

THEORY -- OTHER

ON THE FORMATION OF DEUTERIUM FULLERENE COMPLEXES IN COLLISIONS OF C₆₀ WITH D₂

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It is well known that the highly symmetric C₆₀ fullerene is a very stable cluster [1]. However, C₆₀ is not an inert molecule. For instance, hydrogen can easily react with C₆₀ up to a C₆₀H₃₆ system in the so called Birch reaction [2]. On the other hand, the formation of endohedral C₆₀ or H₂@C₆₀ complexes seem to be not very favored. Weiske et al. [3] detected the formation He@C₆₀ complexes in high energy collision experiments, however the formation of D@C₆₀ or D₂@C₆₀, in collisions of D₂ with C₆₀ under comparable experimental conditions has not been observed [3]. In case of Helium the formation of He@C₆₀ has been verified experimentally [4,5] as well as by computer simulations [6]. However, more recent experiments [7] did show the formation of deuterium-C₆₀ complexes. The formation of endohedral and exohedral complexes have been found in μ -SR experiments on the ultralight hydrogen isotope C₆₀+ μ by Percival and Wlodek [8], and by Niedermayer et al. [9] for C₇₀+ μ . D₂ is of special interest because it has approximately the same mass as He. The calculated lowest barrier for penetration of hydrogen into the C₆₀ cage (3.8 eV [10], resp. 3.0 eV this paper, see section 3.1) is comparable to the penetration barrier of helium (6 eV [4]). In principle, a relatively high D-penetration barrier should offer the possibility of the formation of long living endohedral D@C₆₀ complexes, possibly in a similar way as endohedral He@C₆₀ complexes. Thus on D@C₆₀ and He@C₆₀ complexes the differences in the collision processes of atoms compared to molecules may be studied.

Molecular dynamics simulations of such processes have been successfully performed using empirical interaction potentials. More recently the combination of the Density-Functional-Theory within the Local Density Approximation (DFT-LDA) with Molecular Dynamics (MD) has been realized. A simplified LCAO-DFT-LDA scheme, which enables us to consider the electronic states in the calculation of the forces on the atoms, was developed and applied to simulations of molecular collisions. Furthermore, the relatively small computational effort of the LCAO-DFT-LDA method allows to consider statistics in the collision process, and in this way to calculate reaction cross sections and reaction rates of collisions of clusters or large molecules by (Monte Carlo) integration over impact parameters, averaging over different relative orientations of the collision partners, consideration of internal energies, and calculations at different collision energies.

The collision dynamics of C₆₀ with deuterium has been studied using an approximate LCAO-LDA scheme, combined with the Molecular Dynamics Statistical Trajectory Ensemble (MDSTE) method [11]. The MD simulations of D₂ + C₆₀ collisions show the encapsulation of deuterium, elastic scattering of D₂, dissociative scattering, and formation of exohedral C₆₀-D complexes (Fig. 1). The formation of deuterium C₆₀ complexes shows a distinct maximum between 20 eV and 30 eV collision energy. The kinetic energy in the formation of endohedral and exohedral complexes, respectively, is thermalized (≈ 0.1 eV/atom). Thus D-C₆₀ complexes should be accessible for observation.

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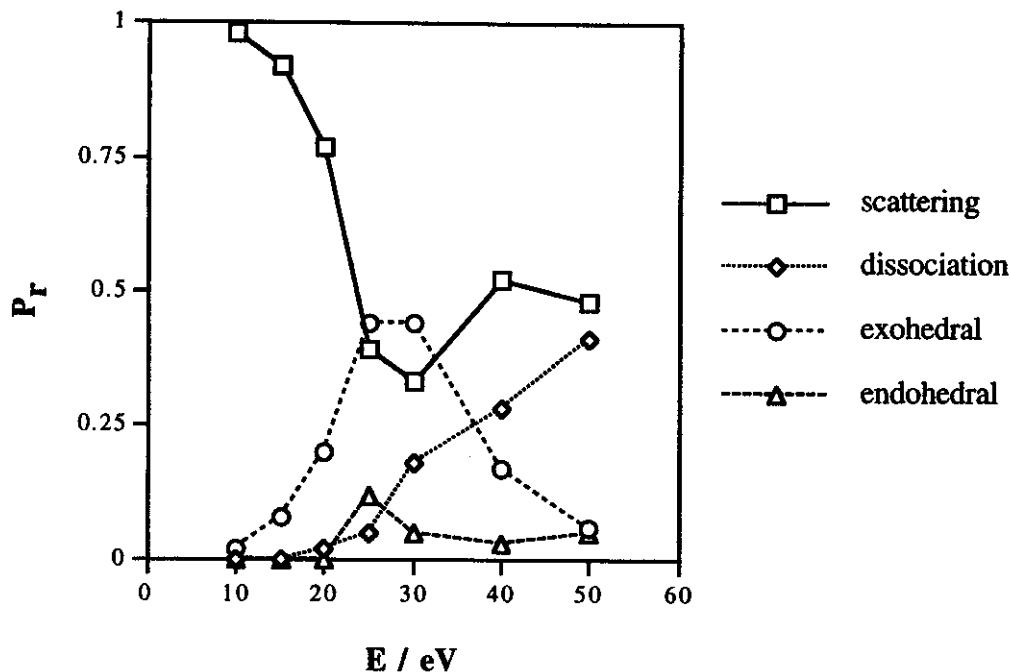


Fig. 1: Reaction probabilities (P_r) for the $C_{60}+D_2$ collision as a function of the center of mass collision energy.

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TIME RESOLVED FRAGMENTATION CROSS SECTION SIMULATION OF $C_{60}^+ + C_{60}$ COLLISIONS

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Recently the first cluster-cluster collision beam experiment has been performed successfully [1]. A cluster beam of laser ionized fullerenes C_{60}^+ (the * denotes that the clusters are thermally excited) was crossed with a C_{60} gas target at center of mass (c.o.m.) beam energies of some 10^2 eV. In this experiment the mass distribution and the energy transfer of the resulting charged reaction products were measured. The thermal excitation has been estimated 30 eV.

We have performed DFT-LCAO Molecular Dynamics Statistical Trajectory (MDSTE) Ensemble simulations of the high energy (500 eV) cross beam collision of $C_{60}^+ + C_{60}$ where the charged collision partner is thermally excited with an average vibrational energy of 30 eV. The electronic and ionic interaction of carbon atoms is approximated using the Hybrid MD-DFT method, i.e., LCAO-LDA as described in [2]. This approach has been successfully applied to the simulation of ion-trap experiments on $C_2^+ + D_2$ [3], and cluster beam experiments on $C_{60} + D_2$ [4], respectively. The application of the LCAO-LDA approximation of electronic interaction is justified by the high collision energy where the energy per atom is still some eV, i.e., there is no need for a full *ab initio* calculation to cover subtle meV details of the potential energy surface. Also, at the studied collision energy electronic excitation is not expected to occur.

The presented simulation suggests that in the 500 eV $C_{60}^+ + C_{60}$ collisions the multifragmentation process is favored opposed to the fission processes that have been suggested in recent high energy coincidence experiments [5]. Kinetic energy is spread uniformly over the colliding molecules soon after they got into contact, and before the first carbon monomers and dimers are evaporating. At the early steps of the collisions $t = 0.36$ ps the quasi-elastic and deep-inelastic collisions are forming large cluster compounds, and preferable dimers. Following the evaporation of small cluster fragments ($t = 0.78$ ps), medium size clusters ($N=20-40$) are formed along with fragments of size $N=2<20$, suggesting that multifragmentation processes have occurred ($t = 1.08$ ps). Though there are still large cluster compounds at this time step, the odd-even effect in the fragmentation spectrum is clearly visible. Thus, we conclude that the most stable fragments are determined during the actual break-off from the fullerene-like cluster compounds, and not by subsequent evaporation processes. This conclusion is supported by the fragmentation spectrum of our final simulation time step ($t = 2.1$ ps) where the fragmentation of the now thermally very excited C_{60} clusters is populating the cross sections of the small and medium cluster sizes, and, at the same time, sharpening the odd-even effect even more. Also, an enhanced formation of C_{10} clusters can be observed which due to its large cross section must have its origin mainly in the multifragmentation of the C_{60} clusters. In our simulation we have found a considerable cross section for finding C_{15} clusters, which is of from the usual odd-even sequence. Experimentally, the medium size cluster fragmentation range has not been investigated well enough yet to confirm the enhanced C_{15} cross section. The fragmentation cross sections of the final step of our simulation ($t = 2.1$ ps) is shown in Fig. 1.

With respect to the cluster' structures, at the beginning of the collisions ($t = 0.098$ ps) the clusters form large cluster compounds with fullerene-like structures ($nc \approx 3$), and small fragments with

chain-like structures ($n \leq 2$). As more fragments of different sizes are formed, a variety of structures with almost uniform distribution of coordination numbers ($1.5 \leq n \leq 3$) can be found. By the time the collision process is over, fullerene-like structures of fragments have decreased in favor of chain-like structures. An analysis of the structure of the $n_c \approx 2$ fragments is subject of current investigations.

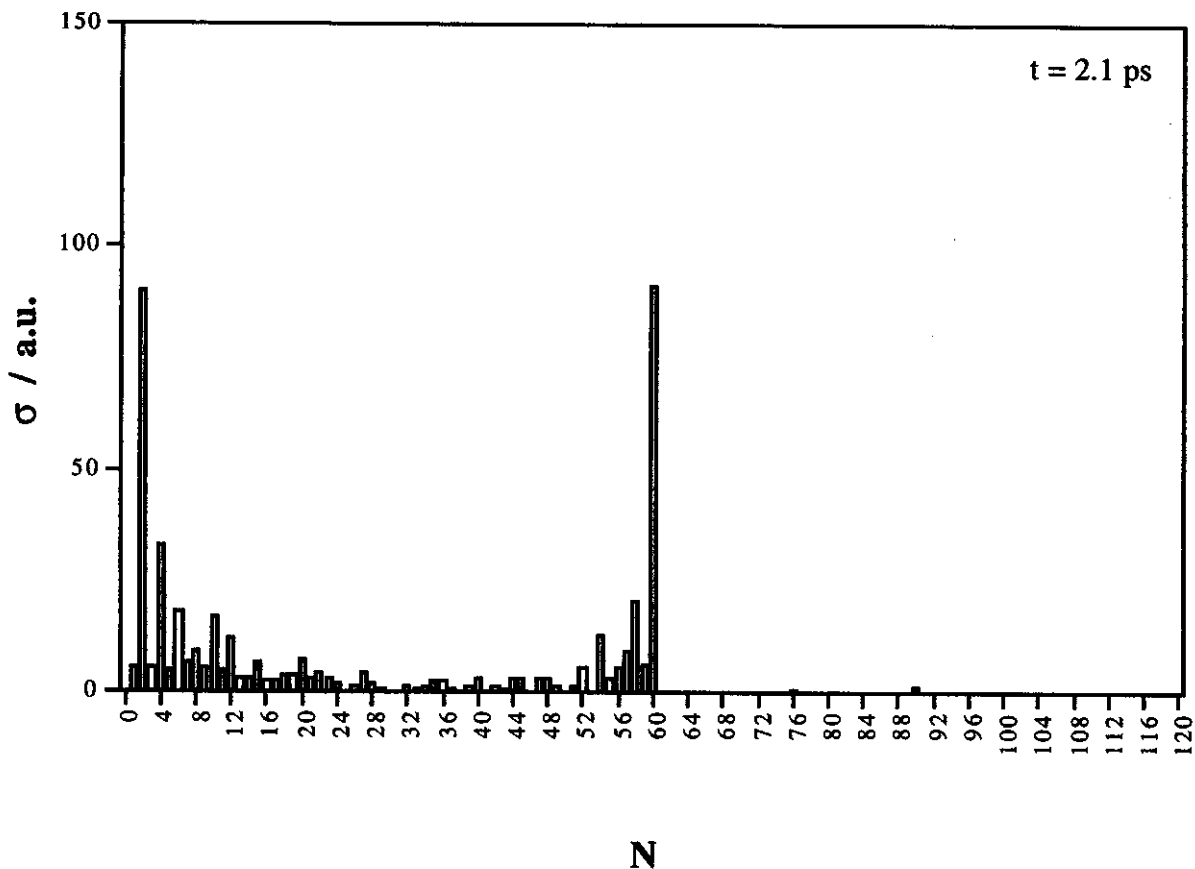


Figure 1: Fragmentation cross section of the simulated $C_{60}^+ + C_{60}$ collisions at simulation time step $t = 2.1$ ps.

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