Decay and fusion as two different mechanisms
of stability loss for the \((C_{20})_2\) cluster dimer

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ABSTRACT

The thermal stability of the \((C_{20})_2\) cluster dimer consisting of two \(C_{20}\) fullerenes is examined using a tight-binding approach. Molecular dynamics simulations of the \((C_{20})_2\) dimer at temperatures \(T = 2000 - 3500\) K show that the finite lifetime \(\tau\) of this metastable system is determined by two fundamentally different processes, the decay of one of the \(C_{20}\) fullerenes and the fusion of two \(C_{20}\) fullerenes into the \(C_{40}\) cluster. The activation energies for these processes \(E_a \approx 3.4\) and \(2.7\) eV, respectively, as well as their frequency factors, have been determined by analyzing the dependence of \(\tau\) on \(T\).
In 2000, after the experimental detection of the smallest fullerene $C_{20}$ [1], Fig. 1a, on the surface of which C-C bonds form only pentagons, whereas hexagons are absent (in contrast to $C_N$ fullerenes with $N > 20$), a problem of synthesizing the condensed phase (fullerite) based on this fullerene by analogue with the known fullerite based on $C_{60}$ fullerenes [2, 3] arised. Interest in this problem is stimulated, because the $C_{20}$ fullerite may be a high-temperature superconductor [4-6]. Indeed, preliminary calculations point to a possibility of formation of three-dimensional crystals consisting of $C_{20}$ fullerenes [4-6]. There is yet disagreement on the crystal structure of such a hypothetical cluster matter [5,6], but all authors agree that $C_{20}$ clusters in it should be connected with each other by strong covalent bonds. This is a fundamental difference of the $C_{20}$ fullerite from the $C_{60}$ fullerite in which clusters are bonded with each other due to a weak van der Waals attraction.

The strong intercluster interaction can significantly distort the shape of the $C_{20}$ clusters in the fullerite with respect to the spherical shape of the $C_{20}$ fullerene and, as a consequence, result in the transition to another crystalline (or even amorphous) modification. It seems to be reasonable to begin the analysis of the stability of the $C_{20}$ fullerite with the analysis of the stability of the simplest system consisting of two interacting $C_{20}$ fullerenes, the $(C_{20})_2$ cluster dimer. Experimental indications of the existence of charged $(C_{20})^\pm_2$ dimers [as well as complexes $(C_{20})^\mp_k$ with $k = 3 - 13$] were obtained in [7]. The dimerization of neutral fullerenes $C_{20}$ was theoretically studied in [4] and, most comprehensively, in [8], where eight different $(C_{20})_2$ isomers were found, their structural and energy characteristics were calculated, and it was shown that the so-called open-[2+2] isomer has the lowest energy, see Fig. 1b (numbers in the square brackets are the numbers of the atoms of each fullerene that are involved in the formation of intercluster bonds).
The aim of this work is to theoretically analyze the stability of the \((C_{20})_2\) dimer with respect to its transition to another atomic configuration. It is known (see, e.g., [9]) that the specific (per atom) binding energy of carbon clusters, which is defined as the difference between the energy of an isolated carbon atom and the specific potential energy of the \(N\)-atomic cluster, \(E_b(N)/N = E(1) - E_{pot}(N)/N\), increases with \(N\) (this is the property of the overwhelming majority of the elements of the Periodic Table, except for metastable clusters of nitrogen, helium, and some other elements [10, 11]). For this reason, it is energetically favorable for two (or several) carbon clusters to merge into one larger cluster, thereby increasing the binding energy [10] (i.e., reducing the potential energy), by analogy with fusion of light atomic nuclei. At the same time, our previous analysis [12] of the thermal stability of the isolated \(C_{20}\) fullerene showed that, when heated, it passes to various energetically unfavorable configurations with lower \(E_b\) values rather than to a more stable isomer with the maximum binding energy ("bowl"). This is due to the ability of carbon structures to form numerous intermediate metastable states separated by high energy barriers from configurations with a lower potential energy.

Since the \(C_{20}\) fullerenes in the \((C_{20})_2\) dimer are, on the one hand, at small distances from each other and hence strongly interact with each other and, on the other hand, both preserve the overall spherical shape (see Fig. 1b), the \((C_{20})_2\) dimer can loose its molecular structure both through the fusion of two \(C_{20}\) fullerenes to the \(C_{40}\) cluster and through the decay of one of them [12]. A question arises of which of two factors, thermodynamic (the minimum of the energy of the final product after fusion) or kinetic (the thermally activated transition to the metastable configuration with a high energy upon decay), finally determines the stability of the \((C_{20})_2\) dimer? To answer this question, we study the dynamics of the \((C_{20})_2\) dimer
numerically at high (sufficient to overcome the corresponding potential barriers \( U \sim 5 \) eV [12]) temperatures.

To calculate the energies of arbitrary atomic configurations, we used the tight binding model [13], which is a reasonable compromise between \textit{ab initio} calculations and too simplified empirical approaches with classical inter-atomic potentials. This model well describes both small clusters and macroscopic carbon structures. Previously, we used it to simulate the fullerenes \( C_{20}, C_{60}, \) and other carbon systems [10, 12, 14-18]. For the binding energy of an isolated \( C_{20} \) fullerene, this method gives \( E_b = 6.08 \) eV/atom [12] (in agreement with a value of \( E_b = 6.36 \) eV/atom obtained in \textit{ab initio} calculations [19]). For the binding energy of the open-[2+2] isomer of the \((C_{20})_2\) dimer, see Fig. 1b, this method gives a value of \( E_b = 6.20 \) eV/atom (which corresponds to the coagulation energy of two fullerenes \( \Delta E = 2E_{pot}[C_{20}]-E_{pot}[(C_{20})_2] = 4.9 \) eV, to be compared with the value \( \Delta E = 6.3 \) eV obtained by the density functional method [8]).

To analyze the thermal (it can also be called kinetic) stability of the \((C_{20})_2\) dimer, we study its dynamics numerically for the initial temperature \( T_{ini} = 2000 - 3500 \) K and fixed total energy \( E_{pot} + E_{kin} = \text{const} \), where \( E_{kin} \) is the kinetic energy in the center-of-mass system. In this formulation of the problem, the system temperature \( T \) is a measure of the energy of the relative motion of atoms (for more details, see [12, 17, 18]). The values of \( T \) were calculated by the formula \( \langle E_{kin} \rangle = \frac{1}{2}k_BT(3N - 6) \), where \( k_B \) is the Boltzmann constant, \( N = 40 \) is the number of atoms in the \((C_{20})_2\) dimer, and the angular brackets stand for averaging over \( 10^3 - 10^4 \) steps of the molecular dynamics simulation (the time of one step is \( t_0 = 2.72 \cdot 10^{16} \) s).

We observed two fundamentally different types of the \( T(t) \) dependence. They are shown
in Fig. 2. In the first case (Fig. 2a), the dimer temperature at $t \approx 4.4$ ns drops stepwise by $\Delta T \approx 200$ K. The decrease in temperature points to a decrease in the kinetic energy and, hence, an increase in the potential energy (because $E_{\text{pot}} + E_{\text{kin}} = \text{const}$). Therefore, the $(C_{20})_2$ dimer passes to a less favorable configuration. Our analysis showed that this transition is caused by the decay of one of the $C_{20}$ fullerenes, whereas the other fullerene preserved the cage shape, see Fig. 3a. The binding energy of the metastable state formed upon the decay is equal to (after the relaxation to the local minimum of the potential energy) $E_b = 6.14$ eV/atom, which is lower than the value of $E_b$ for the initial $(C_{20})_2$ dimer by $\Delta E_b = 0.06$ eV/atom. This $\Delta E_b$ value is consistent with the value $\Delta T \approx 200$ K, taking into account that, in thermal oscillations near the local minimum of the potential energy $E_{\text{pot}}^{\text{min}}$, the average kinetic energy of the system is approximately (up to anharmonic corrections) equal to the average increase in the potential energy $\Delta E_{\text{pot}} = E_{\text{pot}} - E_{\text{pot}}^{\text{min}}$, so that, since the total energy is constant, i.e., $E_{\text{pot}} + E_{\text{kin}} = E_{\text{pot}}^{\text{min}} + \Delta E_{\text{pot}} + E_{\text{kin}} \approx E_{\text{pot}}^{\text{min}} + 2E_{\text{kin}} \approx E_{\text{pot}}^{\text{min}} + 3Nk_B T$, in the $1 \rightarrow 2$ transition from the vicinity of one local minimum to the vicinity of the other local minimum, the relation $E_{\text{pot}}^{\text{min},1} + 3Nk_B T_1 \approx E_{\text{pot}}^{\text{min},2} + 3Nk_B T_2$ is valid, from which it follows that $\Delta T = T_1 - T_2 \approx \Delta E_b / 3k_B$ for $E_{\text{pot}}^{\text{min},2} > E_{\text{pot}}^{\text{min},1}$ taking into account the definition of $E_b$.

On contrary, for the second case (Fig. 2b), the temperature at $t \approx 4.4$ ns increases stepwise by $\Delta T \approx 200$ K. This indicates an increase in the kinetic energy, i.e., a decrease in the potential energy. Therefore, the system passes to the energetically favorable configuration. However, since the initial open-[2+2] isomer has the minimum energy among all $(C_{20})_2$ dimers, this transition indicates that the $C_{20}$ fullerenes loss their individuality and merge into the $C_{40}$ cluster. We analized the atomic structure after the temperature jump and showed that this is indeed the case. The $C_{40}$ cluster formed upon fusion is shown in Fig. 3b. It can be considered
as one of nonclassical, strongly imperfect isomers of the C$_{40}$ fullerene: the C-C bonds in it form not only pentagons and hexagons, but also two 9-member rings. The binding energy of this cluster after relaxation, $E_b = 6.25$ eV/atom, is higher than the value for the (C$_{20}$)$_2$ dimer by $\Delta E_b = 0.05$ eV/atom, which is consistent with a value of $\Delta T \approx 200$ K upon fusion.

We also observed the fusion of the C$_{20}$ fullerenes into isomers with higher binding energies. Fig. 4 shows the $T(t)$ dependence for the case, where an imperfect isomer of the C$_{40}$ fullerene with one heptagon and $E_b = 6.49$ eV/atom is formed upon fusion at $t \approx 0.34$ ns. At $t \approx 0.46$ ns, the annealing of the defect takes place and the C$_{40}$ fullerene with $E_b = 6.53$ eV/atom is formed, on the surface of which the C-C bonds form 12 pentagons and 10 hexagons, see Fig. 5. In this case, the temperature increases sequentially by $\Delta T \approx 1100$ and 150 K, which is consistent with changes $\Delta E_b$, see above. Transitions of the (C$_{20}$)$_2$ dimer into other isomers of the C$_{40}$ fullerene were also observed. The general statistics is as follows ($N_k$ is the number of $k$-gons with $k > 6$ in the C$_{40}$ isomer). Among 57 sets of the initial displacements and velocities of atoms that correspond to different initial temperatures $T_{ini}$, the fusion into the C$_{40}$ cluster with $N_9 = 2$ occurs most frequently (16 times), see Fig. 3b. In addition, the clusters with $N_{10} = 2$ and $N_8 = 1$ (six times); $N_9 = N_8 = N_7 = 1$ (once); $N_8 = 2$ (twice); $N_8 = N_7 = 1$ (once); $N_7 = 1$ (once); and $N_7 = 1$ (once) are formed. In other 29 cases, the decay of one of the C$_{20}$ fullerenes takes place (Fig. 3a). The further evolution of the system after it looses its molecular structure is as follows. The decay of one of the fullerenes in the (C$_{20}$)$_2$ dimer is followed by the decay of the second fullerene, while fusion of two fullerenes into the C$_{40}$ cluster is followed by the decay of this cluster, so that the final product is always a quasi-two-dimensional or quasi-one-dimensional configuration as in the decay of the isolated C$_{20}$ fullerene [12]. We never observed the return of the system to the initial open-[2+2]...
configuration. The fission of the (C\textsubscript{20})\textsubscript{2} dimer into two isolated C\textsubscript{20} fullerenes has not been observed as well.

There is correlation between the value of \(T_{ini}\) and the mechanism of the loss of the stability of the (C\textsubscript{20})\textsubscript{2} dimer. The loss of the molecular structure of the dimer occurs primarily due to fusion of two C\textsubscript{20} fullerenes into the C\textsubscript{40} cluster at \(T_{ini} < 2500\) K, due to the decay of one of the fullerenes at \(T_{ini} > 3000\) K, and due to both those processes at \(2500\) K < \(T_{ini} < 3000\) K, see Fig.6. To determine the activation energies \(E_{a}\) for the decay and fusion, we analyzed the temperature dependence of the lifetime \(\tau\) of the (C\textsubscript{20})\textsubscript{2} dimer, using the Arrhenius formula with the finite-heat-bath correction \([18, 20, 21]\)

\[
\tau^{-1}(T) = A \cdot \exp \left[ -\frac{E_{a}}{k_{B}T(1 - E_{a}/2CT)} \right].
\]  

Here, \(A\) is the frequency factor, \(C\) is the microcanonical specific heat, which we set to \(C = (3N - 6)k_{B}\), where \(N = 40\) (as will be shown below, \(E_{a}/2CT \approx 0.05 << 1\) for \(T \approx 3000\) K). Figure 6 shows the calculated logarithm of \(\tau\) as a function of \((T_{ini}^{*})^{-1}\), where \(T_{ini}^{*} = T_{ini}(1 - E_{a}/2CT_{ini})\), see Eq. (1). It is seen that this dependence in a quite wide range \(T_{ini} = 2000 - 3000\) K is given, in the first approximation, by the straight line for both the decay and fusion processes; i.e., \(A(T) \approx \text{const}\) (since the spread of the points is sufficiently large, particularly for fusion processes, it is impossible to reliably determine the temperature dependence of \(A\)). Using the slopes of these straight lines and the points of their intersection with the ordinate axis, we determined the activation energies \(E_{a} = 3.4 \pm 0.2\) eV and \(E_{a} = 2.7\pm 0.3\) eV, as well as the frequency factors \(A = (1.8\pm 0.3) \cdot 10^{17}\) s\(^{-1}\) and \(A = (5.6\pm 1.1) \cdot 10^{15}\) s\(^{-1}\) for the decay and coalescence processes, respectively. [Since \(E_{a}\) enters both into the nominator of the exponential in Eq. (1) and into the renormalized initial temperature, it is determined self-consistently by successive iterations]. The values found for \(E_{a}\) are one fourth to one third
of the fragmentation activation energy of the C\textsubscript{60} fullerene (frequency factors are smaller by two to four orders of magnitude) [18].

In conclusion, we note that the value $E_a \approx 3.4$ eV for the decay of one C\textsubscript{20} fullerene in the (C\textsubscript{20})\textsubscript{2} dimer is approximately one half of the value $E_a \approx 7$ eV for the decay of the isolated C\textsubscript{20} fullerene [12]. This fact, along with the appearance of the second mechanism of the loss of the molecular structure (fusion of two C\textsubscript{20} fullerenes into the C\textsubscript{40} cluster) with a lower value of $E_a \approx 2.7$ eV, indicates that stability decreases when the (C\textsubscript{20})\textsubscript{2} dimer is formed from two C\textsubscript{20} cages. In three-dimensional cluster structures based on C\textsubscript{20} fullerenes, both the stabilization of the metastable state due to an increase in the number of nearest neighbors of each C\textsubscript{20} fullerene and the appearance of new channels of stability loss can be expected. We are going to study this problem in the next work.
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Fig. 1. (a) C_{20} fullerene with the binding energy $E_b = 6.08 \text{ eV/atom}$ and (b) $(C_{20})_2$ cluster dimer with the binding energy $E_b = 6.20 \text{ eV/atom}$.
Fig. 2. Time dependences of the temperature $T$ of the (C$_{20}$)$_2$ cluster dimer obtained from the molecular dynamics simulation by averaging the kinetic energy over each $10^4$ steps. The total energy of the system is constant. The time of one step is equal to $t_0 = 2.72 \cdot 10^{-16}$ s. The initial temperature is $T_{ini} = 2415 \pm 10$ K (a) and $2285 \pm 10$ K (b).
Fig. 3. (a) Atomic configuration after the decay of one of the C\textsubscript{20} fullerenes in the (C\textsubscript{20})\textsubscript{2} dimer, see Fig. 2a. The binding energy after relaxation is $E_b = 6.14$ eV/atom. (b) The C\textsubscript{40} cluster formed upon fusion of two C\textsubscript{20} fullerenes in the (C\textsubscript{20})\textsubscript{2} dimer, see Fig. 2b. The binding energy after relaxation is $E_b = 6.25$ eV/atom.
Fig. 4. Same as in Fig. 2, for $T_{ini} = 2820 \pm 10$ K.
Fig. 5. (a) Defect isomer of the C\textsubscript{40} fullerene that is formed upon fusion of two C\textsubscript{20} fullerenes in the (C\textsubscript{20})\textsubscript{2} dimer, see Fig. 4. The binding energy after relaxation is $E_b = 6.49$ eV/atom.

(b) The C\textsubscript{40} fullerene formed after annealing of the imperfect isomer. The binding energy after relaxation is $E_b = 6.53$ eV/atom. The distant atoms are not shown for clarity.
Fig. 6. Logarithm of the lifetime $\tau$ (in seconds) of the $(C_{20})_2$ cluster dimer for the processes of the decay of one of $C_{20}$ fullerenes (circles) or fusion of two $C_{20}$ fullerenes into the $C_{40}$ cluster (squares) versus the inverse temperature (Kelvins), taking the finite-heat-bath correction into account, see text. The solid and dashed lines are the linear approximations for decay and fusion, respectively.