Collision of Li^+ and Na^+ with C_{60}: Insertion, Fragmentation, and Thermionic Emission

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Interactions of Li^+ and Na^+ with C_{60} molecules have been studied over the collision energy range from 0 to 150 eV. We observe insertion of the alkali-metal ions to form the endohedral $[LiC_{60}]^+$ and $[NaC_{60}]^+$ species, with energy thresholds of 6 and 20 eV, respectively. At higher collision energies, the excited $[NaC_{60}]^+$ appears to relax mainly by loss of C_2 units from the fullerene cage, yielding $[NaC_{60-2n}]^+$. For $[LiC_{60}]^+$, escape of the Li^+ competes effectively with C_2 loss. For both Li^+ and Na^+, signal for pure carbon fragment ions $C_{60-2n}{}^+$ increases sharply at $\sim$30 eV, which is attributed to thermionic emission.

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Since 1985, gas-phase C_{60} has attracted the interests of many chemists and physicists. Many properties have been investigated experimentally and theoretically, including unimolecular decay [1], electronic structure and UV and visible spectroscopy [2], vibrational Raman and ir spectroscopy [3], and chemical reactivity with atoms and molecules [4]. A review of many aspects of fullerene chemistry and physics has been given recently in a special issue of Accounts of Chemical Research [5]. C_{60} has a stable hollow-cage structure [6], which raises the interesting possibility of preparing compounds where atoms or molecules are trapped inside. Chai *et al.* first prepared metal-doped fullerenes with the metal atom in the endohedral cavity [7]. More recently, Weiske *et al.* [8] reported *insertion* of rare-gas atoms into the endohedral cavity during high-energy collisions of $C_{60}{}^+$ with various atoms and molecules. Independent experiments by Ross and Callahan [9], Caldwell *et al.* [10], and Campbell *et al.* [11] have confirmed this observation. To avoid problems with unknown internal excitation of the $C_{60}{}^+$, and to simplify measurements of collision energetics, we have studied the insertion, fragmentation, and charge-transfer reactions, using collisions of Ne^+ with C_{60} [12].

In this paper, we report on collisions of alkali-metal ions M^+ (M=Li and Na) with C_{60} vapor molecules. These systems are interesting for several reasons. Na^+ is similar in size and is isoelectronic with neon, allowing direct comparison of the results. Li^+ is considerably smaller and lighter (more comparable to helium), and thus may have a very different insertion mechanism. A major difference between the alkali-metal-ion and rare-gas-ion systems is their electronic energies. For the $C_{60}{}^+$ inert-gas-ion system, exoergic charge transfer occurs with a large cross section, releasing over 10 eV, while for the alkali-metal ions, the charge is expected to remain on the alkali atom.

With the exception of the alkali-metal source, the experimental setup for this work is the same as described previously [12,13]. Alkali-metal ions are generated by surface ionization on a hot filament [14]. The nascent M^+ beam is collected by a radio-frequency (rf) octapole ion guide, then accelerated and mass filtered by a magnetic sector. The mass-selected M^+ beam is then decelerated, and injected into a second rf octapole ion guide, operated at 4.34 MHz, which guides the reactant ions through a scattering cell. The cell, which is heated to $\sim$340 °C, holds a capillary tube containing mixed C_{60}/C_{70} powder, which generates C_{60}:$C_{70}\sim$85:15 vapor. The fullerene pressure is conductance limited to $\sim 10^{-7}$ Torr, as estimated by the rate of mass loss and cell conductance. This is well below the vapor pressure of C_{60} at 340 °C [15], which minimizes condensation on the ion optics.

A small fraction of the reactant ions collide with C_{60} molecules, and product ions scattered into the forward hemisphere in the laboratory frame are collected by the octapole. Product and unscattered reactant ions are mass selected by a double focusing electric and magnetic sector mass spectrometer, and detected by an on-axis Daly detector [16]. In the following we give only relative cross sections, due to uncertainties in the absolute pressure of C_{60}, the product collection efficiency, and the alkali-metal ion beam intensities *in the scattering cell.*

The results for $Li^+ + C_{60}$ are summarized in Fig. 1, which gives the relative cross sections for all product channels as a function of collision energy. The main product ion is $LiC_{60}{}^+$, which appears at 6 eV collision energy. At energies above 20 eV, the $LiC_{60}{}^+$ signal decreases, and a series of $LiC_{60-2n}{}^+$ fragment ions appears. This suggests that C_2 loss is an important decay mechanism for excited $LiC_{60}{}^+$. Note that $LiC_{60-2n}{}^+$ fragments for $n > 3$ have negligible intensities—evidently Li loss is favored at the higher energies.

At collision energies above 30 eV, we observe $C_{60}{}^+$ with a cross section about one-fourth as large as for $LiC_{60}{}^+$. As collision energy is increased above 40 eV, the $C_{60}{}^+$ signal decreases and is replaced by a series of C_2 loss fragments: $C_{60-2n}{}^+$. The bottom frame of Fig. 1 gives the total cross sections for formation of fullerene product ions, with and without Li. Note that for the $C_n{}^+$ series, the total cross section is roughly energy independent once the appearance energy is surpassed, while for the $LiC_n{}^+$ series, the cross section is nearly zero for collision energies above 70 eV. (Note that the appearance of the $C_n{}^+$ channels coincides with the decrease in the $LiC_n{}^+$ cross section. From the Na^+ results, we believe

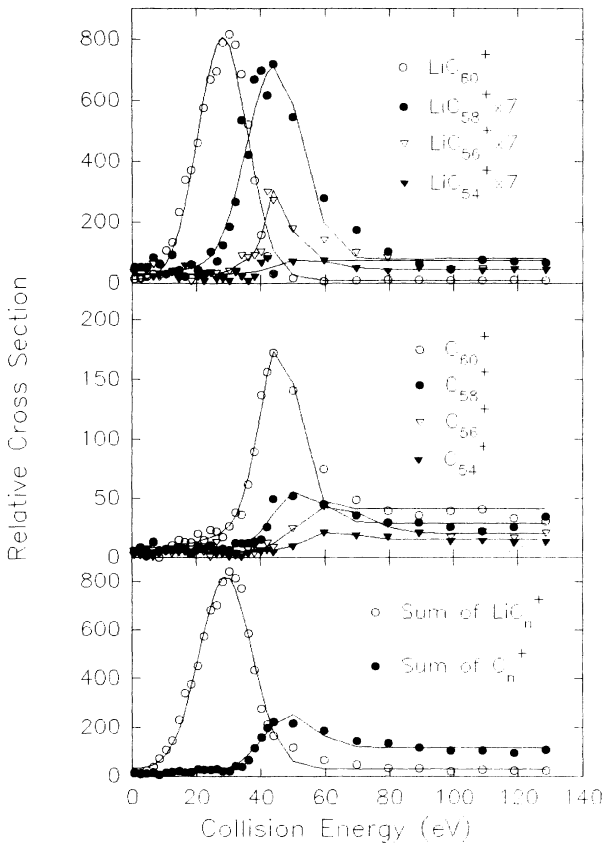

FIG. 1. Relative product cross sections as a function of collision energy for $Li^+ + C_{60}$. The solid lines are simply smooth curves to guide the eye.

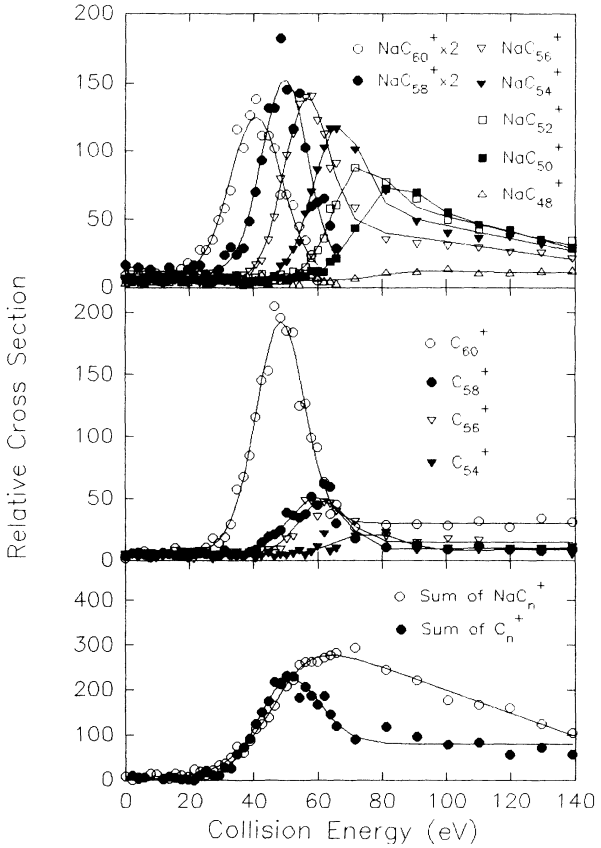

FIG. 2. Relative product cross sections as a function of collision energy for $Na^+ + C_{60}$. The solid lines are simply smooth curves to guide the eye.

this is merely an accident, and not indicative of interchannel competition.)

Figure 2 gives the equivalent data for $Na^+ + C_{60}$. NaC_{60}^+ adduct ions appear at ~20 eV collision energy, and with smaller cross section compared to the lithium case. At energies above 25 eV, we see a series of NaC_{60-2n}^+ fragment ions, predominantly produced by sequential C_2 loss from excited NaC_{60}^+. Note that for Na^+, the intensity of the NaC_{60-2n}^+ sequence continues out to NaC_{50}^+, then drops suddenly for NaC_{48}^+ and smaller fragments. This is in contrast to the LiC_{60-2n}^+ sequence, which effectively terminates at LiC_{54}^+. (Note that the NaC_{60}^+ and NaC_{58}^+ cross sections are not plotted for collision energies above 65 eV. At these high energies, there is background from reaction with the C_{70} impurity in our fullerene sample.)

The middle frame of Fig. 2 gives cross sections for production of bare fullerene fragment ions: C_{60-2n}^+. Note that for $Na^+ + C_{60}$, the appearance energy for C_{60}^+ is 30 eV—nearly identical to the $Li^+ + C_{60}$ case. The bottom frame of the figure gives the total cross sections for product ions with and without Na^+. The NaC_n^+ cross section extends to high collision energies, in sharp contrast to the LiC_n^+ results. On the other hand, the magnitude and energy dependence of the C_n^+ total cross section is nearly identical for Li^+ and Na^+.

Both the collision energy dependence of the MC_{60}^+ (M=Li, Na) signal, and the observed decay by C_2 loss, can best be explained if MC_{60}^+ is an *endohedral* complex, i.e., the alkali atom must be bound inside the fullerene cage. There presumably is an attractive interaction that could bind M^+ on the outside of the cage, but for closed-shell alkali-metal ions, the binding is unlikely to be strong enough to stabilize an exocomplex at the high energies we are probing. In addition, we would expect no activation for this type of binding.

Bakowies and Thiel have estimated, by the modified neglect of differential overlap method, that the energy barriers for Li^+ passage through the six-member and five-member rings of C_{60} are 7.3 and 10.2 eV, respectively [17]. Our appearance energy of 6 eV for LiC_{60}^+ is therefore in reasonable agreement with the calculated barrier. Na^+, which has a hard-sphere radius ~0.3 Å larger than Li^+, must almost certainly break or distort C-C bonds to get into the cage, and our appearance energy for NaC_{60}^+ (~20 eV) is consistent with this picture. Another interesting comparison is with the appearance energy for insertion of Ne atoms into C_{60}^+ (~25 eV) [12], which, as expected, is 3–5 eV higher, since Ne is isoelectronic with and slightly larger than Na^+. (Note that Campbell

et al. found a threshold of 9 eV for inserting Ne atoms into C_{60}^+ [11]. The reasons for the discrepancy between their threshold and ours are not completely clear, but most likely are related to the fact that the C_{60}^+ in their experiments has tens of electron volts of internal excitation [18], while our C_{60} is thermal. This issue is discussed fully elsewhere [19].)

Once the alkali projectile gets inside, the translational energy of the M^+ should be efficiently converted into internal energy of the MC_{60}^+ adduct, thus trapping the M^+. As the collision energy is increased, the resulting internal energy of the endocomplex also increases, and decomposition becomes likely. Radi *et al.* [1] and Yoo, Ruscic, and Berkowitz [20] have estimated that the binding energy of C_{60}^+ with respect to C_2 loss is 4.6 to 6.5 eV. In our experiment, we observe the first C_2 loss product channel at 25 eV for LiC_{58}^+ and 30 eV for NaC_{58}^+. These are the energies at which the lifetime of the MC_{60}^+ activated complex is short enough to allow measurable fragmentation on the experimental time scale ($\sim$1 msec).

Our observation that the series of LiC_{60-2n}^+ fragment ions terminates sooner than the corresponding NaC_{60-2n}^+ series is consistent with the endohedral binding picture. Just as Li^+ can insert into C_{60} more easily than Na^+, it should be able to escape more readily. The large drop of ion signals toward bigger n clearly shows that Li^+ loss competes effectively with C_2 loss:

$$\begin{aligned} LiC_{60}^+ &\rightarrow C_2 + LiC_{58}^+ \rightarrow 2C_2 + LiC_{56}^+ \rightarrow \cdots \\ &\searrow C_{60} + Li^+ \quad \searrow C_{58} + Li^+ \quad \searrow C_{56} + Li^+ . \end{aligned}$$

Since the radius of Na^+ is much larger than Li^+ and it is harder to escape from the cage, we continue to observe the C_2 loss series down to NaC_{50}^+ with no large decrease in intensity.

The other interesting product ion is C_{60}^+, which is observed at 30 eV collision energy for both $Li^+ + C_{60}$ and $Na^+ + C_{60}$. The ionization potentials (IPs) of Li and Na are 5.39 and 5.14 eV, respectively, which are more than 2 eV lower than the IP of C_{60} (7.61 eV) [21]. The mechanism for production of fullerene ions can be formally divided into two channels:

$$M^+ (M = \mathrm{Li,Na}) + C_{60} \rightarrow M + C_{60}^+ \quad (1)$$

$$\searrow M^+ + C_{60}^* \rightarrow M^+ + C_{60}^+ + e^- . \quad (2)$$

The first channel is formally endoergic charge transfer, which can occur through a variety of mechanisms. For example, in large impact parameter collisions, the time-dependent ion-induced polarization can result in electron hopping from C_{60} to the M^+ ion. This mechanism has been investigated for several atom-cluster ion systems [22], and is only efficient when the following condition is satisfied: $R\Delta\mathrm{IP} \sim hv$, where $\Delta\mathrm{IP} = \mathrm{IP}(C_{60}) - \mathrm{IP}(M)$, v is the relative velocity of the M^+ ion to the C_{60}, and R is the interaction range, here about 10 Å. The required collision energy turns out to be $\sim$10 keV for Li^+ and $\sim$35 keV for Na^+, thus this mechanism is insignificant for our energy range. For small collision energy ($\sim$100 eV), a more likely mechanism is endoergic charge transfer resulting from small impact parameter, intimate collisions, which may or may not involve formation of an intermediate complex. There is no literature on the energy dependence of this process for such large molecules; however, for small molecular ions the cross sections typically show a quick increase as energy is raised through the thermodynamic threshold. In our results, there is a small C_{60}^+ signal at low energies, which probably comes from this mechanism, but the large increase of $\sim$30 eV seems to require a different mechanism.

For large stable molecules like fullerenes, thermionic emission may compete favorably with dissociation as an energy loss mechanism for highly excited collision products. For example, Campbell, Ulmer, and Hertel and Wurz and Lykke have examined delayed ionization of laser-heated C_{60}, and concluded that thermionic emission was the mechanism [23]. Maruyama *et al.* have pointed out that thermionic emission is probably the mechanism for laser-induced multiple ionization of giant fullerenes [24]. In our experiment, when an alkali-metal ion collides with C_{60}, part of the kinetic energy will be transferred to internal energy of the C_{60} molecule. For *high-energy* collisions, we can make a crude estimate of the energy transfer by assuming that the alkali-metal ion simply undergoes an elastic collision with a single carbon atom (i.e., assume that the collision is impulsive with the carbon atom that is impacted). In this limit, the C_{60} internal energy after collision is

$$\begin{aligned} E_{\mathrm{int}} &= [4M_A M_C/(M_A + M_C)^2] E_{\mathrm{CE}} + (3N-3)kT_0 \\ &= (3N-3)kT_{\mathrm{final}} , \end{aligned} \quad (3)$$

where M_A and M_C are the alkali and carbon atom masses, E_{CE} is the collision energy, N = sixty carbon atoms, and T_0 is the initial C_{60} temperature (600 K). The second line simply expresses the internal energy as a final temperature, T_{final}. For $E_{\mathrm{CE}} = 30$ eV, where we observe a large increase in C_{60}^+ signal, T_{final} is 2430 K for lithium, and 2370 K for sodium. This is certainly in the temperature range where thermionic emission might be expected.

Klots has calculated the thermionic emission rate of small particles [25]. For a C_{60} molecule, this rate becomes

$$\begin{aligned} k(T) &= (4.16 \times 10^{13}) T (1 + 1.17 T^{1/2} + 0.437 T) \\ &\quad \times \exp(-E_0/kT) , \end{aligned} \quad (4)$$

where T is the internal temperature in a unit of 1000 K, E_0 (=7.61 eV) is the ionization potential of C_{60} [21], and the unit of $k(T)$ is 1/sec. The relationship between the rate $k(T)$ of a single C_{60} molecule and the total C_{60}^+ ion intensity is estimated to be $I(C_{60}^+) \sim 100 k(T)$ for

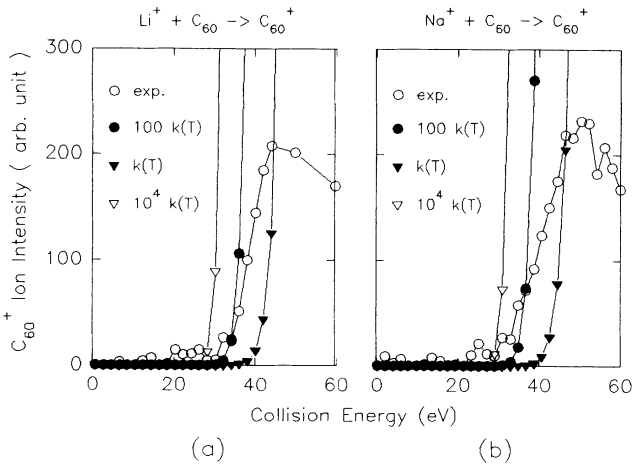

FIG. 3. Thermionic emission model of C_{60}^+ production in $C_{60}+Li^+$ and Na^+ collisions. The experimental data are compared with the theoretical fitting curve $I=A_0k(T)=100k(T)$, where T is calculated from the collision energy by Eq. (3): (a) C_{60}^+ from Li^++C_{60}; (b) C_{60}^+ from Na^++C_{60}. A_0 is a fitting parameter proportional to the C_{60} vapor pressure. $A_0=100$ corresponds to the estimated pressure of 10^{-7} torr. Two other curves, $k(T)$ and $10^4k(T)$, indicate the lower and upper limits of the fitting.

our experimental condition. Using the relationship given above for T_{final}, we plot the thermionic emission rate as a function of collision energy, and compare this with our data in Figs. 3(a) and 3(b). We can see that the experimental data are quite similar to the theoretical curves, which supports our hypothesis that most of our C_{60}^+ is due to thermionic emission.

We recently received a report of a very interesting study of photon-induced thermionic emission by Campbell, Ulmer, and Hertel [26]. They observed delayed ionization when C_{60} molecules absorbed two to four 308-nm (4.03 eV) photons, and fit the results to a thermionic emission model. Although the experiments are quite different, and somewhat difficult to compare quantitatively, their conclusions regarding the temperature (or internal energy) dependence of C_{60} thermionic emission appear to be very similar to ours.

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