Chemical Reactions Dynamics from Sequential Scanning Tunneling Microscopy Images at Solution-Solid Interface

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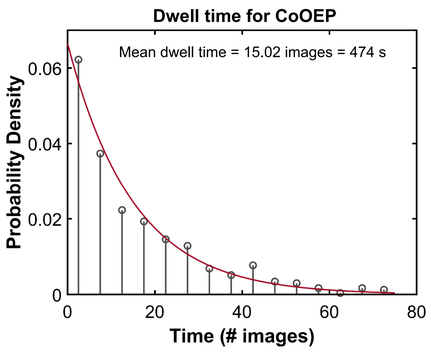
Abstract:

Understanding the process of binding O_2 to metal porphyrins is of importance in biological sciences because porphyrins exist in the active site of many proteins and enzymes such as hemoglobin and myoglobin. These molecules are responsible for the transport and storage of oxygen in mammalian cells. Here we present the dynamics of an unusual oxygen binding system, The metalloporphyrin of interest, CoOEP, *does not bind to oxygen in solution but will bind oxygen when adsorbed on a graphite substrate*. Sequential STM images are used to determine the rate constants for the ligation reaction, stochastically.



CoOEP → O_2-CoOEP	O_2-CoOEP → CoOEP
$k_a \cdot P_{O_2}$	k_d
0.003 s^{-1}	0.017 s^{-1}
$t_{unbound \rightarrow bound}$	$t_{bound \rightarrow unbound}$
6.01%	42.5%

Stochastic Kinetics:

- Useful for studying systems with a small number of molecules
- Uses probability distributions and not concentrations to describe the system

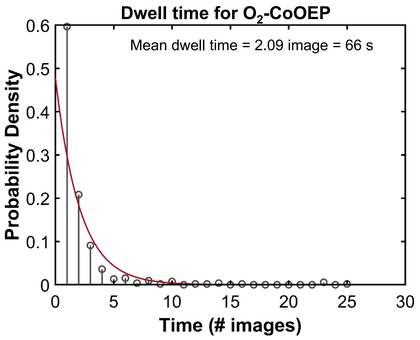
For a general reversible unimolecular reaction

A ↔ B

Rate of change of probability of finding molecule in state A, P_A is

$$\frac{dP_A}{dt} = t_{B\rightarrow A}P_B(t) - t_{A\rightarrow B}P_A(t)$$

Where $t_{B\rightarrow A}$ is the probability of a transition from state B to A



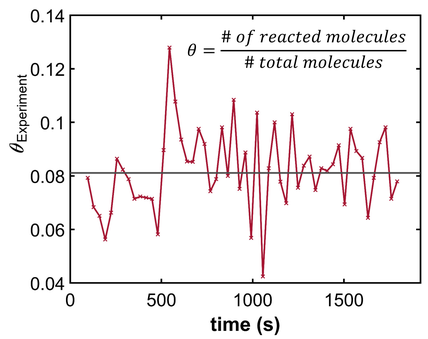
Kinetics from State Dwell Times:

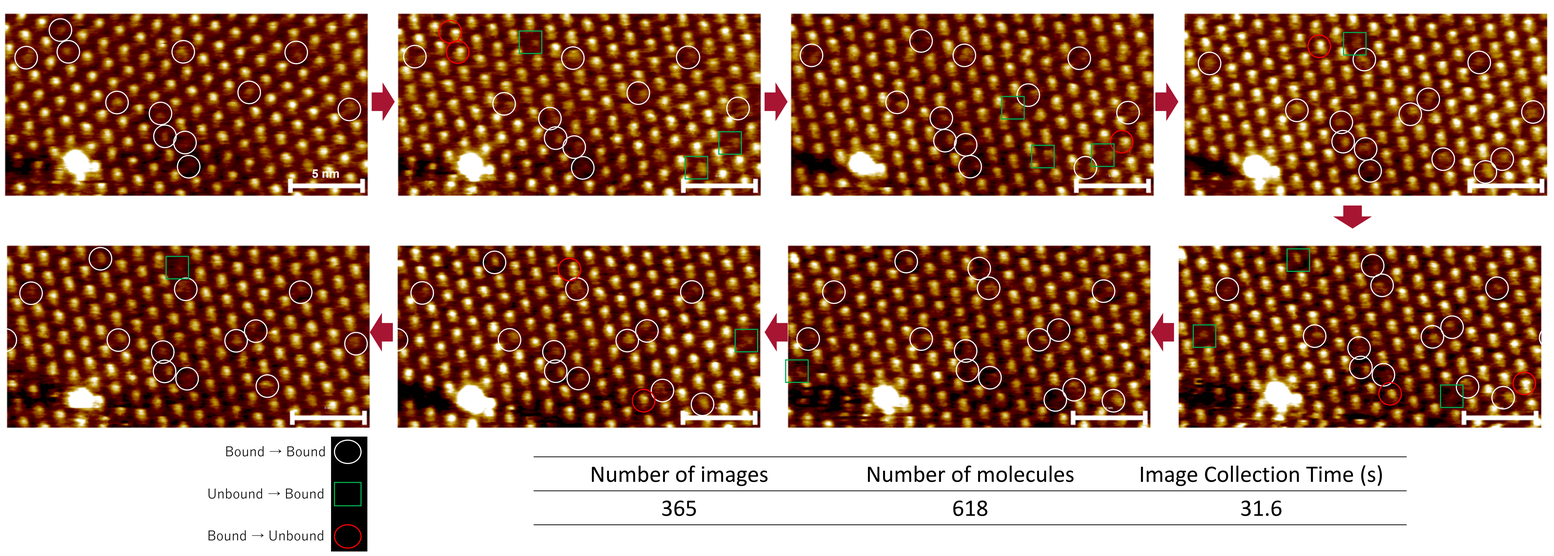
For Markovian systems, systems with no state memory, dwell times are distributed according to an exponential distribution of form:

$$P(t_i|k_i) = k_i e^{-k_i t_i}$$

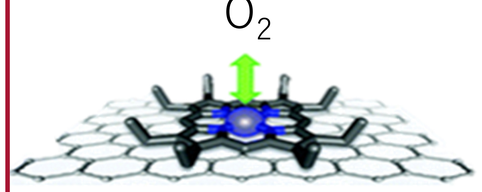
Where P is the probability density function (PDF) of molecule in i^{th} state for dwell time lasting time t_i, and k_i is the stochastic rate constant.

Mean of exponential distribution = mean dwell time = $1/k_i$





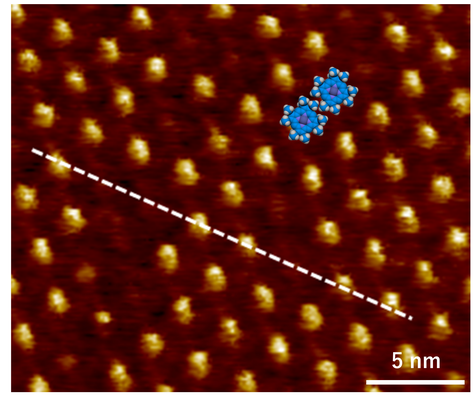
Number of images	Number of molecules	Image Collection Time (s)
365	618	31.6



O_2 + CoOEP/HOPG ⇆ O_2-CoOEP/HOPG

Cobalt(II)octaethylporphyrin (CoOEP)

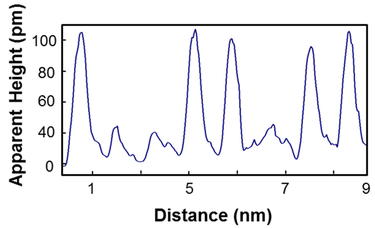
Typical STM image of CoOEP + O_2 system. Bright circles = free porphyrin, Dim circles = O_2-CoOEP adduct



Experimental Details:

CoOEP concentration: 1×10^{-5} M, Partial Pressure O_2 = 608 torr

Solvent: phenyloctane, Substrate: HOPG



Correcting for missed dwells:

Missed dwells arise from sampling time limitations. A missed dwell in state A causes a missed transition into the other state and can lead to erroneously long dwells. Because the dwell times are distributed according to the exponential PDF the fraction of dwell times that are too short to capture f_{missed} are found by considering the area of the distribution less than the scan time.

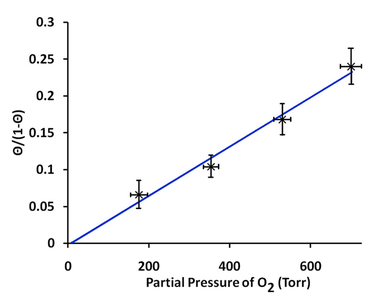
$$f_{missed,A} = 1 - e^{-k_{A\rightarrow B}\tau}$$

$$k_{corrected} = f_{missed} \times k_{corrected} + k_{observed}$$

This results in a set of coupled equations that can be solved numerically through a least squares method in order to correct the rate constants from the effects of missed dwells. With correction rate constants are improved to ~90% accuracy even when rate constants are similar to the acquisition rate.[1]

$$K = \frac{[O_2\text{–}CoOEP]}{P_{O_2}[CoOEP]} = \frac{\Theta}{(1-\Theta)\left(P/P_0\right)} = \frac{k_a}{k_d} = e^{-\Delta G/RT}$$

Oxygenation of Various Porphyrins	CoOEP (this work)	CoOEP[2] (on HOPG)	Co "Picket-fence" porphyrin[3] (in toluene)
K ($torr^{-1}$)	3e-4	4e-4	5e-3
ΔG (KJ/mol), 298K	20	21	13
Referenced to 1 torr standard state			



Langmuir adsorption plot from reference 2. Slope = K.

Comparison to other Co-porphyrins:

Present results match previous results for the same system determined by Langmuir adsorption isotherm analysis. However, are quite different from a specially designed porphyrin for facilitating oxygen binding at room temperature, the picket-fence porphyrin. For this porphyrin >80% are bound to oxygen at room temp. and transient adsorption spectroscopy has shown a adsorption rate constant of 10^7 s^{-1} and desorption of 10^6 s^{-1}. This illustrates the interesting influence of HOPG on adsorbed species reaction dynamics and warrants further study.

References:
(1) Stigler J, Rief M. *Chem. Phys. Chem*. **2012**, *13*, 1079–1086.
(2) Friesen, B. A.; Bhattarai, A.; Mazur, U.; Hipps, K. W. *J. Am. Chem. Soc.* **2012**, *134*, 14897–14904.
(3) Zou, S.; Baskin, J. S.; Zewail, A. H. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, *99*, 9625–9630.
(4) Johnson, K. N.; Mazur, U,; Hipps, K. W. *J. Phys. Chem. Lett*. **2022**, 13, 4918–4923.

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