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Review

Hyperthermal collisions of atomic clusters and fullerenes

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Dedicated to T. D. Märk on the occasion of his 60th birthday.

Abstract

Among the many directions that mass spectrometry of atomic clusters and fullerenes have taken, analysis of their collisions with atoms, molecules, or surfaces has been particularly successful. We will first review experimental and theoretical work pertaining to hyperthermal collisions of charged or neutral clusters, including the formation of endohedral fullerenes. We will then present experimental data on the unimolecular formation of $C_{60}{}^{+}$ and $C_{58}{}^{+}$ from collisionally excited C_{60}. Based on recently proposed rate coefficients for dissociation and ionization of C_{60} and C_{58}, we derive the efficiency of energy transfer, from translational to vibrational modes, for inelastic $C_{60} + K^{+}$ collisions.

Keywords: Cluster; Fullerene; C_{60}; Endohedral; Collision; Energy transfer; Breakdown curve; Thermionic emission

1. Dedication

Two decades ago, a competition ensued between Tilmann Märk's cluster group at the University of Innsbruck and the cluster group at the University of Konstanz that included Ekkehard Recknagel and one of the authors, O.E. We were competing in two "hot" areas, namely characterization of fission reactions of metastable, multiply charged cluster, and formation of negatively charged clusters by electron attachent. In 1985, Tilmann spent a semester at the University of Konstanz where he taught nuclear physics. The competition quickly turned into a collaboration that resulted in several publications [1–6]. The collaboration has prospered ever since, and ever since has it been a pleasure to enjoy the hospitality and excitement that permeates the Institut für Ionenphysik. Thank you, Tilmann, and congratulations!

2. Introduction

A vast number of collisional studies of clusters has been published during the last two decades. We cannot possibly cover this field comprehensively; instead we attempt to provide a broad overview with emphasis on recent developments. Several excellent reviews that focus on particular sub-areas are available; they will be mentioned in the course of this work. In the second part of this article, we will quantitatively derive the efficiency for energy transfer in inelastic collisions between C_{60} and K^{+} ions from the intensity of $C_{60}{}^{+}$ and $C_{58}{}^{+}$ product ions.

This review will not cover collisions at thermal energies. In particular, we will not cover the emerging field of helium-cluster scattering [7,8], or scattering off helium microdroplets [9–11]. Interaction of electrons with clusters which has long attracted the interest of Märk's group [12–16] will not be covered either.

2.1. Gas-phase collisions

Guided-ion-beam mass spectrometry was among the first techniques that provided quantitative information about the stability of metal cluster ions by measuring ion intensities as a function of collision energy. Rate constants and cross sections for reactive scattering have been determined as well. The method has been successfully applied to a large number of elemental clusters [17–21]. Zhang and Cooks investigated collision-induced dissociation of doubly charged sodium chloride cluster ions in an ion trap; small clusters were found to be prone to fission [22]. The different

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pathways of energy transfer (electronic versus momentum transfer) in impulsive collisions between cluster ions and rare gas atoms has been discussed [23,24].

Molecular dynamics has been applied to a variety of systems. Plummer and Chen [25,26] observed that essentially all $H_2O + (H_2O)_n$ collisions ($n \leq 21$) were reactive, i.e., the accommodation coefficient was very close to 1. Charge transfer and fragmentation in collisions of sodium cluster ions with cesium atoms have been investigated by Schmidt and coworkers [27]. Märk and coworkers observed that fragmentation following attachment of thermal xenon ions to argon and neon clusters was less serious than after vertical ionization [28].

Gas-phase collisions between fullerenes and atoms or molecules have been subject of numerous studies; for recent reviews see [29,30]. A variety of topics have been covered. For example, fusion in C_{60}–C_{60} collisions has been investigated by experimental and theoretical methods [31–34], and the scattering cross section for low-energy collisions of alkali cations has been computed [35]. Methods of forming endohedral fullerenes by injecting projectiles into the cage will be discussed in the following section.

2.2. Endohedral fullerenes

A major effort has been underway to force gas atoms or ions, or small molecules, into pre-existing empty fullerenes. One approach involves implantation in the gas phase under single-collision conditions. Most experiments have been done with inert gas atoms or small molecules (or their ions) (see [29,36–38] and references therein), others involved alkali ions [39–42] and transition metal ions [43]. These experiments have been augmented by theoretical studies [44–55].

The experiments provide direct information about threshold energies for insertion although it should be kept in mind that, at very low collision energies, complexes other than endohedrals may be formed [43,56–58]. If the threshold for insertion of species A is sufficiently low, the intact collision complex $A@C_{60}{}^+$ can be identified in a mass spectrum; this is the case for collisions with He, Ne, Li, and Na (or there ions) which have thresholds of 30 eV or less. A compilation of published values is shown in Table 1. For larger atoms such as Ar, Kr, Xe, and K, the intact collision complex is not observed in gas-phase experiments because the lifetime of the highly excited complex becomes too short for mass spectrometric detection. However, the threshold energy may be estimated from the appearance energy of fragments ion $A@C_n{}^+$, $n \leq 58$ [37,39,42]. These values, too, are listed in Table 1, together with various computed thresholds.

The agreement among the experimental values reported for He is poor; it is also poor for Ne. It has been argued that the variability reported for insertion of He reflects the existence of two distinct thresholds, corresponding to insertion through hexagonal and pentagonal carbon rings, respectively [38], plus a dependence on the internal energy of the C_{60} target [59] (but see [50] for a molecular dynamics study of collisions with the isoelectronic Li^+). For Ne, on the other hand, the low 9-eV threshold observed in early experiments [62] seems to be due to insertion into defective C_{60} structures [37,38]. Campbell et al. have suggested that the remaining difference between their experimental value of 18 eV [38], and the much higher value of 28–30 eV reported by Anderson and coworkers [37,70] is due to the higher excess energy in the fullerene target ions used in the former study.

Table 1
Threshold energies (in eV) for insertion of atoms or ions into C_{60}

Projectile	Experiment	Theory
He	3[a], 3.5[b], ≤4.4[c], 6[d,e], 15[f], 17[e]	6[g,e], 9[h], 9.4[i], 9[j], 11[e], 13[k]
Ne	9[d], 10[e], 18[e], ≤22[c], 30[l]	36[h]
Ar	38[l]	48[h]
Kr	41[l]	67[h], 80[m]
Xe	43[l]	
Li	6[n], 10[o]	4.9[p], 5[q], 28[r], 29[p]
Na	18[n], 25[s], 29.6[t]	>50[q]
K	40[k], 46[u]	
N	1.57[v]	

Some of the experimental values have been estimated from the appearance of endohedral fragment ions, or from the thermal stability of the endohedral system. Some studies report two distinct thresholds pertaining to different insertion mechanisms [38,50].

[a] [59].
[b] [60].
[c] [61].
[d] [62].
[e] [38].
[f] [63].
[g] [64].
[h] [45].
[i] [65].
[j] [66].
[k] [46].
[l] [37].
[m] [53].
[n] [39].
[o] [40].
[p] [50].
[q] [47].
[r] [67].
[s] [68].
[t] [41].
[u] [42].
[v] [69].

That explanation is not quite compelling though, because the initially cold C_{60} in Anderson's experiment is excited by 14 eV upon exothermic charge transfer between the incoming Ne^+ projectile and C_{60} [37]. This extra energy is not available in the experiments by Campbell and co-workers which involve $Ne + C_{60}{}^+$ collisions. Another problem with the explanation is the absence of a correlation between the internal C_{60} energy and the insertion threshold in a molecular dynamics study of $Li^+ + C_{60}$ by Bernshtein and Oref [50]. Furthermore, the 30 eV insertion threshold observed for $Ne^+ + C_{60}$ [37] agrees with the value observed for $Na^+ + C_{60}$ by Deng and Echt [41]. Why should these two thresholds agree? Exothermic charge transfer will occur between Ne^+

and C_{60} well before the actual collision [37], hence the projectiles being inserted in these two studies will have the same electronic configurations and, being adjacent elements in the Periodic Table, nearly the same size [71]. Hence, the close agreement of the observed thresholds may be seen as a confirmation that the 14 eV excess energy released upon charge transfer *does not* affect the insertion threshold.

The excitation energy in the collision complex will, however, leave its mark on the breakdown energy of $A@C_{60}^+$, i.e., the collision energy at which the intensity of the complex rapidly diminishes because its lifetime becomes too short. Barring exothermic charge transfer, the total excitation energy in the intact complex $A@C_{60}^+$ is the sum of the collision energy, the thermal (vibrational) energy of C_{60} before collision, and the complexation energy. The latter is usually not well known, but much smaller than the first two terms. It has been shown that, indeed, an increase in the thermal energy in the C_{60} target will shift the breakdown energy to a correspondingly lower value, in agreement with the computed heat capacity of C_{60} [72]. Careful modeling of the breakdown curves can provide the activation energy for dissociation of $A@C_{60}^+$. For $Na@C_{60}^+$ which, like most other endohedral fullerenes dissociates by C_2 loss, the activation energy was found to be identical to that of empty C_{60}^+ [41].

A powerful alternative to gas-phase ion implantation has been pioneered by Saunders and coworkers [73,74] (also see [75]). They found that rare gas atoms can be inserted if a fullerene sample is heated to some 650 °C under high pressure of helium, neon, argon, krypton, or xenon. $Kr@C_{60}$ has been isolated from these samples by HPLC [76]. An open question is the mechanism by which the endohedrals form. The threshold of 3.5 eV estimated from the experimental conditions for insertion of helium [60] is much lower than thresholds measured in gas-phase $He + C_{60}$ collisions. A so-called “window” mechanism for atom insertion, or escape, has been proposed [60,77]. However, radical impurities in the C_{60} samples, or formation of C_{60} dimers, could also be responsible for a significant reduction of the insertion barriers [64,78].

Another promising development has been the formation by ion implantation of macroscopic amounts of $N@C_{60}$ and $P@C_{60}$ [69,79,80]. These systems can be dissolved in organic solvents; they are stable in air at room temperature. They can be reacted with addends without losing the atomic character of the guest atom. For these endohedrals, the insertion threshold has been determined from the reverse reaction, namely the escape of the captured atom [69].

The stability of endohedral fullerenes has been probed by gas-phase collisions. Saunders and coworkers [74,81,82] studied collisions of $Ar@C_{60}$ ions with rare gas atoms. While $Ar@C_{60}$ cations predominantly fragment into smaller $Ar@C_n^+$ until the cage breaks below $n = 48$ (shrink-wrapping effect), the anions fragment to C_{60}^+, i.e., the caged atom is lost. Likewise, Compton and coworkers [83] collided $A@C_{60}^+$ (A = Ca, Sr, La, and Gd) to find C_2 loss; the reactivity of $A@C_n^+$ with oxygenated compounds was studied as well. An ion trap has been used for collisional formation of $Mg@C_{60}^+$ as well as for analyzing its stability by collision-induced dissociation [84]. C_2 loss was also observed by Lorents et al. for $Gd@C_{82}^+$ and $La@C_{82}^+$ [85]. Schwarz and coworkers [86] observed that collisions of $Kr@C_{60}^+$ with helium leads to $HeKr@C_{60}^+$.

Another possibility to incorporate atomic ions into pre-existing fullerenes is by implantation into C_{60} films [68,87–89]. As an advantage, the matrix stabilizes endohedral complexes that would not survive the time required for mass spectrometry in gas-phase collisions. It has been suggested that efficient synthesis of $H@C_{60}$ is possible [54]. On the downside, it is more difficult to determine insertion thresholds from these experiments because of energy straggling. Campbell and coworkers have been able to isolate $Li@C_{60}$ from their samples and determine their thermal stability in vacuum and air [87,90].

Another option is the use of radioactive nuclides [91–96]. The recoil in nuclear reactions (e.g., (γ, n) and $(d, 2n)$) produces energetic atoms that may implant into C_{60} if an appropriate, intimate mixture of the activated compound with C_{60} is used. Some elements (e.g., Be, Ar, Kr, Xe) were found to insert into the fullerene cage while others insert into the carbon network. These studies have been augmented by molecular dynamics simulations [95].

2.3. *Collisions at high energies or energy transfers*

Whereas mild excitation of C_{60} primarily results in sequential emission of C_2 [97,98] and, for neutral fullerenes, electron emission, new channels open when the C_{60} excitation energy exceeds some 80 eV [99]. In a molecular dynamics study, it was shown that collision of C_{60} with He or Ne at 200 eV leads to direct, non-statistical fragmentation [48]. A variety of charged and neutral fragments have been identified in collisions of 75 keV C_{60} ions with H_2 using multi-coincidence techniques [100–102]. The dependence of the fragmentation pattern on the energy in collisions with H^+, He^+, and Ar^+ has been reported [103–105]. A strong dependence of the fragmentation pattern on the atomic number of the atomic target is observed [106,107]. Slow collisions of highly charged atomic ions prepare highly charged C_{60} ions with little initial vibrational energy that subsequently undergo fission [108–112]. Collisions at MeV energies with highly charged ions Xe^{35+} lead to fragment distributions that have been modeled with a percolation theory [113,114]. Highly charged sodium clusters that are near the Rayleigh limit (fissility parameter $X = 1$) have been formed by collisions with energetic protons or highly charged ions [115,116]; fission of clusters that exceed the Rayleigh limit have been modeled by molecular dynamics [117].

At extremely high excitation energies, a liquid-vapor phase transition is expected to occur [118–120]. Evidence for this phenomenon has been reported for collisionally excited C_{60} [34,121]. Direct evidence for the transition has been observed by constructing the caloric curve of hydrogen clusters from a complete event-by-event analysis of all their fragments [122–124].

In the Coulomb-explosion imaging technique, very fast small molecules or clusters are passed through a thin foil [125]. If the atoms are stripped of all their electrons and their directions and momenta are measured in coincidence for each event, the geometric structure of the species upon passage through the foil can be constructed. The method has been applied to carbon clusters containing up to eight atoms [126].

2.4. *Surface collisions*

Impact of energetic clusters on surfaces leads to extremely high compression and energy densities that cannot be achieved by atomic ion impact [127–132]. For some time, it appeared that the local temperatures reached upon impact of deuterated water clusters at some 300 keV are high enough to cause deuteron–deuteron fusion [133,134]. The experimental evidence turned out to be an artifact [135]; but other novel processes may occur at sufficiently high energies. For example, energetic cluster ion beams may be used for shallow ion implantation and to create nanostructures [136–138]. Clusters have been used to smooth surfaces at the atomic level [139,140]. Details of this application for which a commercial system is available [141] have been investigated with molecular dynamics [142,143].

Cooks and Miller have pioneered collisions of polyatomic ions with surfaces at lower energies; for recent reviews see [144], and the article by Herman elsewhere in this volume [145]. Collision-induced dissociation of atomic clusters combined with analysis of the kinetic energy and, in some studies, the angular distribution of scattered products provides information about the scattering mechanism and the energy transfer efficiency; this topic has been investigated by experiment [146–151] and molecular dynamics [152–155]. Märk and coworkers have determined the degree of dissociation as a function of collision energy as well as energy content in the projectile [156]. The observed fragmentation patterns demonstrate that unimolecular dissociation dynamics controls the formation of product ions [157].

Another intriguing phenomenon occurring upon low-energy impact of charged fullerenes and metal clusters is the emission of electrons as a result of neutralization; it occurs on a picosecond or even femtosecond time scale [158,159].

Collisions of fullerenes with surfaces have attracted considerable attention. Scattering of $C_{60}{}^{+}$ and $C_{60}{}^{-}$ ions with surfaces were among the first experiments to demonstrate the exceptional stability of fullerenes [160]. A comprehensive picture of the ion/surface collision dynamics has emerged from a variety of experimental studies [161–168] and from molecular dynamics simulations [159,169,170]. In general, the results depend on the energy and angle of the incident fullerene ion, and on the nature of the surface. For energies ranging from about 100 to 500 eV, incident angles not much larger than 45°, and targets like silicon, graphite, diamond, or metals coated with hydrocarbons, the findings may be summarized as follows: The majority of the primary ions is neutralized upon impact. The scattered neutrals autoionize by thermally activated electron emission if their internal excitation energy is sufficiently high. The kinetic energy of the scattered parent ion stays remarkably constant at about 5–10 eV over the full range of collision energies. The major part of the collision energy is transferred to the substrate.

A few studies have involved endohedral fullerenes. In one such study, $Y@C_{82}{}^{+}$, $Ca@C_{82}{}^{+}$, and $Ca@C_{84}{}^{+}$ were collided with silicon and gold surfaces, and with self-assembled monolayer films [171,172]. The degree of fragmentation strongly depended on the nature of the surface. C_2 loss was the only reaction channel; escape of the endohedral metal ion was not observed.

While most cluster–surface collision experiments involve charged projectiles, Kolodney and coworkers have developed a method to accelerate neutral C_{60} to energies up to 50 eV [173]. One interesting observation is the formation of $C_{60}{}^{-}$ in collisions of hyperthermal C_{60} with a nickel surface covered with a monolayer of carbon [174]. Kappes and coworkers have shown that, for grazing-incidence scattering of larger neutral fullerenes, the intensity of anions correlates with the electron affinity of the neutral projectile [175].

Deposition of size-selected clusters has been another goal in cluster science. These clusters or cluster ions are usually hyperthermal, and it is difficult to reduce their kinetic energies to much less than ≈1 eV per monomer. It had been demonstrated in a molecular dynamics study that prior deposition of a neon film may provide for "soft landing" of the cluster in spite of these high energies [176]. This technique has been successfully applied to deposit small size-selected metal cluster ions in inert gas layers [177,178].

2.5. *Energy transfer in inelastic collisions of K^+ with C_{60}*

In the following, we will present the intensities of $C_{60}{}^{+}$ and $C_{58}{}^{+}$ ions that are formed as a result of collisions between K^+ ions and a molecular beam of C_{60}. The experiment monitors the intensity of ions but is blind to neutrals; in this situation several reaction mechanisms could conceivably give rise to fullerene ions:

$$K^{+} + C_{60} \rightarrow K^{+} + C_{60}{}^{*} \qquad \text{(inelastic collision)} \tag{1a}$$

$$K^{+} + C_{60} \rightarrow K + C_{60}{}^{+} \qquad \text{(charge exchange)} \tag{1b}$$

$$K^{+}+C_{60} \rightarrow K@C_{n}{}^{+} + \tfrac{1}{2}(60-n)C_{2} \quad \text{(insertion + fragmentation)} \tag{1c}$$

Our assertion is that inelastic collisions (1a), followed by autoionization of the vibrationally excited C_{60} or its neutral fragments, is responsible for the appearance of empty fullerene ions. Charge exchange (1b) would be endothermic by 3.26 eV and therefore very inefficient for the range of collision energies studied here. Experimental evidence for K^+ insertion followed by fragmentation (1c) has been reported [39,42]. However, the large insertion threshold of about 46 eV in the center-of-mass system [42] implies a similarly large activation energy for escape of K^+; hence (1c) cannot contribute to the $C_n{}^+$ signal unless the fullerene ion becomes so small that it can no longer cage the atom [179,180].

A main objective of this study is to determine the efficiency of energy transfer in inelastic collisions (1a). To this end, we model consecutive unimolecular reactions of excited $C_{60}{}^*$ and its products. Dissociation and autoionization will be considered, in any order. We find that the frequently neglected channel of dissociation of neutral fullerenes followed by autoionization is important; in fact it is the major channel through which $C_{58}{}^+$ is formed in our experiments (also see [88,181,182]). This finding invalidates simplified models that assume that all fullerene fragment ions formed by statistical reactions from excited C_{60} pass through a transient $C_{60}{}^*$ ion [39,165,183].

3. Experiment

Fig. 1 shows the experimental setup. A metal ion gun provides a beam of potassium ions that are generated by surface ionization. These ions have a small kinetic energy spread of about $2\,k_BT \approx 0.3$ eV [184]. We use cylindrical, resistively heated cartridges capped with a 0.25 in. diameter porous tungsten plug, coated with aluminasilicate glass which is doped with potassium [185]. The continuous beam of K^+ emitted from the tungsten plug is accelerated, decelerated, and then chopped into bunches of 2 μs duration at a repetition rate of 5–10 kHz by an electrostatic ion gate. The energy dependence of the ion current can be measured before or after taking spectra by moving an electrode into the ion beam at the position where it intersects the C_{60} beam.

The metal ion beam is intersected at 90° by a molecular beam of C_{60} (purity 99%) that emerges from a stainless steel Knudsen cell kept at 570 °C. The C_{60} flux is monitored during the experiment by a quartz microbalance, see Fig. 1. All data presented in this work are corrected for the energy dependence of the ion current from the metal ion gun as well as any possible changes of the C_{60} flux.

Product ions that are formed as a result of collisions between metal ions and C_{60} are accelerated by pulsed extraction potentials towards the ion detector at the end of a drift tube. The time-of-flight mass spectra shown in this work reflect the ion distributions approximately 14 μs after the collision. Any ions that might form from neutrals by thermionic emission at a later time will add a tail to the resolved time-of-flight peaks, but we do not see any clear evidence for that process. This may seem surprising, but the pulsed extraction technique bunches events with small delays into the main peak and therefore partly suppresses the appearance of a tail [186]. On the other hand, ions that form within the first few microseconds and then fragment after a time exceeding >14 μs, will contribute to the parent ion peak in the spectrum. Further experimental details may be found elsewhere [41,42].

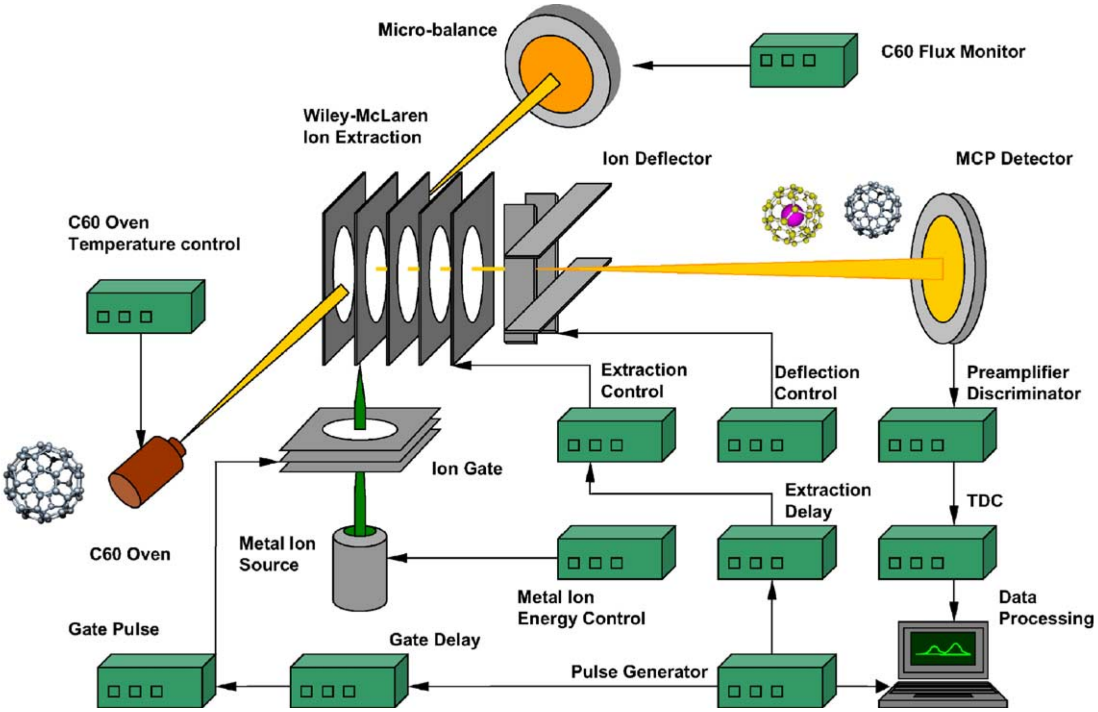


Fig. 1. Experimental setup. A beam of C_{60} vaporized at 570 °C collides with a pulsed beam of K^+ ions that are emitted from a surface ionization source and accelerated to the desired energy. Product ions formed during or shortly after the collision are extracted into a time-of-flight mass spectrometer by pulsed electrostatic potentials.

4. Experimental results

In Fig. 2, we display the intensities of $C_{60}{}^{+}$ and $C_{58}{}^{+}$ ions (full and open circles, respectively), formed as a result of collisions of C_{60} with K^{+} ions. The abscissa display the collision energy in the lab and the center-of-mass system. The lines show the result of our kinetic model as explained in the next section. The experimental $C_{60}{}^{+}$ ion intensity peaks at $E_{cm} \approx 48$ eV, some 6 eV below the $C_{58}{}^{+}$ ion. Qualitatively similar shifts between $C_{60}{}^{+}$ and $C_{58}{}^{+}$ have been observed under a variety of experimental conditions. For example, in electron impact ionization of C_{60}, a shift of about 7 eV between the appearance energies of $C_{60}{}^{+}$ and $C_{58}{}^{+}$ was reported [187]; $C_n{}^{+}$–C_2 dissociation energies have been computed from these shifts [183,188]. Shifts of this magnitude are also observed in the intensity of endohedral $A@C_{60}{}^{+}$ and $A@C_{58}{}^{+}$ ions formed by reactive collisions between atomic ions A^{+} and C_{60} [39,41,43,70]. An order of magnitude larger shifts are found when singly or multiply charged C_{60} ions collide with surfaces; these large shifts reveal that the efficiency of energy transfer is very small [162,165,168,189,190].

The shifts are often interpreted as evidence for a sequential process, in our case for the reaction

$$C_{60}{}^{*} \rightarrow C_{60}{}^{+} + e \rightarrow C_{58}{}^{+} + e + C_2. \qquad (2)$$

The experimentally observed shift would then depend on the activation energy for dissociation of $C_{60}{}^{+}$ as well as the efficiency of energy transfer in the primary collision that leads to the formation of $C_{60}{}^{*}$.

However, in the present case, a conclusion in favor of sequential decay, reaction 2, would be premature. This will become apparent when we model the kinetics, but it is already suggested by the unusual observation that the peak intensity of $C_{58}{}^{+}$ in Fig. 2 is five times weaker than that of $C_{60}{}^{+}$.

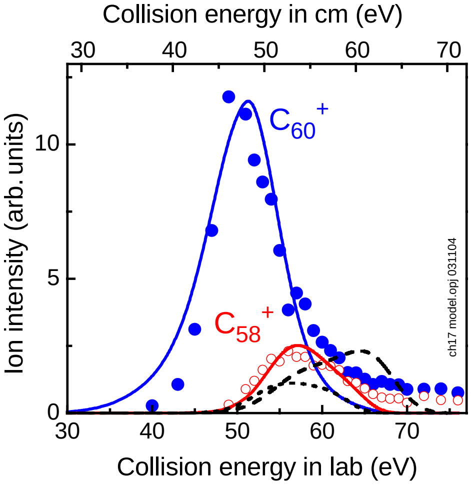
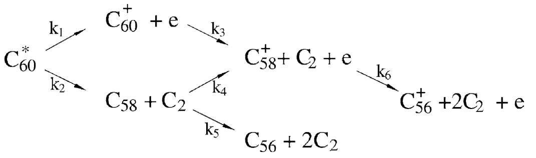


Fig. 2. (Solid circles) Intensity of $C_{60}{}^{+}$ product ions versus collision energy. (Open circles) Intensity of $C_{58}{}^{+}$. The lines result from modeling the system with Eqs. (12)–(14) (see text).

5. Modeling the kinetics

In this section, we will assume that all empty fullerene ions observed in the experiment are formed as a result of inelastic, non-reactive collisions between K^{+} and C_{60} (reaction 1a). The vibrationally excited $C_{60}{}^{*}$ is, like any other neutral product, not observable, but it may lead to ion formation through a series of competing reaction channels:



(3)

To model the kinetics, we need expressions for the dependence of the rate coefficients k_i ($i = 1$–6) on the excess energy E^{*} of the parent ion of the corresponding reaction. We express the rate coefficients in Arrhenius form

$$k_i = \nu_i \exp\left(-\frac{E_i}{k_B T_b(E^{*})}\right) \qquad (4)$$

where T_b is the "isokinetic temperature", i.e., the temperature of a fictitious heat bath for which the rate $k(T_b)$ would equal $k(E^{*})$. The relation between T_b and E^{*} is [191–193]

$$E^{*} = E(T_b) - k_B T_b + \frac{E_i}{2} + \frac{E_i^2}{12(C - k_B)T_b} \qquad (5)$$

E_i is the activation energy for the reaction, and C is the specific heat of the parent in units of the Boltzmann constant k_B. $E(T_b)$ is the caloric curve of a canonical ensemble. For C_{60}, we use an expression calculated for $1500 < T < 4000$ K from the vibrational frequencies of C_{60} [194]

$$E(T_b) = 0.0143 T_b - 7.55. \qquad (6)$$

with T_b in kelvin and E in eV. Note that the quantities T_b, $E(T_b)$, C, and E^{*} in Eqs. (4) and (5) refer to a specific parent. For fullerenes smaller than C_{60}, we assume that C scales as the classical number of degrees of vibrational freedom.

For the frequency factors and activation energies in Eq. (4), we use values recently derived by Tomita et al. from a photo-excitation study of C_{60} [195]. The authors determined the intensity of delayed $C_{58}{}^{+}$ and $C_{60}{}^{+}$ ions in coincidence with electrons. Their analysis included radiative cooling and allowed for different frequency factors for the rate coefficients k_1 through k_5. Specifically, we use the following values in agreement, or near agreement, with their results: $\nu_1 = 10^{15}\,s^{-1}$, $\nu_2 = 3.4 \times 10^{21}\,s^{-1}$, $\nu_3 = 1.7 \times 10^{21}\,s^{-1}$, $\nu_4 = 5 \times 10^{14}\,s^{-1}$, $\nu_5 = \nu_6 = 2 \times 10^{19}\,s^{-1}$, $E_1 = IE_{C_{60}} = 7.6$ eV, $E_2 = D_{C_{60}} = 10.8$ eV, $E_3 = D_{C_{60}{}^{+}} = 10.26$ eV, $E_4 = IE_{C_{58}} = 7.06$ eV, $E_5 = D_{C_{58}} = E_6 = D_{C_{58}{}^{+}} = 8.36$ eV. Here we have, for later use, introduced new symbols that are more descriptive than E_i.

Of all these values, only the ionization energies $IE_{C_{60}}$ and $IE_{C_{58}}$ have been determined directly in experiments [196,197]; their difference of 0.54 eV determines the difference between $D_{C_{60}}$ and $D_{C_{60}{}^{+}}$. The ionization energy of

C_{56} appears to be close to that of C_{58} [198], therefore we have used $D_{C_{58}^+} = D_{C_{58}}$. We also assumed $\nu_6 = \nu_5$. The frequencies for electron emission adopted here are an order of magnitude smaller than usually assumed for fullerenes [199], and the frequency factors for C_2 loss from C_{60} and $C_{60}{}^+$ are two orders of magnitude larger than the values used by others [98,200–202]. However, the activation energies for C_2 loss from C_{60} and $C_{60}{}^+$ are commensurable with other recent experimental [98,200–204] and theoretical [198,205] work.

Eq. (4) assumes that dissociation and electron emission are statistical processes and that the excitation energy E^* is fully randomized over all energetically accessible degrees of freedom. As far as electron emission is concerned, this assumption has been questioned by some authors [206–209], one reason being the assertion that the lowest triplet state in C_{60} may be very long lived [210]. This is, in fact, true at low temperature, but recent experiments show that the lifetime of the triplet state decreases rapidly with increasing vibrational excitation, and that the absorbed photon energy is fully thermalized within $\ll 10^{-7}$ s when E^* reaches 10 eV [211–213]. Concerning the nature of fragmentation reactions, it appears that they are statistical as long as the total excitation energy in C_{60} remains below 80 eV [48,99].

We now discuss how the excitation energies of the decaying complexes are computed. The internal energy E^* of the collisionally excited C_{60} molecule is the sum of the energy ΔE that is absorbed in the collision (the determination of ΔE is the main goal of our kinetic model), plus the internal energy E_{ov} of the neutral C_{60} before collision, minus the energy lost by radiation since the collision

$$E^*_{C_{60}} = \Delta E + E_{\text{ov}} - \kappa_{\text{rad}} t, \tag{7}$$

E_{ov} is the average internal energy of a canonical ensemble of C_{60} that emerges from the Knudsen cell at temperature T_{ov}. The caloric curve of C_{60} may be computed from its vibrational frequencies; a temperature of 843 K corresponds to $E_{\text{ov}} = 5.22$ eV [41]. Expressions for the radiative energy loss $\kappa_{\text{rad}} t$ have been computed and experimentally determined by the Aarhus group [195,204,214]. We use the expression

$$\kappa_{\text{rad}} = 4.5 \times 10^{-17} T^6 \ \text{eV/s} \tag{8}$$

for all sizes and charge states. The rate for neutral C_{60} is reduced due to the large HOMO–LUMO gap [195], but radiative cooling does not have a substantial effect over the time scale of our experiment, $t \le 14\,\mu\text{s}$, therefore our approximation will not introduce significant errors.

Based on Eq. (7), the internal energies of the direct reaction products of $C_{60}{}^*$ are as follows:

$$E^*_{C_{60}^+} = \Delta E + E_{\text{ov}} - \kappa_{\text{rad}} t - \text{IE}_{C_{60}} - 2k_B T_{C_{60}^+} \tag{9}$$

$$E^*_{C_{58}} = \Delta E + E_{\text{ov}} - \kappa_{\text{rad}} t - D_{C_{60}} - 2k_B T_{C_{58}} \tag{10}$$

$$E^*_{C_{58}^+} = \Delta E + E_{\text{ov}} - \kappa_{\text{rad}} t - D_{C_{60}} - 2k_B T_{C_{58}} - \text{IE}_{C_{58}} - 2k_B T_{C_{58}^+} \tag{11}$$

Here the term $2k_B T$ accounts for the kinetic energy release in the decay channel [215,216]. The temperatures refer to the product of the reaction, as specified in the subscripts.

We are now in the position of computing the rate at which products form from collisionally excited $C_{60}{}^*$at time t:

$$I_{C_{60}^+}(t) = I_0 \int_0^\infty k_1(E(t))\, e^{-[k_1(E(t))+k_2(E(t))]t} \rho(E(t))\, dE, \tag{12}$$

$$I_{C_{58}}(t) = I_0 \int_0^\infty k_2(E(t))\, e^{-[k_1(E(t))+k_2(E(t))]t} \rho(E(t))\, dE. \tag{13}$$

I_0 is a normalization constant. The first factor under the integrals is the rate at which the species ($C_{60}{}^+$ and C_{58}, respectively) are formed; the exponential is the rate at which the parent is being depleted by electron emission or dissociation.

$\rho(E)$ is the internal energy distribution. The internal energy of the collisionally excited C_{60} includes a distribution that arises from the kinetic energy spread of the K^+ ions from the surface ionization source, and from the distribution of the initial internal energy of C_{60}. The combined energy spread (standard deviation) due to these factors is estimated to be 1 eV [41], but increasing it to 3 eV had negligible effect on the computed ion intensities. Another major contribution to the internal energy distribution $\rho(E)$ will come from the energy transfer in the collision. The efficiency of energy transfer will depend on the orientation of C_{60} and the impact parameter. Experimentally, we average over all orientations and impact parameters; we did not attempt to fit the width of the distribution.

$C_{58}{}^+$ ions arise from decay of $C_{60}{}^+$ as well as auto-ionization of C_{58}. Their intensity is determined by the double integral

$$\begin{aligned} I_{C_{58}^+}(t) = \int_0^\infty \rho(E(t))\, dE \int_0^t dt' \{ & I_{C_{60}^+}(t-t') k_3 \\ & \times \exp[-k_3(E(t-t'))(t-t')] \\ & + I_{C_{58}}(t-t') k_4(E(t-t')) \exp[-(k_4(E(t-t')) \\ & + k_5(E(t-t')))(t-t')]\}. \end{aligned} \tag{14}$$

The total ion intensities are obtained by multiplying the expressions in Eqs. (12)–(14) with a decay factor of the form $\exp(-k_i t)$ where k_i is the rate coefficient for decay of the ion under consideration, and integrating over the time window set in our instrument, $0 \le t \le 14\,\mu\text{s}$. For example, for the $C_{58}{}^+$ product ion the decay factor is $\exp(-k_6 t)$.

6. Discussion

The primary objective of the present work is to determine the relation between the collision energy in the center-of-mass system, E_{cm}, and the amount of energy, ΔE, that is converted from translational to vibrational modes in an inelastic collision between C_{60} and K^+ (reaction 1a). For a given set of parameters (primarily the frequency factors ν_i and the activation energies E_i in the Arrhenius relations, Eq. (4)), our model lets us predict the intensities of $C_{60}{}^+$ and $C_{58}{}^+$ as a function of ΔE. In principle, we could find the ΔE values that best match the experimental results for each spectrum, recorded for collision energies ranging from 40 to 76 eV. However, a more robust result is obtained if we parameterize the energy transfer in the form

$$\Delta E = \alpha E_{\mathrm{cm}} - \beta. \tag{15}$$

The values of α and β are varied systematically. Theoretical ion intensities are computed for each pair and compared with experiment. The best values are

$$\alpha = 0.52 \pm 0.02 \quad \text{and} \quad \beta = 16 \pm 2\,\mathrm{eV} \tag{16}$$

The ion intensities computed for these parameters are shown in Fig. 2 by solid lines. The fit is moderately successful. It does reproduce two characteristic features of the experiment, namely the shift of ≈6 eV between the maxima of the $C_{60}{}^+$ and $C_{58}{}^+$ ions, and the greatly reduced intensity for $C_{58}{}^+$. Hence, the set of parameters that we used (frequency factors and activation energies) is consistent with our data.

How sensitive are the modeled intensities to the input parameters? As a demonstration, we have computed the ion intensities after either increasing ν_5 and ν_6 from $2 \times 10^{19}\,\mathrm{s}^{-1}$ to $2 \times 10^{20}\,\mathrm{s}^{-1}$, or increasing $D_{C_{58}}$ and $D_{C_{58}{}^+}$ from 8.36 to 8.86 eV (Fig. 2, dotted and dashed lines, respectively). The quality of the fit deteriorates dramatically. By contrast, the computed intensity profile of $C_{60}{}^+$ changes very little; the different curves (not shown) could hardly be distinguished if plotted together in Fig. 2.

However, the fit has an obvious deficiency, the peaks fall off too quickly towards high energies. Given the strong dependence of the rate coefficients on E^*, this observation implies that, even at very high collision energies, a fraction of the excited $C_{60}{}^*$ has a rather low excitation energy. In other words, the energy transfer has a much broader distribution than assumed in the analysis. Successful attempts to also fit the width of the energy transfer distribution have been reported for experiments involving collisions between $C_{60}{}^+$ and surfaces [165,168], but a larger number of fragment ions would have to be considered here to render such an analysis meaningful. Our analysis is more involved than the ones applied to the surface collision data because we do not ignore the formation of fragment ions through the neutral channel.

In Fig. 3, we plot the energy transfer ΔE (Eq. (15), solid line) versus collision energy. For comparison, we show ΔE computed in a molecular dynamics study of $Li^+ + C_{60}$ collisions [50], together with experimental results derived from the appearance of $C_{60}{}^+$ and $C_{58}{}^+$ after collisions of energetic $C_{60}{}^+$ with a hydrocarbon-covered stainless surface [168] and HOPG [165] (dotted and dash-dotted lines, respectively). The surface collision data pertain to much higher collision energies; in Fig. 3, we linearly extrapolated them to lower energies. For example, the energy at which the intensity of $C_{60}{}^+$ product ions drops as a result of fragmentation to 50% is $E_{\mathrm{cm}} = 450\,\mathrm{eV}$ in collisions with a hydrocarbon-covered stainless surface [168], whereas it is only 52 eV in our experiments. Accordingly, the fitted slope efficiencies for energy transfer, $\eta = \mathrm{d}\Delta E/\mathrm{d}E_{\mathrm{cm}}$, differ by nearly an order of magnitude (52% in our experiments versus 6.8% in the experiment by Fiegele et al.).

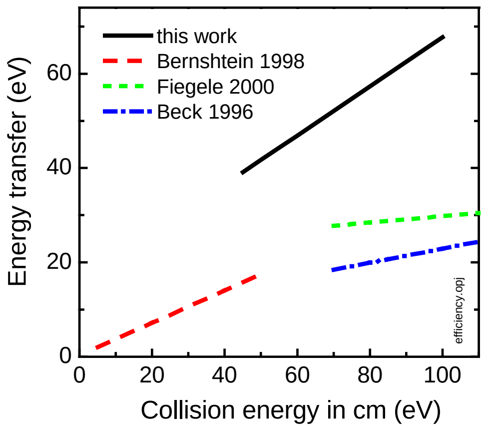


Fig. 3. The amount of energy transferred in inelastic collisions from translational to vibrational modes for $K^+ + C_{60}$ (this work, solid line) and $Li^+ + C_{60}$ (molecular dynamics study [50], dashed line), and in $C_{60}{}^+$ collisions with HOPG [165] and hydrocarbon-covered stainless steel [168] (dash-dotted and dotted lines, respectively).

Generally, the slope efficiencies are small for collisions of C_{60} with surfaces, but they vary considerably. For example, Kolodney and coworkers reported a value of less than 2% for neutral C_{60} scattered off nickel with impact energies below 50 eV [173]. Kappes and coworkers [165] deduced an efficiency of 15% for collisions of $C_{60}{}^+$ with clean HOPG under 45° (dash-dotted line in Fig. 3), but only 8% if the surface was contaminated with pump oil vapor. In a molecular dynamics simulation of C_{60} impacting on a hydrogen-terminated diamond surface, Mowrey et al. [169] obtained 24–27%.

Also apparent from Fig. 3 is a large difference between our experimental results for $K^+ + C_{60}$ collisions, and the molecular dynamics results for $Li^+ + C_{60}$ collisions [50]. In the latter work, the slope efficiency is approximately 34%, not much less than in our experiments, but the offset (β in Eq. (14)) is small. A tentative explanation may be obtained by viewing the reaction as an impulsive (elastic) collision between the ion and a small, distinct group of n carbon atoms in the fullerene; after escape of the ion, the energy absorbed by this group is randomized. In this model, the energy transfer depends on the mass of the projectile and the number n. For a Li projectile (most abundant isotope 7 u), one computes an energy transfer of 92, 68, 52, and 42% for $n = 1, 2 3, 4$, respectively, whereas the values are 75, 96, 100, and 97%, respectively, for K (mass 39 u). Hence, the light mass of Li is not favorable for efficient energy transfer. Within the impulsive model it is possible to correlate the measured energy transfer, $\Delta E(E_{\mathrm{cm}})$, with the number of carbon atoms $n(E_{\mathrm{cm}})$ that participate in the primary collision [63]. Some experimental results have been interpreted in terms of this model [37–39]. However, we abstain from showing this correlation because it is impossible to assess the merit of the impulsive model under our experimental conditions.

As mentioned before, the shift in Fig. 2 between $C_{60}{}^+$ and $C_{58}{}^+$ could possibly be seen as evidence for sequential decay, Eq. (2). However, analysis of the computed rates k_i clearly shows that the major contribution to the $C_{58}{}^+$ signal is through the neutral channel

$$C_{60} \rightarrow C_{58} \rightarrow C_{58}{}^+ \qquad (17a)$$

rather than via

$$C_{60} \rightarrow C_{60}{}^+ \rightarrow C_{58}{}^+ \qquad (17b)$$

In fact, the ratio of rate coefficients k_2/k_1 will increase with increasing excitation energy, because C_2 loss (k_2) has a higher activation energy than electron emission (k_1). Note that this finding is in agreement with the direct experimental result $k_2 \gg k_1$ deduced from photo-excitation data measured in our lab [217].

The conclusion that reaction (17a) dominates over reaction (17b) contradicts a scenario often applied in the analysis of unimolecular formation of fragment ions. For example, the appearance of $C_n{}^+$ after collisions of energetic C_{60} ions with surfaces [165,168,190], or after electron impact ionization of C_{60} and C_{70} [183,188] has been modeled under the assumption that increasingly smaller ions form with increasing excitation energy as a result of sequential C_2 emission from the ions. In the electron impact studies, dissociation energies of $C_n{}^+$ could thus be derived from the shift in their appearance energies. However, the recent findings of rather large dissociation energies (10 eV or higher for $C_{60}{}^+$) conflicts with the observed shifts of 7 eV or less between adjacent fullerene sizes. The conflict can be resolved if ion formation through the neutral channel is included in the data modeling (also see [195]). Although there is ample evidence for sequential loss of C_2 units from metastable, singly, or multiply charged fullerene cations [97,218–220], it is not necessarily the only channel.

We conclude with a discussion of $C_n{}^+$ and $A@C_n{}^+$ data that Basir and Anderson recorded in collisions between rare gas ions ($A^+ = Ar^+, Kr^+, Xe^+$) and C_{60} [37]. The authors concluded (without presenting a detailed quantitative analysis of their data) that the efficiency of energy transfer in collisions that lead to $C_n{}^+$ is sharply bimodal, with 85% of the collisions leading to little energy transfer, and the other 15% leading to near 100% efficient energy transfer. Part of this apparent discrepancy with our analysis comes from the fact that $C_{60}{}^+$ is easily formed in collisions with rare gas ions by exothermic charge transfer. This process gives rise to $C_{60}{}^+$ ions which represent the most intense signal for all collision energies, but the process is not viable for collisions of K^+ with C_{60}. The 100% efficiency that Anderson and coworkers estimate for the minority of collisions, i.e., those that have small impact parameters, is significantly larger than the slope efficiency of 52% that we find, but the total efficiency $\Delta E/E_{\mathrm{cm}}$ in our experiments at, say, 50 eV is 84%, not much less than the estimate given by Anderson and coworkers. The efficiency that we have derived (Eq. (15)) is near 100% for collisions energies near 40 eV, but it decreases with increasing collision energy. This trend agrees with the results of a molecular dynamics study of $Ne + C_{60}$ collisions by Schmidt and coworkers [48].

7. Conclusion

We have analyzed the intensities of $C_{60}{}^+$ and $C_{58}{}^+$ ions that form after inelastic $K^+ + C_{60}$ collisions in the gas phase. The basic assumption is that all reactions are statistical, with full equilibration of the excitation energy. Although a large number of input parameters are required in the model that are not well known, we show that a set of values recently derived by Tomita et al. from a very different experiment [195] does lead to reasonable agreement between the model and experiment when just two parameters, describing the efficiency of energy transfer, are adjusted. The model reveals that the main contribution to the $C_{58}{}^+$ signal is via dissociation of C_{60} followed by ionization, rather than via ionization followed by dissociation. This result invalidates an assumption frequently found in the literature.

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