The threshold displacement energy of buckminsterfullerene $C_{60}$ and formation of the endohedral defect fullerene He@$C_{59}$

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We have measured the threshold center-of-mass energy for knocking out a single carbon atom from $C_{60}$ in collisions with He. Combining this experimental result with classical molecular dynamics simulations, we determine a semi-empirical value of $24.1 \pm 0.5$ eV for the threshold displacement energy, the minimum energy needed to remove a single carbon atom from $C_{60}$. In collisions with He, $C_{60}$ is the lowest energy dissociation channel [20, 21], this leads to the well-known statistical product distribution dominated by fragments with even numbers of carbon atoms, $C_{60-2n}$, $n = 1, 2, ...,$. In collision experiments like those presented here, products with odd numbers of C atoms like $C_{59}$ have occasionally been observed [19, 20, 22, 23]. These products are fingerprints of non-statistical fragmentation, where carbon atoms are displaced in billiard-ball like collisions [3]. This process takes place on timescales that are too short (sub-femtoseconds) for local excitations to distribute over the whole molecular system. The exceptionally low yield of $C_{59}$ relative to statistical fragmentation products has so far precluded systematic experimental studies of this mechanism.

Here, we have developed a refined approach to determine displacement energies for free molecules in collisions with particles that improves upon earlier such methods in an important way, namely by eliminating the (usually dominant) contribution of statistical fragmentation from the product distribution. This is achieved by colliding He with $C_{60}$ and measuring the threshold behavior for the formation of negatively charged fragments $e.g., C_{59}$ and $C_{58}$. Because the electron affinity of $C_{60}$ (2.664 eV [24]) is much lower than any of the dissociation energies of the system ($> 10$ eV [20, 21]), any trajectories depositing enough energy to induce statistical unimolecular dissociation most likely lead to electron loss and thus do not contribute to the negative ion product spectrum. In this way, we select those trajectories where essentially all the excitation energy is transferred to the primary knock-on atom, and as little as possible to the other atoms in the $C_{60}$ cage. By eliminating the major source of background from the measurement, greater sensitivity to minute cross-sections for non-statistical fragmentation is achieved, without which the present results for $C_{60}$ would not be possible. We combine experimen-
tional measurements of the threshold center-of-mass energy for non-statistical fragmentation of C\textsubscript{60} in collisions with He with classical Molecular Dynamics (MD) simulations of the knockout process and a statistical model of electron loss to determine the threshold displacement energy \( T_d \). Because the extra electron in C\textsubscript{60} does not affect the binding between C atoms, this result is valid for neutral as well as anionic C\textsubscript{60}.

Continuous beams of C\textsubscript{60}\textsuperscript{−} were produced by means of ElectroSpray Ionization [25]. In the ion source, the C\textsubscript{60}\textsuperscript{−} ions undergo many low-energy collisions and are assumed to equilibrate to roughly room temperature. Mass selected C\textsubscript{60}\textsuperscript{−} ions were accelerated to 3–15 keV and passed through a collision cell containing He gas. This C\textsubscript{60}\textsuperscript{−} kinetic energy range corresponds to center-of-mass energies, \( E_{CM} \), of 20–80 eV. Both negatively and positively charged product distributions were measured using an electrostatic energy analyzer equipped with a position-sensitive microchannel plate detector [26].

Electron affinities for C\textsubscript{60}, C\textsubscript{59}, and C\textsubscript{58}, and dissociation energies for C\textsubscript{60}\textsuperscript{−} → C\textsubscript{59}\textsuperscript{−}+C, C\textsubscript{60}\textsuperscript{−} → C\textsubscript{58}\textsuperscript{−}+C\textsubscript{2}, and C\textsubscript{59} → C\textsubscript{58}+C were determined from Density Functional Theory (DFT) structure calculations at the B3LYP/6-31+G(d) level using Gaussian 09 [27]. Complete results of these calculations are presented in the Supplemental Material.

Classical molecular dynamics simulations of collisions between C\textsubscript{60} and He were carried out using the LAMMPS software package [28]. We used the reactive Tersoff potential [29, 30] to describe the bonds between C atoms and the Ziegler-Biersack-Littmark (ZBL) potential [31] for the He-C\textsubscript{60} interaction. For each collision energy 10,000 randomly oriented trajectories were simulated (with random orientations of the C\textsubscript{60} molecule) and followed for 500 fs with a time step of 5 \( \times \) 10\textsuperscript{−12} s. Videos of selected trajectories showing the formation of endothermic reaction products are included in the Supplemental Material.

For MD trajectories leading to C\textsubscript{59}, the probability for survival under the present experimental conditions is calculated using a statistical model. The excitation energy deposited in the C\textsubscript{59} is calculated taking the nuclear scattering on 60 carbon atoms into account. In addition, we add small energy contributions from electronic stopping obtained by scaling the results by Schlahthöller et al [32] to the collision velocity in the present experiment, and the internal energy of C\textsubscript{60} before the collision. The latter is taken to be 0.44 eV for 298 K C\textsubscript{60} as calculated by Yoo et al. [33]. This gives a total internal energy \( E_{int} \) for each trajectory, an internal temperature \( T[K] = 1000 + (E_{int}[eV] - 7.4)/C \) [34], and an effective temperature \( T_{eff} = T - E_b/2C \), where \( C = 0.136 \) K/eV is the heat capacity of C\textsubscript{59} (found by scaling that of C\textsubscript{60} [34]), and \( E_b = 3.34 \) eV is the electron affinity of C\textsubscript{59} according to our DFT calculations (see Supplemental Material). We calculate the survival probability for C\textsubscript{59} ions as a function of their internal energy \( E_{int} \) by applying an Arrhenius expression for the electron detachment rate \( k = \nu e^{-E_b/k_BT_{eff}} \) [25]. Here the pre-exponential factor \( \nu \) is taken to be 10\textsuperscript{13} s\textsuperscript{−1} [35], and \( k_B \) is Boltzmann’s constant. By relating these calculated detachment rates to the time it takes for the ions to pass from the gas cell to the analyzing system (10–40 \( \mu s \), depending on the collision energy) we can select those C\textsubscript{59} fragments that are cool enough to survive on our experimental timescale.

In Fig. 1 we show distributions of positively charged (upper panel) and negatively charged (lower panel) reaction products of C\textsubscript{60}\textsuperscript{−}+He collisions at 77 eV center-of-mass energy. The putative mass corresponding to the kinetic energy of a fragment of that mass with the same velocity as incident C\textsubscript{60} is indicated on the upper horizontal scale. The observed energy loss (due to the combination of the change in mass and the energy transfer to the molecular system) is indicated in the lower horizontal scale. Both scales are common to both panels.

FIG. 1. Kinetic energy loss spectra for (upper panel) positively and (lower panel) negatively charged products of C\textsubscript{60}+He collisions at 77 eV center-of-mass energy. The putative mass corresponding to the kinetic energy of a fragment of that mass with the same velocity as incident C\textsubscript{60} is indicated on the upper horizontal scale. The observed energy loss (due to the combination of the change in mass and the energy transfer to the molecular system) is indicated in the lower horizontal scale. Both scales are common to both panels.

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ner and the internal degrees of freedom of the molecule and this reduces its kinetic energy relative to the putative mass. Neglecting these effects, the energy loss due to loss of mass is approximately $3 N_C^{\text{loss}} \times E_{\text{CM}}$ where $N_C^{\text{loss}}$ is the number of C atoms lost.

Positively charged products due to $C_{60}^+ + \text{He}$ collisions are shown in the upper panel of Fig. 1. These products are due to trajectories leaving sufficient energy in the fullerene system for double ionization. The energy transferred may be sufficient also for delayed statistical fragmentation in one or several steps, which leads to the products $C_{58}^+$, $C_{56}^+$ and smaller even-numbered fragments ranging down to $C_{50}^+$ (not shown in Fig. 1). Two cation product peaks are found just below the putative mass $672$ amu.

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Below: mean energy losses of reaction products in units of $E_{\text{CM}}$; filled symbols: experiment, open symbols: MD simulations. The uncertainties in the mean position are smaller than the symbols.

The collision products contributing to the energy spectra in the lower panel in Fig. 1 are those which are sufficiently cool to retain their negative charge after non-statistical knockout fragmentation. The two distributions are dominated by the parent ion beam at zero energy loss ($720$ amu). For $C_{60}^- + \text{He}$, four fragment peaks are observed: two just below the $C_{58}^-$ putative mass ($708$ amu or $\sim 3 \times E_{\text{CM}}$), and two just below the $C_{56}^-$ putative mass ($696$ amu or $\sim 6 \times E_{\text{CM}}$). By analogy with the positive ion spectrum, we assign in both cases the higher energy peaks to endohedral complexes. This is the first observation of an endohedral defect fullerene complex with an odd number of C atoms, namely $\text{He} @ C_{59}^-$. The observed $C_{58}^-$ and $\text{He} @ C_{59}^-$ products are most likely due to secondary losses of loosely bound C atoms from $C_{59}^-$ and $\text{He} @ C_{59}^-$, respectively. We have calculated the $C_{59}^- \rightarrow C_{58}^- + C_2$ has a dissociation energy of $10.13$ eV according to our calculations (similar to the $10-11$ eV for neutral and cationic $C_{60}$ [20, 21]) and is not competitive with electron emission (2.664 eV [24]) and thus should not contribute significantly to the negative product spectrum.

In the upper panel of Fig. 2, we show a series of $E_{\text{loss}}$ spectra recorded at different values of $E_{\text{CM}}$. Below: mean energy losses of reaction products in units of $E_{\text{CM}}$; filled symbols: experiment, open symbols: MD simulations. The uncertainties in the mean position are smaller than the symbols.
arise from a common mechanism with a single threshold energy.

In the lower panel of Fig. 2 we give the mean energy loss for each of the observed product ions as a function of center-of-mass energy. The peaks assigned to endothermic complexes are shifted by between 0.25 to 0.5 units of $E_{CM}$ relative to the putative positions of $C_{59}^-$ and $C_{58}^-$ i.e. $3 \times E_{CM}$ and $6 \times E_{CM}$, respectively, indicated by horizontal lines. This is different from the situation when atoms like He are captured by intact $C_{60}$, where the increase in mass induces a well-defined kinetic energy shift equal to $E_{CM}$ [36], as seen in the positive product spectrum in Fig. 1. Here, the knocked out carbon atom carries away some energy and energy shifts (relative to the putative mass) less than $E_{CM}$ are possible. Knockout collisions without capture giving $C_{59}^-$ and $C_{58}^-$ have a broader range of possible energy transfers and are thus shifted by larger energies on average. Mean energy losses from our MD simulations are in good agreement with the experimental values for He@$C_{59}^-$ and $C_{59}^-$. The energy shifts of the observed He@$C_{58}^-$ and $C_{58}^-$ products relative to the putative mass of $C_{58}^-$ are similar to those of $C_{59}^-$ and He@$C_{59}^-$, respectively. This is consistent with our view that these products originate from secondary statistical fragmentation following knockout i.e. $C_{59}^- \rightarrow C_{58}^- + C$. Our MD simulations do not include statistical fragmentation and thus no $C_{58}^-$ is observed.

As discussed above, the four different reaction channels leading to the production of He@$C_{59}^-$, $C_{59}^-$, He@$C_{58}^-$, or $C_{58}^-$ fragments are all non-statistical in nature and can be considered to be due to a common mechanism. Accordingly, we deduce the total absolute cross section for non-statistical fragmentation from our mass spectra by summing the intensities of all four anion fragment peaks and relating these to the $C_{60}^-$ primary beam intensity and its attenuation in the gas cell [26] (measured separately, see Supplemental Material). The total experimental cross section for all $C_{60}^- +$He collisions yielding negatively charged fragments is given in the upper panel of Fig. 3.

Also included in Fig. 3 are the results of our MD simulations. In the upper panel we give the cross section for single carbon knockout and in the lower panel the average energy transfer to the molecular system $\langle \Delta E_{He} \rangle$ in collisions leading to C knockout. Included in both of these quantities are only those trajectories which leave the resulting $C_{59}^-$ sufficiently cool to survive the timescale of our experiment, according to the our statistical model vide supra. This model gives an internal energy cutoff of 24-25 eV. The effects of these considerations are negligible for $E_{CM} < 60$ eV but there are significant corrections for higher energies.

We model the experimental and MD cross section assuming that the primary process is an elastic binary collision between a He projectile with kinetic energy equal to the He-$C_{60}$ center-of-mass $E_{CM}$ and a free C atom at rest. This is justified in that the knockout process happens on an ultrafast timescale on which the remaining 59 C atoms are standing still. For such collisions, Chen et al. [39] give the following expression, based on Lindhard scattering theory [40], for the cross section $\sigma_{KO}$ leading to energy transfer above a given fixed value (here the displacement energy $T_d$):

$$\sigma_{KO} = \frac{A/E_{CM}}{\pi^2 \arccos^{-2}(\sqrt{E_{th}/E_{CM}}) - 4}.$$  \hspace{1cm} (1)

where $E_{th}$ is here the minimum center-of-mass energy required to transfer $T_d$. We take $A$ and $E_{th}$ as fit parameters, yielding $E_{th}^{exp} = 35.8 \pm 0.5$ eV and $E_{th}^{MD} = 41.8 \pm 1.5$ eV. As seen in Figure 3, this simple model accurately reproduces both the experimental and MD cross sections above $E_{th}$. There is some deviation close to threshold due to the fact that $T_d$ is not single-valued, but rather varies somewhat with respect to the angles between the imparted momentum and the molecular bonds [17, 41].

The threshold energy $E_{th}$ is projectile dependent [12]; to obtain the intrinsic threshold displacement energy $T_d$ we need the energy transferred from the projectile (He).
to the target at threshold, which we extract from our MD simulations. From a power-law fit to \( \langle \Delta E_{th} \rangle = c \times E_{CM}^{-d} \) we obtain the mean energy transfer at the experimental knockout threshold \( E_{CM} = E_{th}^{exp} \). This is our semi-empirical value for the \( C_{60} \to C_{59} + C \) threshold displacement energy, \( T^S_d = 24.1 \pm 0.5 \text{ eV} \). The uncertainty given here is calculated from the uncertainty in the power-law fit parameters \( c \) and \( P \), \( E_{th}^{exp} \). Our semi-empirical value of \( T_d \) is much higher than generally assumed previously for fullerenes (around 15 eV [2, 6, 18, 19]), and is similar to that determined for the planar \( sp^2 \)-hybridized carbon systems graphene (23.6 eV [13, 14]) and PAHs (23.3 \pm 0.3 eV [15]). As our MD simulations give somewhat higher threshold energy we find a correspondingly higher threshold displacement energy \( T^{MD}_d = 26.5 \pm 0.8 \text{ eV} \), which is slightly lower than previous simulation-based results [17].

This is the first determination of a threshold displacement energy for free fullerenes or for any type of fullerene based material. An intrinsic material property, this is a key parameter for modeling radiation damage in many contexts, for example during electron microscopy imaging [13] or gas-phase reactions in the interstellar medium [12]. Finally, the surprising observation of the endohedral defect fullerene complex \( \text{He}@C_{59} \) is a remarkable testament to the intriguing complexity of fullerene reactions, which continue to fascinate more than 30 years after their discovery.

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