The nanometre limits of ballistic and diffusive hot-hole mediated nonlocal molecular manipulation

H G Etheridge¹, K R Rusimova¹,²,³ and P A Sloan¹,²

¹ Department of Physics, University of Bath, Bath, BA2 7AY, United Kingdom
² Centre for Nanoscience and Nanotechnology, University of Bath, Bath, BA2 7AY, United Kingdom
³ Centre for Photonics and Photonic Materials, University of Bath, Bath, BA2 7AY, United Kingdom

E-mail: p.sloan@bath.ac.uk

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Abstract
We report an experimental investigation into the surface-specific and experimental limits of the range of STM induced nonlocal molecular manipulation. We measure the spot-size of the nonlocal manipulation of bromobenzene molecules on the Si(111)-7 × 7 surface at room temperature at two voltages and for a wide range of charge-injection times (number of hot charge-carriers) from 1 s up to 500 s. The results conform to an initially ballistic, 6–10 nm, and then hot-hole diffusive, 10–30 nm, transport away from the localised injection site. This work gives further confirmation that nonlocal molecular manipulation by STM directly reveals the ultrafast transport properties of hot-charge carriers at surfaces.

Keywords: hot electron, ballistic transport, diffusive transport, STM, molecular manipulation

(Some figures may appear in colour only in the online journal)

Introduction

An understanding of ultra-fast hot-electron dynamics is key to, for example, controlling matter at the atomic scale by scanning tunnelling microscopy (STM) molecular manipulation, and to breaking the Shockley–Queisser efficiency limit in solar cells [1–4]. In the latter the rapid time-scale of thermalization (loss of energy) of light generated hot-carriers sets the length-scale over which hot-carriers would have to be captured before they have lost most of their energy. However, direct measurement of hot-carrier dynamics, to underpin and develop hot-charge carrier theory, is difficult owing to their short lifetimes (femtoseconds) and length-scales (nanometres).

The tip of an STM is a local source of tunable hot-charge carriers. These hot-charges can lead to manipulation of individual atoms and molecules on a surface with atomic precision. Such molecular level control is the cutting edge of bottom-up nanoscience and in conventional STM manipulation is restricted to the tunnel junction [5–12]. Although these manipulations are driven by the hot-charges, since the only measurable outcome is whether the manipulation was successful or not, they give little information as to the underlying hot-charge carrier dynamics.

In nonlocal manipulation, however, charge injected from the tip of an STM results in the manipulation of many molecules within a distance, typically a few nm, of the tip injection site. Critically the distant molecules only react to the charge if it still has energy above a certain threshold, that is, they only react to charge carriers while they remain hot. Nonlocal molecular manipulation, therefore, has the signature of hot-charge dynamics directly imprinted in real-space on the pattern of the manipulation. Such nonlocal manipulation by STM has been reported in noble metals [13–18] and on the Si(111)-7 × 7 surface [19–21], the surface of primary interest for this research.
The surface and molecule were chosen as they exhibit a large and easily measured nonlocal manipulation signal. This system is well characterised and has been extensively studied by us and others and is therefore the ideal testbed for developing a surface-specific theory of hot-charge carrier dynamics that underlies the nonlocal manipulation.

Combining automated experimental and analysis techniques has allowed us to explore the parameter space of both local \cite{22, 23} and nonlocal \cite{24–28} manipulation with unprecedented range and resolution revealing the hot-electron dynamics that govern both modes of manipulation on the Si(111)-7 × 7 surface.

Here we show that the hot-charge carrier transport model developed in \cite{27, 28} is more general than those reports. We explicitly deconvolve the measured raw signal (image) of nonlocal manipulation into its three constituent parts: molecular properties, experimentally set properties and, crucially, the hot-charge carrier dynamics. This work is therefore an important step towards robustly linking STM mediated molecular manipulation to hot-charge carrier dynamics. It should now be possible to engineer the properties of this model system to directly measure the effect on the hot-charge dynamics so that nonlocal manipulation can act as a test-bed for controlling, measuring, and understanding hot-charge dynamics.

**Experimental**

Experiments were performed with a room temperature Omicron STM1 at a base pressure of \(\sim 1 \times 10^{-10}\) mbar. Si(111)-7 × 7 samples (n-type, phosphorous doped, 0.001–0.002 \(\Omega\)cm) were prepared upon entering the vacuum chamber by an initial degassing at \(\sim 660\) °C for several hours, as well as daily automatic heating to \(\sim 1250\) °C 10 times followed by a slower reconstructive cooling from 960 °C prior to scanning. Tungsten tips were electrochemically etched using a 2 M NaOH solution and degassed via resistive heating. Sample dosing of bromobenzene gas was controlled by an automated leak valve, providing an accurate and reproducible dose of 2 Langmuirs. Bromobenzene was purified by a freeze-pump-thaw routine and verified by mass spectrometry.

**Results**

Figure 1 shows a set of STM images taken before (left hand side) and after (right hand side) hole injection \(\sim 2.1\) V, 900 pA at the location indicated and at increasing injection times from 5 to 500 s corresponding to \(10^{10}\) to \(10^{12}\) injected holes. In these relatively large-scale images, the speckled dark-spots are in fact individual bromobenzene molecules chemisorbed to neighbouring adatom-restatom pairs with a binding energy of 1.4 eV \cite{29, 30}. They are stable at room temperature and unreactive to the imaging parameters used to capture these large scale and high resolution STM images, yet are highly reactive to hot-charge carriers.

Injections occur at a position towards the top left corner of the scanned area in order to maximise the possible observed radial distance from the injection site. A thermal drift-correction program minimised the drift to <1 nm during the longest 500 s injections—much less than the resulting nonlocal area of manipulation. For a 5 s injection of hot-holes the immediate area surrounding the injection site is cleaned of molecules. Some manipulated molecules appear as new adsorbrates further away, but the majority desorb from the surface completely. In our site-by-site analysis we can filter out such re-adsorption to focus purely on the number of molecules that were manipulated. At 50 s injection time the radius of this nonlocal manipulation is evidently increased, and at our longest injection times of 500 s we find a large radius of \(\sim 30\) nm has been cleared of its original molecular coverage.

The ‘spot-size’ of the clean area has been shown to be invariant to the presence of multiple steps within the region \cite{31}. Assuming a tunnel gap of \(\sim 10\) Å, and with a step height of 3.14 Å there would be significant variation in the strength of the tip-surface E-field at the top of a step or the bottom of multiple steps. Yet no change in the nonlocal manipulation
spot-size was observed. Therefore we ruled out any active role for the tip-sample E-field in the manipulation process.

To quantify the nonlocal manipulation the precise crystallographic locations of all the molecules and the injection sites are found using a suite of in-house written computer programs to analyse pairs of ‘before’ and ‘after’ STM images. Further analysis compares the occupation of the same individual adsorption sites before and after injection to determine the probability of manipulation $P(r) = N(r)/N_0(r)$: the ratio of the number of molecules manipulated $N(r)$ to the number of original molecules $N_0(r)$ within an annulus at radius $r$.

Figure 2 shows a series of measured $P(r)$ data-sets as a function of the injection time. Each data-set at a particular injection-time is the average from at least two ‘before’ and ‘after’ experiments (∼34 000 manipulation events were recorded in total during this work). To quantify the size of the nonlocal manipulation we define the half-radius, $r_{1/2}$, as the radius at which the probability of manipulation is half that of the maximum measured manipulation probability. For each data-set $r_{1/2}$ is indicated by the short vertical black line. For long enough injections, the maximum probability reaches a consistent maximum at ∼0.8. This upper threshold is due to the presence of immovable contaminants on the surface which are included in the $P(r)$ analysis. At short duration injections the maximum probability may be less—not all molecules in an annulus, even near the injection site, are driven to desorb. For short injection-times at −2.1 V, the nonlocal manipulation occurred near the injection site with $r_{1/2} = (9 ± 2)$ nm. At longer injection-times the size of the nonlocal effect increased with a corresponding increase in the half-radius. For 500 s injections $r_{1/2} = (34 ± 2)$ nm, the longest injection and largest half-radius of our −2.1 V experiments. Although the increase in half-radius with injection duration is monotonic, it is not linear.

Figure 3 shows the main result of this work, the injection-time dependence of $r_{1/2}$ for two injection voltages, −1.6 and −2.1 V. These voltages were chosen to be near threshold (−1.6 V) of a surface-state (labelled $s_4$ in [28]) in order to minimise any possible ballistic transport, and well beyond the threshold (−2.1 V) to maximise any ballistic transport. Using site-specific STS we previously showed that each manipulation voltage threshold corresponds to the onset of a site-specific surface state. With each state having slightly different diffusive and ballistic transport ranges [28, 32]. Here, for both voltages, below ∼10 s there is an initial constant minimum region in $r_{1/2}$, (4 ± 2) nm and (9 ± 2) nm respectively, followed by a logarithmic increase. Does our model, developed from the voltage and temperature dependence of nonlocal manipulation, extend to explain this injection-duration $r_{1/2}$ dependence?
Discussion

The model for nonlocal manipulation has the stepwise form: (i) an electron (or hole) is injected from the STM tip into a specific surface electronic state at a specific atomic site of the surface; (ii) it evolves for a few fs in that state from its initial conditions that are set by the properties of the band (dispersion etc.) and the quantum tunnelling process. This is simply ballistic transport; (iii) the electron (or hole) undergoes multiple scattering events to become quasi-thermally equilibrated at the bottom (or top) of the band and from there undergoes isotropic 2D diffusive transport with a lifetime of, here, 200 fs; (iv) during this diffusive phase the charge has a chance to localise on a molecule and, by a desorption induced by an electronic transition process, induce the molecule to detach from the surface and desorb. Given the mismatch of the time between tunnelling charges, ~100 ps, and the life-time of the hot-charge of ~100 fs, we can assume that this process repeats identically and independently for each charge carrier injected into the surface during the current-pulse. This results in the probability of manipulation per charge carrier being independent of the tunnelling current, as previously observed [28, 33].

The probability of manipulation $P(r) = N(r)/N_0\delta(r)$ derived for this model is

$$P(r) = 1 - \exp \left[ -\left( \frac{\sigma \kappa_r}{\tau_i} \right) \times \left( \frac{slie}{e} \times C(r) \right) \right]. \quad (1)$$

This expression highlights the three factors that control the shape of the nonlocal manipulation: (i) molecular manipulation properties through $\kappa_r$, the probability per injected charge carrier of inducing molecular desorption, $\sigma$ the molecular cross-section (taken as $(1.5 \text{ Å})^2$ [34]) and $\tau_i$ the lifetime of an electron in the surface-state here taken as 200 fs [35] (Note, in comparison with our earlier work, here we have introduced this additional $\tau_i$ term for the lifetime of the charge in the surface-state. This allows us to express $\kappa_r$ as a probability of manipulation per injected electron. This minor (book keeping) correction does not change the form of the results here or earlier, but is a more correct form for the expression); (ii) experimental conditions that determine the number of injected electrons $n_e = slie$/ where $t$ is the injection duration, $I$ the injection (tunnelling) current and $s$ the fraction of the current injected into the surface state (taken as unity); and (iii) the hot-charge carrier dynamics themselves through $C(r)$, the time-integrated charge density of a single carrier. It is this last term that describes the underlying hot-electron dynamics that drives the nonlocal manipulation.

Diffusive model

A single-electron 2D diffusive model with a single unreactive decay channel gives

$$C(r) = \frac{2\tau_i}{\pi \lambda^2} K_0 \left( \frac{2\tau}{\lambda} \right), \quad (2)$$

see [27] for derivation. The 2D charge diffusion is described by the diffusion length $\lambda$ and the diffusion time $\tau_i$. These are related as usual for 2D diffusion through $\lambda = \sqrt{4D\tau_i}$ with $D$ the diffusion coefficient. Furthermore, combining equations (1) and (2), for $r > \lambda$ the half-desorption radius as a function of injection duration can be approximated as

$$r_{1/2} = \frac{\sqrt{2} \lambda}{2} \log \left( \frac{r_0}{\tau_i} \right) \quad (3)$$

With the characteristic time-scale given by $t_0 = (\pi \lambda^2/2\sigma \kappa_r I_e)$. We perform an iterative fitting routine to determine robust values for $\lambda$ and $\kappa_r$. We initially find these parameters (and a contamination scaling factor) by fitting the model given by equations (1) and (2) to the data as shown in figure 2. Each injection time generates unique fitting parameters $\lambda$, $\kappa_r$ and a contamination scaling factor.

From these values we determine the half-radius for each injection time, shown in figure 3. We then fit the logarithmic dependence given by equation (3) and so extract another measure of $\lambda$ but here this value is fitted across all the data (injection times) for a particular voltage. The dashed lines of figure 3 show the excellent fit of this logarithmic model to the experimental results, resulting in $\lambda = 7 \pm 2 \text{ nm}$ for $-1.6 \text{ V}$ and $\lambda = 11 \pm 3 \text{ nm}$ for $-2.1 \text{ V}$ in agreement with [28].

We use this value of $\lambda$ to refit the data of figure 2 but now with just $\kappa_r$ and the contamination scaling factor as fitting parameters. By this route we minimise the effect of the inherent statistical variation we have in our experimental results and extract the best values for hot-charge carrier dynamics. We find that the half-radii extracted from figure 2 are relatively insensitive to variations in $\lambda$, and so further iterative fitting does not significantly affect our final values. A weighted average over all injection times gives the probability per electron of manipulation $\kappa_r = (2 \pm 2) \times 10^{-7}$ at $-1.6 \text{ V}$ and $\kappa_r = (8 \pm 5) \times 10^{-7}$ at $-2.1 \text{ V}$.

The local manipulation probability of toluene molecules on the same surface with $-1.3 \text{ V}$ holes is remarkably similar at $k_r = 3 \times 10^{-7}$ [33]. Both bromobenzene and toluene are simple derivatives of benzene and bond in near identical fashion onto the Si(111)-7×7 surface and exhibit near identical molecular manipulation properties. For local injections the molecule ‘experiences’ the whole injected charge interaction, whereas for nonlocal manipulation the charge is spread out and so only a fraction of any one charge interacts with any one adsorbate. To relate the local manipulation probability $k_r$ to the nonlocal probability $\kappa_r$ we note that $k_r$ is the probability of inducing any desorption and that the fraction of the spread-out charge that interacts with the molecule will simply be the geometric fraction of the spot-size that was covered by molecules, here ~0.4. Additionally, nonlocal manipulation has a longer interaction lifetime than local manipulation, ~200 fs to ~10 fs respectively, and so we assume a linear increase [23] in probability of about an order of magnitude giving the approximate relationship $k_r \times 0.4 \times 200/10 \sim \kappa_r$. It is therefore reasonable, in our case, for the nonlocal probability per injected charge carrier to be of the same order as its local counterpart, just as we find.

At room temperature, thermal drift plays more of a role and the maximum time of a single-position experiment is set by the mechanical stability of the microscope. We go to great
experimental lengths to perform stable injections up to 500 s at room temperature. Due to the logarithmic nature of the manipulation spot-size, attaining a spot-size larger than 35 nm would require unfeasibly long injections. At cryogenic temperatures STMs are more stable, but the thermally driven (though still hot) diffusive charge transport is slowed reducing λ and hence ultimately the spot-size [27].

At injection times lower than 10 s this purely diffusive model does not fit the experimental data. This is partly due to approximations taken in the derivation of equation (3), but even the full diffusive expression does not generate the observed plateau region at small injection duration.

Ballistic model

In [28] we developed the diffusive transport model further, whereby injected charge carriers were modelled to undergo an initial ballistic (unperturbed) transport away from the injection site before intra-band thermalization and diffusion (as above). In this ballistic region the charge carriers are not observed to interact with adsorbed molecules and so, for certain injection voltages, can result in a reduction in the measured probability P(r) of manipulated molecules close to the injection site. In essence, the charge only becomes ‘active’ some short distance from the injection site.

Consequently, the initial spatial distribution of charge density before diffusion is not a Dirac delta function at the injection site, as is assumed in the purely diffusive case described by equation (2). Instead, for the initial ballistic transport a simple 2D cylindrical Schrödinger model (and an equivalent 2D tight-binding model) predicted nearly a constant charge carrier density out to a distance R set by the properties of the surface-state and the ballistic lifetime. Values for R typically ranged from 5 to 15 nm [28]. For the half-radius desorption measurement in figure 3 this implies a lower limit, just as we observe, set by the physical properties of the surface electronic state as the electrons undergo this ultrafast ballistic transport.

To model this initial ballistic phase and its effect on the nonlocal spot-size r1/2 we calculate the diffusion, again with a single decay channel, from an initial constant charge density across a disc of radius R centred on the injection site. Due to its linear and separable properties we use the superposition principle to calculate the total charge density C(r) that feeds into equation (1)

\[ C(r) = \frac{1}{\pi R^2} \int_R 2\pi \frac{2\pi}{\pi^2} K_0(2\pi r'/\lambda) dA, \]

where \( r' \) is the distance between a point on the initial disc and the radial distance from the injection site r. The solid lines in figure 3 show the excellent fit to this ballistic-diffusive model for all of the data, giving for −1.6 V injections \( R = (5 \pm 1) \) nm, and for −2.1 V injections \( R = (8 \pm 1) \) nm. These are in good agreement with our earlier work [28].

Conclusions

This work supports the ballistic-diffusive model for hot-charge carrier transport developed to model nonlocal STM manipulation. It sets physical limits on the maximum and minimum size of the nonlocal manipulation effect and demonstrates that molecular, experimental and surface factors can be distinguished and measured. It opens the way to engineering and altering surface properties, for example doping level, to enhance (or suppress) the ultra-fast hot-charge carrier dynamics and hence the nonlocal manipulation itself.

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ORCID iDs

K R Rusimova @ https://orcid.org/0000-0002-3679-9948
P A Sloan @ https://orcid.org/0000-0002-0810-8468

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