Charge transfer from polycharged ions: C_{60}^{n+} as a model system

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A geometric model is presented which considers the effects of Coulombic repulsion upon gas-phase charge-transfer reactions of multiply charged molecular ions. Special consideration is given to multiply charged cations of buckminsterfullerene, C_{60}, which appears ideal as a model system for studies of polycation charge-transfer chemistry because of the very high structural rigidity and well-defined geometry of the parent neutral. The effects of Coulombic repulsion are discussed in relation to previous reports of photo- and electron-impact ionization of fullerenes. We predict that the fullerene polycations C_{60}^{n+}, up to at least $n=6$, should be stable against Coulombic explosion.

1. Introduction

The gas-phase chemistry of molecular monocations has been a wide field of study for several decades. Charge transfer,

$$A^+ + B \rightarrow A + B^+ , \qquad (1)$$

is one of the most frequently reported product channels of ion/molecule reactions, and is generally rapid when exothermic. A substantial body of results exists concerning charge-transfer reactions of monocations.

The field of gas-phase dication/molecule chemistry has been studied to a substantially lesser degree, and much of the emphasis to date has been on the chemistry initiated by a wide range of atomic dications typified by C^{2+} [1], Mg^{2+} [2,3], Ar^{2+} [4–8], and the transition-metal dications La^{2+} and Y^{2+} [9]. While much theoretical and experimental study has also been focused on molecular dications [10], much of the experimental work has concerned unimolecular processes such as fragmentation or Coulombic explosion, rather than bimolecular reactivity. The relative paucity of available data on molecular dication reactivity is related, in part, to the comparative difficulty in generating molecular dications in sufficient quantity and purity for experimental investigation. The recent discovery [11] and synthesis [12] of buckminsterfullerene, C_{60}, has resulted in the intensive study of many aspects of fullerene chemistry [13,14], including the thermal-energy gas-phase chemistry of the dication C_{60}^{2+} [15–28]. In consequence, studies of C_{60}^{2+} chemistry now form a substantial fraction of the available literature on gas-phase dication/molecule chemistry. The ion/neutral chemistry of trications has been studied to a much lesser degree again: to the best of our knowledge, the only reports of gas-phase molecular trication chemistry are studies of the fullerene trications C_{56}^{3+}, C_{60}^{3+} and C_{70}^{3+} [16,29]. The outstanding features of C_{60}'s structure – high rigidity and essentially spherical symmetry – make it an appropriate model for the study of molecular polycation chemistry. Fullerenes are highly resistant to fragmentation processes, as we have witnessed in a study of the reaction of $He^{+\cdot}$ with C_{60} [30]: in this reaction, the sole products are singly *and doubly* charged C_{60} cations, with no detectable fragmentation despite the very large difference in ionization energies ($IE(He) - IE(C_{60}) = 16.98 \pm 0.02$ eV). The comparatively large number of reports on multiply charged fullerene ions provides an indication of the relative ease of multiple ionization, over dissociative ionization, of fullerenes.

While the occurrence of reaction (1) is largely dependent only upon the exothermicity of this process, the reaction

$$A^{n+} + B \rightarrow A^{(n-1)+} + B^{+} , \tag{2}$$

involving the transfer of one charge from a multiply charged ion to a neutral, will not necessarily occur even if exothermic. This is because reaction (2) initially produces two cationic species in relatively close proximity, and the heat of formation of such a like-charged ion pair will exceed the heat of formation of the products at infinite separation by a quantity of energy equal to the Coulombic repulsion between the product ions. This effect was first discussed by Spears et al. [2]. Roth and Freiser have noted [9] that a consequence of the Coulombic interactions is that there exists a minimum separation between A^{n+} and B within which reaction (2) is "endothermic". Long-range charge-transfer processes appear to occur with atomic and small molecular dications [9], but we have proposed [19] that charge transfer from the fullerene dications C_{60}^{2+} and C_{70}^{2+} is generally only short-range, occurring at a separation of 3 Å or less. We have demonstrated [19] that the discrepancy between determinations of the second ionization energy of C_{60} by photo- and electron-impact ionization [31–34], and by "bracketing" via ion/molecule reactions [15,16,19], can be reconciled using a simple model for the charge distribution upon the fullerene surface. In this context, the Coulombic repulsion between products is manifested as a barrier to insufficiently exothermic charge-transfer reactions.

In the present work, we extend our model [19] for Coulombic constraints to polycationic charge transfer, in order to predict the ion/molecule reactivity of C_{60}^{n+} species ($n>2$), and of other molecular polycations of well-defined geometry.

2. Discussion

For a polycation A^{n+}, there are $\frac{1}{2}n(n-1)$ distinct pairs of like charges. Between each of these pairs there exists a Coulombic repulsion $V_{i,j}$, dependent upon the intercharge separation $r_{i,j}$,

$$V_{i,j} = q_i \phi_{r_{i,j}} = \frac{q_i q_j}{4\pi\epsilon_0 r_{i,j}} . \tag{3}$$

The sum of the repulsive interactions between all the charges can be expressed as

$$V_{\text{tot}} = \sum_{i=1}^{n} \sum_{j=1}^{i-1} V_{i,j} . \tag{4}$$

When a charge-transfer reaction of type (2) occurs, the reaction exothermicity

$$-\Delta H^0 = \Delta H_f^0(A^{(n-1)+}) + \Delta H_f^0(B^+) - \Delta H_f^0(A^{n+}) - \Delta H_f^0(B) , \tag{5}$$

$$= \mathrm{IE}(A^{(n-1)+}) - \mathrm{IE}(B) \tag{6}$$

effectively includes a term due to the loss of $n-1$ repulsive interactions between the transferred charge and those charges which have not been transferred. However, at the point of charge transfer the products $A^{(n-1)+}$ and B^+ are not at infinite separation, and thus the repulsive interactions

$$V'_n = \sum_{i=1}^{n-1} V_{i,n} \tag{7}$$

between the charges upon $A^{(n-1)+}$ and the charge upon B^+ can be considered as constituting a barrier to the occurrence of charge transfer. Another effect which will contribute to this barrier is that, at the point of charge transfer, the charge distribution upon $A^{(n-1)+}$ will be perturbed by its proximity to B^+. The quantity

$$V''_{n-1} = \sum_{i=1}^{n-1} \sum_{j=1}^{i-1} q_i (\phi_{r_{i,j}} - \phi_{r'_{i,j}}) \tag{8}$$

is therefore an additional component of the activation energy which may impede charge transfer: $E_a = V'_n + V''_{n-1} + \Delta H^0$. For efficient charge transfer to occur, the exothermicity $-\Delta H$ must outweigh the Coulombic V'_n and V''_{n-1}. Fig. 1 shows the expected energy profile for a reaction of type (2).

We use, as a model, an idealized spherically symmetric C_{60}^{n+} polycation of radius equal to that of the parent neutral, $r_{60} = 3.5$ Å [35], upon which all charges (while very probably delocalised) are, at any point in time, at the maximum mutual separation attainable upon a sphere of this size. Thus, for example, a C_{60} trication has a trigonal planar configuration of charges; a C_{60} pentacation has its charges deployed in a trigonal bipyramid upon its surface. V_{tot} is tabulated for C_{60}^{n+} ($n = 2$–6) in Table 1. Charge transfer to a neutral B is assumed to occur at a specific separation, x, of B from C_{60}^{n+}, and the height of

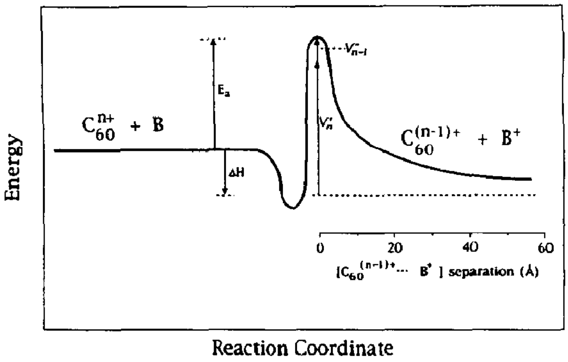

Fig. 1. Schematic diagram illustrating the Coulombic factors involved in charge transfer from a polycation C_{60}^{n+} ($n \geqslant 3$) to a neutral B. In the case shown, charge transfer is exothermic but is impeded by an activation energy barrier $E_a = V'_n + V''_{n-1} + \Delta H$. The condition for efficient charge transfer, which requires $E_a \leqslant 0$, is therefore $-\Delta H \geqslant V'_n + V''_{n-1}$.

the barrier to charge transfer is thus the net difference in Coulombic interactions at x and at infinite separation of $C_{60}^{(n-1)+}$ and B^+. We assume that the influence of attractive ion/dipole, ion/induced dipole, and dipole/induced dipole interactions is negligible in comparison to the repulsive Coulombic interaction: if this is not so, then the barrier height will be reduced.

The separation value x is taken as the separation required to account for the discrepancy between the least uncertain photoionization value of IE($C_{60}^{+\cdot}$), 11.39±0.05 eV [34], and the threshold ionization energy IE(B) = 9.59±0.11 eV for charge transfer from C_{60}^{2+} to B. The latter value is obtained by ICR [15,16] and SIFT [19] bracketing experiments which have determined that charge transfer occurs with *m*-nitrotoluene (IE = 9.48 eV [36]) and with a wide variety of neutrals having lower IE, but not with allene (IE = 9.69 eV [36]) or neutrals of higher IE. The difference, IE($C_{60}^{+\cdot}$) − IE(B) = 1.80±0.16 eV, is assumed to equate with the Coulombic repulsion between $C_{60}^{+\cdot}$ and B^+ at the point of charge transfer, and yields an intercharge separation of 8.0±0.7 Å. If the charge on $C_{60}^{+\cdot}$ is diametrically opposed to the charge upon B^+ (which is plausible given the likely charge distribution immediately prior to charge transfer [19]), then $x = 1.0 \pm 0.7$ Å. Note that if ion/dipole or other attractive interactions have a significant effect upon the height of the barrier to charge transfer, a smaller separation value x is required to account for the observed difference between IE($C_{60}^{+\cdot}$) and the threshold IE(B) for charge transfer from C_{60}^{2+} to B: yet x cannot feasibly be much smaller than the apparent value of 1.0±0.7 Å. A typical C–C, C–N, or C–O bond length is 1.4–1.5 Å: at separations below this value, the interaction between C_{60}^{2+} and B is thus expected to become repulsive.

We adopt the value of 1.0±0.7 Å in the present work: while there is no reason for separation between the reactants at the point of charge transfer to be independent of the charge upon the reactant ion C_{60}^{n+}, we have presented arguments in a companion Letter [37] which suggest that the separation of C_{60}^{3+} and B at the point of charge transfer is very similar to the value of 1.0±0.7 Å used here.

We note that this value of 1.0±0.7 Å is very much smaller than the maximum separation (the "critical transfer radius") for which charge transfer from me-

Table 1
Cumulative Coulombic repulsion V_{tot} existing between the charges on the polycations C_{60}^{n+} (n = 2–6)

n	Charge configuration	$r_{i,j}$ (Å)	$V_{i,j}$ (eV)	$N(i,j)$ [a]	V_{tot} (eV)
2	linear	7.0	2.06	1	2.06
3	trigonal planar	6.06	2.38	3	7.13
4	tetrahedral	5.72	2.52	6	15.10
5	trigonal bipyramidal	4.95	2.91	6	26.64
		6.06	2.38	3	
		7.0	2.06	1	
6	octahedral	4.95	2.91	12	41.08
		7.0	2.06	3	

[a] $N(i,j)$ is the number of degenerate charge–charge interactions for the intercharge separation $r_{i,j}$ given. All other parameters are as defined in the text.

tallic dications is often observed. The results reviewed by Roth and Freiser [9] include examples of charge transfer from transition-metal-containing dications to neutrals at separations of up to 15 Å, as interpreted upon the basis of the calculated distance for curve crossing between the reactant $(A^{2+}+B)$ and the product $(A^{+}+B^{+})$ potential energy curves. Our studies of C_{60}^{2+} charge-transfer reactivity [19] suggest that only close interactions of the reactants result in effective curve crossing (charge transfer is not observed to species for which $x>1.7$ Å), in sharp contrast to the occurrence of charge transfer, for example, in the reaction of $Mg^{2+}+CO_2$ ($x=11.7$ Å) [2]. This is, perhaps, not too surprising. The chemical and physical effects governing the reactivity of atomic or small molecular dications are likely to differ considerably from those involved in the reactivity of large molecular dications featuring delocalised charges. The much smaller intercharge separation which exists in atomic and small molecular dications greatly inhibits charge transfer in close interactions of the dication X^{2+} and the neutral B, since the Coulombic repulsion (which must be considered as a destabilising potential energy term) between the product ions X^{+} and B^{+} is very large for small intercharge separations: in contrast, the expected charge separation of 7.0 Å in the fullerene dication (and 6.06 Å in C_{60}^{3+}) does not engender such extreme Coulombic interactions. In addition we expect that, in the charge-separating reactions of fullerene polycations, a close interaction of the ion and the neutral is necessary in order to localise the charge which is to be transferred [19].

Two cases for charge transfer from C_{60}^{n+} must be distinguished. In one scenario, which we term "unrelaxed charge transfer" and which is depicted in fig. 2a, only the charge to be transferred from C_{60}^{n+} to B is displaced upon charge transfer; all the charges remaining upon the fullerene are unperturbed and remain oriented to each other in the configuration which prevailed prior to charge transfer. Relaxation of $C_{60}^{(n-1)+}$ to the optimum geometry thus occurs after charge transfer, concomitantly with separation of $C_{60}^{(n-1)+}$ and B^{+}. In the other scenario, which we refer to as "relaxed charge transfer" and which is shown diagrammatically in fig. 2b, some relaxation of the charges upon $C_{60}^{(n-1)+}$ occurs simultaneously with the charge-transfer step, to produce a $[C_{60}^{(n-1)+}...B^{+}]$ ion pair possessing the lowest overall Coulombic repulsion V_{tot}; further relaxation of $C_{60}^{(n-1)+}$ occurs as the products separate. It is not clear to us which of these models is appropriate since it is not known how mobile are the charges upon fullerene polycations (although it seems reasonable to expect that all charges are somewhat delocalised), and thus we have calculated barrier heights for both cases. Tables 2 and 3 detail the structures of the "unrelaxed" and "relaxed" ion pairs $[C_{60}^{(n-1)+}...B^{+}]$, respectively, and the calculated contributions to Coulombic repulsion within these ion pairs.

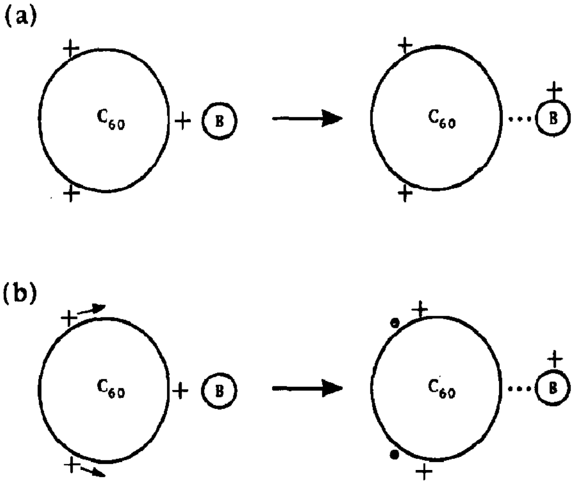

Fig. 2. "Unrelaxed" and "relaxed" charge transfer, illustrated for $C_{60}^{3+}+B$. In "unrelaxed" charge transfer (a), the charges remaining on $C_{60}^{(n-1)+}$ in the transition state $[C_{60}^{(n-1)+}...B^{+}]$ are unmoved from their original configuration. In the "relaxed" model (b), all the charges upon the $[C_{60}^{(n-1)+}...B^{+}]$ ion pair are distributed so as to achieve the minimum overall Coulombic repulsion V_{tot} possible within the prevailing geometric constraints (which are, that all charges except one are located on the fullerene surface; the remaining charge is localised upon B at a distance x from the fullerene surface). The small shaded circles in fig. (b) denote the sites of the untransferred charges prior to reaction: the amount of charge displacement shown in this figure for "relaxed" charge transfer is somewhat exaggerated for illustrative purposes.

There is no distinction between "relaxed" and "unrelaxed' charge transfer from C_{60}^{2+} to B. The structure of the lowest-Coulombic-energy ion pair $[C_{60}^{(n-1)+}...B^{+}]$ ($n=3$–6), for our model of "relaxed charge transfer", can be determined (in principle) by solution of the differential equations:

Table 2
Geometries (upper part) and contributions to Coulombic repulsion (lower part) in $[\mathrm{C}_{60}^{(n-1)+}...\mathrm{B}^+]$ (n=3–6) ion pairs, calculated for "unrelaxed" charge transfer

n [a]	σ (deg)	ϑ (deg)	$r_{1,i}$ (Å)	$r_{1,n}$ (Å)	$r_{i,j}$ (Å)	$r_{i,n}$ (Å)
geometry						
3	60	26.1±2.6	–	–	6.06	6.95±0.63
4	70.53	30.5±3.1	–	–	5.72	6.56±0.60
5 [b]	90	38.3±4.4	4.95	8.0±0.7	6.06	5.72±0.55
6	90	38.3±4.4	4.95	8.0±0.7	4.95 [c]	5.72±0.55

n	V_{tot} (eV)	V'_n (eV)	V''_{n-1} (eV)	barrier (eV)
Coulombic factors				
3	6.55±0.38	4.18±0.38	0.32	4.50±0.38
4	14.19±0.61	6.64±0.61	0.43	7.07±0.61
5 [b]	25.28±0.89	9.44±0.89	0.74	10.18±0.89
6	39.35±0.38	11.96±0.38	0.75	12.72±0.38

[a] Geometric parameters for $n=3, 4$ are as shown in fig. 3a; parameters for $n=5, 6$ areas shown in fig. 3b.

[b] Angles, distances and energies are calculated for the case of transfer of an "axial" charge from $\mathrm{C}_{60}^{5+\cdot}$ having a trigonal bipyramidal charge distribution.

[c] There exists also $r_{i,k}$= 7.0 Å for two pairs of charges in this charge configuration.

Table 3
Geometries (upper part) and contributions to Coulombic repulsion (lower part) in $[\mathrm{C}_{60}^{(n-1)+}...\mathrm{B}^+]$ (n=3–6) ion-pairs, calculated for "relaxed" charge transfer

n [a]	σ (deg)	ϑ (deg)	$r_{1,i}$ (Å)	$r_{1,n}$ (Å)	$r_{i,j}$ (Å)	$r_{i,n}$ (Å)
geometry						
3	62.1±1.5	26.9±2.0	–	–	6.19±0.09	6.87±0.58
4	72.4±1.4	31.2±2.6	–	–	5.78±0.05	6.48±0.55
5 [b]	87.9±1.5	39.0±3.9	5.04±0.07	8.0±0.7	6.06±0.01	5.60±0.48
6	88.3±1.2	38.8±4.1	5.02±0.06	8.0±0.7	4.95±0.01 [c]	5.62±0.50

n [a]	V_{tot} (eV)	V'_n (eV)	V''_{n-1} (eV)	barrier (eV)
Coulombic factors				
3	6.55±0.38	4.24±0.38	0.27±0.03	4.51±0.40
4	14.18±0.62	6.69±0.58	0.35±0.05	7.05±0.62
5 [b]	25.28±0.91	9.56±0.81	0.61±0.11	10.17±0.92
6	39.35±1.16	12.11±1.05	0.59±0.12	12.71±1.16

[a] Geometric parameters for $n=3, 4$ are as shown in fig. 3a; parameters for $n=5, 6$ are as shown in fig. 3b.

[b] Angles, distances and energies are calculated for the case of transfer of an "axial" charge from $\mathrm{C}_{60}^{5+\cdot}$ having a trigonal bipyramidal charge distribution.

[c] There exists also $r_{i,k}$= 6.995±0.005 Å for two pairs of charges in this charge configuration.

$$-\frac{\mathrm{d}(1/r_{i,j})}{\mathrm{d}\sigma}=\frac{2\mathrm{d}(1/r_{i,n})}{\mathrm{d}\sigma}\quad(n=3)\,, \tag{9}$$

$$-\frac{\mathrm{d}(1/r_{i,j})}{\mathrm{d}\sigma}=\frac{\mathrm{d}(1/r_{i,n})}{\mathrm{d}\sigma}\quad(n=4)\,, \tag{10}$$

$$-\frac{\mathrm{d}(1/r_{1,i})}{\mathrm{d}\sigma}=\frac{\mathrm{d}(1/r_{i,j})}{\mathrm{d}\sigma}+\frac{\mathrm{d}(1/r_{i,n})}{\mathrm{d}\sigma}\quad(n=5)\,, \tag{11}$$

$$-\frac{\mathrm{d}(1/r_{1,i})}{\mathrm{d}\sigma}=\frac{\mathrm{d}(1/r_{i,j})}{\mathrm{d}\sigma}+\frac{\mathrm{d}(1/r_{i,n})}{\mathrm{d}\sigma}+\frac{1}{2}\frac{\mathrm{d}(1/r_{i,k})}{\mathrm{d}\sigma}\quad(n=6)\,. \tag{12}$$

(However, in practice the derivatives of eqs. (9)–(12) are not readily soluble and so the characteristic angle σ was instead determined by an iterative method of calculating the total Coulombic energy V_{tot} as a function of σ.) The relevant geometrical parameters are illustrated in fig. 3. Calculation of the intercharge separation $r_{i,n}$ and other relevant charge separations ($r_{1,i}$, $r_{i,j}$ etc.) is achieved by application of simple trigonometric principles to the parameters shown in fig. 3.

A comparison of the energetic parameters in tables 2 and 3 indicates that the effect of "relaxation" (of the polycation product $C_{60}^{(n-1)+}$ occurring concomitantly with the transfer of a charge to the adjacent neutral B) is indeed very small: to a very good approximation, the barrier heights determined using the unrelaxed structures in table 2 are the minimum possible barrier heights within the constraints of the present model. The very slight differences in V_{tot} for relaxed and unrelaxed structures indicate that small relative motion of the charges is not likely to affect the overall Coulombic repulsion greatly: thus, even in the initial ion pair $[C_{60}^{(n-1)+}...B^{+}]$ each charge upon the fullerene surface is likely to be somewhat delocalised. Given the probable aromatic nature of the fullerene polycations discussed here, a treatment of the loss of delocalisation energy involved in charge-transfer reactions seems relevant: however, there is no information presently available concerning the degree of delocalisation energy within the polycations C_{60}^{n+}, nor how much delocalisation energy is lost in the initial formation of the ion pair $[C_{60}^{(n-1)+}...B^{+}]$. We have proposed [19] that charge transfer from C_{60}^{2+} to B requires a close approach of the neutral B in order to localise one of the charges upon the fullerene: in this instance the loss of delocalisation energy is balanced by the ion-induced dipole attraction between C_{60}^{2+} and B. The ion-induced dipole interaction is expected to increase in magnitude with increasing polycation charge, so it is possible also that a loss of delocalisation energy may not constrain charge transfer from higher charge states C_{60}^{n+} ($n \geqslant 3$).

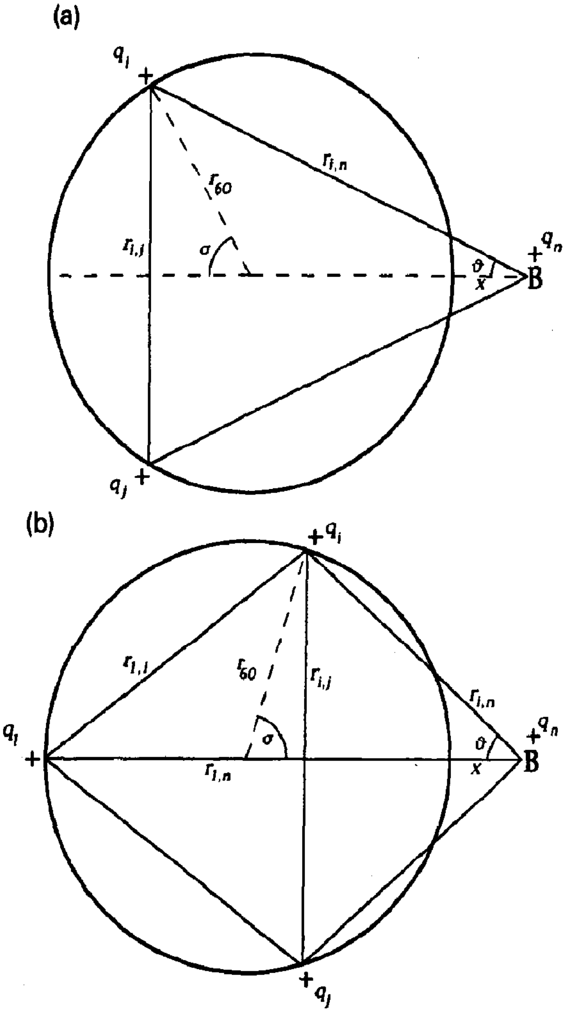

Fig. 3. Depiction of geometric parameters for $[C_{60}^{(n-1)+}...B^{+}]$ for (a) $n=3$ or 4, and (b) $n=5$ or 6.

Walter et al. [38] have stated that the observed stability of C_{60}^{4+} in mass-spectrometric experiments indicates that charge shielding and/or delocalisation inhibits the fragmentation of the quadruply charged ion by Coulomb explosion. However, C_{60}^{4+} will be stable against Coulombic explosion even in the absence of charge shielding and delocalisation effects: we feel that the arguments of Walter et al. [38] ignore the difference in character between the chemical bonding within the fullerene framework and the electrostatic repulsion between the multiple charges. The probable lowest-energy fragmentation process for C_{60}^{4+} is $C_2^{+\cdot}$ loss:

$$C_{60}^{4+} \rightarrow C_{58}^{3+\cdot} + C_2^{+\cdot}. \qquad (13)$$

Walter et al. use a binding energy of 4.6 eV for C_2 in C_{60} [39] and a Coulombic repulsion energy of 6.2/α eV (where α accounts for structural deformation of the ion, and charge screening) to estimate that a "classical" (spherically symmetric, localised charge) C_{60}^{4+} ion would be unstable against Coulombic explosion by reaction (13). This finding is based on the model of Tománek et al. [40] which proposes that the criterion for Coulombic explosion of multiply charged metallic, ionic, or van der Waals-type clusters is that the Coulombic repulsion between the charged fragments exceeds the binding energy between these fragments. This is not a reasonable criterion for fragmentation of the covalent cluster C_{60}^{4+}: the chemical bonding between $C_{58}^{3+\cdot}$ and $C_2^{+\cdot}$ will be essentially completely dissipated at a separation (of the $C_2^{+\cdot}$ fragment from the surface of the $C_{58}^{3+\cdot}$ remnant) of only 2 or 3 Å, while at this distance considerable Coulombic repulsion will remain. The Coulombic repulsion between one charge and the other three in C_{60}^{4+} is 7.55 eV for a symmetric (tetrahedral) charge distribution: at a $C_2^{+}...C_{58}^{3+\cdot}$ separation of 3 Å the repulsion between the two fragments will still be 5.5 eV or more, so the Coulombic energy released over this separation, to counteract C–C bond fragmentation energy requirements, is only ≈2.0 eV. This is *not sufficient* to permit this fragmentation channel unless the chemical bonding is very substantially weaker than in the neutral fullerene. We propose that the necessary condition for Coulombic explosion of multiply charged fullerenes (and similar clusters) is

$$-\Delta q\phi_r(C_x^{n+}...C_y^{m+}) \geqslant \Delta \mathrm{BE}(C_x^{n+}...C_y^{m+})$$
$$\text{for all } r(C_x^{n+}...C_y^{m+})\,, \qquad (14)$$

that is, that for all separations $r(C_x^{n+}...C_y^{m+})$ between the fragments, the cumulative energy released by Coulombic relaxation to that separation must exceed the energy expended in diminishing the binding between the fragments to that separation. (In practice, of course, thermalised clusters will have available thermal energy which may also contribute to fragmentation, and clusters may also exist in excited states which may fragment more readily.)

Similar arguments to those presented above can be advanced for the likely stability of $C_{60}^{5+\cdot}$ and C_{60}^{6+} against Coulombic explosion, and we expect that high-level theoretical calculations on $C_{60}^{5+\cdot}$ and C_{60}^{6+} will indicate that these are stable structures; however, there are likely to be considerable experimental difficulties in generating quintuply and sextuply charged fullerenes (by electron bombardment or similar methods) in conventional ion sources because the electrostatic lenses used in focusing the ion signal are likely to deposit considerable kinetic energy into these multiply charged ions, facilitating their destruction by collisions with neutrals. In this light, it is very interesting to note that although no reports have yet appeared of $C_{60}^{5+\cdot}$ generated by electron bombardment, there has been a tentative identification of $C_{60}^{5+\cdot}$ in a charge-stripping study of C_{60}^{4+} [41].

4. Conclusion

We have developed a model which predicts the magnitude of Coulombic barriers for charge-transfer reactions of a polycharged fullerene ion C_{60}^{n+} ($n=3$–6) to a neutral B. In all cases the largest component of the Coulombic barrier is the repulsion between the product ions $C_{60}^{(n-1)+}$ and B^+; a minor component (<10%) arises from the deformation of the $C_{60}^{(n-1)+}$ charge configuration by the adjacent B^+. The magnitude of the barrier is very well approximated by assuming that the positions of the nontransferred charges (i.e. those remaining on $C_{60}^{(n-1)+}$ do not change in the charge-transfer step. Assuming a separation of 1.0 Å between C_{60}^{n+} and B at the moment of charge transfer, the barrier height is 4.46 eV ($n=3$), 7.01 ev ($n=4$), 10.12 eV ($n=5$), or 12.64 eV ($n=6$) above the energy of the products: reaction exothermicity must exceed this barrier height for the reaction to proceed efficiently at thermal energy. In an accompanying Letter [37], we have used the calculated barrier height to determine IE(C_{60}^{2+}), the third ionization energy of C_{60}, by the experimental technique of ion–molecule bracketing.

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