Mass Transport in Surface Diffusion of van der Waals Bonded Systems - Boosted by Rotations?: Supporting Information

Holly Hedgeland,*†‡ Marco Sacchi,¶ Pratap Singh,§ Andrew J. McIntosh,†
Andrew P. Jardine,† Gil Alexandrowicz,‖ David J. Ward,† Stephen J. Jenkins,⊥
William Allison,‡ and John Ellis‡

†School of Physical Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK
‡Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge, CB3 0HE, UK
¶Department of Chemistry, University of Surrey, Guildford, GU2 7XH, UK
§The Perse School, Cambridge, CB2 8QF, UK
‖Department of Chemistry, Technion - Israel Institute of Technology, Haifa 32000, Israel
⊥Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

E-mail: holly.hedgeland@open.ac.uk
Bayesian Methods

Figure 1: Panel (a) shows a typical variation of the polarization, $P/P_o$ as a function of the spin-echo time, in this case for $\Delta K = 1.8 \text{ Å}^{-1}$ in the $<100>$ with the measurements shown as blue circles and the red line, a single exponential function of form $ae^{-\alpha t} + c$. Panel (b) shows the Bayesian probability function (pdf) of the dephasing rate $\alpha$. The red data point corresponds to those shown in Figures 2 and 4 of the main manuscript and illustrates the peak and credible interval of the distribution. We note the least squares solution corresponds to the mode of the pdf.

Figure 1(a) of the SI shows a typical $I(\Delta K, t)$ measurement at a specific value of $\Delta K$ along with a single exponential function of form $ae^{-\alpha t} + c$. We take a Bayesian approach to determine best value of the dephasing rate, $\alpha$. We find the relative probability that $a, \alpha$ and $c$ have particular values for a given $I(\Delta K, t)$. We then integrate out $a$ and $c$ to leave the relative probability of $\alpha$ as a function of $\alpha$ as illustrated in SI Figure 1(b). The data points in Figures 2 and 4 of the main manuscript show the maxima of the probability distribution functions while the error bars are the credible intervals found by integrating under the probability distribution function. The error bars are asymmetric because they reflect the skewed nature of the probability distributions (which is related in physical terms to the requirement for the constant term $c \geq 0$). We present the credible interval corresponding to the 67% highest posterior density interval: the credible interval is guaranteed to span the mode (least squares solution) and indicates credible maximum and minimum values either side of the most likely value. If the distribution were normal, this would give the same data point as a conventional least squares point with a 1-$\sigma$ error bar. The key point is that the
skewed distributions provide a strong lower bound on the rates we observe.

A Bayesian method is also used to determine the Arrhenius slope, where the probability of fitting the measured ISF, in each direction, was found as function of both pre-exponential factor and activation energy and then marginalized to give a probability distribution function that is a function of activation energy. The maximum in this distribution gives the effective activation energy, with the uncertainties found in a comparable manner to that described previously for the dephasing rates.

### Langevin Molecular Dynamics

For adsorption to the hollow site, the translational part of the potential, $V_{\text{trans}}$, is parameterized in terms of the barriers over the top and bridge sites ($E_T$ and $E_B$), which can be varied independently, and is given by:

$$V_{\text{trans}}(x, y) = \frac{E_B}{2} + \frac{E_T}{4} \left[ 1 + \cos \left( \frac{2\pi x}{a} \right) + \cos \left( \frac{2\pi y}{a} \right) \right]$$

$$+ \frac{1}{4} (E_T - 2E_B) \cos \left( \frac{2\pi x}{a} \right) \cos \left( \frac{2\pi y}{a} \right).$$

(1)

The rotational potential, $V_{\text{rot}}$ is added to the translational part and varies as a function of the angle of rotation of the molecule about a central, perpendicular axis, $\theta$. The range of variation is dependent on the $x, y$ position of the molecule and varies smoothly between values defined at the hollow adsorption site, $E_{\text{rot},H}$ and at the edge of the surrounding unit cell linking the bridge and top sites $E_{\text{rot,edge}}$, with $E_{\text{rot,diff}} = E_{\text{rot,edge}} - E_{\text{rot},H}$, such that:

$$V_{\text{rot}}(x, y, \theta) = \frac{1}{2} \left [ 1 + \cos(12.\theta) \right ] \times \left [ E_{\text{rot},H} + (E_{\text{rot,diff}}) \left( \frac{1}{4} \left[ 1 + \cos \left( \frac{2\pi x}{a} \right) + \cos \left( \frac{2\pi y}{a} \right) \right] + \frac{1}{2} - \frac{1}{4} \cos \left( \frac{2\pi x}{a} \right) \cos \left( \frac{2\pi y}{a} \right) \right) \right ],$$

(2)
with $x$ and $y$, displacements parallel to the surface and $a$, the substrate primitive lattice spacing.

The total potential is hence defined by four parameters but these are further constrained by the experimental data. The ratio of the translational barriers $E_T$ and $E_B$ is constrained by the relative magnitudes of the dephasing rate along the two azimuths, and their magnitude by the measured Arrhenius data, such that values of 172 meV and 122 meV are obtained, respectively. When the rotational part of the potential is added, if either $E_{\text{rot,edge}}$ or $E_{\text{rot,}}$ were to be too low (order of kT) then the mode would become a free rotor and distort the diffusion barrier, hence the minimum for $E_{\text{rot,edge}}$ is 30 meV. As the role of the rotational potential is to provide an increased density of states at the transition state, the ratio of $E_{\text{rot,edge}}$ to $E_{\text{rot,}}$ is significant, rather than than their absolute values. In SI Figure 2 we demonstrate the effect of altering $E_{\text{rot,}}$ between 120 and 240 meV while keeping $E_{\text{rot,edge}}$ fixed at 30 meV to reproduce the experimental Arrhenius energy. The final factor to consider in constraining the four energies is the friction parameter, as this will affect the curvature of the simulated $\alpha(\Delta K)$ and so does not permit arbitrary pairings of $E_{\text{rot,}}$ and $\eta$ if the full set of experimental data is to be considered. (The same friction parameter is used for the translational co-ordinates and rotational degrees of freedom and determines the rate at which random impulses are received, both linearly to the translational co-ordinates and also rotationally, where the angular momentum is considered in terms of the moment of inertia of the molecule about its central axis and its rate of rotation.)

As we consider the role of rotations in the measured diffusion rate, it is appropriate also to comment as to whether we also consider them to influence the scattering of the helium atoms from the adsorbed molecules and the measured dephasing rate. In addition to our data here demonstrating the characteristic of translational (jump) diffusion, previous studies of small aromatic systems have shown no evidence of direct sensitivity to rotational motion within the regime we consider here, for example, previous simulations of benzene on a graphite surface found a negligible contribution of rotational motion in coherent scattering below
Figure 2: Showing the experimental results (solid circles with error bars) alongside dephasing rates obtained from optimized simulations with translation only (dashed lines) and with translation+rotation (solid lines). The shaded region around the solid lines shows the effect of altering the corrugation of the rotational potential at the adsorption site from 120–240 meV while keeping that at the transition state at 30 meV.

2 Å\(^{-1}\). The reason for the lack of sensitivity may be related to some combination of: the scattering form-factor; the fact that the scattering is coherent; or the different time scales for rotation and diffusion.

It is also interesting to compare the diffusion barriers with the molecular desorption energies: we note that benzene adsorbed on other facets of copper has desorption energies between 360–750 meV,\(^4\),\(^5\) 4 to 8 times greater than the diffusion barriers we observe.

**Density Functional Theory**

Further to the details given in the Experimental Methods section of the main manuscript, we have converged our DFT calculations and used essentially the same parameters for cut-off energy, k-point grid sampling, vacuum layers, etc as in our previous publications on several aromatics:\(^6\)–\(^8\) 300 eV energy cut-off, a (4×4×1) k-point grid, 0.05 eV/Å force tolerance. Calculations are for a p(4×4) cell, which corresponds to a coverage of 0.06 monolayers (defined by number of adsorbate molecules per substrate atom). For benzene adsorption on a bridge site, increasing the k-point sampling, from a (4×4×1) grid to a (5×5×1) grid
does not significantly improve the accuracy of the adsorption energy calculations (3 meV difference, less than 0.3%). Similarly, increasing the cut-off energy to 320 eV has a very minor effect on the adsorption energy (-10 meV, meaning a difference of less than 1%).

In Table 1 we present the calculated adsorption energies for benzene adsorbed on the high symmetry sides, at a number of rotational orientations. The initial angle is the angle at the starting point of the optimization, while the final angle is the rotational angle when the structure was optimized around the particular local minimum. No distance was kept constant as both the molecular height and C-H bond angles will adjust when relaxed, depending on the exact position and orientation of the molecule with respect to the surface close-packed rows. The adsorption energy, \( E_a \), of the benzene is determined by the difference in energy between the initial state, given by the isolated molecule in gas phase plus a clean relaxed Cu(001) surface, and the final state, where the molecule is adsorbed in the same surface unit cell. The difference between experimental and DFT diffusion barriers, as reported here for benzene/Cu(001), remains an important point in terms of benchmarking methods for dispersion correction.

<table>
<thead>
<tr>
<th>Site</th>
<th>Hollow</th>
<th>Hollow</th>
<th>Hollow</th>
<th>Hollow</th>
<th>Top</th>
<th>Top</th>
<th>Top</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial angle (°)</td>
<td>15</td>
<td>10</td>
<td>5</td>
<td>0</td>
<td>15</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Final angle (°)</td>
<td>15.3</td>
<td>9.8</td>
<td>6.5</td>
<td>0</td>
<td>15.1</td>
<td>4.1</td>
<td>0</td>
</tr>
<tr>
<td>( E_a ) (eV)</td>
<td>-1.473</td>
<td>-1.435</td>
<td>-1.441</td>
<td>-1.415</td>
<td>-0.973</td>
<td>-0.950</td>
<td>-0.947</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>Bridge</th>
<th>Bridge</th>
<th>Bridge</th>
<th>Bridge</th>
<th>Bridge</th>
<th>Bridge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial angle (°)</td>
<td>30</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Final angle (°)</td>
<td>30.1</td>
<td>25.8</td>
<td>20.3</td>
<td>17.4</td>
<td>8.4</td>
<td>0</td>
</tr>
<tr>
<td>( E_a ) (eV)</td>
<td>-1.105</td>
<td>-1.122</td>
<td>-1.112</td>
<td>-1.105</td>
<td>-1.068</td>
<td>-1.054</td>
</tr>
</tbody>
</table>
References


(8) Lechner, B. A.; Sacchi, M.; Jardine, A. P.; Hedgeland, H.; Allison, W.; Ellis, J.; Jenk-