Long Jumps in the Surface Diffusion of Large Molecules

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We have studied the diffusion of the two organic molecules DC and HtBDC on the Cu(110) surface by scanning tunneling microscopy. Surprisingly, we find that *long jumps,* spanning multiple lattice spacings, play a *dominating* role in the diffusion of these molecules—the root-mean-square jump lengths are as large as 3.9 and 6.8 lattice spacings, respectively. The presence of long jumps is revealed by a new and simple method of analysis, which is tested by kinetic Monte Carlo simulations.

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Adsorbate diffusion has been observed directly and at the atomic scale in a large number of instances by either field ion microscopy (FIM) for metals on metals [1] or by scanning tunneling microscopy (STM) for metal, semiconductor, or simple gaseous adatoms [2,3] on a wide range of surfaces. Similar, detailed studies on the surface mobility of larger organic molecules are still very scarce [4]. They are, however, strongly warranted both due to a fundamental scientific interest [5,6] and because of the important role played by the diffusion of such species in the formation of, e.g., self-assembled monolayer molecular films or surface-bound nanostructures [7].

In the simplest picture of surface diffusion, the migration of adsorbates occurs by random jumps between nearest neighbor (*nn*) sites [1]. So-called *long jumps,* spanning multiple lattice spacings, are, however, also believed to contribute to the diffusion in cases of weak adsorbate-substrate interaction [5], but the experimental evidence for such long jumps is still rather limited and restricted to the mobility of metal adatoms [2,8,9].

Attempts to extract information on jump lengths from diffusion constant prefactors have been hampered by notoriously large statistical uncertainties on prefactors derived from Arrhenius analysis [10]. An alternative approach to unravel contributions from double and triple jumps to metal-on-metal diffusion [2,8] was introduced by Ehrlich and co-workers [8], and focuses on the entire atomic displacement distribution function. This approach is, however, experimentally challenging since it requires a very large, lattice-resolved data set for the diffusivity of adatoms. Furthermore, the approach is unsuitable if large deviations from the simple single-jump diffusion picture occur (see also [11]).

In this Letter, we report on the diffusion of the two largish molecules, decacyclene (DC) and hexa-*tert*-butyl-decacyclene (HtBDC), illustrated in Figs. 1a and 1b, on the Cu(110) surface. We introduce a new and simple approach to determine root mean-squared (rms) jump lengths λ in the surface diffusion. Our approach is based on the fundamental and well known relation between the mean-squared displacement $\langle(\Delta x)^2\rangle$ and the hopping rate h [5],

$$\langle(\Delta x)^2\rangle = \lambda^2 h t\,. \tag{1}$$

By deriving $\langle(\Delta x)^2\rangle$ and h independently from time-resolved, variable temperature STM data with the time period t, we have determined λ for DC/HtBDC and surprisingly find that *long jumps* play a *dominating* role in the diffusion of these molecules. The rms jump lengths are as large as $\lambda = 3.9 \pm 0.2$ and 6.8 ± 0.3 Cu *nn* distances for DC and HtBDC, respectively.

Both molecules studied here consist of an aromatic π system which adsorbs parallel to the Cu substrate [12]. HtBDC differs from DC solely by having six additional *tert*-butyl spacer groups which raise the aromatic plane of HtBDC away from the surface. As will be shown below this leads to a 4 orders of magnitude higher diffusion constant for HtBDC compared to DC in the investigated temperature range. This demonstrates that the diffusion properties of molecules can be tailored, which is especially interesting since HtBDC/DC possess key characteristics thought to be important in building blocks for possible future molecular electronics devices [13].

The DC/HtBDC molecules were deposited in ultrahigh vacuum from a glass crucible, resistively heated to

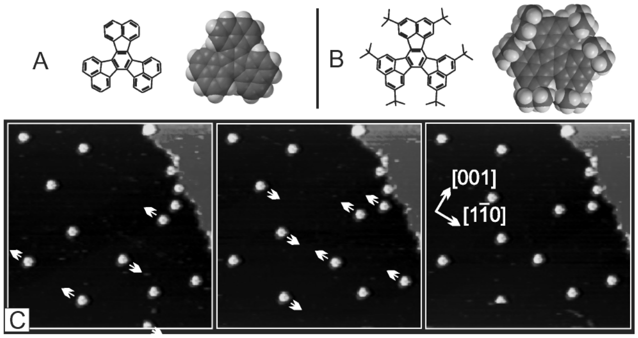

FIG. 1. Chemical structure and space filling model of (a) decacyclene (DC, $C_{36}H_{18}$) and (b) hexa-*tert*-butyl decacyclene (HtBDC, $C_{60}H_{66}$). DC consists of a disklike aromatic ring system and HtBDC additionally holds six peripheral *tert*-butyl groups. (c) Stills from a constant-current STM movie of HtBDC molecules, imaged as bright spots, on Cu(110) at $T = 194$ K ($V = -1768$ mV, $I = -0.61$ nA, 500×500 Å^2, $\Delta t = 13.9$ s). Molecular displacements can clearly be discerned; arrows indicate the direction in which molecules will have moved in the successive image.

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450/470 K, onto a clean Cu(110) surface held at or below 300/250 K during deposition. For HtBDC this was the maximum permissible temperature to avoid a local chiral restructuring of the Cu surface induced by the molecules at higher temperatures [12]. The molecular coverage was kept sufficiently low to make intermolecular interactions negligible (Fig. 1c).

The molecular diffusion was studied by acquiring time-resolved STM movies with a variable-temperature STM [14]. Tip influences on the diffusion process could be excluded by scanning with a tunneling resistance above 5 GΩ in which case variations in the interaction time between the tip and the adsorbate did not give differences in the derived values for h or $\langle(\Delta x)^2\rangle$. For both molecules around 10 STM movies were recorded at specific temperatures in the interval 172–200 K/218–251 K for HtBDC/DC. Each movie comprised 400–2500 image-to-image observations of individual, diffusing molecules, as exemplified in Fig. 1c (see Ref. [15]). For both DC and HtBDC, the molecular diffusion was observed to be strongly one dimensional, occurring parallel to the close-packed $[1\bar{1}0]$ direction of the Cu(110) substrate.

Our quantitative analysis starts from an evaluation of the molecular displacements along $[1\bar{1}0]$ between consecutive images [2]. The resulting displacement distributions were binned according to the lattice constant of Cu(110) along the $[1\bar{1}0]$ direction (2.56 Å) [16]. The molecular mean-squared displacement $\langle(\Delta x)^2\rangle$ during the image acquisition time t can be calculated directly from these displacement distributions.

To obtain the molecular hopping rate h we focus on the probability $P_0 = N_0/M$ of finding a molecule at the same position in two consecutive images [N_0 is the number of the observations with zero net displacement ($\Delta x = 0$), and M is the total number of observations in the displacement distribution [17]]. In the simplest approximation P_0 is related to the hopping rate via

$$P_0 = \exp(-ht), \tag{2}$$

which we use to determine h (systematic errors in this approach will be discussed in detail below).

Arrhenius plots of h and the one-dimensional diffusion constant $D = \langle(\Delta x)^2\rangle/2t$ are shown in Fig. 2 for both molecules. Activation energies and prefactors from these plots are summarized in Table I. As expected, the activation energies from the two analyses agree well for both molecules [1]. It is interesting that HtBDC has a lower activation barrier for diffusion than DC. We attribute this difference to the six *tert*-butyl spacer groups on HtBDC which increase the distance between the surface and the aromatic π system generally believed to interact strongly with the substrate.

The central new finding from our analysis is presented in Fig. 3 where we, inspired by Eq. (1), plot $\langle(\Delta x)^2\rangle$ versus the product ht. The data points for HtBDC and DC fall on straight lines with significantly different slopes; we can only attribute this to different rms jump lengths for these two molecules. By fitting to Eq. (1) we obtain $\lambda = 3.9 \pm 0.2$ and 6.8 ± 0.3 Cu *nn* distances for DC and HtBDC, respectively. Long jumps of several lattice spacings thus appear to *dominate* the diffusion of both these molecules on the Cu surface even at temperatures where the molecular mobility is fairly low.

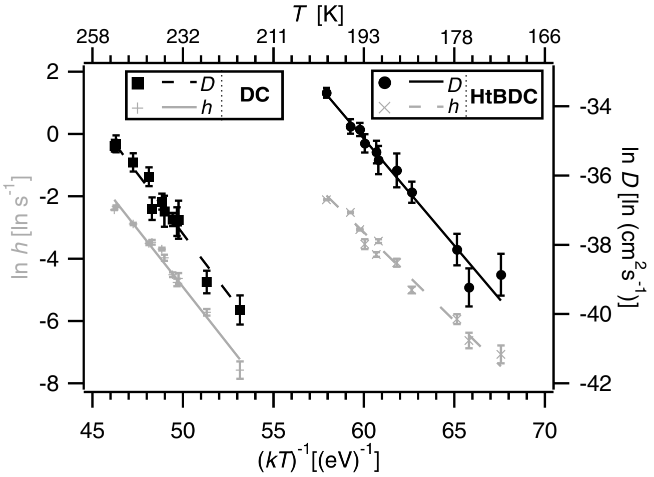

FIG. 2. Arrhenius plots of the hopping rates h and tracer diffusion constants D for DC and HtBDC. The lines are best fits to the Arrhenius expression for h and D, yielding the parameters in Table I.

For comparison we have included in Fig. 3 the data for diffusion of Pt on the Pt(110)-(1 × 2) surface which we previously have found to be dominated by single jumps [2]. As expected from Eq. (1) the Pt data fall on a line with a slope close to unity (see below also), confirming that the HtBDC/DC molecular diffusion differ strongly from the simple single jump picture.

To critically and quantitatively assess the precision of our new approach for determining rms jump lengths, we performed kinetic Monte Carlo (KMC) simulations of one-dimensional random walks, incorporating multiple site jumps, for different jump rates h_{in} and rms jump lengths λ_{in} (all simulations were for $t = 1$). The probability p_i for performing a jump of length i was assumed to be exponentially distributed: $p_i = c\exp(-ai)$ [5,18], with c and a adjusted to fulfill $\sum_i p_i = 1$ and $\sum_i i^2 p_i = \lambda_{\mathrm{in}}^2$ [19]. The simulation time was incremented according to the overall jump rate h_{in}, using standard procedures [20]. From the simulated displacement distributions (1000 observations) a hopping rate h_{out} was determined from Eq. (2) and a value for the rms jump length λ_{out} was calculated from Eq. (1).

In Fig. 4a we compare input and output values for h for different λ (black lines). We find that the hopping rate is systematically underestimated and increasingly so for larger values of ht. This is due to Eq. (2) neglecting the possibility of a molecule performing several jumps between consecutive images conspiring to bring it back to its starting point before it is observed again. Hence, the analysis always underestimates h and has the highest precision for $ht \ll 1$, i.e., where several jumps between

TABLE I. Diffusion parameters for DC and HtBDC derived from analyses of the mean-squared displacements ("dis") and the hopping rates ("hop").

	DC		HtBDC	
	dis	hop	dis	hop
E_D/eV	0.71 ± 0.05	0.74 ± 0.03	0.62 ± 0.04	0.57 ± 0.02
h_0/s^{-1}	...	$10^{13.9\pm0.7}$	...	$10^{13.5\pm0.4}$
$D_0/\mathrm{cm}^2\,\mathrm{s}^{-1}$	$10^{-1.0\pm1.0}$	...	$10^{0.9\pm1.0}$	...

observations are less likely to occur. What may initially seem surprising, is that the analysis works *better* the *larger* the rms jump length. This because $\lambda_{\mathrm{in}} > 1$ implies the participation of jumps of different lengths in the random walk, making accidental observations of $\Delta x = 0$ less likely.

We will next directly examine the confidence by which λ can be determined from an analysis of the simulation data. Figure 4b shows the ratio $\lambda_{\mathrm{out}}/\lambda_{\mathrm{in}}$ versus the two parameters most relevant from an experimental point of view, $\langle(\Delta x)^2\rangle$ and $h_{\mathrm{out}}t$. The rms jump length is determined least precisely for high $h_{\mathrm{out}}t$ and for small λ_{in} (i.e., towards the left in the plot), reflecting the behavior of h_{out} described above. Overall, λ_{in} is, however, regained with reasonable confidence for the displayed parameter space. Using Fig. 4b we have evaluated the confidence by which we expect to be able to determine λ for all data points displayed in Fig. 3, and conclude that the expected systematic error on the determined rms jump lengths is at most 5% for each of these data points.

For the case where all molecular jumps are of *identical* length (i.e., $\lambda = 1$), the expression

$$P_0 = \exp(-ht)I_0(ht) \tag{3}$$

constitutes an improvement over Eq. (2) by precisely accounting for the described effects of multiple jumps between images (I_0 is the modified Bessel function of the first kind of the order 0) [8]. The results obtained by analyzing the simulation data by this expression instead of Eq. (2) are included in Fig. 4a (gray lines). As expected, Eq. (3) is more precise compared to Eq. (2) for λ close to unity, but is not found to improve the precision generally for larger λ relevant to the situation in the present experiments. It is noteworthy that Eq. (2)/Eq. (3) systematically under/overestimates h and thereby leads to an over/underestimation of λ, respectively. This allows a bracketing of the correct value for the rms jump length. From Eq. (3) we obtain values for λ approximately 0.3 *nn* distances lower than those based on Eq. (2).

We now briefly return to the Pt/Pt(110)-(1 × 2) diffusion data included in Fig. 3 [2]. The diffusion in this system is dominated by single jumps, but has contributions

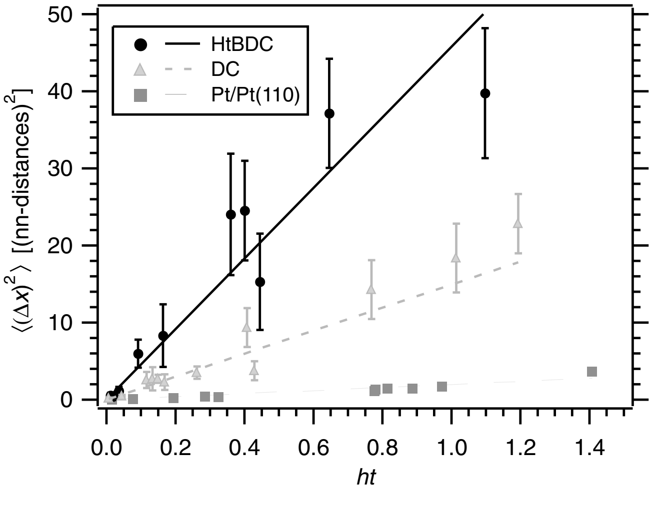

FIG. 3. Plot of the mean-squared displacement $\langle(\Delta x)^2\rangle$ versus ht for HtBDC and DC. Also shown are data for diffusion of Pt on Pt(110) [2]. The lines are the best fits to Eq. (1) yielding the rms jump lengths mentioned in the text.

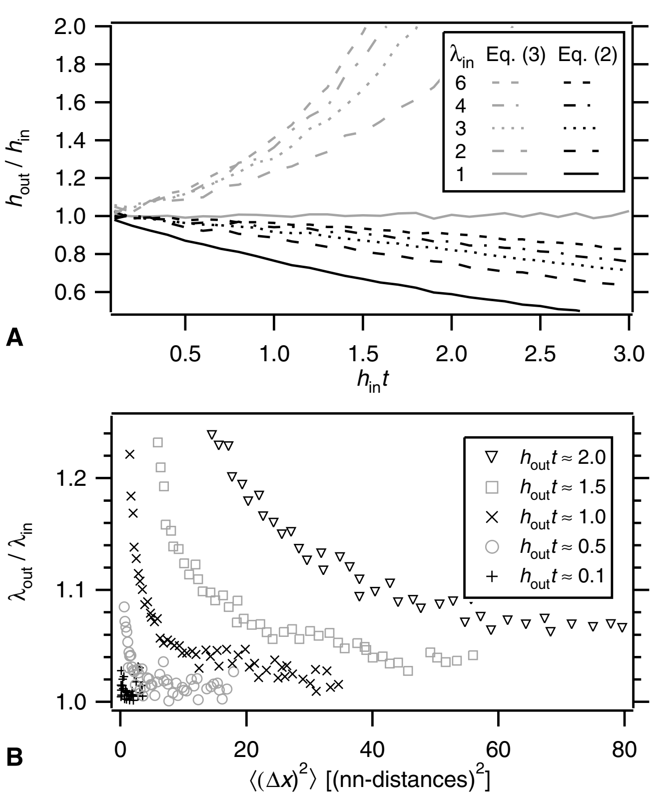

FIG. 4. Results based on KMC simulations. (a) Precision by which the hopping rate h_{out} can be determined for different input values of h_{in} and λ_{in}, using either Eq. (2) (black lines) or Eq. (3) (gray lines). (b) Confidence by which the rms jump length λ_{out} can be determined from Eq. (2), for different values for the two experimentally relevant parameters $\langle(\Delta x)^2\rangle$ and $h_{\mathrm{out}}t$ (see text for details). For a given trace with a specific value for $h_{\mathrm{out}}t$, the different $\langle(\Delta x)^2\rangle$ correspond to different $\lambda \in [1, 6]$.

from ~7% double jumps [21] as revealed from an analysis of the obtained displacement distributions by the detailed method originally introduced by Ehrlich [8]. If we analyze the Pt data with the approach outlined in the present paper, we find $\lambda = 1.41 \pm 0.06$ or $\lambda = 1.11 \pm 0.01$ Pt *nn* distances using Eqs. (2) or (3), respectively. The latter result is in excellent agreement with the value $\lambda = 1.10$ derived from the hopping rates for single/double jumps found by the elaborate analysis in Ref. [2].

Finally we consider what information regarding long jumps can be gained from an analysis of Arrhenius prefactors alone, as has been attempted before in the literature. From Table I we see that h_0 is close to the value typically anticipated (10^{13} s^{-1}), while D_0 is significantly increased compared to what is expected for single jump diffusion (10^{-3} cm^2 s^{-1}). Since $D_0 = \lambda^2 h_0/2$, this clearly reflects the large rms jump lengths in the present system. From the prefactors alone we obtain $\lambda = 2 \pm 3$ for DC and $\lambda = 28 \pm 39$ for HtBDC, which is in agreement with the conclusions reached above, but underscores how the statistical uncertainty associated with Arrhenius prefactors is typically too large to make them useful for obtaining information on diffusion jump lengths.

To summarize, we have performed the first thorough study of the diffusion of organic molecules on metal surfaces by time-resolved STM. We have presented a new method of analysis to reveal the presence of long jumps in surface diffusion which is simple, but, to the best of our knowledge, has been overlooked in the existing literature. Surprisingly, we find the diffusion of the two molecules studied, DC and HtBDC, to be *dominated* by long jumps with rms jump lengths close to four and seven Cu lattice spacings, respectively. This is in strong contrast to the conventional nearest-neighbor hopping picture.

Furthermore, our results demonstrate the possibility of tailoring molecular diffusion properties: By raising the aromatic plane common to DC/HtBDC away from the surface by spacer groups in the case of HtBDC, this molecule is endowed with an approximately 4 orders of magnitude higher diffusion constant compared to DC. The higher diffusivity is both due to larger rms jump lengths and a lower activation barrier for diffusion.

At present it cannot be ruled out that the dominating role of long jumps in the diffusion of DC/HtBDC is particular to these specific molecules, but it seems more likely that this result has implications for the way we should think about the surface diffusion of large organic molecules in general. Further experimental studies and new theoretical developments are certainly warranted.

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