PHYSICAL REVIEW A VOLUME 52, NUMBER 5 NOVEMBER 1995

Fullerene-fullerene collisions: Fragmentation and electron capture

H. Shen, P. Hvelplund, and D. Mathur*
Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

A. Bárány, H. Cederquist, and N. Selberg
Stockholm University, S-104 05 Stockholm, Sweden

D. C. Lorents
SRI International, Menlo Park, California 94025

(Received 27 February 1995)

In this paper, we describe collisions between high-energy (100-keV) fullerene ions ($C_{60}{}^{+}$, $C_{60}{}^{2+}$, $C_{70}{}^{2+}$, and $C_{70}{}^{3+}$) and C_{60}. The fast, forward-directed charged collision products are identified, leading to information on electron capture and loss as well as fragmentation. Similar studies are performed on rare-gas targets (He and Xe), and the fragmentation patterns and charge-exchange cross sections are compared and discussed. The electron-capture cross sections are two orders of magnitude larger for collisions with C_{60} as compared to Xe, while the smaller cluster-ion fragment peaks are only 3–6 times more intense. These observations are discussed in the light of the low ionization energy and the large mass and size of C_{60}.

PACS number(s): 34.70.+e, 36.40.−c

I. INTRODUCTION

Since the discovery of methods for preparing fullerenes in bulk [1], a large number of collision studies involving these cagelike structures have been reported [2]. C_{60} ions ranging from $C_{60}{}^{2-}$ to $C_{60}{}^{7+}$ have been produced in conventional ion sources [3] and at present, we routinely produce accelerated beams of $C_{60}{}^{-}$ and $C_{60}{}^{+}$ in the 10–100 nA intensity range. A target containing C_{60} in the gas phase is also at hand [4]. By heating C_{60} powder to temperatures of ~500 °C, a vapor pressure around 1 mTorr is obtained [5].

Collisions between fullerene ions and molecular or atomic gas targets have been found to lead to fragmentation [6], electron capture [7], electron loss [6], and atom insertion into the cage [8]. In collisions between energetic ions and thermal C_{60} molecules, both fragmentation and charge transfer have been studied [9].

Molecular fusion and deep inelastic scattering in $C_{60}{}^{+}$ + C_{60} collisions have been reported at energies around 200 eV in the center-of-mass system [10]. These experiments are ones where atomic cluster-cluster collisions (CCCs) are performed under well controlled conditions, and it is interesting to note that $C_{120}{}^{+}$ can be formed in collisions at these energies.

The present work probes the interactions involved in collisions between fullerene ions and C_{60} at collision energies of 50 and 100 keV in the laboratory frame. Fusion is not believed to be important at these energies where an energy of 25 keV would have to be absorbed as internal energy, as compared to a typical binding energy of a C_2 dimer of only around 10 eV. The dominating reaction channel in the present high-energy cluster-cluster collisions is electron transfer from the neutral to the charged, moving fullerene ion. We measure the single-electron-capture cross section to be as large as $(2–3)\times 10^{-14}$ cm^2. To compare the CCCs with collisions between cluster ions and atomic gases, experiments with He and Xe targets are also reported. Fragmentation leading to fast, charged collision products is also observed in the CCC. The relative intensity distribution within the fragmentation pattern is similar to that observed in atomic gases, but the total fragment intensity is larger.

The general questions that arise are as follows. How do these extended structures interact and how does electron capture occur? The former relates to the definition of concepts such as impact parameter, which have long been of use in collision physics, whereas the latter has important implications for developing insights into the dynamics of collisions involving such massive entities. Is it most appropriate to consider the fullerenes as conducting spheres, with a "sea" of electrons populating very delocalized orbitals and, consequently, with well defined single- and multiple-ionization energies? Or is a nonaromatic picture involving a large degree of localization of the electron-density distribution on the surface of the cage more realistic? In the latter case, the dynamics of the electron-capture process in CCCs should be similar to that obtained in collisions involving singly charged ions. Moreover, the low-ionization-energy values for multiply charged fullerenes, as compared with multiply charged *atomic* ions, should lead to effects that would normally only be expected in ion–solid-surface interactions.

II. EXPERIMENT

The apparatus (Fig. 1) used in these measurements is essentially the same as that described in previous publications [6,7]. The main difference is that we now use a 180° hemispherical electrostatic analyzer with a radius of 15 cm, resulting in better energy resolution. The positive fullerene ions are produced by electron bombardment in an ion source and then electrostatically accelerated to energies in the 50–

---

*Permanent address: Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India.

1050-2947/95/52(5)/3847(5)/$06.00

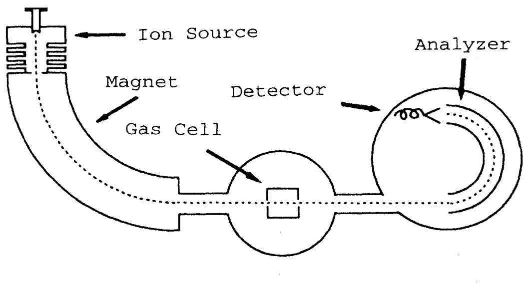

FIG. 1. Schematic of experimental setup.

100 keV range. The energetic fullerenes are magnetically mass selected and directed to a gas cell where they undergo single collisions with target atoms or molecules. After exiting the target cell, the charged fast fragments are electrostatically deflected into a channeltron detector operated in the particle-counting mode. Fragments scattered less than 0.5° in the target cell are accepted by the electrostatic energy analyzer. The deflection voltage is swept over the appropriate range in order to separate the fragmented and charge-changed ions. The energy is proportional to mass for these high-energy ions and therefore the deflection voltage is a measure of their mass-to-charge ratios. Typical spectra are shown in Fig. 2.

For the He and Xe experiments, the target cell is a 3-cm-long, differentially pumped gas cell with 1- and 2-mm-diam entrance and exit apertures, respectively. The target cell in the C_{60}-target experiments is a resistively heated, 6-cm long stainless-steel tube. During the experiment, the tube was heated to temperatures between 400 °C and 500 °C. The central 3-cm portion of the tube is made into a target cell by apertures like those used in the gas cell. The 99.9% pure C_{60} powder is placed in the midsection of the tube and degassed at high temperatures (~ 550 °C) for several hours prior to the measurements. Care was also taken to check that the charge-exchange yield vs temperature curve is reproducible before starting measurements of cross sections. The absolute target thickness is obtained from the measured oven temperature, using the vapor-vs-temperature values measured by Abréfah *et al.* [5]. The cross sections are deduced from the signal-vs-target-thickness measurements.

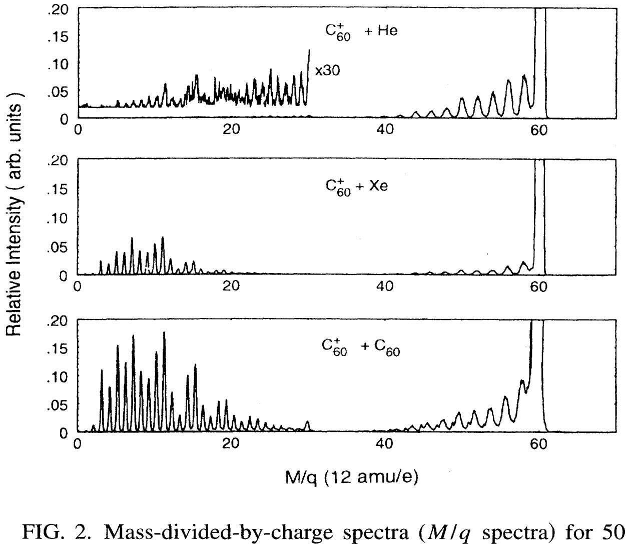

FIG. 2. Mass-divided-by-charge spectra (*M/q* spectra) for 50-keV $C_{60}{}^{+}$ colliding with He, Xe, and C_{60}. The intensities shown on the vertical scales in the three spectra are measured with the same product between target thickness and the number of $C_{60}{}^{+}$ projectiles passing the target cell. This means that ratios between fragment-peak intensities from the same or different spectra yield direct information on the corresponding relative cross sections (ignoring the fact that multiple-collision corrections differ in each case). The primary-peak intensities are 1 (He), 0.65 (Xe), and 3.90 (C_{60}), and the corresponding target pressures were 0.78, 1.3, and 0.53 mTorr, respectively.

III. RESULTS

A. Fragmentation

Fast product-ion spectra resulting from collisions of 50-keV $C_{60}{}^{+}$ ions with He, Xe, and C_{60} are shown in Fig. 2. As also observed earlier by several groups, for different energies and target gases, the fragment spectra consist of a low- and a high-mass group. The high-mass group is, as earlier reported [6], dominant for collisions with He. In this group, only even-numbered fullerenes are observed, indicating consecutive C_2 loss as a result of the collision. Both the relative and absolute intensities in this group are similar for He and C_{60}, while the absolute intensity is lower in the Xe case.

The low-mass group is dominant in collisions with both Xe and C_{60}. The absolute intensity is larger by a factor of ~ 4 for the C_{60} case. The low-mass ion peaks may be ascribed to both odd- and even-numbered carbon species. The well known increased relative abundance of $C_7{}^{+}$, $C_{11}{}^{+}$, $C_{15}{}^{+}$, $C_{19}{}^{+}$, and $C_{23}{}^{+}$ is observed for all targets, but most clearly in the C_{60} case. The occurrence of the "magic numbers" 7, 11, 15, 19, and 23 has been explained by Bach and Eyler [11] in terms of a low value of ionization energy for these $4n+3$ ($n=1$–5) clusters compared with neighboring clusters. This implies that the fragment pattern is most likely different for neutral clusters, and we have indeed shown [12] that the negative-fragment distribution is distinctly different from that obtained for positive fragments. The distribution within the low-mass group is broader in the C_{60} case and, in particular, $C_3{}^{+}$ is quite abundant on a relative scale. It should also be noted that in the C_{60} case, a peak is observed at $m/q=30$. This peak is believed to be caused by $C_{60}{}^{2+}$ ions originating from electron-loss collisions and some of the peaks in the upper 20s are most probably due to doubly charged fragment fullerene ions.

When discussing such collision-induced fragmentation spectra, it is customary to invoke the center-of-mass (c.m.) energy in the collision. The c.m. energies pertinent here are 0.28 keV (He), 7.7 keV (Xe), and 25 keV (C_{60}); these values represent the *maximum* energy transfer that can occur in the course of the collision. For collisions involving large molecules, there is a distribution of transferred energy that is subsequently randomized over all the available degrees of freedom, leading to a fragmentation pattern in which the relative intensities of the fragment ion peak yield an indication of relative bond strengths. A larger amount of c.m. energy is normally believed to result in more violent collisions and, consequently, in a larger amount of fragmentation and more intense low-mass peaks. However, it should be empha-

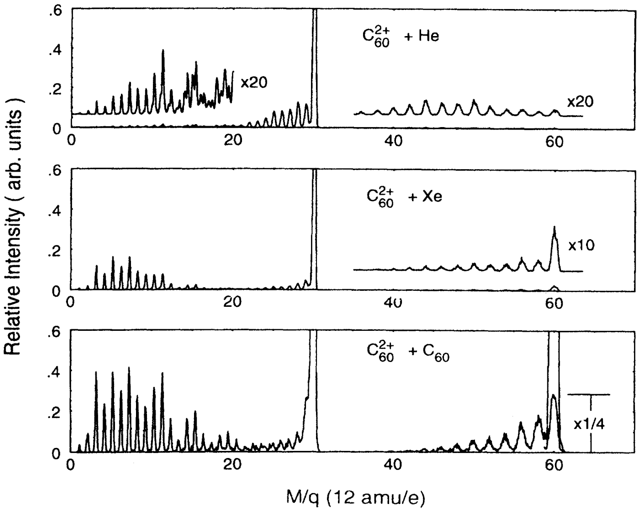

FIG. 3. M/q spectra for 100-keV ${C_{60}}^{2+}$ colliding with He, Xe, and C_{60} normalized in the same way as the spectra in Fig. 2. The right-hand part reflects the singly charged fullerene components, including the ${C_{60}}^{+}$ component resulting from electron capture. The primary-peak intensities are (at $m/q=30$) 1 (He), 1.1 (Xe), and 7.8 (C_{60}).

sized that large impact-parameter collisions, where only a small fraction of the available c.m. energy is transferred, dominate in these collisions.

Our data show that the fragmentation spectrum resulting from collisions with C_{60} is not qualitatively different from that resulting from collisions with heavier rare gases, despite the significantly different values of c.m. energy. A more intense and broader distribution of low-mass fragment ions is obtained in the former case. It should also be mentioned that the peak at $m/q=30$ could, in principle, originate from molecular fusion in the ${C_{60}}^{+}+C_{60}$ collision. In such a case, an energy of 25 keV would have to be absorbed as internal energy in the C_{120} molecule. However, Campbell *et al.* [10] have shown that fusion is unlikely to occur at energies larger than ~500 eV.

It is clear that even semiquantitative correlation between c.m. energy and the observed fragmentation patterns is difficult to achieve with the present data. We therefore postulate that the measured fragmentation pattern, particularly in the case of CCCs, may be very strongly influenced by the electron-capture processes that also occur in the course of the collision.

B. Electron capture

Figure 3 displays spectra in which single-electron capture by ${C_{60}}^{2+}$ leading to ${C_{60}}^{+}$ results in a peak at $m/q=60$. For He as a target gas, the capture cross section is extremely small. The peak observed in the spectrum at $m/q=60$ is mostly due to capture in the rest gas. Electron capture does take place in collisions with Xe, but in collisions with C_{60} it is the dominating reaction channel. Similar experiments were performed with ${C_{70}}^{2+}$ and ${C_{70}}^{3+}$ and, as shown in Fig. 4, the interaction of ${C_{70}}^{3+}$ with C_{60} results in both single- and double-electron capture.

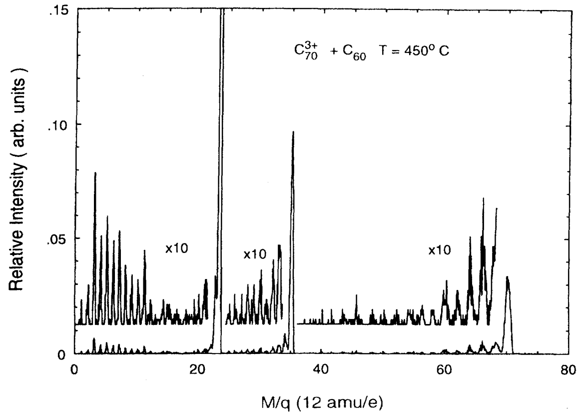

FIG. 4. Same as Fig. 3, but for 100-keV ${C_{70}}^{3+}$ on C_{60}. The dominant reaction products are ${C_{70}}^{2+}$ and ${C_{70}}^{+}$ resulting from single- and double-electron capture. The primary-peak intensity (at $M/q=23.33$) is 1.

Capture cross sections in collisions of 100-keV ${C_{60}}^{q+}$ ($q=1,2$) and ${C_{70}}^{q+}$ ($q=2,3$) with the target gases in question are listed in Table I. The most striking observation is the very large, nonfragmenting electron-capture cross section for collisions with the C_{60} target. This cross section, $\sim 2\times 10^{-14}$ cm^2, is large both on an absolute scale and also in comparison with the capture cross section in the Xe gas.

The following question now arises: how can we visualize electron capture in a ${C_n}^{q+}+C_{60}$ collision? First, we list some values that may be of significance in this discussion. The first ionization energy E_1^{ioniz} is 12.13 eV for Xe [13] and 11.26 eV for C [13]. For C_{60}, $E_1^{\text{ioniz}}=7.6$ eV [14] and $E_2^{\text{ioniz}}=11.5$ eV [15]. For C_{70}, $E_1^{\text{ioniz}}=7.6$ eV [14], $E_2^{\text{ioniz}}=11.5$ eV [15], and $E_3^{\text{ioniz}}=15.6$ eV (estimated to be equal to the value for C_{60}) [16].

Capture cross sections larger than 10^{-14} cm^2 are known in collisions between "ordinary" low charge-state ions and atoms. They are normally associated with what is known as symmetric electron capture. As an example, Lorents, Black, and Heinz [17] found cross sections larger than 10^{-14} cm^2 for $\text{Li}^{+}+\text{Li}\rightarrow\text{Li}+\text{Li}^{+}$ at energies in the interval from 0.01 to 1 keV. For Li, $E_1^{\text{ioniz}}=5.4$ eV [13]. For nonsymmetric electron capture, the reported cross sections are normally substantially smaller. On the other hand, large cross sections can occur in such instances under so-called accidental resonance conditions, i.e., in cases where the energy of an excited state of the incoming ion matches the electronic ground-state energy of the target atom. In this case, the energy defect in the collision ΔE is equal to zero. For large molecules, coupling between the electronic and the rovibronic degrees of freedom may lead to accidental resonance conditions ($\Delta E=0$). Accordingly, one explanation of the large cross section for ${C_n}^{q+}+C_{60}$ capture reactions could be that resonant conditions ($\Delta E=0$) occur.

In another scenario, similar to the one used by Petrie, Wang, and Bohme [18], we model the positively charged fullerene ions in a time-dependent picture as cages with well defined positive charges that can move over the surface. The charges are delocalized, i.e., they are not bound to a specific atom in the cluster, but are moving from one atom to another.

TABLE I. Cross sections in cm^2 for the process described. The estimated uncertainty is about ±30%.

Target	Projectile	σ_{21}	σ_{32}	σ_{31}	σ_{1-1}	σ_{tot}
C_{60}	C_{60}	2.6×10^{-14}			1.3×10^{-17}	$\sim5\times10^{-14}$
C_{60}	C_{70}	2.1×10^{-14}	2.1×10^{-14}	0.63×10^{-14}		
Xe	C_{60}	3.3×10^{-16}			3.1×10^{-21}	7×10^{-15}
Xe	C_{70}	3.3×10^{-16}	3.5×10^{-16}			

In the multiply charged fullerenes, the positive charges will be correlated to minimize the Coulomb repulsion that exists between them [18]. The detailed validity of this picture is connected with the question of aromaticity of the fullerenes. Walter *et al.* [19], for example, mention that the aromaticity should imply that "the positive charges should be delocalized and distributed throughout the molecule."

When a multiply charged fullerene-projectile ion approaches a gas-phase fullerene target, the strong polarizability of the latter (the dipole polarizability of C_{60} is about 500 times larger than for the hydrogen atom [20]) will tend to orient the initially delocalized positive charges on the projectile so that one positive charge will be at minimum distance to the target [Fig. 5(a)]. At the same time, the target will become polarized so that if an electron is transferred, it will start out from the point on the target that is closest to the projectile. This makes it possible that the electron transfer from the target to the projectile in the first approximation could be modeled as a singly charged ion-atom collision, with an ion-atom separation equal to the minimum distance between the two surfaces. According to a simple classical-barrier argument [21], which assumes a quasicontinuum of excited states on the projectile, and using $E_1^{\mathrm{ioniz}}=7.6$ eV, the critical ion-atom distance for electron capture is $R_{c1}=11a_0$. With a fullerene radius of $a=6.7a_0$, the cross section for soft-electron capture (no fragmentation, i.e., the cages do not touch) becomes

$$\sigma_{c1}=q/(q+1)\pi[(2a+R_{c1})^2-(2a)^2]$$
$$\approx 2.5\times10^{-14}\ \mathrm{cm}^2 \quad \text{for} \quad q=2,3.$$

The factor $q/(q+1)$ is a factor that approximately takes care of the fact that in a slow collision, the electron has time to resonate back and forth several times during the collision time, but that it prefers to stay on the ion of charge q [21]. This result compares favorably with all the measured CCC single-capture cross sections (Table I). The model also fits nicely with the very small cross sections measured for single capture from Xe. This is first because Xe has a much smaller polarizability than C_{60} and therefore cannot be expected to localize and orient the positive charges on the projectile to the same extent that C_{60} can as target. Also, the transfer of an electron from Xe to the singly charged fullerenes C_{60} or C_{70} is an endothermic reaction. Such reactions are known to have small cross sections in slow collisions, which fits with the fact that our model treats the multiply charged fullerenes as being locally singly charged.

In a more refined treatment, the fullerene surface beneath the positive charge might, of course, influence the estimated cross section through polarization effects. According to preliminary evaluations of a recent model for ion collisions with atoms, clusters, and solids [22], these effects seem to be rather small.

To explain the double-electron capture by a triply charged fullerene colliding with a fullerene, we consider the relation between the geometry of the two positive charges left on the projectile after capture of the first electron and a positive charge now residing on the target. Since the two ions are already rather close to each other, there are two different configurations possible.

In one, which is most favorable for larger impact parameters, the positive charge on the target is repelled by the projectile and resides on the far side of the fullerene cage. The two charges on the projectile are also on the far side of their fullerene [Fig. 5(b)]. This configuration does not lead to any further electron capture.

In the other configuration, which is only stable for smaller impact parameters, the three positive charges all fall on a straight line, which goes through the fullerene centers [Figs. 5(c)–5(e)]. The reason for the stability of this configuration is the polarization attraction on one of the positive charges of the projectile by the target (having its own positive charge still on the far side). A simple estimate of the competition between this attraction (using the dipole polarizability $540a_0^3$ for the target [20]) and the Coulomb repulsion from the target positive charge (assuming no charge shielding [23]) gives a critical distance R_{c2} of about $7a_0$. Since the classical-barrier condition for symmetric single-electron capture is fulfilled, the cross section for soft double-electron capture (no fragmentation) by a triply charged fullerene projectile from a fullerene target thus becomes [Figs. 5(c)–5(f)]

$$\sigma_{c2}=\tfrac{1}{2}\pi[(2a+R_{c2})^2-(2a)^2]=1\times10^{-14}\ \mathrm{cm}^2.$$

This, once again, compares rather favorably with the measured cross section (Table I).

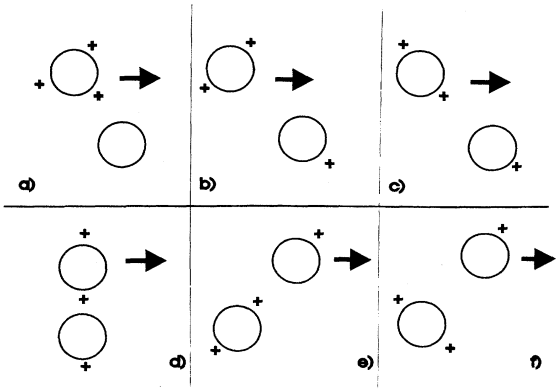

FIG. 5. Schematic picture of double-electron capture by a triply charged fullerene ion from a fullerene. See the text for an explanation.

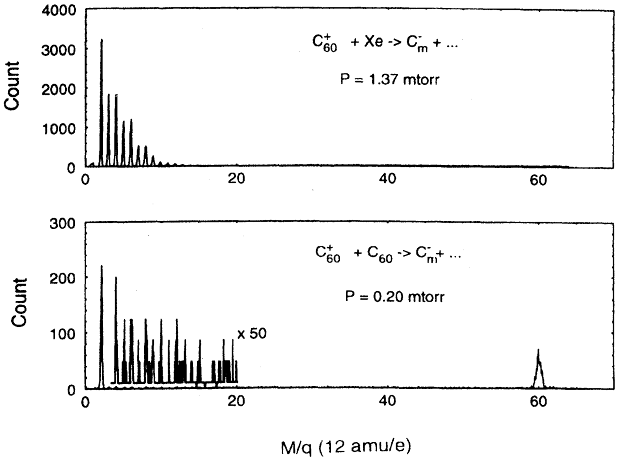

FIG. 6. M/q spectra displaying negatively charged collision products resulting from collisions between 50-keV C_{60}^{+} and Xe and C_{60}.

Double-electron capture by C_{60}^{+} leading to C_{60}^{-} cannot easily be visualized in a simple curve-crossing model or in the classical over-the-barrier model. The cross section for this process is only 1.3×10^{-17} cm^2 and most probably a more refined theory has to be invoked. The dominant reaction channel in this case is fragmentation, resulting in neutral and positive fragments. Spectra displaying negative cluster ions resulting from collisions with Xe and C_{60} are shown in Fig. 6. It should also be noted that double capture in Xe is almost nonexistent. As for the fragment distribution, a striking difference in the two spectra is observed. In collisions with C_{60}, C_2^{-} is by far the most dominating negative-fragment ion, whereas in collisions with Xe, clusters (linear chains) with sizes up to C_{10}^{-} are observed.

IV. CONCLUSIONS

We have shown that the distribution of fast, forward-directed charged fragmentation products resulting from collisions of C_{60}^{+} with C_{60} is similar to the distribution resulting from $C_{60}^{+}+\mathrm{Xe}$ collisions. It is also found that electron capture in collisions between fullerenes and C_{60} leads to cross sections that are two or three orders of magnitude larger than the cross sections in atomic gases. These large cross sections can be explained in a model in which the charges on the projectile fullerene are localized on the surface and one of them is close to the target due to polarization forces. With this localization, electronic transitions are viewed as being governed by the barrier condition for a (singly charged) ion-atom collision.

ACKNOWLEDGMENTS

This project has been supported by the Swedish National Science Research Council and the Danish National Research Foundation through the Aarhus Center for Advanced Physics.

---

[1] W. Krätschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, Nature **347**, 354 (1990).

[2] E. E. B. Campbell, R. Ehlich, M. Westerburg, and I. V. Hertel, in *Proceedings of the XVIIIth International Conference on the Physics of Electronic and Atomic Collisions*, edited by T. Andersen *et al.*, AIP Conf. Proc. No. 295 (AIP, New York, 1993), p. 697; P. Hvelplund, *ibid.*, p. 709.

[3] P. A. Limbach, L. Schweikhard, K. A. Cowen, M. T. McDermott, A. G. Marshall, and J. V. Coe, J. Am. Chem. Soc. **113**, 695 (1991); see also Refs. [7] and [23].

[4] G. Walder and O. Echt, Int. J. Mod. Phys. B **6**, 3881 (1992).

[5] J. Abréfah, D. R. Olander, M. Balooch, and W. J. Siekhaus, Appl. Phys. Lett. **60**, 1313 (1992).

[6] P. Hvelplund, L. H. Andersen, H. K. Haugen, L. Lindhard, D. C. Lorents, R. Malhotra, and R. Rouff, Phys. Rev. Lett. **69**, 1915 (1992).

[7] P. Hvelplund, L. H. Andersen, C. Brink, D. H. Yu, D. C. Lorents, and R. Ruoff, Z. Phys. D **30**, 323 (1994).

[8] E. E. B. Campbell, R. Ehlich, A. Hielscher, J. M. A. Frazao, and I. V. Hertel, Z. Phys. D **23**, 1 (1992).

[9] B. Walch, C. L. Cocke, R. Voelpel, and E. Salzborn, Phys. Rev. Lett. **72**, 1439 (1994).

[10] E. E. B. Campbell, V. Schyja, R. Ehlich, and I. V. Hertel, Phys. Rev. Lett. **70**, 263 (1993).

[11] S. B. H. Bach and J. R. Eyler, J. Chem. Phys. **92**, 358 (1990).

[12] D. Mathur, C. Brink, P. Hvelplund, N. Jensen, and D. H. Yu, Rapid Commun. Mass Spectrom. **9**, 114 (1995).

[13] A. A. Radzig and B. M. Smirnov, in *Reference Data on Atoms, Molecules and Ions* (Springer-Verlag, Berlin, 1985), p. 87.

[14] I. V. Hertel, H. Steger, J. de Vries, B. Weisser, M. Honka, B. Kamke, and W. Kamke, Phys. Rev. Lett. **68**, 784 (1992).

[15] H. Steger, J. de Vries, B. Kamke, and W. Kamke, Chem. Phys. Lett. **194**, 452 (1992).

[16] G. Javahery, H. Wincel, S. Petrie, and D. K. Bohme, Chem. Phys. Lett. **204**, 467 (1993).

[17] D. C. Lorents, G. Black, and O. Heinz, Phys. Rev. A **137**, 1049 (1965).

[18] S. Petrie, J. Wang, and D. K. Bohme, Phys. Lett. A **204**, 473 (1993).

[19] C. W. Walter, Y. K. Bae, D. C. Lorents, and J. R Peterson, Chem. Phys. Lett. **195**, 543 (1992).

[20] A. A. Scheidemann, V. V. Kresin, and W. D. Knight, Phys. Rev. A **49**, R4293 (1994).

[21] A. Bárány, in *Proceedings of the XVIth International Conference on the Physics of Electronic and Atomic Collisions*, edited by A. Dalgarno *et al.*, AIP Conf. Proc. No. 205 (AIP, New York, 1990), p. 246.

[22] A. Bárány and C. J. Setterlind, Nucl. Instrum. Methods Phys. Res. Sect. B **98**, 184 (1995).

[23] P. Scheier and T. D. Märk, Phys. Rev. Lett. **73**, 54 (1994).