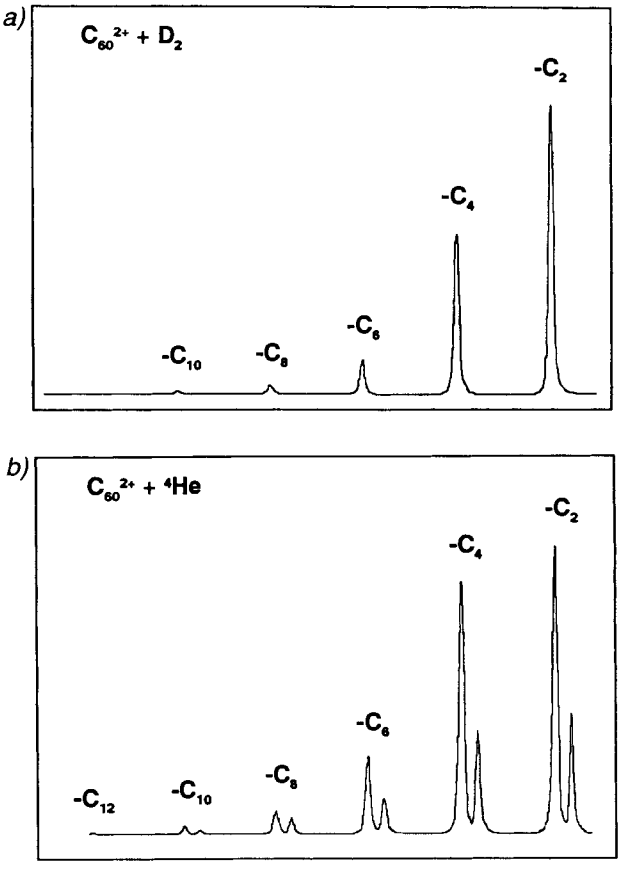

Fig. 5. *CA Mass spectra for* C_{60}^{2+} *with* D_2 (a) *and* ^4He (b) ($E_{lab.}$ = 6 keV; linked scan with B/E = const.)

argument [3e, i] that loss of 'C_m' units is accompanied by a 'self-repair' of the cluster-cage applies, the $C_{60}He^{+\cdot}$ ion generated in the bimolecular reaction of $C_{70}^{+\cdot}$ with He corresponds to the endohedral fullerene-noble gas complex.

Experiments aimed at incorporating noble gases others than He were also successful with Ne (*Fig. 4*), but not with Ar[7]). As demonstrated in *Fig. 4*, the *even-numbered* fragment ions $C_{60-m}^{+\cdot}$ ($m = 2, 4, 6, \ldots$) generated in the reaction with Ne are accompanied by 'satellite' signals at higher masses corresponding to the incorporation of Ne, except for $m = 2$ and 4 for which the satellite signal cannot be assigned with confidence. The cross-section for the reaction with Ne is by a factor of *ca.* 10 smaller than in the case of He, and the origin of this effect will be discussed further below.

The successful incorporation of He in fullerene radical cations, $C_x^{+\cdot}$, together with the propensity of fullerenes to form multiply-charged fullerene cations C_x^{n+} ($n \geq 2$) [15b, d, e, h, j] prompted us [11c] to perform high-energy beam-experiments of C_{60}^{n+} ($n = 2, 3$) with He[8]). The injection of He into C_{60}^{2+} was investigated at laboratory energies of 6, 8, 10, and 16 keV, and the results obtained at 6 keV are shown in *Fig. 5*, where they are compared with D_2 (top). While for D_2, there was no evidence for retention of the collision gas at the sensitivity of the experiments, He retention was observed at all four kinetic energies, decreasing in efficiency with increasing energy. The accompanying fragmentation which occurs by loss of *even-numbered* C units is in agreement with results obtained in collision-induced dissociation experiments conducted elsewhere in which O_2 [15b, d, g] or Xe [15j] were used as the collision gases without observing incorporation of these gases. In our experiments, up to 16 C-atoms were lost from C_{60}^{2+} at 6 keV and 20 C-atoms at 16 keV laboratory energies.

The retention of He by C_{60}^{3+} was monitored at a kinetic energy of 9 keV (primary ions were accelerated through a potential of 3 keV). The experiments were more difficult due to the lower signal intensities, but *Fig. 6* clearly demonstrates the fragmentation with loss of 16 C-atoms in *even-numbered* C units which has previously been reported without evidence for the inclusion of the collision gas [15d, g]. In the present experiment, it is obvious that He is retained in the cluster fragment ions (*Fig. 6b*) while, at the sensitivity of the experiment, D_2 is not (*Fig. 6a*).

Before addressing the central question of the *location* of the noble gases He and Ne in the fullerene ion, *i.e. endohedral vs. exohedral* carbon clusters, we will briefly discuss the results of high-energy beam experiments aimed at generating $C_{60}He^{+\cdot}$ *without* fragmentation [11d] [12].

3.2. *Injection Experiments of* C_{60}^{n+} ($n = 1, 2$) *without Fragmentation.* Although first-principle consideration may suggest that the probability of detecting the *intact* product $C_{60}N^{n+}$ of a high-energy, bimolecular reaction of C_{60}^{n+} with a collision gas N is quite small [17], the chances of generating $C_{60}N^{n+}$, actually, are not that remote provided low-mass

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[7]) *Gross* and coworkers reported [12b, c] that high-energy ($E_{cm} = 421$ eV) collisions of $C_{60}^{+\cdot}$ with Ar cause incorporation of Ar and decomposition to form a series of *odd-numbered* C species $C_xAr^{+\cdot}$ ($x = 49, 51, 53$, and 55). This result differs completely from what has been observed for fullerene ions, which metastably [15a, c, i], by collisional activation [11] [12] [15b, d, e, g, h, j], and by photoactivation [3b] [16] eliminate only *even-numbered* C neutrals. Although a possible explanation for the exclusive formation of *even-numbered* fragment ions has been discussed by *Smalley* [3b], the situation remains an enigma.

[8]) Due to the smaller cross-section of the experiments of $C_{60}^{+\cdot}$ with Ne and the negative results with Ar, the experiments with C_{60}^{n+} ($n = 2, 3$) were confined to He.

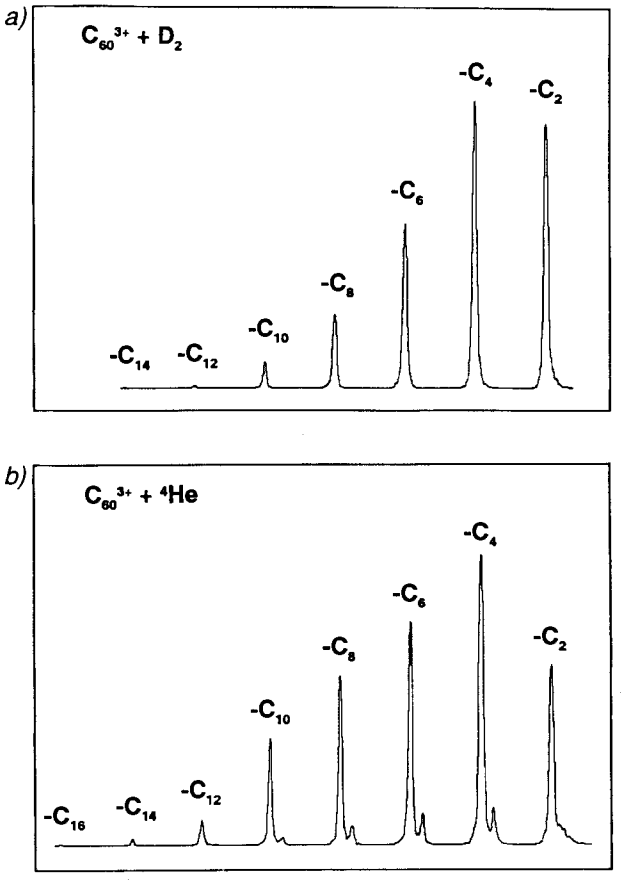

Fig. 6. *CA Mass spectra for* C_{60}^{3+} *with* D_2 (a) *and* ^{4}*He* (b) ($E_{lab.}$ = 9 keV; linked scan with B/E = const.)

stationary target gases N and appropriate laboratory energies of the projectile ions C_{60}^{n+} are used to ensure relatively small center-of-mass energies, E_{cm}. In fact, in our earliest experiments on the reaction of $C_{60}^{+\cdot}$ with ^{4}He and ^{3}He, in addition to the signals shown in *Fig. 2*, we *did* observe signals at *m/z* 724 and 723, when using 8 keV. However, we did not report this observation in our communications [11a, b], as we realized that *i*) the cross-section for He attachment is strongly dependent on the laboratory energy, and *ii*) the linked-scan mode used in our initial experiments for fundamental reasons (interference signals due to the occurrence of translational energy loss of $C_{60}^{+\cdot}$ ions in collision with He) was not ideal for an *unambiguous* detection of the intact encounter-complex $C_{60}He^{+\cdot}$. This matter was discussed at great length with the research group of Dr. *M. M. Ross*, Naval Research Laboratory, Washington, D. C., who also noted the strong energy dependence for the cross-section of generating $C_{60}He^{+\cdot}$. In fact, by using a *ZAB-2FQ* tandem mass spectrometer *Ross* and *Callahan* [12a] were able to unambiguously demonstrate the direct formation of $C_{60}He^{+\cdot}$ in keV collisions of $C_{60}^{+\cdot}$ with He. This result was later confirmed by

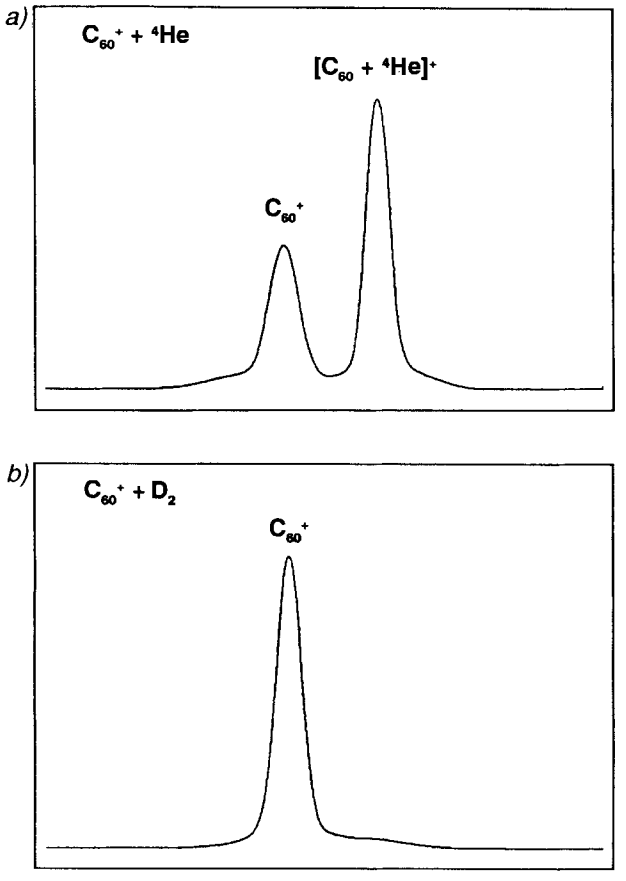

Fig. 7. a) *B(2)/E(2) = const. linked scan in the vicinity of the center of* m/z *724 with an initial kinetic energy of 6 keV for* C_{60}^+. The large peak on the right represents the $C_{60}He^+$ adduct ion, and the peak on the left arises from cutting the energy-loss tail of C_{60}^+ in the B(2),E(2) two-dimensional surface. b) *Similar collision experiments with* D_2 *as a target gas.* There is no real evidence for $C_{60}D_2^+$ adduct ion on the right of the energy-loss peak.

Gross and coworkers [12b, c] using a four-sector mass-spectrometer. Our measurement also demonstrates that retention of He by C_{60}^+ is achievable at laboratory energies of 4, 5, 6, and 8 keV, it is optimal at kinetic energies in the range from 5 to 6 keV, and that it falls at higher and lower energies. When the B/E = constant linked scan is chosen optimally with full recognition of possible complications due to the presence of an energy loss peak, the $C_{60}He^+$ is easily visible and separated from the energy-loss peak for C_{60}^+ as shown in *Fig. 7a* for a laboratory energy of 6 keV. As shown in *Fig. 7b*, no significant, if any, addition of D_2 and C_{60}^+ is apparent at 6 keV nor was it observed at 3, 4, and 8 keV. The latter observation is at variance with the recent findings of *Gross* and coworkers [12b, c]. They report for the reaction of C_{60}^+ with D_2 the formation of weak, though clearly recognizable signals at *m/z* 724 and 722, which they assign to the formation of $C_{60}D_2^+$ and $C_{60}D^+$. In line with our findings (*Fig. 1*), the apparent non-inclusion [12b, c] of deuterium

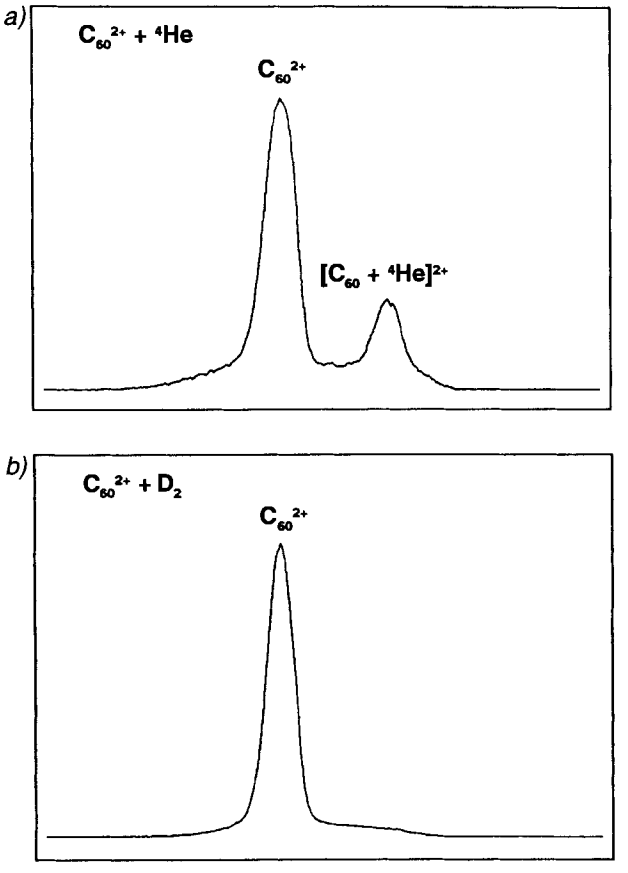

Fig. 8. a) *B(2)/E(2) = const. linked scan in the vicinity of the $C_{60}He^{2+}$ adduct ion with an initial kinetic energy of 6 keV with ^4He as a target gas.* The small peak on the right represents the $C_{60}He^{2+}$ adduct ion, and the large peak on the left arises from cutting the energy-loss tail of C_{60}^{2+} in the B(2),E(2) two-dimensional surface. b) *Similar experiments with D_2 as a target gas.* There is no real evidence for a $C_{60}D_2^{2+}$ adduct ion on the right.

(D or D_2) in all fragment ions suggests that the deuterium is *not* trapped *inside* the cage but rather bound externally and split-off in the course of fragmentation[9]).

We have also conducted collision experiments of C_{60}^{2+} with He and D_2 at a laboratory energy of 6 keV as shown in *Fig. 8*. Again, there is clear evidence for the formation of an intact $C_{60}He^{2+}$ adduct ion (*Fig. 8a*), while similar experiments with D_2 did not show adduct formation (*Fig. 8b*).

3.3. *Location of He in the $C_{60}He^{+}$ Cluster.* The location of the He-atom in the C_xHe^{n+} clusters ($n \geqslant 1$), of course cannot be determined with the experiments described, but there are indirect indications that *we are almost certainly dealing with intra-cavity bonding*

[9]) Although not directly related to *Gross'* experiments of $C_{60}^{+\cdot}$ with D_2, it should be recalled that partial hydrogenation of fullerenes, giving rise to *exohedral* products, has been reported: [18]. For collisional experiments of protonated exohedral fullerenes, $C_{60}H^+$ and $C_{70}H^+$, see [19].

rather than with cluster ions in which He is attached to the outer sphere of the fullerene cage. i) If the He-atom would form an exohedral complex one would normally expect that also higher noble gases due to their larger polarizabilities would form cluster adducts with $C_x^{+\cdot}$. This is not observed experimentally. Rather, the cross section, σ, for adduct formation follows the qualitative order $\sigma_{He} > \sigma_{Ne}$; for the noble gas Ar we do not have evidence for the formation of $C_xAr^{+\cdot}$. *ii)* The process $C_{60}^{+\cdot} \rightarrow C_{58}^{+\cdot} + C_2$ requires at least 4–5 eV according to *Lifshitz et al.* [15h] and *Smalley et al.* [16], while the binding energy of He to $C_6H_6^{+\cdot}$, for example, is less than 0.2 eV according to MP2/6-31G**//MP2/3-21G* *ab initio* MO calculations[10]). Consequently, if the He-atom was not trapped inside the cage but bound externally, on thermochemical and kinetic grounds He rather than C_m should be eliminated from the $C_xHe^{+\cdot}$ fullerenes. This is not observed experimentally. *iii)* Mass-selected $C_xHe^{+\cdot}$ ions ($x = 60, 58$) lose not He, but C_2 unimolecularly. This behavior contrasts with the $C_{60}Fe^{+\cdot}$ system, which upon collision-induced dissociation generates $C_{60}^{+\cdot}$ and *no* $[C_{60-m}Fe]^{+\cdot}$ fragments [10]. Therefore, we conclude that $C_{60}He^{+\cdot}$ and, by analogy, also the other species $C_xHe^{n+\cdot}$ ($x \leqslant 70$; $n = 1$–3) are *endohedral fullerene/helium clusters* [11] [12]. Most likely, this also applies to the $C_xNe^{+\cdot}$ system [11] [12b, c][11]).

How much energy is required to penetrate the carbon shell and to bring a noble gas inside the $C_x^{+\cdot}$ cage? We have sought to answer this question by performing model calculations in which the noble gas is forced through the center of a C_6H_6 or $C_6H_6^{+\cdot}$ plane. At the 3-21G*//3-21G* level of theory, the transition state for the perpendicular passage of He through C_6H_6, is 12.5 eV higher in energy than completely separated C_6H_6 and He. At higher levels of theory, this barrier drops for the neutral system to 11.2 eV (MP2/3-21G*//MP2/3-21G*) and 10.7 eV (MP2/6-31G**//MP2/3-21G*); for the ionic system $C_6H_6^{+\cdot}$/He, at the highest level of theory used, we obtain a barrier of < 10 eV. As this energy barrier is clearly smaller than the kinetic energy which is available to the collision complex $C_x^{+\cdot}$/He (< 30 eV for $x = 60, 70$), the penetration of the cluster shell and the inclusion of a He-atom inside the cage is energetically possible. For the injection of Ne, preliminary MO calculations result in a barrier which is > 2 eV higher then the one calculated for the He system[12]) and for the injection of Ar even larger barriers (> 15 eV) have to be overcome. While such energies are available in collisions of $C_x^{+\cdot}$ with Ar, we think, however, that the large center-of-mass energy available to this system will produce collision-induced dissociations rather than penetration of the cage, resulting in the formation of stable endohedral $C_xAr^{+\cdot}$ complexes.

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[10]) We expect that calculations with larger basis sets will lead to *smaller* values for the binding energy of $C_6H_6^{+\cdot}$/He, which we used as a crude model for attaching He externally to $C_x^{+\cdot}$ fullerenes.

[11]) The most direct and unambiguous evidence for the existence of endohedral He C_{60} complexes was recently provided by successful neutralization/reionization (NR) of $C_{60}He^{+\cdot}$: the NR mass spectrum of $C_{60}He^{+\cdot}$ reveals the presence of a recovery signal for $C_{60}He$ which requests that the noble gas is physically trapped inside the carbon cage, see [20].

[12]) In a recent experiment [21] on the collision energy dependence of He and Ne capture by $C_{60}^{+\cdot}$ the threshold for He capture was determined to 6 ± 2 eV and that for Ne to $9 \pm$ eV.

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