Collision Energy Dependence of Molecular Fusion and Fragmentation in $C_{60}^+ + C_{60}$ Collisions

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(Received 4 December 1995)

Interactions between systems with a large but finite number of degrees of freedom play an important role in many branches of physics ranging from nuclear collisions to collisions between galaxies. We report the first experimental collision energy dependence of the fusion cross section for atomic cluster-cluster collisions and compare the results with quantum molecular dynamics calculations and a phenomenological fusion model. In addition, we discuss the similarities and differences to nuclear heavy ion collisions. [S0031-9007(96)00086-5]

PACS numbers: 36.40.–c

In order to obtain a more complete understanding of the dynamical behavior of systems with a large but finite number of degrees of freedom and to develop phenomenological models which are able to describe the basic behavior of such systems, covering many orders of magnitude in size, it is necessary to extend systematic experimental investigations, until now only available for nuclear collisions [1], to larger bodies. Calculations of metallic cluster-cluster collisions [2–5] have predicted the occurrence of reaction channels which show very close similarities to those observed in heavy ion collisions and have been termed "complete fusion," "quasielastic scattering," and "deep inelastic scattering," in analogy to nuclear collisions [2]. An experimental verification of these predictions is, however, not feasible at the present time due to the difficulties of obtaining mass selected projectile and target metal clusters of sufficient intensity to enable collision experiments to be carried out. For this reason we have decided to carry out the first systematic experimental and theoretical investigations for fullerene-fullerene collisions.

Our experimental setup has been discussed in detail before [6,7] and consists of a C_{60}^+ ion beam, a target gas chamber containing neutral fullerenes heated to a temperature of about 450 °C, and a reflectron time-of-flight mass spectrometer to detect the product ions with an acceptance angle of $0° \pm 0.6°$. A number of improvements have been made to the experiment since the initial report where we showed that fusion products could be formed between fullerenes at collision energies between 200 and 500 eV [6]. The laser desorption ion source has been replaced with an electron impact ionization source which provides better control and reproducibility and allows us to work at a higher repetition rate thus improving the signal to noise ratio. The mass selection of the projectile beam has been improved to ensure that we have only C_{60}^+ present and we use pure (>99%) C_{60} as the target material. The primary ion beam intensity is monitored by deflecting the ions before they enter the collision cell and measuring the current with a channel plate detector. This, along with the careful control of the temperature of our collision cell, allows us to determine absolute values for the fusion cross section. Details will be given elsewhere [8]. The improved experimental setup has enabled us to show that the initial, preliminary results obtained at a relatively high collision energy in the center of mass frame of 200 eV, reported in [6], were due predominantly to collisions between fullerene ions and C_{70} [8].

Figure 1 shows experimentally determined cross sections for the fusion of C_{60}^+ with neutral C_{60} (>99% purity) as a function of $1/E$ under single collision conditions. All collision energies discussed below will be in the center-of-mass frame of reference. The fusion signal can first be observed for collision energies between 60 and 70 eV, reaching a maximum at approximately 140 eV and disappearing abruptly at about 200 eV. (In our initial report [6]

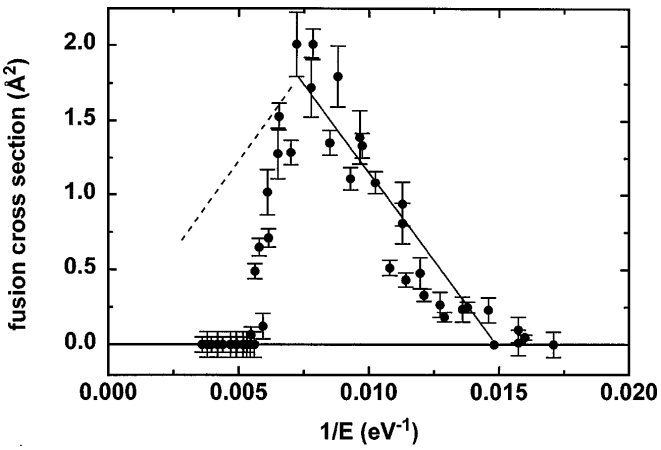

FIG. 1. Experimental absolute fusion cross sections as a function of $1/E$. The full line is a least squares fit to the experimental data points in the low energy range [≤130 eV Eq. (2)], the dashed line is the expected energy dependence if the instability of the fused compound is due to centrifugal fragmentation [Eq. (4)].

of the occurrence of molecular fusion in fullerene collisions we observed a fusion signal at 200 and 250 eV which we now know to be due to collisions between fullerene ions and C_{70} [8].) In Fig. 2 we have plotted the maximum, minimum, and average cluster sizes produced from the fusion reaction as a function of collision energy. At low energies very little fragmentation is observed. The product mass distribution broadens and moves to lower masses as the collision energy is increased.

It is to be expected that the hot C_{120}^+ formed in the collision will cool by successive evaporation of C_2 molecules on the time scale of the experiment. The full line in Fig. 2 gives the cluster size we would expect to see if such a cooling mechanism was taking place. We have ignored the effects of additional cooling channels such as radiative cooling [9] in this simple model. For the peanutlike structures of the fusion compounds (see below) relatively low binding energies of some few eV are expected [10]. Therefore, no release of binding energy has been considered. The calculations, based on an evaporation model discussed by Klots [11], provide a plausible explanation for the observed shift in the mass distribution of the products but cannot explain the abrupt disappearance of a product signal for $E \approx 200$ eV.

In order to obtain microscopic insight into the collisional dynamics we have performed a systematic investigation of $C_{60}^+ + C_{60}$ collisions using molecular dynamics combined with density-functional theory in the local density approximation and in a linear combination of atomic orbitals representation (hereafter referred to as quantum molecular dynamics). The ingredients of our approach have been described previously [12–14]. A large number of collision events with randomly chosen initial orientations of the two fullerenes was simulated to explore the whole range of fusion-relevant incident energies $E \approx 0, \ldots, 250$ eV and impact parameters $0 \leq b \leq R_{12}$ with $R_{12} = R_1 + R_2 \approx 14a_0$, the contact radius of the two cages.

At high collision energies ($E = 500$ eV) we have previously found the dominant reaction channel to be multifragmentation connected with collective-flow effects [11,12]. Within the energy range of interest here, $E \leq 250$ eV, the observed reaction channels can be classified according to three categories: complete fusion, deep inelastic collisions, and fragmentation reactions, as illustrated in Fig. 3. In complete fusion a compound C_{120}^+ cluster is formed which completely loses its memory of the entrance channel. Full momentum transfer occurs and the excited compound decays by subsequent evaporation of small fragments. In deep inelastic scattering, the two-cluster system decays into two deformed and highly excited products with masses in the vicinity of the projectile and target mass. The interaction time is very short (typically a few tenths of a picosecond). In a fragmentation

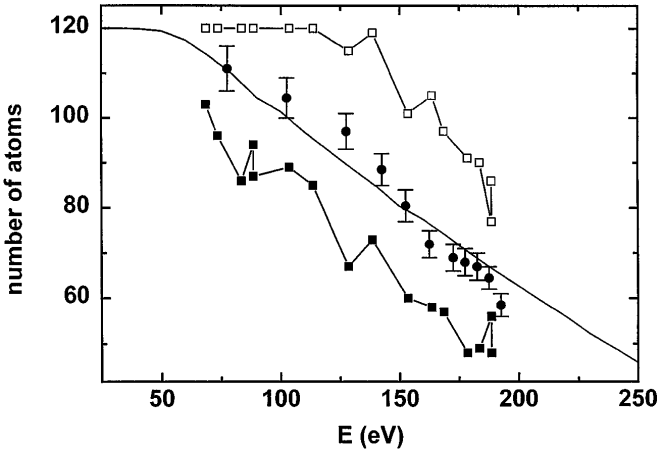

FIG. 2. Maximum (open squares), minimum (full squares), and average (full circles) carbon cluster mass observed experimentally as the product of a fusion reaction as a function of collision energy. The double points at some energies are the result of two separate measurements. The full line is an estimate of the cluster size that would be expected assuming a statistical thermal evaporation of C_2.

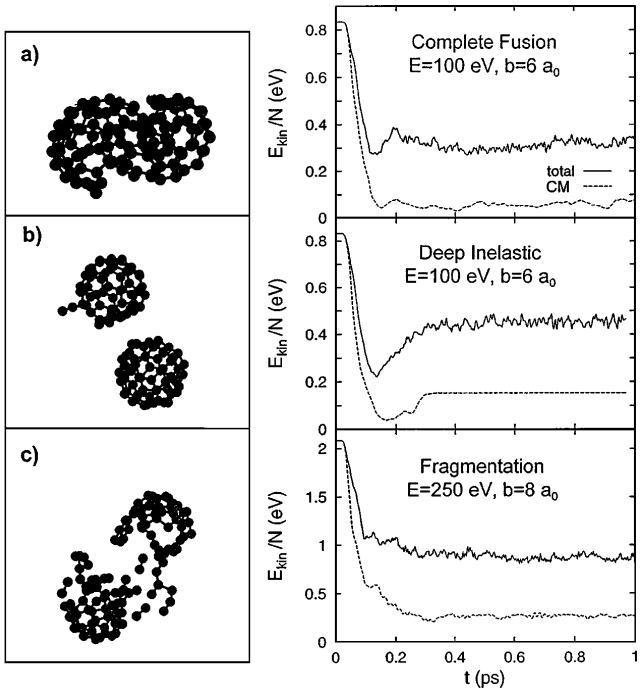

FIG. 3. Left: Snapshots from the time evolution in quantum molecular dynamics simulations of $C_{60}^+ + C_{60}$ collisions for three typical events characterizing the reaction channels (a) complete fusion (after $t = 1$ ps), (b) deep inelastic collision (after $t = 0.36$ ps), and (c) fragmentation (after $t = 0.24$ ps). Different (randomly chosen) initial orientations of the C_{60} cages are used for the two events with $E = 100$ eV and $b = 6a_0$ (a) and (b). Right: Calculated total kinetic energy per atom (full lines) and center-of-mass kinetic energy per atom of the relative motion between the two C_{60} clusters (dashed lines) for the same quantum molecular dynamics simulations. The difference between the curves represents the internal vibrational excitation energy of the system.

event the two-cluster system formed during the approach (ca. 0.1 ps) decays simultaneously into a number of products within some tenths of picoseconds.

Because of the small acceptance angle of the reflectron in the experiments the reaction products observed will come predominantly from complete fusion. The thermal evaporation of dimers or other small fragments should not deflect the heavy product ions from the beam sufficiently to lead to a loss of signal. On the other hand, deep inelastic scattering and fragmentation would be expected to lead to large scattering angles for the product ions which could therefore not be detected with the present experimental setup. The onset of fragmentation is the most likely reason for the abrupt disappearance of the fusion signal seen experimentally. The collision energy at which this occurs ($\approx$200 eV) is in very good agreement with the quantum molecular dynamics calculations.

In our quantum molecular dynamics calculations, no complete fusion events are found for energies below 80 eV. This upper-limit estimate of the fusion barrier (V_B) agrees very well with that obtained in tight-binding molecular dynamics studies which found a barrier of 84 eV [15], whereas classical molecular dynamics calculations give a considerably larger value of approximately 120 eV [16]. These values are larger than the experimental value of 66 $\pm$ 7 eV (see discussion below and Fig. 1), however, in the experiment, the projectile ion beam has a finite temperature which will lower the fusion barrier. When the classical [16] and tight-binding [15] molecular dynamics simulations were carried out at an initial temperature of 2000 K in both clusters the fusion barrier was seen to lie in the region between 60 and 70 eV for both studies. The temperature in these simulations was somewhat higher than that estimated for the experimental conditions so it would seem that they slightly overestimate the fusion barrier.

The dissipation of the impact energy into irreversibly stored heat energy of the intrinsic degrees of freedom is one of the necessary conditions of any fusion process between complex particles. The energy-dissipation process of a typical fusion event is shown in the upper part of Fig. 3. The most important aspect of these results concerns the behavior of the total kinetic energy of the system after fusion which is less than the impact energy and remains practically constant on the time scale of the simulations. This is in striking contrast to the fusion mechanism predicted for metallic cluster-cluster collisions [2] as well as that in nuclear fusion [1] where, due to the gain of binding energy, the total kinetic energy in the fused system is generally larger than the impact energy. The same would be the case in the fusion of two C_{60} if the most stable cagelike isomer of the fused compound cluster C_{120} was produced ($\Delta E \approx 20$ eV [10]). Instead, a highly deformed "peanut" isomer is formed in typical fusion events (cf. Fig. 3). This effect is a consequence of the strongly directed covalent bonds in the fullerenes in contrast to the nondirected bonds in metallic clusters and atomic nuclei. It drastically reduces the final vibrational energy and thus stabilizes the fused compound against evaporation. This is the main reason why even C_{120} clusters can be observed experimentally (on a time scale of microseconds) up to large collision energies of about 120 eV as shown in Fig. 2.

The second characteristic result concerns the general increase of the center-of-mass (and also total) kinetic energy after the system has reached the distance of closest approach (corresponding to the first minima of the kinetic energy in Fig. 3). This "bouncing off" mechanism clearly shows that part of the stored potential energy can be converted back into that of relative motion. This nondissipative mechanism has important consequences for the absolute value of the fusion cross section (see below). Fragmentation, however, occurs on a shorter time scale (see caption of Fig. 3), inhibiting complete transformation of the collision energy into internal energy. As a consequence there is no minimum in the kinetic energy curve in Fig. 3 for this reaction channel, and therefore no bouncing off mechanism is observed.

The third basic property of $C_{60}^+ + C_{60}$ collisions is that, at a given impact energy and impact parameter, the observed reaction channel is strongly dependent on the initial orientation of the two clusters. This is demonstrated in the upper and middle parts of Fig. 3 where different reaction channels (complete fusion and deep inelastic scattering) are observed in the exit channel for the same impact parameter and impact energy but different initial orientations of the colliding clusters. This effect originates from the strong directional dependence of the interatomic forces in these covalent systems which results in an orientational-dependent effective force between both clusters. This important property of the dynamics, together with the nondissipative bouncing off mechanism discussed above, finally leads to the "fingerprint" of fusion between two C_{60}: Fusion appears to be a very rare process, from the 228 simulated trajectories in the energy range $80 \leq E \leq 100$ eV above the fusion barrier only a very small fraction (13 events) leads to fusion, resulting in a mean fusion probability $\overline{P}$ of only $\approx$0.057. This is in striking contrast to fusion between metallic clusters [2] as well as atomic nuclei [1].

Besides the exact quantum molecular dynamics calculations phenomenological fusion models based on transparent assumptions about the underlying mechanism can provide an intuitive picture of the real situation. In the following, we derive a simple phenomenological model for $C_{60}^+ + C_{60}$ collisions and point out the similarities and differences to the fusion of metallic clusters [2–5] and atomic nuclei [1].

The angular momentum $l_{CF}(E)$ below which fusion occurs can be estimated from the centrifugal barrier

$$E \approx V_B + \hbar^2 l_{CF}^2(E)/2\mu R_{12}^2 , \qquad (1)$$

where μ is the reduced mass of the collision partners. It is assumed that the barrier radius does not depend on l and is located in the vicinity of the contact radius R_{12}. One obtains by integration

$$\sigma_{CF}(E) = \pi R_{12}^2(1 - V_B/E)\overline{P} \quad (2)$$

for the fusion cross section as a function of E. In this "sharp cutoff" approximation, $\overline{P}$ is the mean fusion probability (assumed to be energy and angular momentum independent) and $l_{CF}(E)$ the maximum angular momentum which contributes to fusion. In nuclear heavy ion collisions this probability is $\overline{P} = 1$ due to very strong frictional forces between the two nuclei [1]. One may expect $\overline{P} \leq 1$ for the fusion of metallic clusters because the strong energy and angular momentum dissipation leads to an irreversible transfer of relative kinetic energy into intrinsic heat [2–4]. As discussed above, in $C_{60}^+ + C_{60}$ collisions the kinetic energy of the relative motion is not completely converted into heat energy. This bouncing off mechanism, together with the very sensitive dependence of the observed reaction channel on the initial orientation of the colliding clusters, leads to typical values of $\overline{P} \ll 1$ as one of the basic properties of fullerene fusion.

The linear fit in the low energy region of Fig. 1 allows us to determine the fusion barrier to be 66 ± 7 eV and, by making use of Eq. (2) with $R_{12} = 13.4a_0$ we can obtain a mean fusion probability of $\overline{P}^{\text{exp}} = 0.022$. This can be compared directly with the theoretical value of $\overline{P} \approx 0.057$ obtained by quantum molecular dynamics (above). Regarding the fact that there are fairly large experimental uncertainties in the determination of the absolute cross section as well as in the statistics of our calculations, this is a good agreement between theory and experiment and one may conclude that the phenomenological fusion model with the parameter $\overline{P}$, determined microscopically is, on average, well able to reproduce the absolute value of the measured cross section.

Equation (2) is, of course, only valid if the fused compound is stable against centrifugal fragmentation, i.e., if l_{CF} is smaller than a critical angular momentum l_{cr} [5]. Thus, for energies larger than

$$E_{cr} = V_B + \hbar^2 l_{cr}^2/2\mu R_{12}^2 \quad (3)$$

one expects a decrease of the fusion cross section as a function of E according to

$$\sigma_{CF} = (\pi\hbar^2/2\mu E)l_{cr}^2\overline{P}, \quad E \geq E_{cr}\,. \quad (4)$$

This result is represented by the dashed line in Fig. 1. From the maximum in the experimental fusion cross section one obtains $E_{cr} \approx 133$ eV and, hence, for the maximum angular momentum contributing to fusion $l_{cr} \approx 24 \times 10^3$ (or, equivalently, for the impact parameter $b_{cr} \approx 9.0a_0$). These values are again in very good agreement with the quantum molecular dynamics calculations where complete fusion has been observed only for impact parameters $b \leq 9.0a_0$. The decrease of the experimental fusion cross section above E_{cr} is, however, much stronger than that predicted by Eq. (4). As discussed above, this is most likely due to the onset of the fragmentation channel (Fig. 3) and may be indicative of a kind of "phase transition" occurring in the fused compound [17].

We thank K. Hansen for his help with the evaporative ensemble calculations and A. Glotov for his help with the experimental measurements. The work was supported by the DFG through SFBs 276 (Freiburg) and 337 (Berlin) and the EU through HCM Network "Formation, Stability and Photophysics of Fullerenes."

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