Bridging the gap between theoretical and experimentally inferred reorganization energy

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Overview

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- Motivation
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Background - Biology

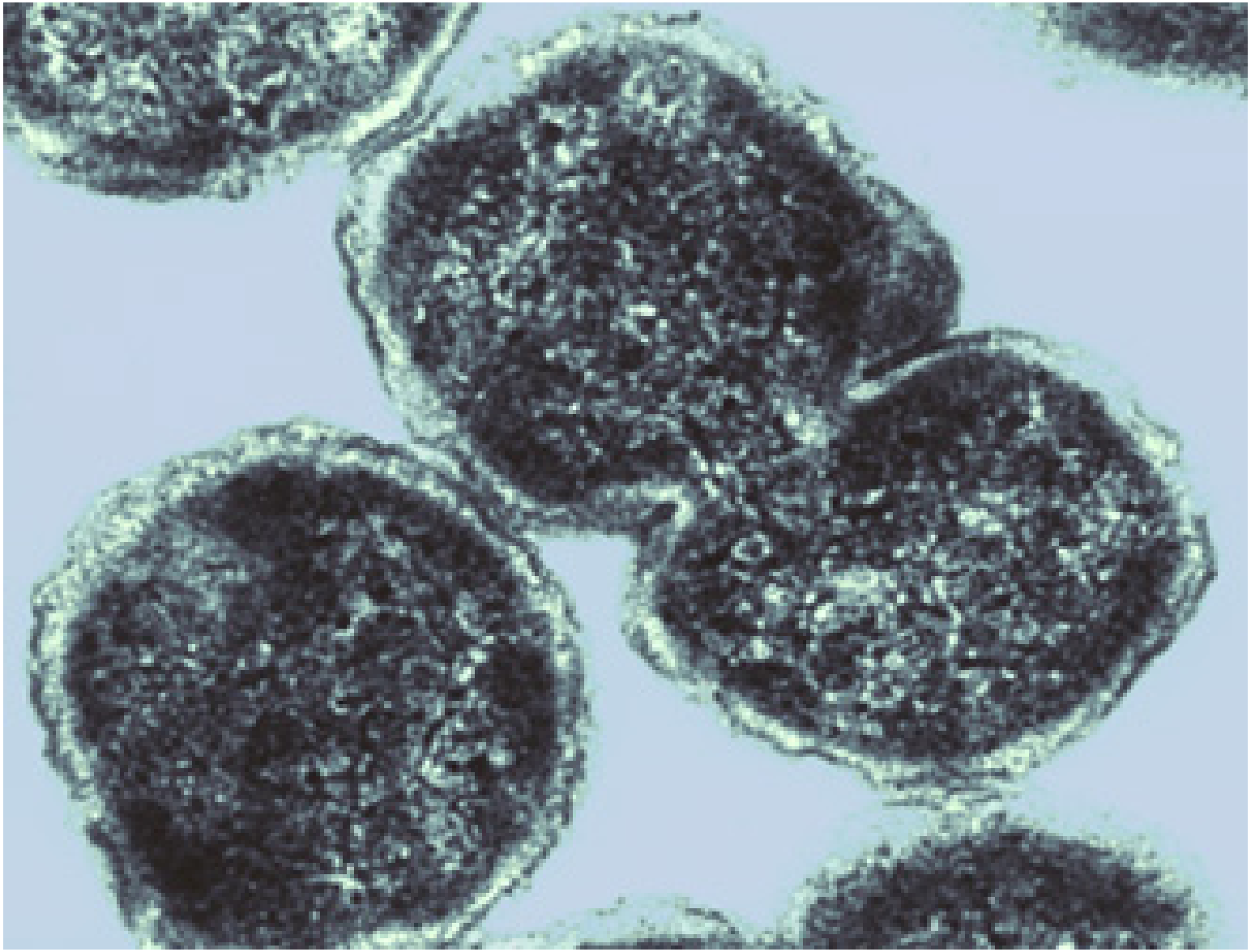
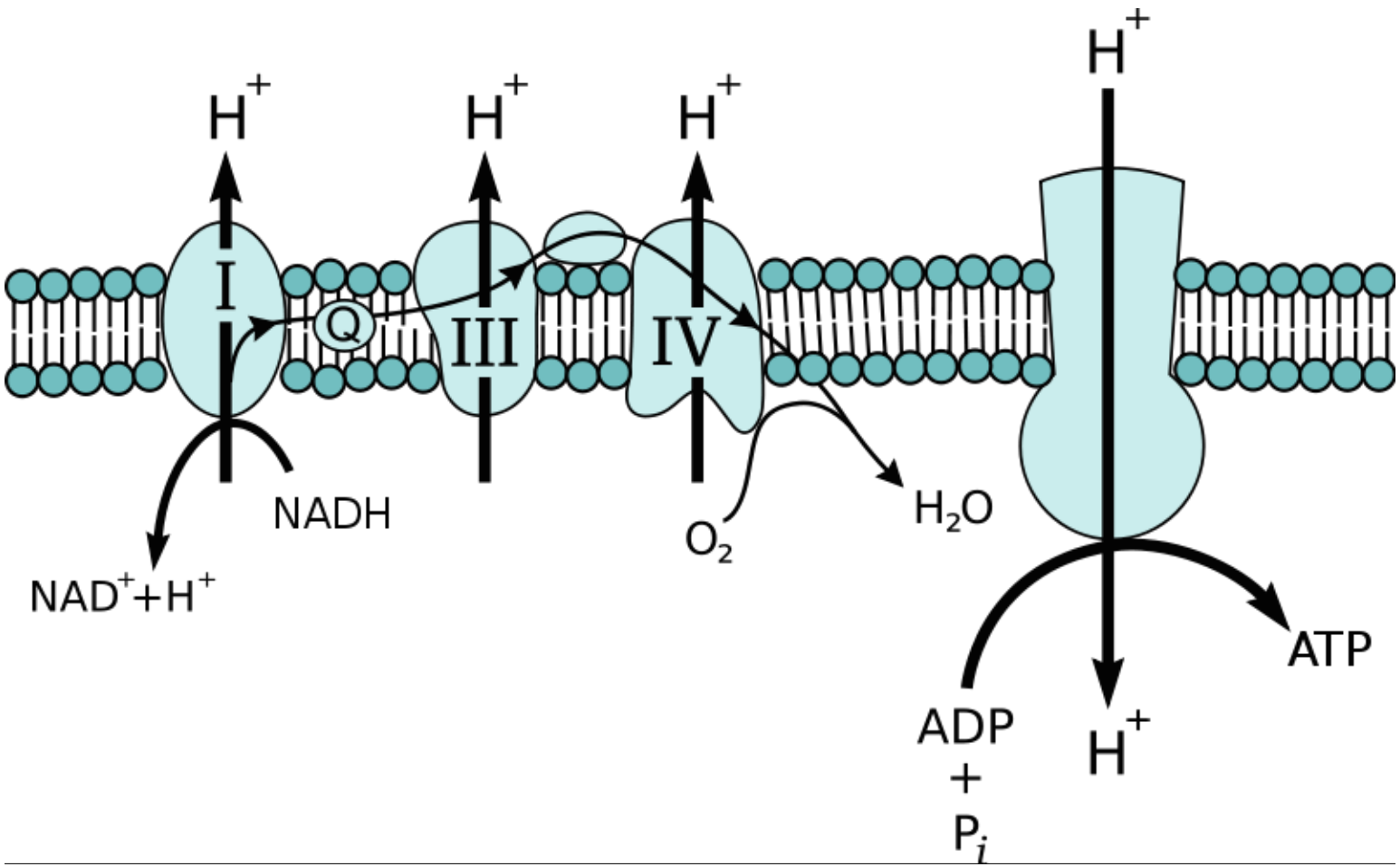
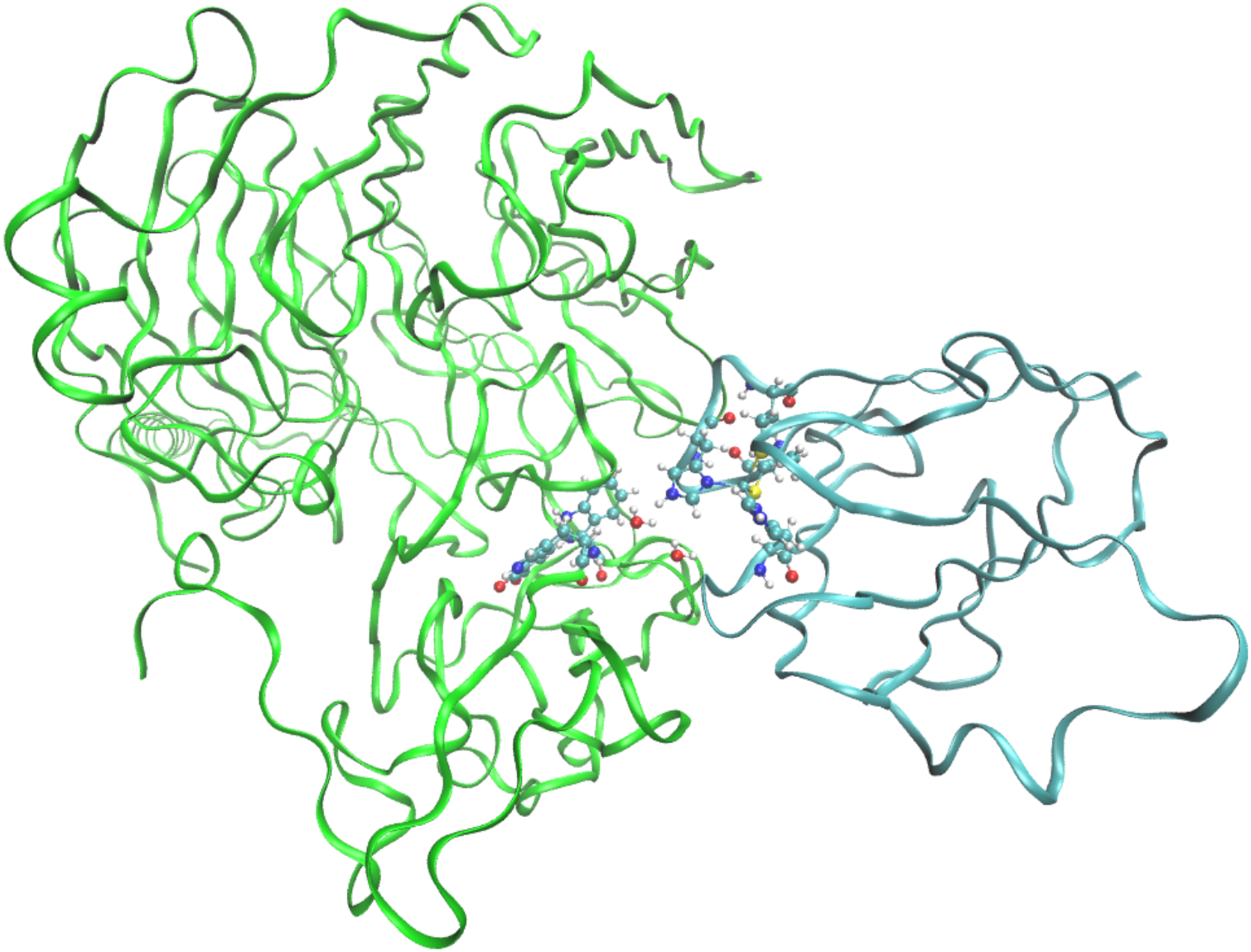


Photo credit: Richard Evans-Gowing at the University of East Anglia


H+
H+
H+
H+
I
Q
III
IV
NADH
NAD+ + H+
O2
H2O
ADP
+
Pi
H+
ATP



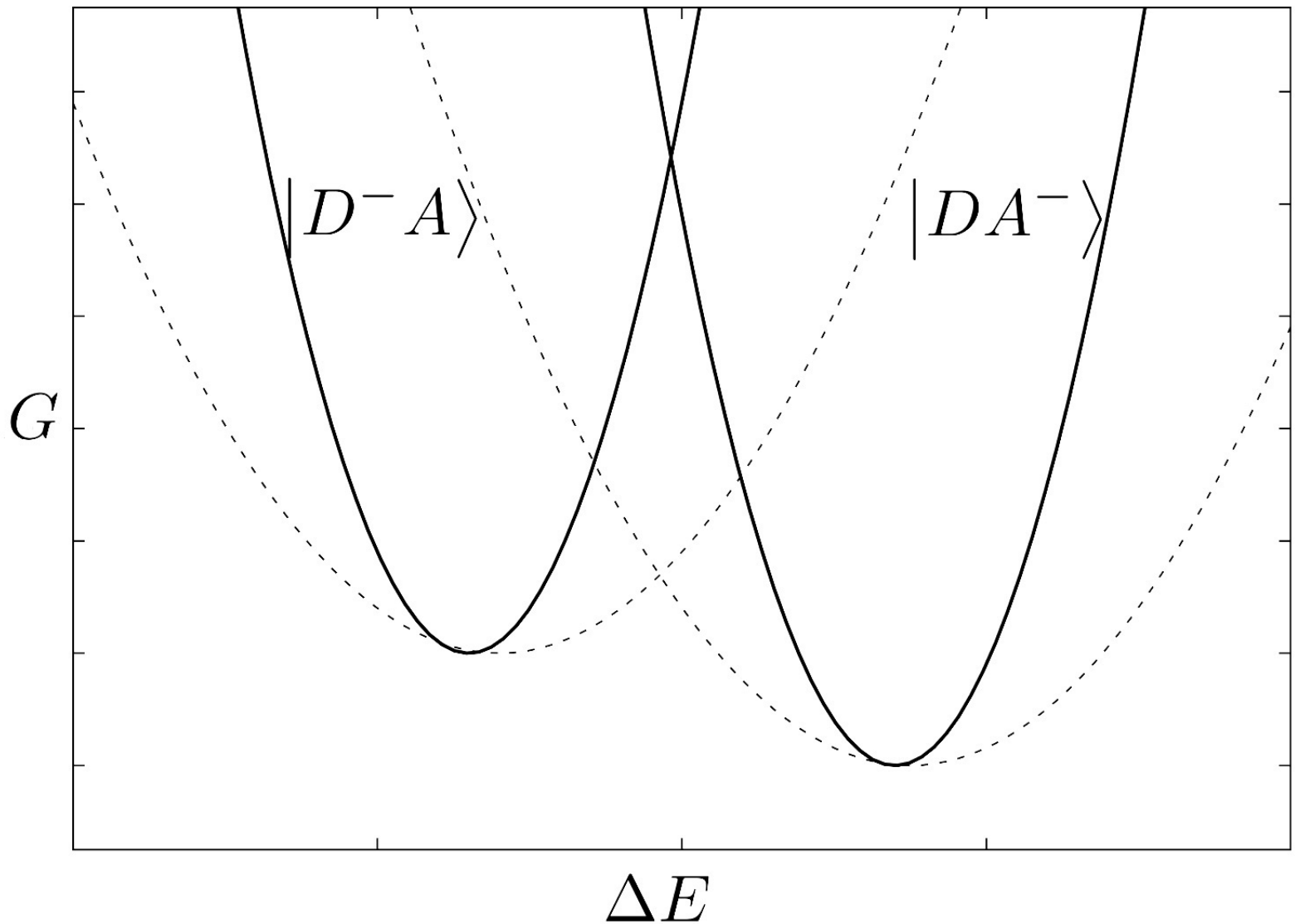
Background - Physical Chemistry

Marcus Theory

$$k_{\mathrm{ET}} = \frac{2\pi}{\hbar}|H_{AB}|^2 \frac{1}{\sqrt{4\pi k_{\mathrm{B}} T}} \exp\left(-\frac{(\lambda + \Delta G^{\circ})^2}{4\lambda k_{\mathrm{B}} T}\right)$$

$$\lambda_{\mathrm{St}} = -\frac{\langle V_{\mathrm{os}} \rangle}{2} \qquad \lambda_{\mathrm{var}} = \lambda_{\mathrm{St}} - \frac{\langle \delta V_{\mathrm{os}} \delta V_{\mathrm{o}p} \rangle}{2 k_{\mathrm{B}} T}$$

Martin, D and Matyushov, D. JCP, 2015.


$|D^- A\rangle$
$|D A^-\rangle$
G
ΔE

Problem

Disagreement between the theoretically calculated and experimentally inferred reorganization energy for the MADH-amicyanin complex.

Motivation

Efficient, site-selective electron transfer is crucial for effective metabolic processes.

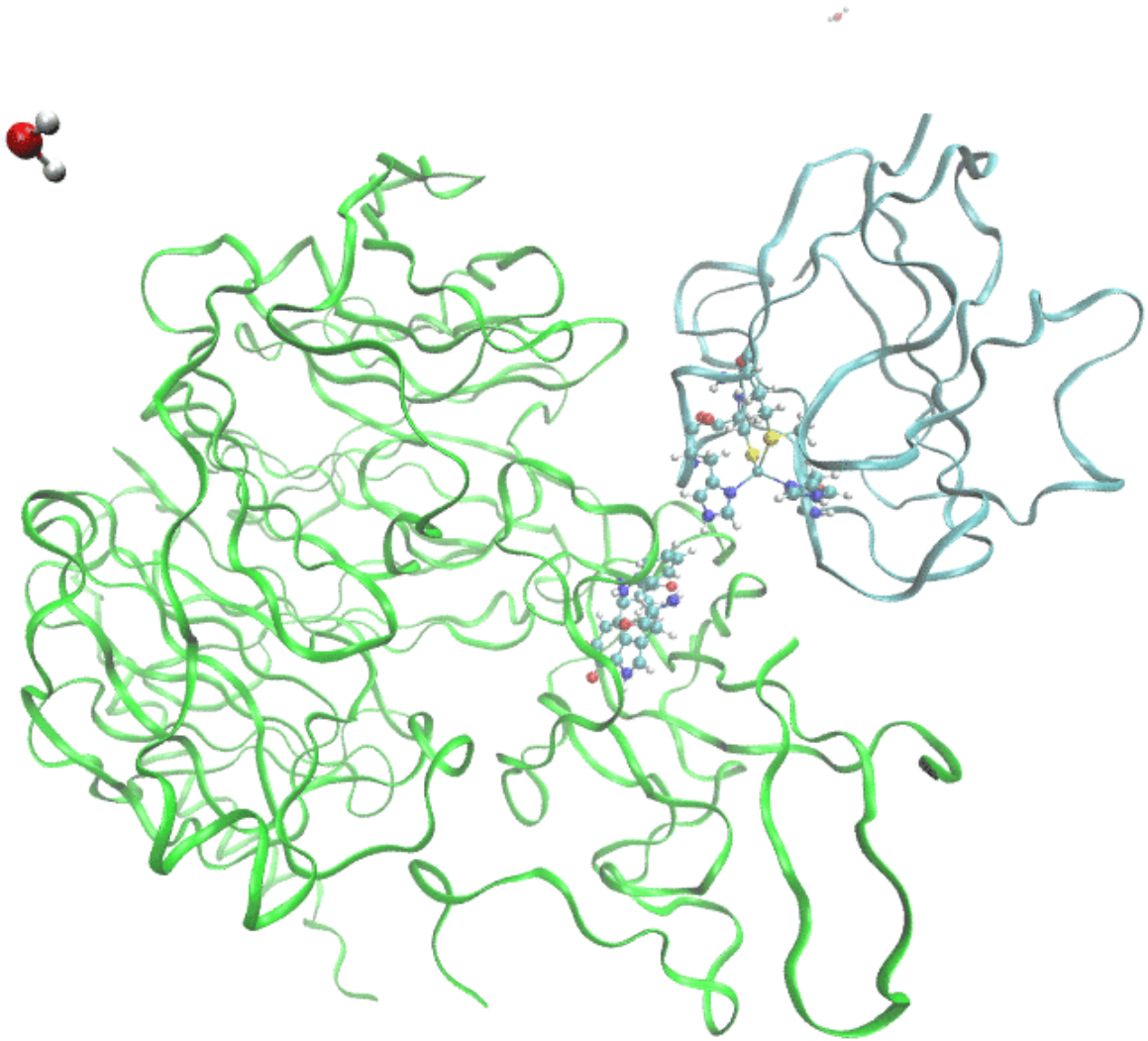
Diseases associated with free radical production.

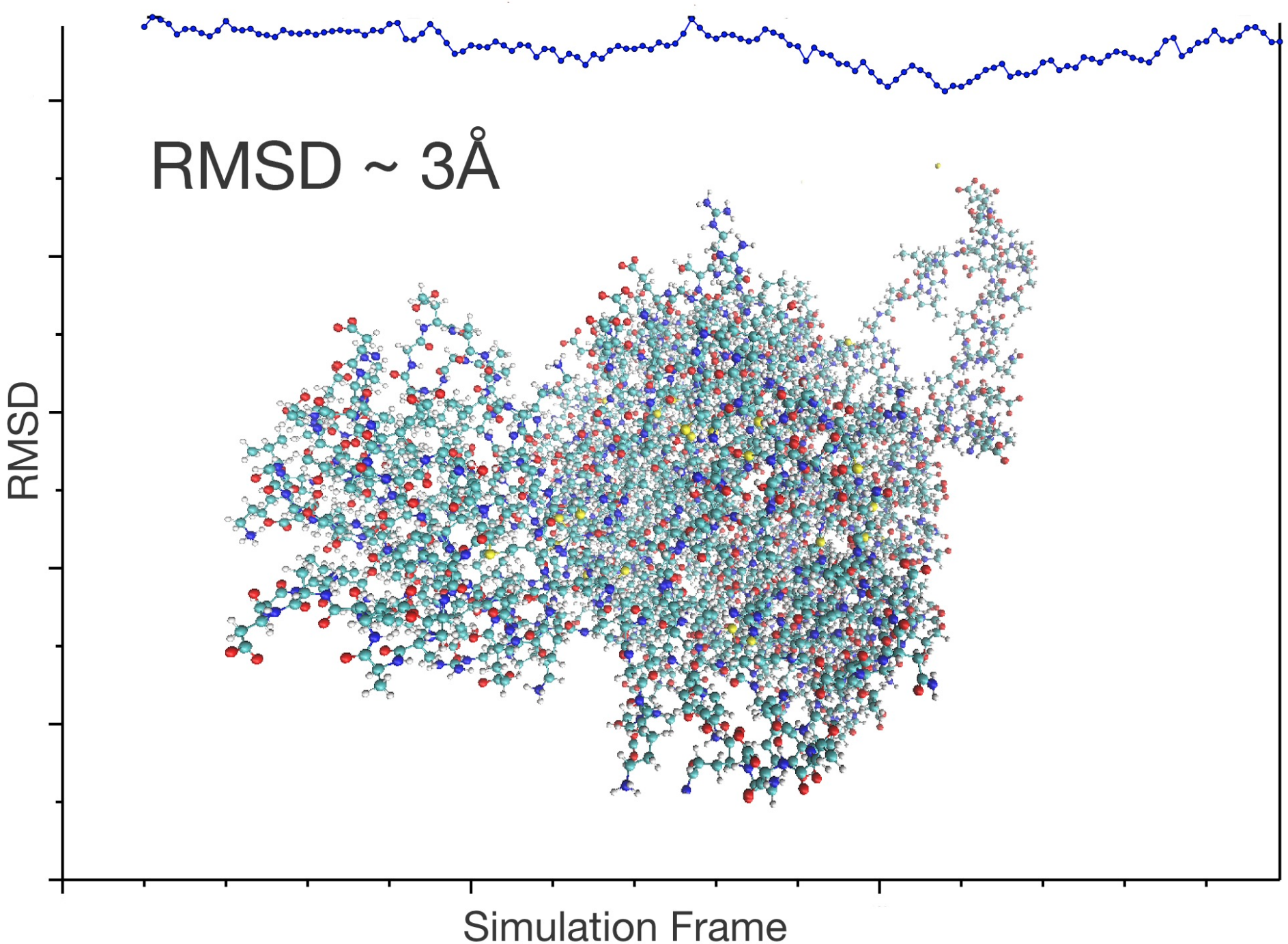
Characterize efficient atomic scale wires.

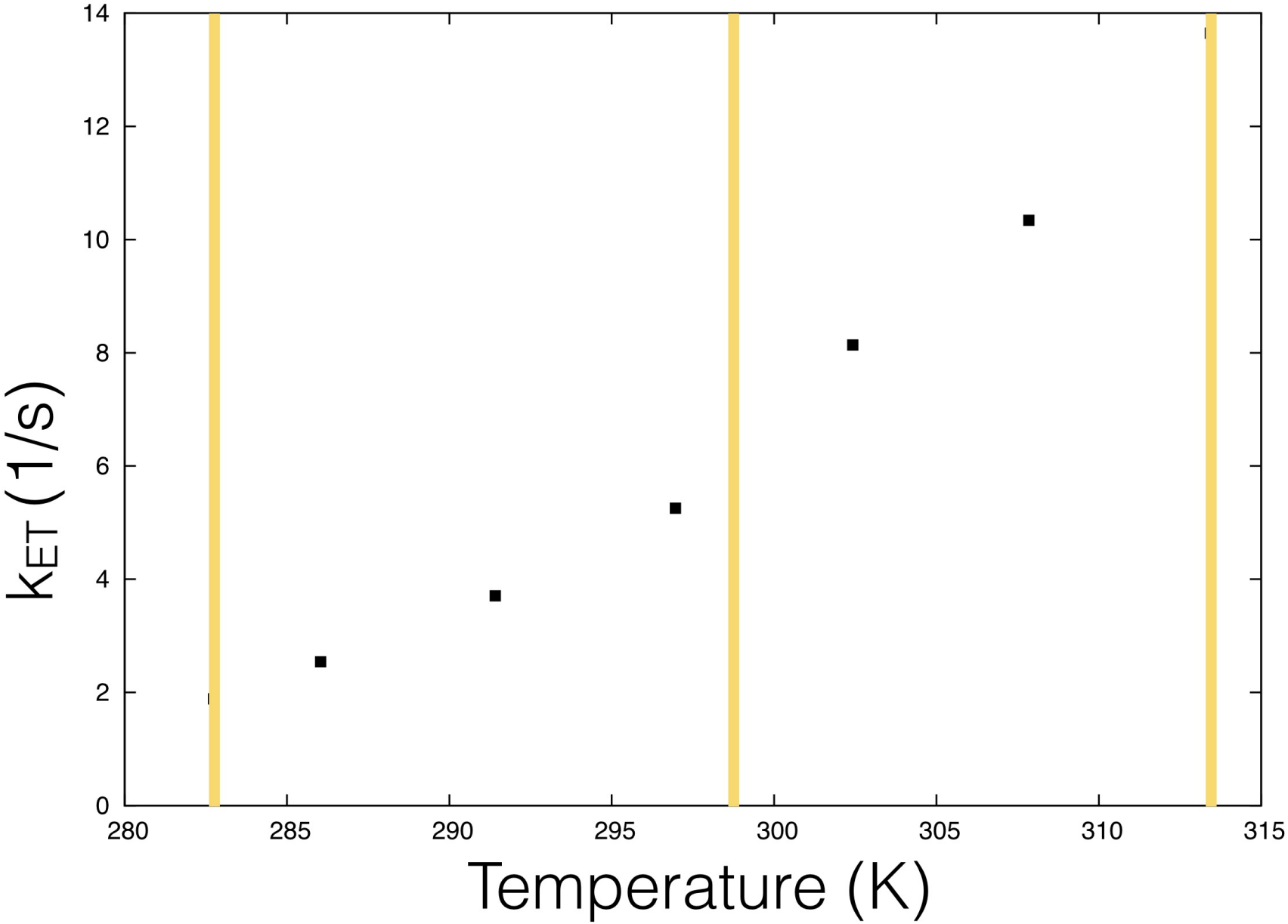
Methods

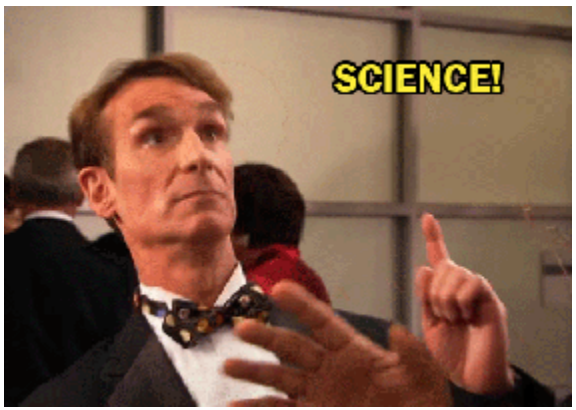
- Apply the two-parameter model to the MADH-amicyanin system.
- Quantum calculations using density functional theory.
- Classical calculations using molecular mechanics, and molecular dynamics.
- Combined classical and quantum.

Results



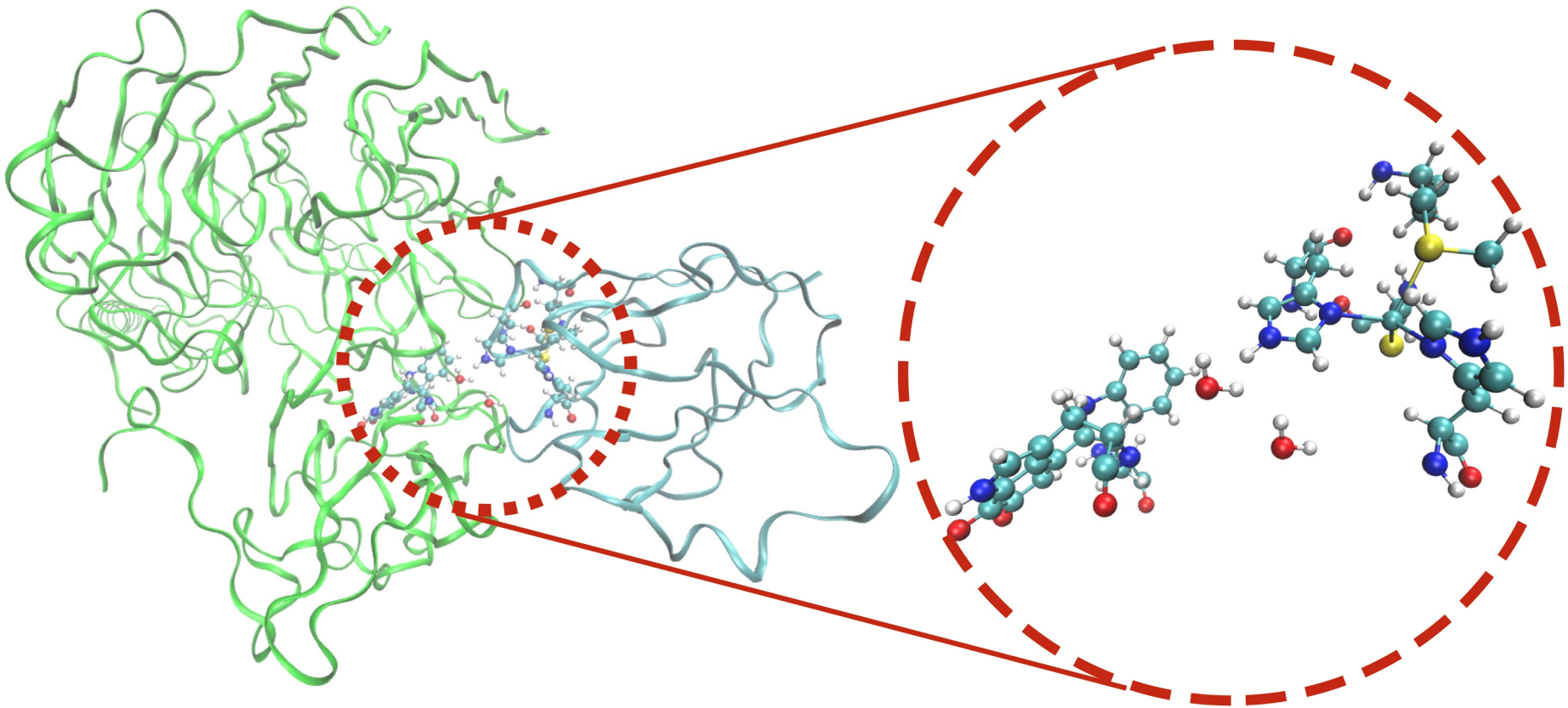

RMSD ~ 3Å
RMSD
Simulation Frame


14
12
10
8
6
4
2
0
280
285
290
295
300
305
310
315
k_{ET} (1/s)
Temperature (K)


SCIENCE!

Discussion

- Simulations allow us to probe inaccessible time and length scales.
- Fluctuations in how the protein rearranges itself and surrounding solvent is vital.
- λ_{var} is an attempt to account for these fluctuations.

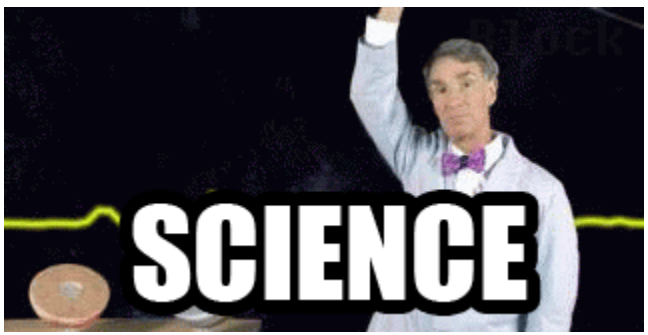


Conclusion

- Disagreement in theoretical and experimentally inferred λ in MADH-amicyanin.

- Claim: two-paramenter model, accounting for statistics around protein-solvent electrostatic interactions can bridge the gap between theory and experiment.

- Novelty: application of the two-parameter model to MADH-amicyanin.


SCIENCE

Thank you, merci!