Resonant Electron Transfer in Collisions between Two Fullerene Ions

H. Bräuning,* R. Trassl, A. Diehl, A. Theiß, and E. Salzborn
Institut für Kernphysik, Justus-Liebig-Universität, Leihgesterner Weg 217, D-35392 Giessen, Germany

A. A. Narits and L. P. Presnyakov
P.N. Lebedev Physical Institute, 117924 Moscow, Russia
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Fullerenes are a direct link between atoms with discrete electronic energy levels and solids with a band structure and a well-defined surface. In this Letter, we report on the first ever experiment on resonant electron transfer in collisions between two fullerene ions. Total cross sections have been measured for the reaction $C_{60}^{+} + C_{60}^{2+} \rightarrow C_{60}^{2+} + C_{60}^{+}$ at center-of-mass energies ranging from 27 to 69 keV. Surprisingly, within the error bars, these cross sections are identical to the respective cross sections for $C_{60}^{+} + C_{60}$ measured by Rohmund and Campbell [J. Phys. B **30**, 5293 (1997)]. We show that the experimental data for both collision systems are very well reproduced by a quantum mechanical treatment of the reaction based on the concept of hole particles and the polarizability of the fullerene molecule.

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Fullerenes in general and fullerene ions, in particular, offer new opportunities to study the interaction of extended structures. In collision experiments, both between energetic ions and neutral C_{60} molecules [1] as well as between charged fullerene projectiles and neutral targets [2–4], the fundamental processes of electron transfer and ionization have been studied extensively. In the case of electron transfer, fullerenes are often considered as a conducting sphere with the valence electrons populating very delocalized orbitals. The electrons can therefore move freely on the sphere in a manner that is similar to the free electron movement in the conduction band of a solid. This is reflected in the large dipole polarizability [5] of 540 a_0^3 (a_0 is the Bohr radius) as compared to 140 a_0^3 for sodium, which has one of the largest dipole polarizabilities for an atom. The importance of polarization in a fullerene target has already been shown using electron-impact ionization of negatively charged fullerene ions [6] and in an earlier work by Shen *et al.* [4] who have proposed a model based on sequential single-electron transfer to explain their measured cross section for double electron capture by C_{70}^{3+} from neutral C_{60}. Within this model the cross section is determined by the single-electron transfer cross section from the intermediate C_{60}^{+} ion to the intermediate C_{70}^{2+} ion and thus by the collision dynamics between two fullerene ions.

In this Letter, we present the first ever experimental data on collisions between two fullerene ions. We have investigated the resonant electron transfer for the reaction $C_{60}^{+} + C_{60}^{2+} \rightarrow C_{60}^{2+} + C_{60}^{+}$ which probes directly the validity of the model proposed by Shen *et al.* [4]. We further present a quantum treatment expanding on this model, which also reproduces very well the experimental data for the reaction $C_{60}^{+} + C_{60} \rightarrow C_{60}^{+} + C_{60}$ at much lower collision energies [7].

Our ion-ion crossed beams experimental arrangement (Fig. 1) [8,9] provides an ideal tool to enable studies of a wide range of ion-ion collision systems. In the present Letter, two electron cyclotron resonance (ECR) ion sources [10] provide a C_{60}^{+}-ion beam with 3 keV energy and a C_{60}^{2+}-ion beam with energies in the range of 80–180 keV. The ion beams are crossed at an angle of 17.5° in an ultrahigh vacuum collision chamber. After the interaction, the product ions are separated from the parent beams by electrostatic analyzers and detected by a Channeltron (low energy beam) and a position sensitive Micro-Channel Plates (MCP) detector (high energy beam). In order to minimize the background contribution from collisions with the residual gas in the interaction region, a pressure of better than 10^{-10} mbar is maintained. In spite of this low pressure the background contribution on the detectors is still a factor of 10^3 to 10^4 (depending on the ion) higher than the reaction rate of 0.4 true events per second for typical beam currents of about 1 to 2 nA. However, the coincident detection of the product ions in their respective detector provides a

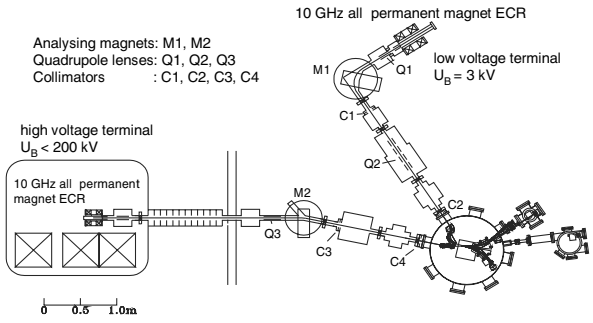

FIG. 1. Schematic overview of the Giessen ion-ion experiment [8,9].

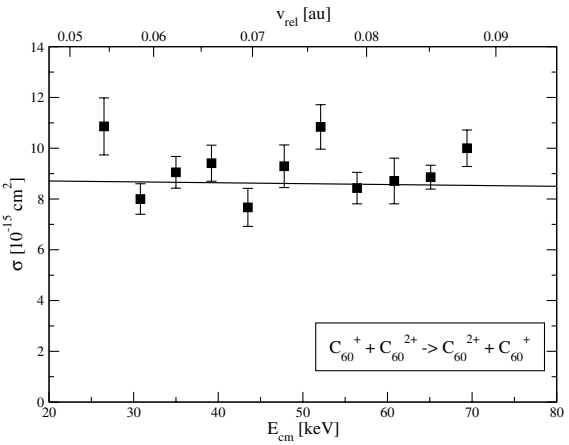

FIG. 2. Total cross sections for the resonant electron transfer in $C_{60}^{+} + C_{60}^{2+}$ collisions vs the center-of-mass energy. Solid squares, present experimental data; solid line, present theoretical calculations. The error bars represent the statistical error at 67% confidence level.

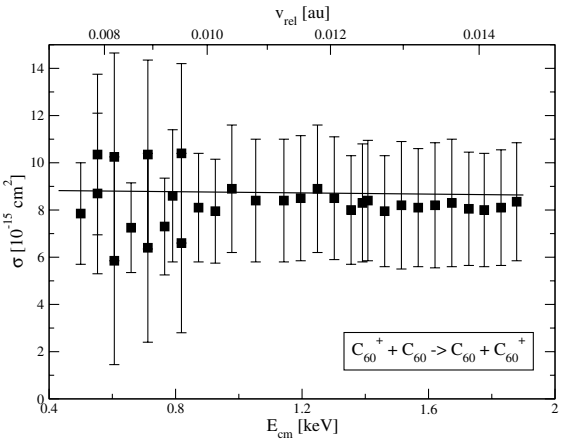

FIG. 3. Total cross sections for the resonant electron transfer in $C_{60}^{+} + C_{60}$ collisions vs the center-of-mass energy. Solid squares, experimental data by Rohmund and Campbell [7]; solid line, present theoretical calculations.

powerful tool for signal recovery and gives a clear signal of the electron transfer reaction. The use of a position sensitive detector for the C_{60}^{+} reaction products in principle enables the measurement of the scattering angle of these ions. It also provides information about possible fragmentation, which, however, contributes only very weakly.

The measured absolute cross sections for the reaction $C_{60}^{+} + C_{60}^{2+} \rightarrow C_{60}^{2+} + C_{60}^{+}$ as a function of the center-of-mass energy is shown in Fig. 2 together with our theoretical calculations. The systematic error of the experimental data is mainly determined by the error of the detector efficiencies. These have been measured and are $(64 \pm 14)\%$ for the Channeltron and $(31 \pm 1)\%$ for the MCP, respectively. The efficiencies are significantly lower than for atomic ions of comparable energy, which we attribute to the very low velocities of the heavy fullerenes. The systematical error thus amounts to 22%.

Most surprisingly, the measured cross sections virtually coincide with the data by Rohmund *et al.* [7] for the reaction $C_{60}^{+} + C_{60} \rightarrow C_{60} + C_{60}^{+}$ at much lower collision energies between 0.5 and 1.9 keV (Fig. 3). As is expected from a resonant system, no significant dependence on the collision energy is found within the error bars.

We therefore analyze our experimental data for resonant electron transfer between singly and doubly charged fullerene ions, $C_{60}^{+} + C_{60}^{2+}$, jointly with those [7] for collisions of singly charged ones with neutral fullerenes, $C_{60}^{+} + C_{60}$. For both processes, we use the same model in which we consider the positively charged fullerene ions in a collision as cages with well-defined positive charges that can move freely over the surface [4,11]. According to Shen *et al.* [4], the positive charges of the colliding fullerene ions should be localized along the intermolecular axis in the region of the closest approach (Fig. 4) as a result of the strong polarizability of the fullerenes. Electron transfer occurs in the vicinity of the closest approach near the axis between the centers of the colliding ions [Fig. 4(b)]. The two outermost positive charges in this figure are screened by the respective fullerene cage and the dynamics of the electron transfer process in $C_{60}^{+} + C_{60}^{2+}$ collisions is the same as in $C_{60}^{+} + C_{60}$ collisions if the relative velocity of the colliding particles is much smaller than the orbital velocity of the transferred electron. With a maximum collision velocity of 0.09 a.u. in our experiments as compared to an orbital velocity of 0.75 a.u. for the active electron this condition is clearly fulfilled. A similar polarization effect has been also observed [6] for the case of electron-impact ionization of negatively charged fullerene ions.

In the theory of many-particle systems, the analysis of the behavior of vacancies, i.e., hole particles, instead of real particles is a well-known tool, e.g., in the theory of the atomic spectra of complex atoms [12] and in solid state physics [13,14]. In this approach, a reduction of the many-body to a few-body problem helps to simplify

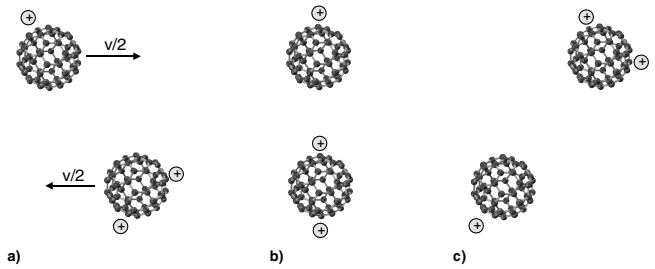

FIG. 4. Representation of the electron transfer process $C_{60}^{+} + C_{60}^{2+} \rightarrow C_{60}^{2+} + C_{60}^{+}$ in terms of moving positive charges. For large distances before (a) and after (c) the collision the localization of the positive charges is determined by their mutual repulsion. At closest approach (b) the positive charges align along the axis due to the polarizability of the fullerene.

greatly all the calculations, especially in relation to the permutation properties of the many-particle systems. Another important question is the symmetry group of the two colliding fullerenes. The isolated (free) fullerene molecule C_{60}, neutral or ionized, posesses icosahedral symmetry [15,16] whereas the symmetry of the two C_{60} fullerenes at slow collisions cannot be higher than cylindrical (uniaxial-isotopic). The model discussed above corresponds to this lower symmetry, which is exactly the same as for atomic (i.e., ion-atom or ion-ion) collisions. Therefore, one can apply the well established theories of ion-atom collisions [17].

We consider electron transfer as the under- and overbarrier transition of a hole particle from the target to the projectile. At small relative velocities one can neglect the fragmentation of the fullerenes. More precisely, we consider peripheral collisions, which give the main contribution to the cross section. The problem of the shape of the static barrier between two isolated, infinitely conducting spheres is of interest for many applications. Recently this problem was solved [18] in terms of an infinite series, which is rather complicated. We are interested only in the description of the barrier in the close vicinity of the axis between the centers of the two spheres and use simple analytical models for identical spheres with very large radii [19]. In all cases, one gets a symmetric barrier for the resonant electron transfer in symmetric collision systems. Both methods, [18,19], result in identical expressions in the region of interest.

Near the axis between the centers of projectile and target, the barrier reduces to one dimension. The Schrödinger equation then reads

$$\left\{\frac{d^2}{dx^2} + \frac{2m}{\hbar^2}[E(R) - U(R|x)]\right\}\psi(R|x) = 0. \qquad (1)$$

Here $\hbar$ is the Planck constant, x and m are the electron coordinate and mass, respectively, and $E(R)$ is the binding energy of the electron including the static Stark shift. $U(R|x)$ is the potential energy of the barrier and will be discussed in a forthcoming more specialized paper. The distance between the centers of the two fullerenes, $R = R(b, t)$, is considered as a given function of the time and the impact parameter. The cases of $E - U > 0$ and $E - U < 0$ correspond to the overbarrier and underbarrier transitions, respectively. It is well known that the barrier between two isolated, infinitely conducting spheres has Coulomb-type poles at the points where the axis between the centers of the two spheres intersects the surface of each sphere (see [18,19]). These poles result in additional nonphysical eigenstates of Eq. (1). Quantitatively, these states are visible in so-called phase-shift jumps that follow from the Levinson theorem (see, for example, [20,21]). In order to eliminate this nonphysical effect, we cut the potential near the two spheres and obtain two identical potential wells of finite depth separated by the barrier. The potential wells have a maximum depth at which the nonphysical states vanish. In our case, the depth of the potential well relative to the limit of the one-electron continuum was $U_0 = 15.2$ eV. This value results from a numerical solution of the phase equations [20,21] discussed below [see Eqs. (9) and (10)]. It is more convenient to take the energy values in Eq. (1) relative to the bottom of the potential well. Using $k^2(R) = (2m/\hbar^2)[E(R) + U_0]$ and $2V(R|x) = (2m/\hbar^2)[U(R|x) + U_0]$ we substitute

$$\frac{2m}{\hbar^2}[E(R) - U(R|x)] = k^2(R) - 2V(R|x), \qquad (2)$$

and solve Eq. (1) with the help of the phase-shift approach [20,21]. Both k^2 and $2V$ are positive, and their difference is positive for the overbarrier transitions and negative for the underbarrier penetration.

For a symmetric barrier, we employ the odd (ψ_o) and even (ψ_e) solutions of this equation as follows:

$$\psi_o(x) = k^{-1/2}A(x)\sin[kx + \delta(x)], \qquad (3)$$

$$\frac{d\psi_o(x)}{dx} = k^{1/2}A(x)\cos[kx + \delta(x)], \qquad (4)$$

$$\psi_e(x) = k^{-1/2}B(x)\cos[kx + \gamma(x)], \qquad (5)$$

$$\frac{d\psi_e(x)}{dx} = -k^{1/2}B(x)\sin[kx + \gamma(x)]. \qquad (6)$$

Here the amplitudes A and B are even functions of x and the phases δ and γ odd ones. In any symmetric interval $-x_0 \le x \le x_0$ the transition and reflection coefficients can be expressed in terms of the phase functions only; these are

$$T(x_0) = \{\exp[i\delta(x_0) + i\gamma(x_0)]\}\cos[\delta(x_0) - \gamma(x_0)], \qquad (7)$$

$$Q(x_0) = \{-i(\exp[i\delta(x_0) + i\gamma(x_0)])\}\sin[\delta(x_0) - \gamma(x_0)], \qquad (8)$$

respectively. The two independent phase equations have the form

$$\frac{d\delta}{dx} = -\frac{2V}{k}\sin^2(kx + \delta), \qquad \delta(0) = 0, \qquad (9)$$

$$\frac{d\gamma}{dx} = -\frac{2V}{k}\cos^2(kx + \gamma), \qquad \gamma(0) = 0, \qquad (10)$$

where $k = k(R)$ includes the static Stark shift and $V = V(R|x)$. In our case we have $x_0 = \frac{R}{2} - a$, where a is the radius of the conducting sphere. The phase equations (9) and (10) were solved numerically. It is worth noting that contributions from underbarrier transitions result in an increase of 10% to the total cross sections.

Integration over all values of t can be done with the help of the so-called decay model [17]. The electron

transfer probability is equal to

$$P(b) = 1 - \exp\left\{-\int_{-\infty}^{\infty} dt |T\left[\frac{R(b,t)}{2} - a\right]|^2\right\}. \quad (11)$$

Here the integral should be evaluated over the straightline or hyperbolic Coulomb trajectory for collisions $C_{60}^+ + C_{60}$ and $C_{60}^{2+} + C_{60}^+$, respectively. In our case, however, the difference between the straightline and hyperbolic trajectory calculations is very small for peripheral collisions.

In order to use the general quantum mechanical analysis, we employ the correspondence principle that connects the impact parameter b with the orbital momentum quantum number l of the relative motion for large l: $Mvb = \hbar l$. Here M is the reduced mass of the colliding system and v the relative velocity. The barrier transition probability (11) then corresponds to the scattering matrix element for the electron transfer process at a given orbital momentum l.

$$P(b) = |S_{if}(l)|^2. \quad (12)$$

It is worth noting that the characteristic values of the orbital momentum are rather large with $l \approx 10^4$ even when the relative velocity is not larger than $10^{-2}v_0$, where $v_0 = 2.19 \times 10^8$ cm s^{-1} is the atomic unit of velocity. The total cross section for charge transfer is equal to

$$\sigma = \pi a_0^2 \left(\frac{mv_0}{Mv}\right)^2 \sum_l (2l+1)|S_{if}(l)|^2, \quad (13)$$

where $a_0 = 0.529 \times 10^{-8}$ cm is the Bohr radius, m is the electron mass, and M and v are the reduced mass of the colliding system and the velocity of the relative motion, respectively. The quantal form (13) may be more suitable in some respects than the semiclassical one, especially for the analysis of the angular differential cross sections.

The model of screened outer charges (see Fig. 4) used here reduces electron exchange between the two fullerene ions to exchange between the neutral and singly ionized fullerenes. Comparison of the experimental data with the theory in Figs. 2 and 3 confirms the applicability of this model. The calculations of the $C_{60}^{2+} + C_{60}^+$ collision system without screening the outer charges result in cross sections being a factor 2 lower than the experimental data. In our calculations we used the following parameters: the radius of C_{60}, C_{60}^+, and C_{60}^{2+} is the same and equal to 8.2 a.u. [22] and the ionization potential of C_{60} is equal to 7.6 eV [23].

The cross sections for both processes are virtually equal to each other and depend logarithmically on the center-of-mass energy. The equality of the two cross sections confirms that the model discussed here may be considered a realistic description for slow collisions. This is also different from collision systems with atomic ions or small molecules, where significant differences between ion-atom and ion-ion collisions are found. It clearly shows the status of fullerenes as a bridge between atoms and solids.

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*Electronic address: Harald.Braeuning@strz.uni-giessen.de

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