

Controlling preferential motion of chiral molecular walkers at a surface.

Supporting Information

David Abbasi-Pérez¹, Hongqian Sang^{1,2}, Lluïsa Pérez-García³, Andrea Floris⁴,
David B. Amabilino⁵, Rasmita Raval⁶, J. Manuel Recio⁷ and Lev Kantorovich¹

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¹Department of Physics, King’s College London, London, WC2R 2LS, (UK)

²Institute for Interdisciplinary Research, Jiangnan University, Wuhan 430056, (China)

³School of Pharmacy, University of Nottingham, University Park, Nottingham, NG7 2RD, (UK)

⁴School of Mathematics and Physics, University of Lincoln, Brayford Pool, Lincoln LN6 7TS, (UK)

⁵School of Chemistry GSK Carbon Neutral Lab. for Sust. Chemistry, University of Nottingham, Triumph Road, NG7 2TU(UK)

⁶Surface Science Research Centre, Department of Chemistry, University of Liverpool Liverpool L69 3BX (UK)

⁷MALTA-Consolider Team and Department of Analytical and Physical Chemistry, Universidad de Oviedo, Oviedo, 33006, (Spain).

1 Rate pre-factors

Within the Harmonic Transition State Theory the prefactor ν is calculated via the Vineyard formula [1] as $\nu = W^{min}/W^{TS}$, where W^{min} is the product of all vibrational frequencies at the minimum of the potential well corresponding to the initial state (either A_i or B_i) and W^{TS} is the product of all vibrational frequencies, with the exception of the imaginary one, at the saddle point (transition state) connecting the two minima.

Description	prefactor (ps ⁻¹)
from A_i to B_i (to the right)	13.9217
from A_{i+1} to B_i (to the left)	36.0214
from B_i to A_{i+1} (to the right)	10.5505
from B_i to A_i (to the left)	4.0776

Table 1: DFT calculated pre-factors for the diffusion of the enantiomer (R)*.

2 Diffusion mechanism

Full animation of the diffusion of both the (S) and (R)* conformers are provided as separated animated gif files. For each conformer views from the legs and tail perspectives are provided.

3 Density difference maps of a negatively charged system

The electronic density difference map between the molecule on the surface with a single extra electron (a negative charge) and the neutral system (both in the same geometry to ease the comparison) is shown in Fig. 1. It can be seen that the molecule allocates a part of the charge, the rest of the charge is spread out across the upper layer of the surface; at the same time, the character of the bonding of the molecule to the surface remains the same.

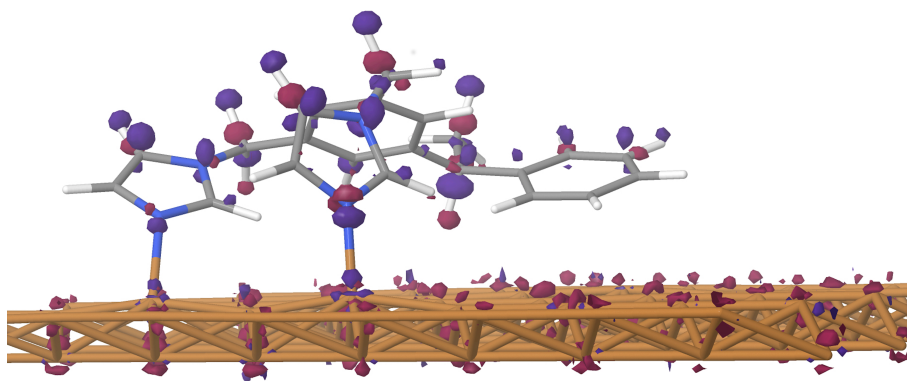


Figure 1: Electronic density difference map between a negatively charged and a neutral system. Purple isosurfaces show excess of charge and red ones indicate depletion, at the values of $\pm 0.00045 \text{ e}/\text{\AA}^3$, respectively.

References

- [1] G. H. Vineyard. Frequency factors and isotope effects in solid state rate processes. *J. Phys. Chem. Solids*, 3:121, 1957.