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Photochemical dissipative structuring of the fundamental molecules of life

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Instituto de Física UNAM

Abstract: It has been conjectured that the origin of the fundamental molecules of life, their proliferation over the surface of Earth, and their complexation through time, are examples of photochemical dissipative structuring, dissipative proliferation, and dissipative selection, respectively, arising out of the non-equilibrium conditions created on Earth's surface by the solar photon spectrum. Here I describe the non-equilibrium thermodynamics and the photochemical mechanisms involved in the synthesis and evolution of the fundamental molecules of life from simpler more common precursor molecules under the long wavelength UVC and UVB solar photons prevailing at Earth's surface during the Archean. Dissipative structuring through photochemical mechanisms leads to carbon based UVC pigments with peaked conical intersections which endow them with a large photon disipative capacity (broad wavelength absorption and rapid radiationless dexcitation). Dissipative proliferation occurs when the photochemical dissipative structuring becomes autocatalytic. Dissipative selection arises when fluctuations lead the system to new stationary states (corresponding to different molecular concentration profiles) of greater dissipative capacity as predicted by the *universal evolution criterion* of non-equilibrium thermodynamics established by Onsager, Glansdorff, and Prigogine. An example of the UV photochemical dissipative structuring, proliferation, and selection of the nucleobase **adenine** from an aqueous solution of HCN under UVC light is given.

Keywords: origin of life; disspative structuring; prebiotic chemistry; adenine

Thermodynamic Dissipation Theory of the Origin and Evolution of Life

Life´s Function;
Sunlight --> Heat

1. Dissipative Structuring
2. Dissipative Proliferation
3. Dissipative Selection

Michaelian, K., Thermodynamic Origin of Life, *Cornell ArXivv,* arXiv:0907.0042 [physics.gen-ph] 2009.
Michaelian, K., Thermodynamic Dissipation Theory for the Origin of Life, *Earth Syst. Dynam.,* 2 (2011) 37-51.

Physical Conditions at Life's Origin (Sunlight?)

3,850,000,000 years ago

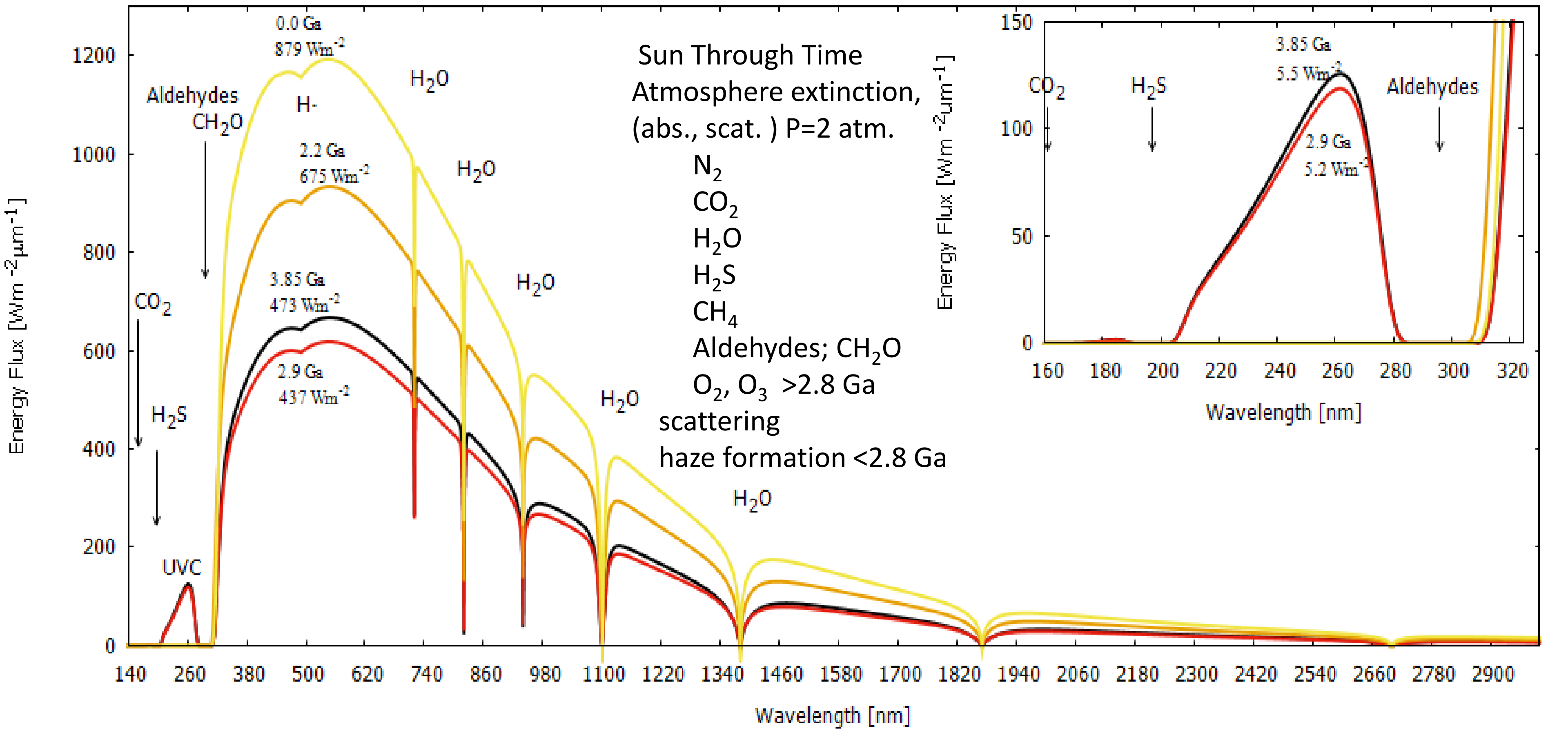
Vulcanos H_2S, H_2O, CO_2

Hot seas, 85°C

Atmosphere;
N_2, CO_2, H_2O, CH_4, H_2
No O_2, no O_3
UV light intense

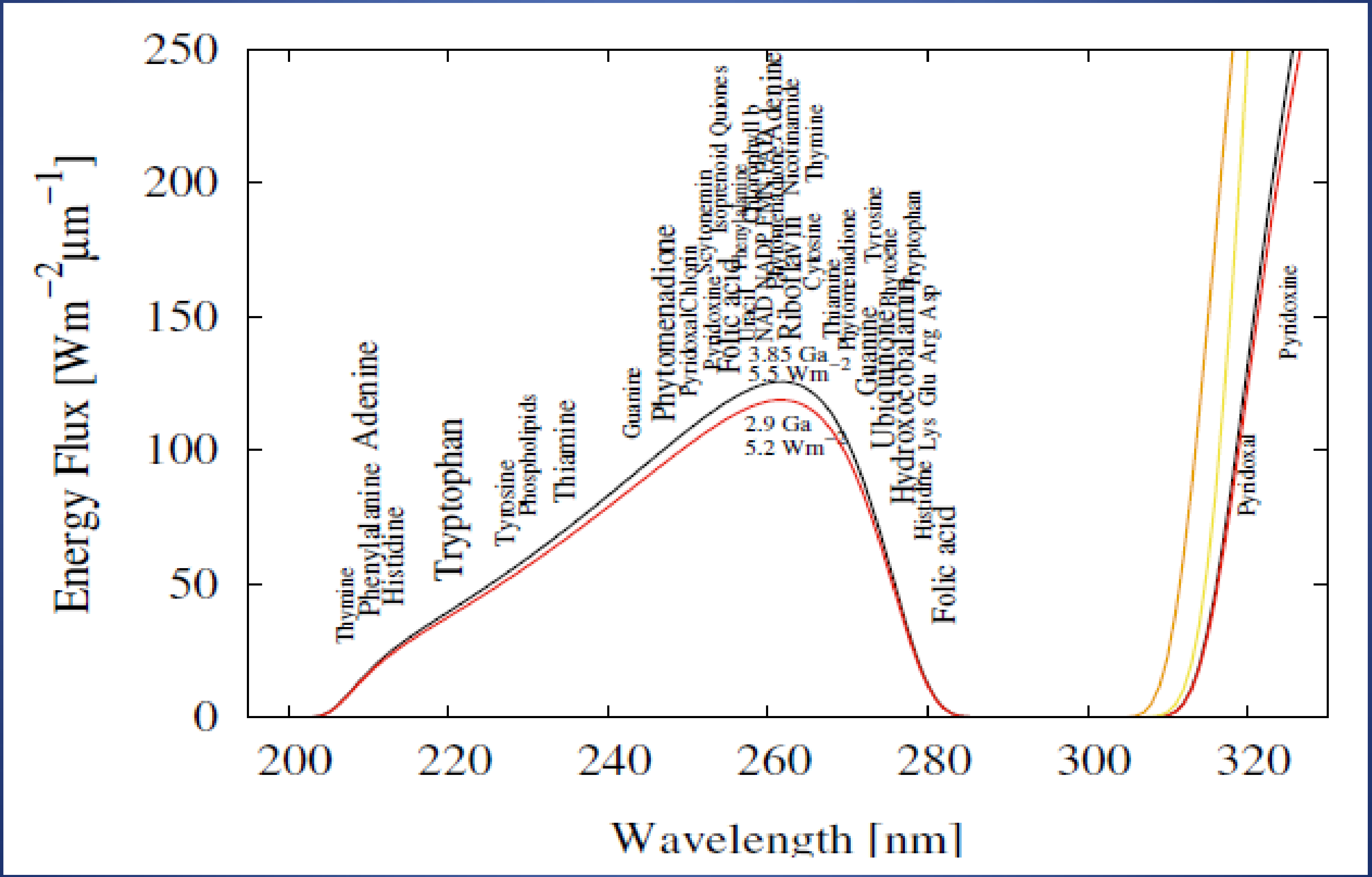
Solar spectrum?

Solar Spectrum, Earth's Surface



Michaelian, K. and Simeonov, A., *Biogeosciences* **12**, 4913—4937 (2015).

Nucleic acids, amino acids, fatty acids, coemzymes, are UV-C Pigments

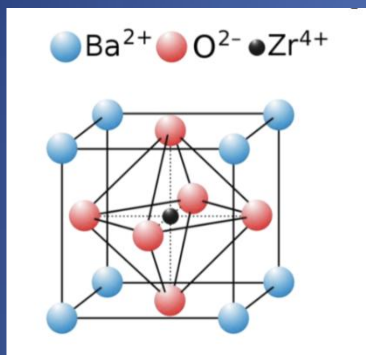


Michaelian, K. and Simeonov, A., *Biogeosciences* **12**, 4913—4937 (2015).

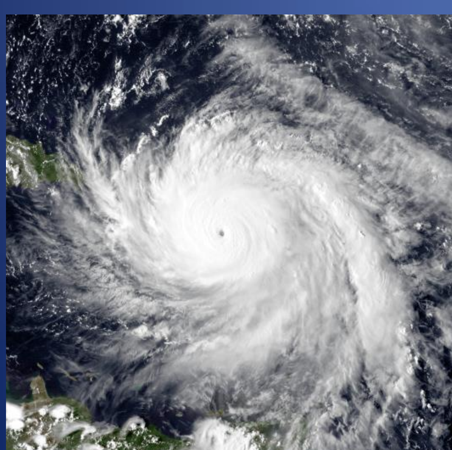
Dissipative Structuring

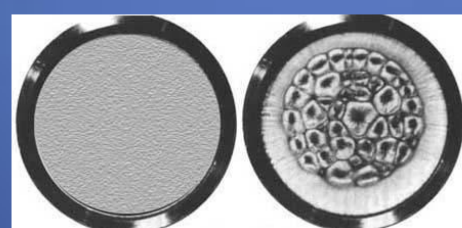
Two classes of structures;

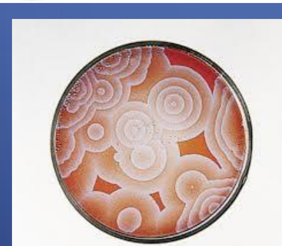
1) Equilibrium – minimization of Gibb’s potential



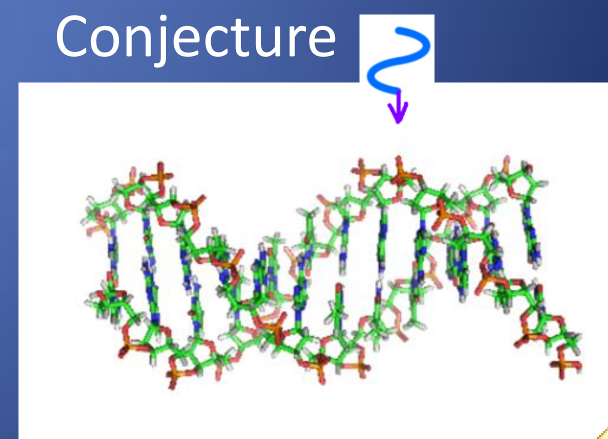
2) Non-equilibrium – optimization of dissipation







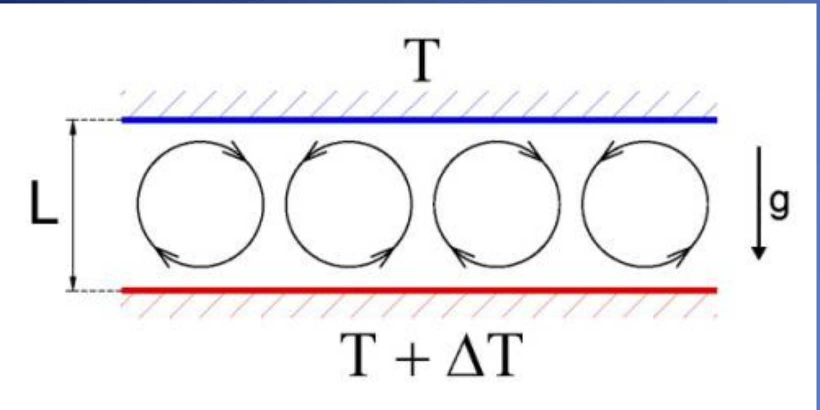
Conjecture

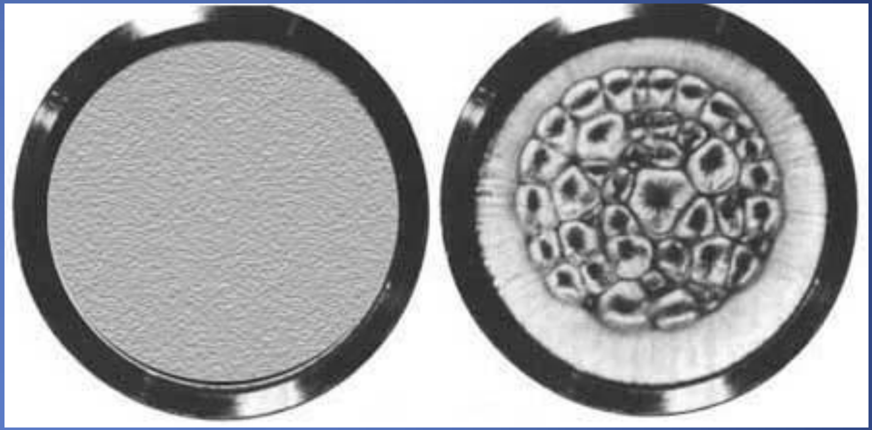


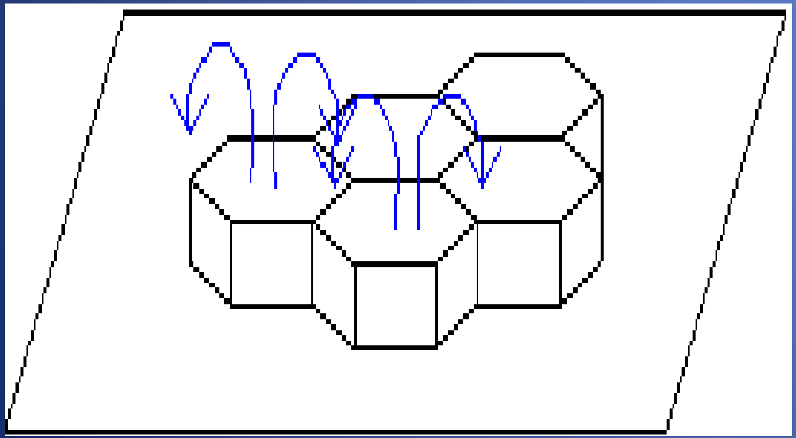
Michaelian, K. Earth Sys. Dyn. 2011

Dissipative Structuring

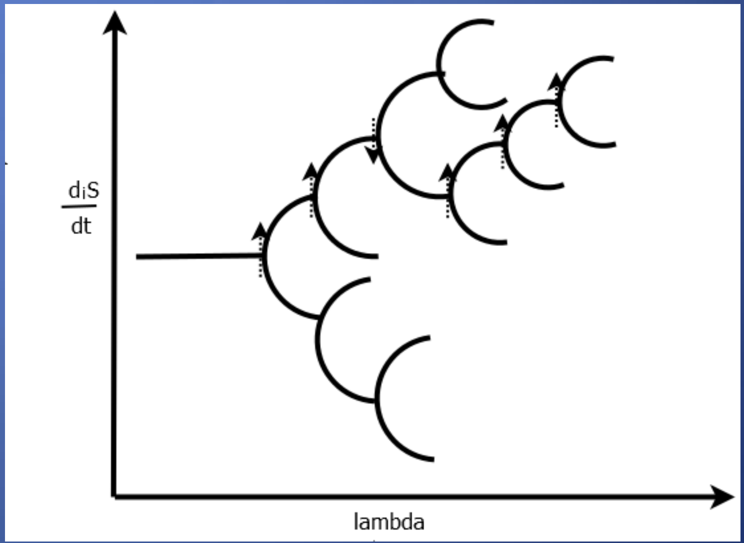
Macroscopic – coordinate degrees of freedom, e.g. Bénard Cell







$$\sigma = J \cdot X = -J_{th} \cdot \nabla \left(\frac{1}{T} \right),$$

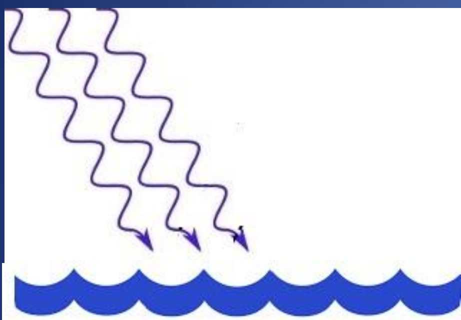


Non-linear relation; X, J

Microscopic Dissipative Structuring

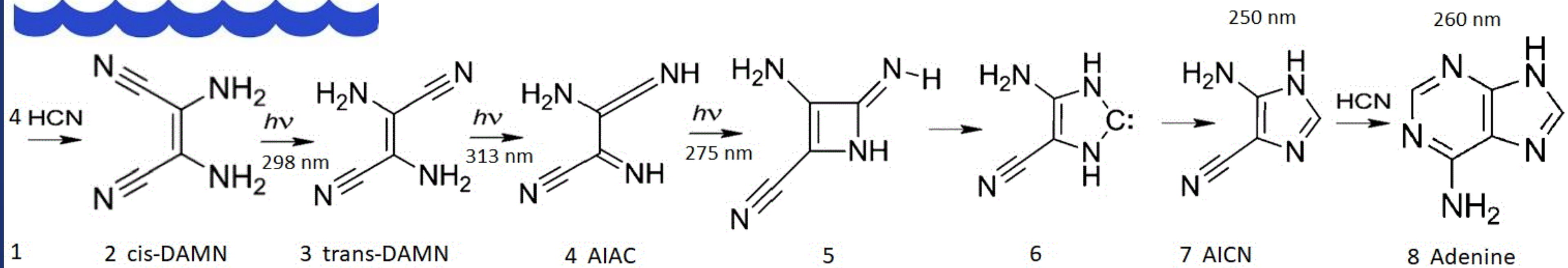
Microscopic – molecular degrees of freedom

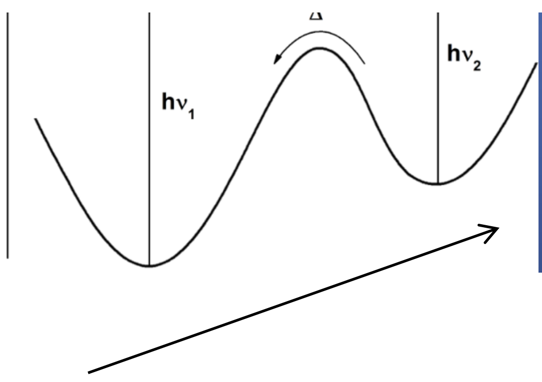
-- isomerizations, tautomerizations, rotations around bonds, charge transfer, exciplex formation, etc. (molecular reconfigurations)



e.g. Adenine (Ferris and Orgel, 1966)

Boulanger et al., Angew. Chem. Int. Ed. 2013, 52, 8000

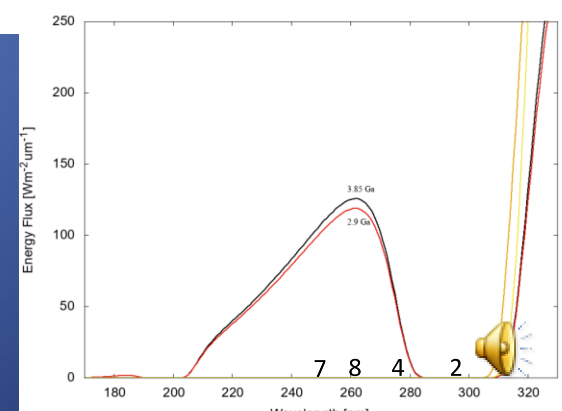


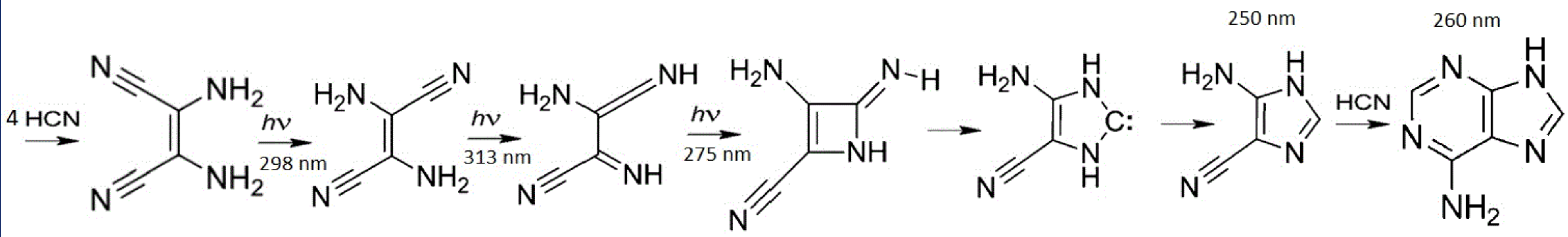


Reactions can go "up hill" in energy or "down hill" in entropy

Structuring to dissipate photon potential.

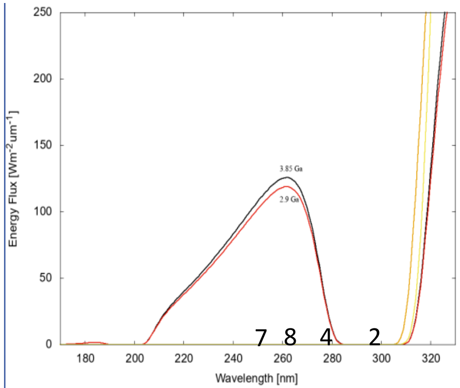
Michaelian, K., Microscopic Dissipative Structuring and Proliferation at the Origin Of Life, *Heliyon*, **3** e00424 (2017)



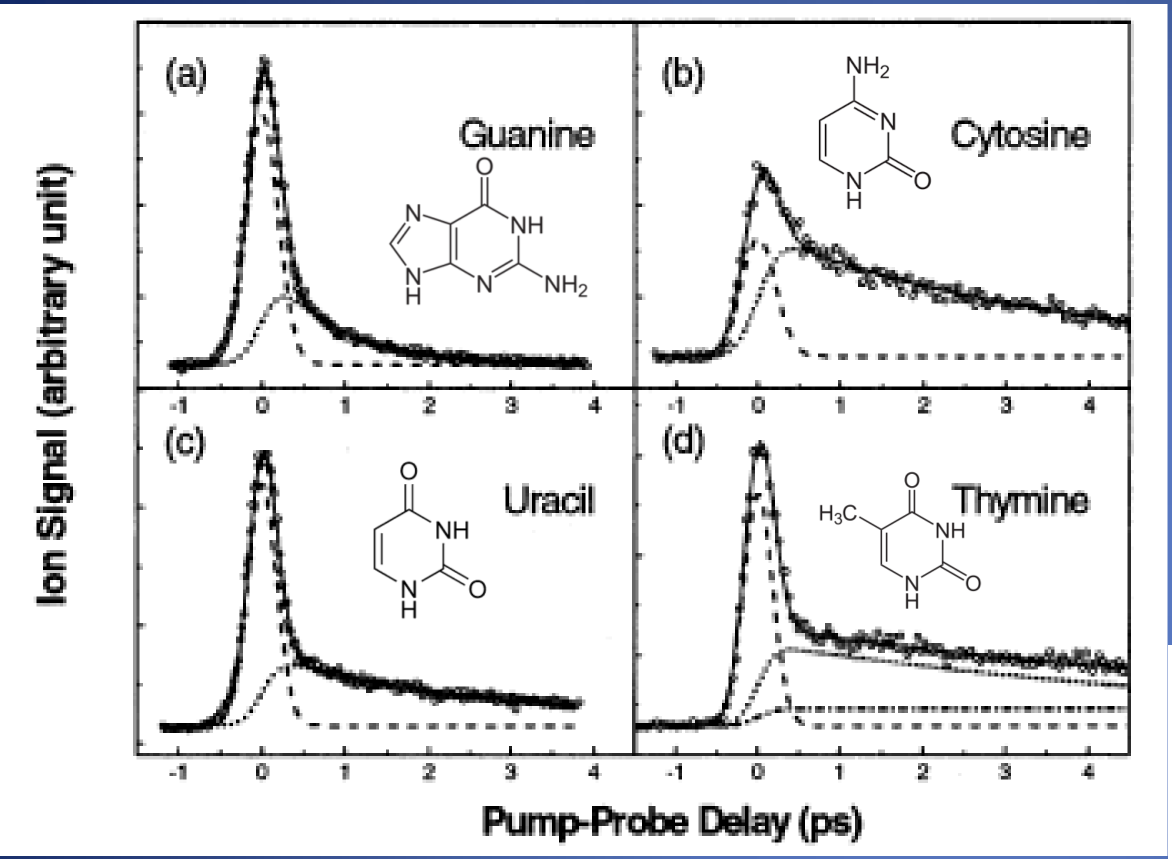


1 2 cis-DAMN 3 trans-DAMN 4 AIAC 5 6 7 AICN 8 Adenine

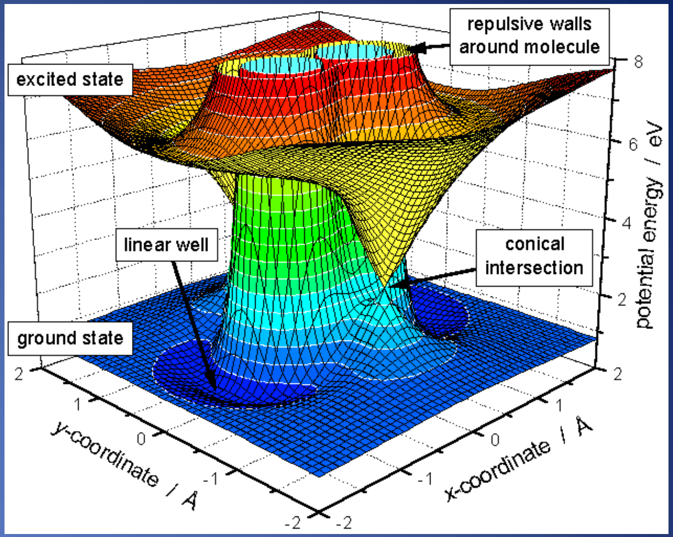
Step (Fig. 3)	Molecule	λ_{isom} (nm)	Φ	λ_{max} (nm)	ε (M^{-1} cm^{-1})
1	4HCN	thermal			
2	cis-DAMN	254 [4]	0.045 [2]	290 [1], 298 [2],	14,000 [2],
				295 [4],	12,000 [4],
				295 [8]	13,500 [8]
3	trans-DAMN	<325 [4]	0.0034 [2]	326 [1], 313 [2]	8,500 [2],
				314 [4], 310 [7]	8,000 [5]
4	AIAC	275 [9]	–	255–290 [4]	–
7	AICN	thermal		250 [2]	10,700 [2],
				247 [3]	
				245–250 [4], 246 [7]	11,000 [3]
8	adenine			260 [6]	14,000 [6]
				261 [10]	13,400 [10]
				259 [11]	15,040 [11]



Rapid UV-C Dissipation RNA/DNA

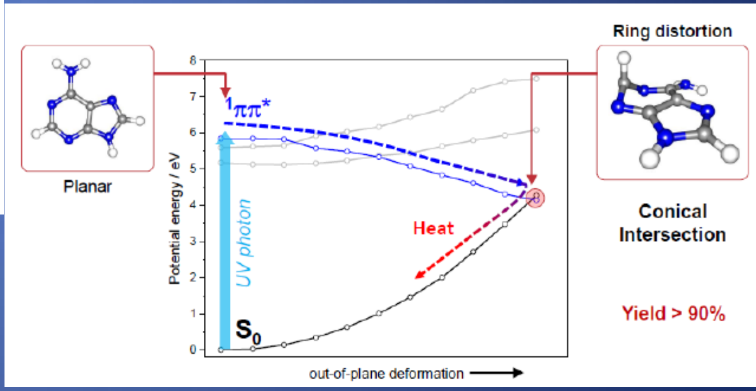


Kang et al., *JACS* **124**, 12958-12959 (2002)



Conical Intersection

Canuel et al., *J. Chem. Phys*. **122**, 074316 (2005)

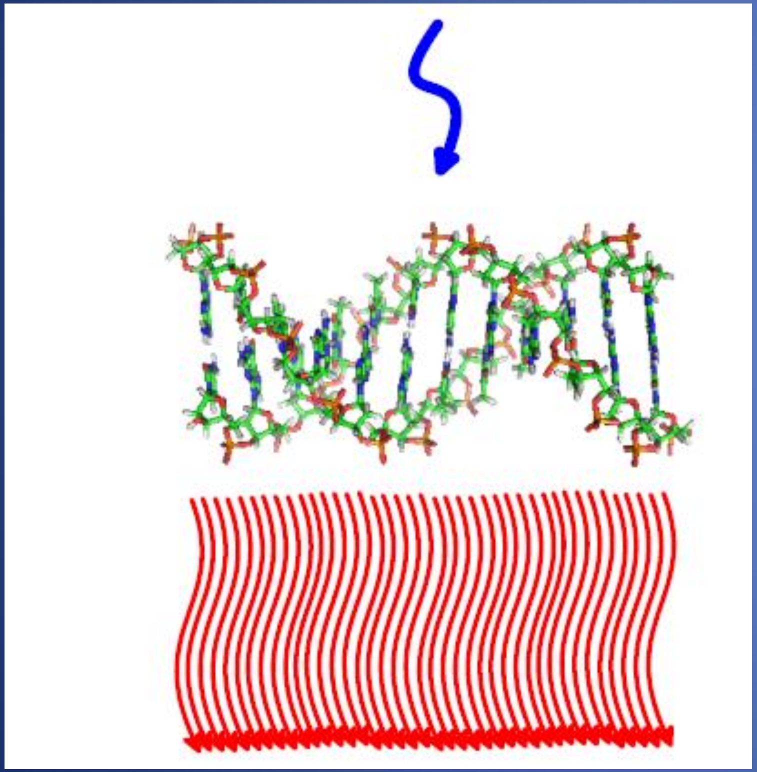


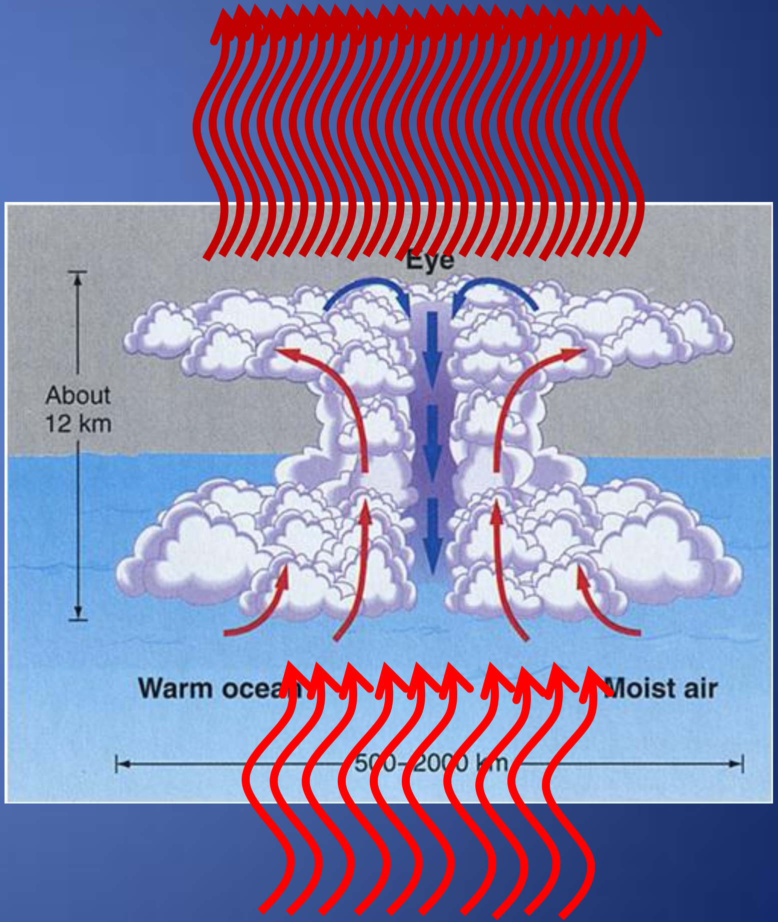
Kleinermanns *et al., Int. Rev. Phys. Chem.* **32,** 308 (2013)
Barbatti et al., *PNAS* **107,** 21453 (2010)

RNA/DNA bases extremely rapid dissipators
RNA/DNA resistant to destruction by UV light

Dissipation

RNA and DNA are Excellent Dissipative Structures



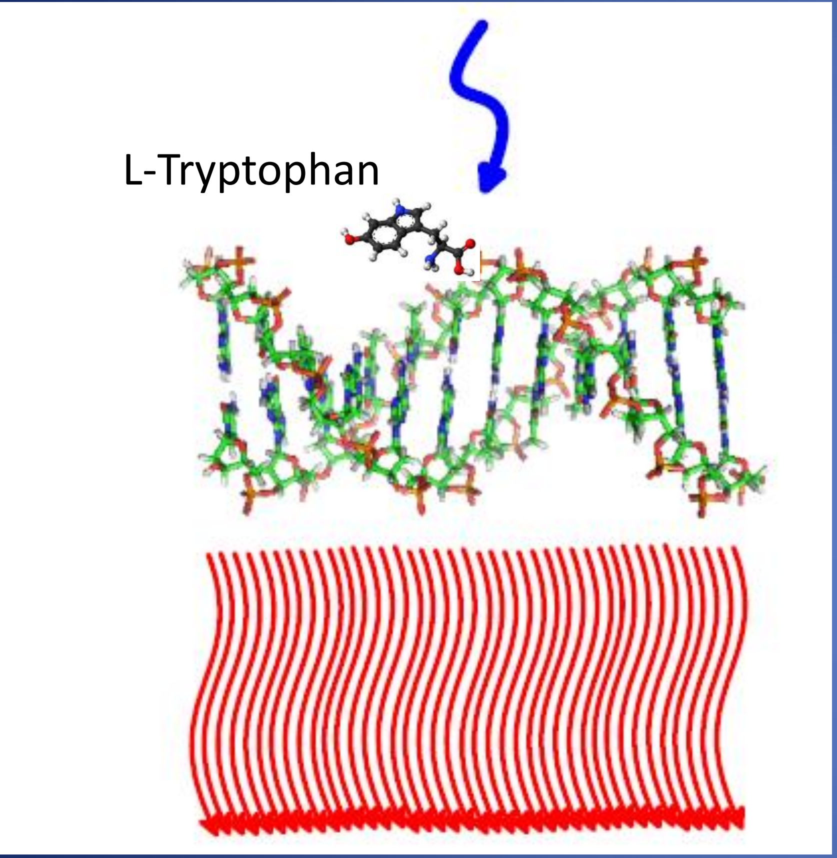


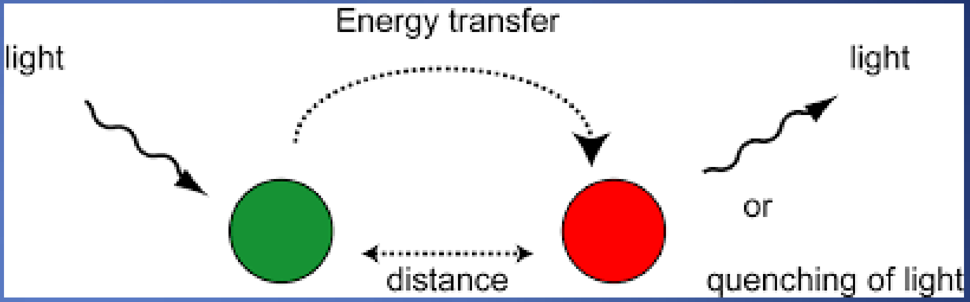
Microscopic, UVC

Macroscopic, Infrared

Not all fundamental molecules have a conical intersection

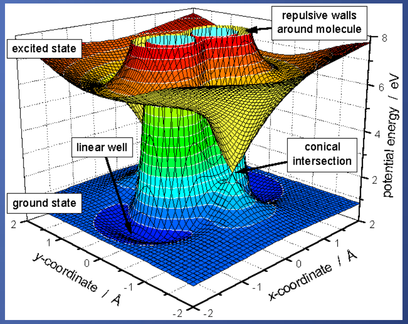
Resonant Energy Transfer





Donor
Tryptophan

Aceptor
DNA



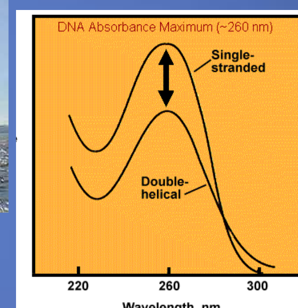
Tryptophan has affinity to DNA codon.

Complex is greater dissipating system.

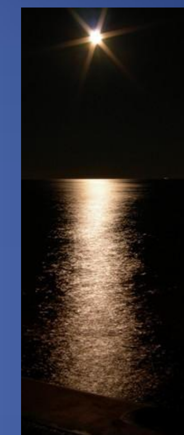
Evolution => Complexation => Greater dissipation

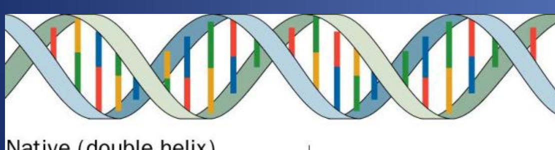
Dissipative Proliferation of RNA/DNA (enzymeless)
UV and Temperature Assisted Reproduction (UVTAR)

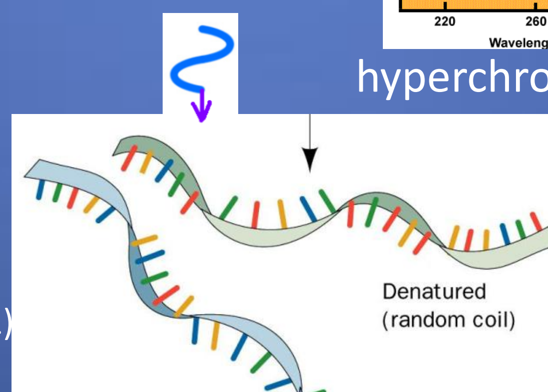
Ocean temp < 85°C

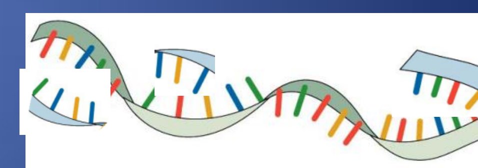


hyperchromism









Michaelian, *Earth Syst. Dynam*. **2**, 37–51 (2011)

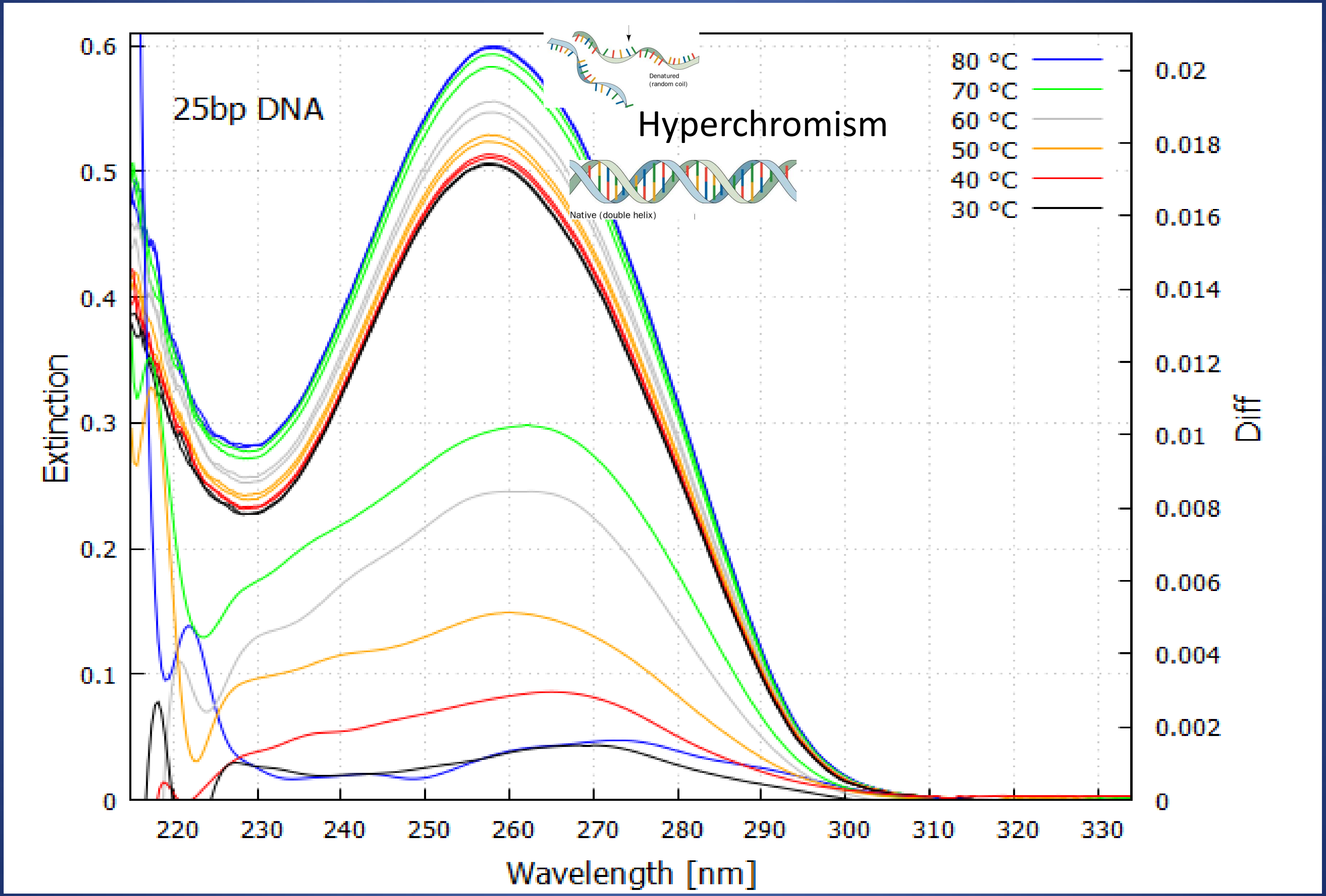
Template directed autocatalytic photochemical reaction

Replication tied to photon dissipation – entropy production.

Experiment

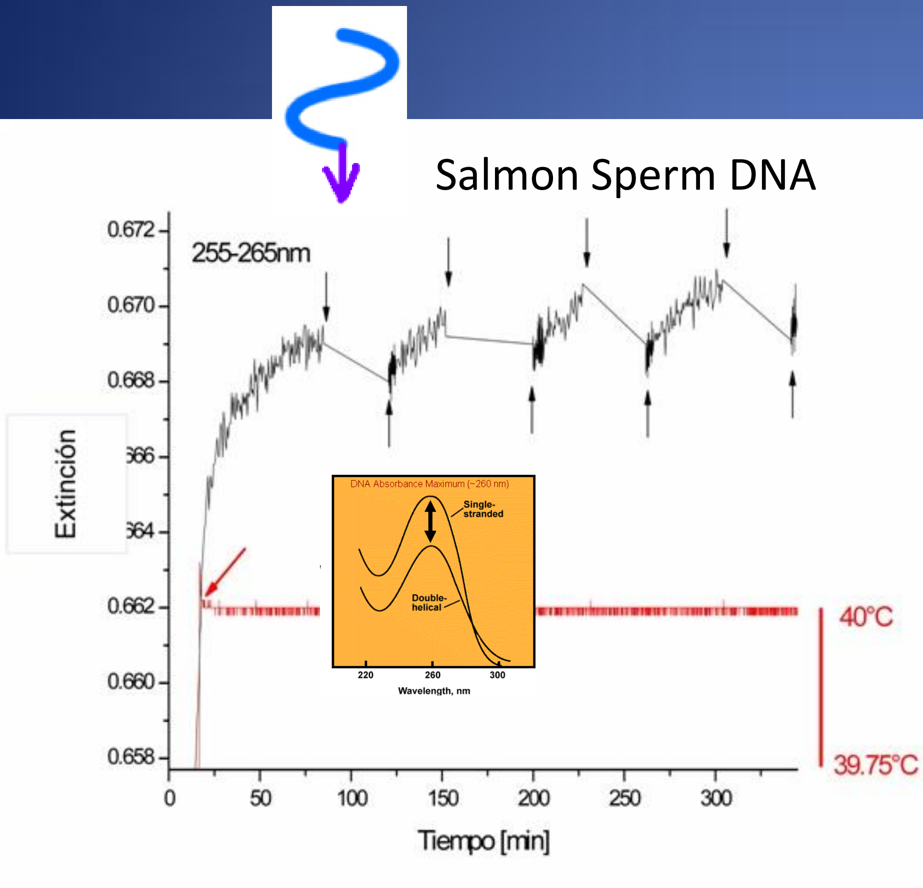

DT-MINI-2-GS
Fundamentos de
ECUACIONES DIFERENCIALES
qpod
RED TIDE
SONY
HR4000CG-UV-NIR
Ocean Optics
28 11 2013

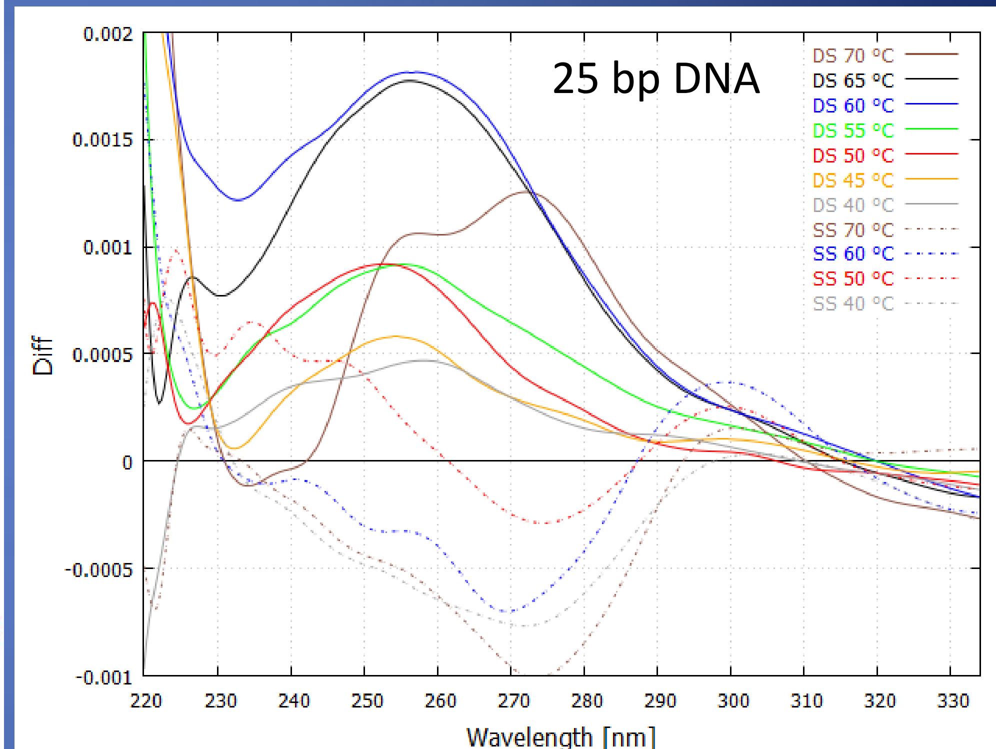
Absorption Spectrum DNA



Michaelian, K. and Santillán Padilla, N., *Heliyon* 5, e01902 (2019).

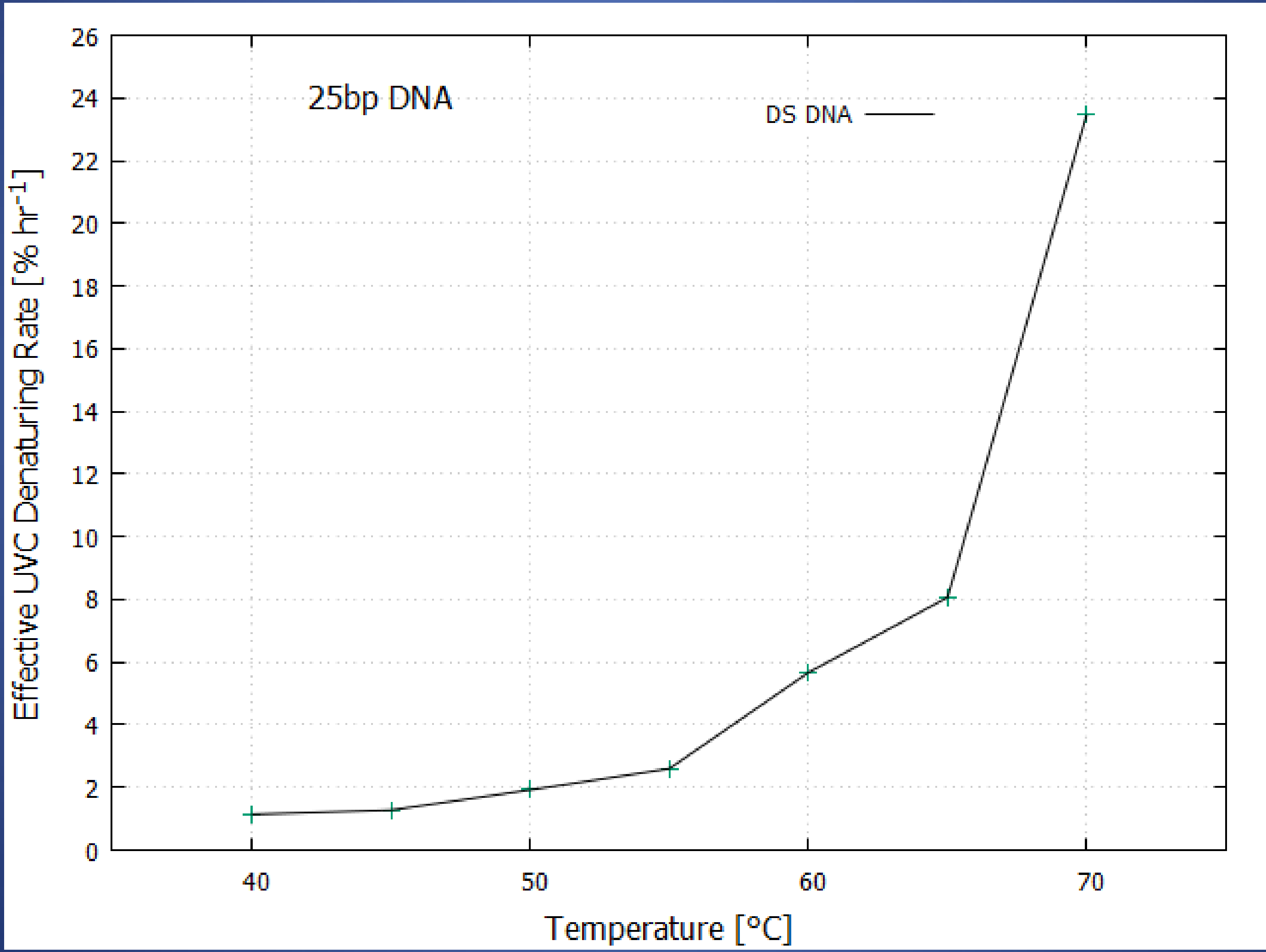
Expt.--UVC Light-induced Denaturing





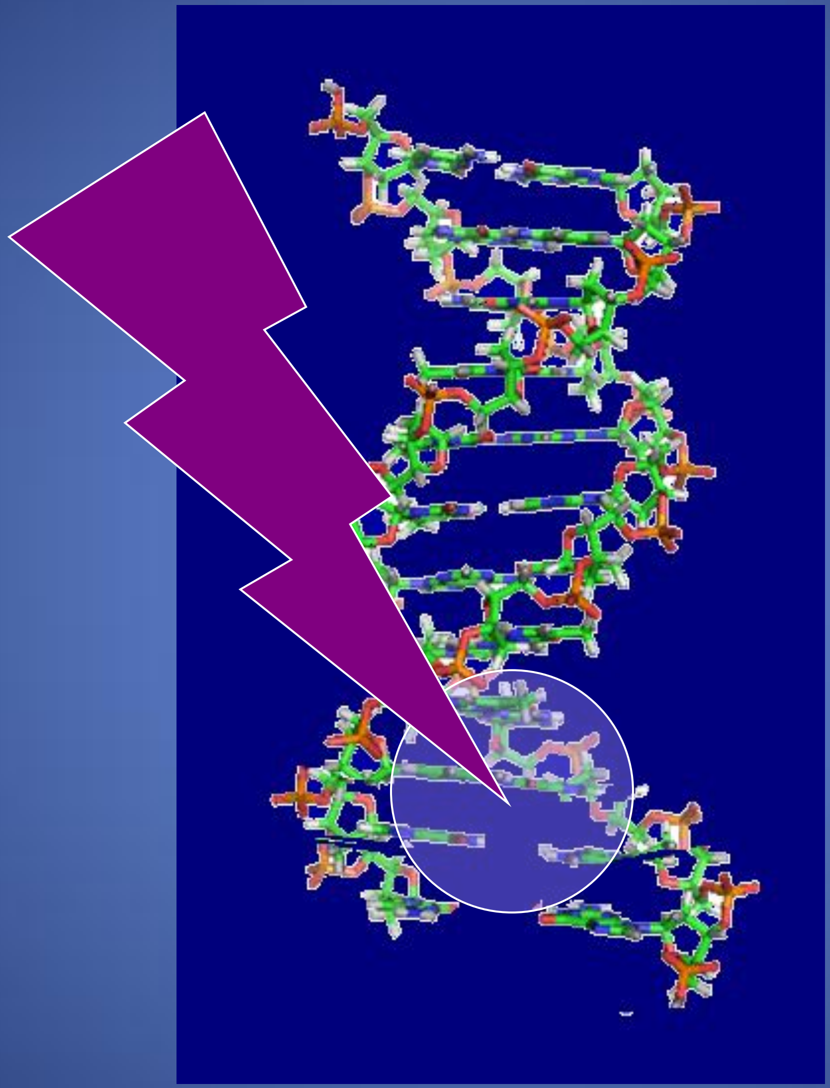
Michaelian, K. and Santillán Padilla, N., *Heliyon* 5, e01902 (2019).

Temperature Dependence of UVC Light-induced Denaturing



Michaelian, K. and Santillán Padilla, N., *Heliyon* 5, e01902 (2019).

UVC –induced Denaturing



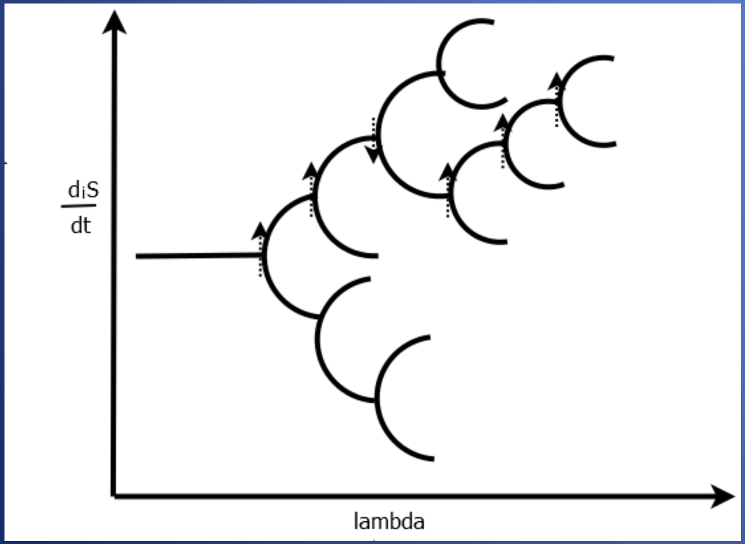
Dissipative Selection

$$\sigma \equiv \frac{P}{V} = \frac{d_i S/dt}{V} = \sum_{k=1,n} X_k J_k = \sum_{k=1,n} \frac{A_k}{T} J_k \geq 0.$$

$$\frac{dP}{dt} = \frac{d_X P}{dt} + \frac{d_J P}{dt},$$

$$\frac{d_X P}{dt} = \int \sum_{k=1,n} J_k \frac{dX_k}{dt} dV; \qquad \frac{d_J P}{dt} = \int \sum_{k=1,n} X_k \frac{dJ_k}{dt} dV,$$

Non-linear relation; X, J

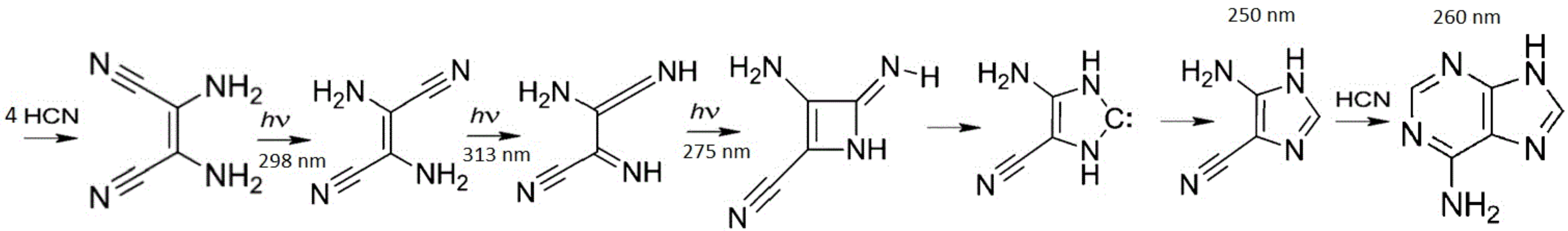


$$\frac{d_X P}{dt} \leq 0.$$

Universal Evolution Criterion
Glansdorff-Prigogine Criterion

For autocatalytic chemical reactions

$$\frac{d_X P}{dt} \leq 0 \Rightarrow \frac{dP}{dt} \geq 0.$$



1   2 cis-DAMN   3 trans-DAMN   4 AIAC   5   6   7 AICN   8 Adenine

$$H_e \to H \tag{5}$$

$$H \to^{k_0} F \qquad k_0 = k_1/H \quad (k_0/k_1 \approx 1 \text{ as long as } 0.01 < H < 0.1 \text{ M}) \text{ [34]} \tag{6}$$

$$4H \to^{k_1} C \qquad k_1 = 5.787 \times 10^{-6} \text{ M/s} \quad \text{when } H = 1.0 \tag{7}$$

$$4H \to^{k_2} T \qquad k_2/k_1 = 1/10 \tag{8}$$

$$4H + T \to^{k_3} C + T \qquad k_3/k_1 = 2.0 \tag{9}$$

$$4H + T \to^{k_4} 2T \qquad k_4/k_1 = 4.0 \tag{10}$$

$$\gamma_{298} + C \to C^* \qquad \lambda_{max} = 298 \text{ nm}, \ \epsilon_{298} = 14,000. \text{ [35]} \tag{11}$$

$$C^* \to^{k_6} C \qquad k_6 = 1.0 \tag{12}$$

$$C^* \to^{k_7} T \qquad k_7/k_6 = 0.045 \text{ [35]} \tag{13}$$

$$\gamma_{313} + T \to T^* \qquad \lambda_{max} = 313 \text{ nm}, \ \epsilon_{313} = 8,500 \text{ [35]} \tag{14}$$

$$T^* \to^{k_8} T \qquad k_8 = 1.0 \tag{15}$$

$$T^* \to^{k_9} J \qquad k_9/k_8 = 0.0034 \text{ [35]} \tag{16}$$

$$\gamma_{275} + J \to J^* \qquad \lambda_{max} = 275 \text{ nm}, \ \epsilon_{275} = 9,000. \text{ [36] [34]} \tag{17}$$

$$J^* \to^{k_{10}} J \qquad k_{10} = 1.0 \tag{18}$$

$$J^* \to^{k_{11}} I \qquad k_{11} = 1.0 \tag{19}$$

$$\gamma_{250} + I \to I^* \qquad \lambda_{max} = 250 \text{ nm}, \ \epsilon_{250} = 10,700. \text{ [35]} \tag{20}$$

$$I^* \to^{k_{12}} I \qquad k_{12} = 1.0 \tag{21}$$

$$I + H \to^{k_{13}} A \qquad k_{13} = 0.6 \tag{22}$$

$$\gamma_{260} + A \to A^* \qquad \lambda_{max} = 260 \text{ nm}, \ \epsilon_{260} = 15,000 \tag{23}$$

$$A^* \to^{k_{14}} A \qquad k_{14} = 1.0 \tag{24}$$

$$A \to^{k_{15}} A_e \qquad k_{15} = 1.0 \times 10^{-6} \tag{25}$$

$$
\begin{aligned}
\frac{dH}{dt} &= D_H \frac{\partial^2 H}{\partial x^2} - k_0 H - k_1 H^2 - k_2 H^2 - k_3 H^2 T - k_4 H^2 T \\
&= D_H \frac{\partial^2 H}{\partial x^2} - H k_0 - H^2 (k_1 + k_2 + T(k_3 + k_4)) \qquad (27)
\end{aligned}
$$

$$\frac{dF}{dt} = k_0 H \qquad (28)$$

$$\frac{dC}{dt} = k_1 H^2 + k_3 H^2 T + k_6 C^* - \frac{I_{298}(1 - 10^{-x\epsilon_{298} C - x\alpha_{298}})}{x N_A} \qquad (29)$$

$$\frac{dC^*}{dt} = \frac{I_{298}(1 - 10^{-x\epsilon_{298} C - x\alpha_{298}})}{x N_A} - k_6 C^* - k_7 C^* \qquad (30)$$

$$\frac{dT}{dt} = k_2 H^2 + k_4 H^2 T + k_7 C^* + k_8 T^* - \frac{I_{313}(1 - 10^{-x\epsilon_{313} T - x\alpha_{313}})}{x N_A} \qquad (31)$$

$$\frac{dT^*}{dt} = \frac{I_{313}(1 - 10^{-x\epsilon_{313} T - x\alpha_{313}})}{x N_A} - k_8 T^* - k_9 T^* \qquad (32)$$

$$\frac{dJ}{dt} = k_9 T^* + k_{10} J^* - \frac{I_{275}(1 - 10^{-x\epsilon_{275} I - x\alpha_{275}})}{x N_A} \qquad (33)$$

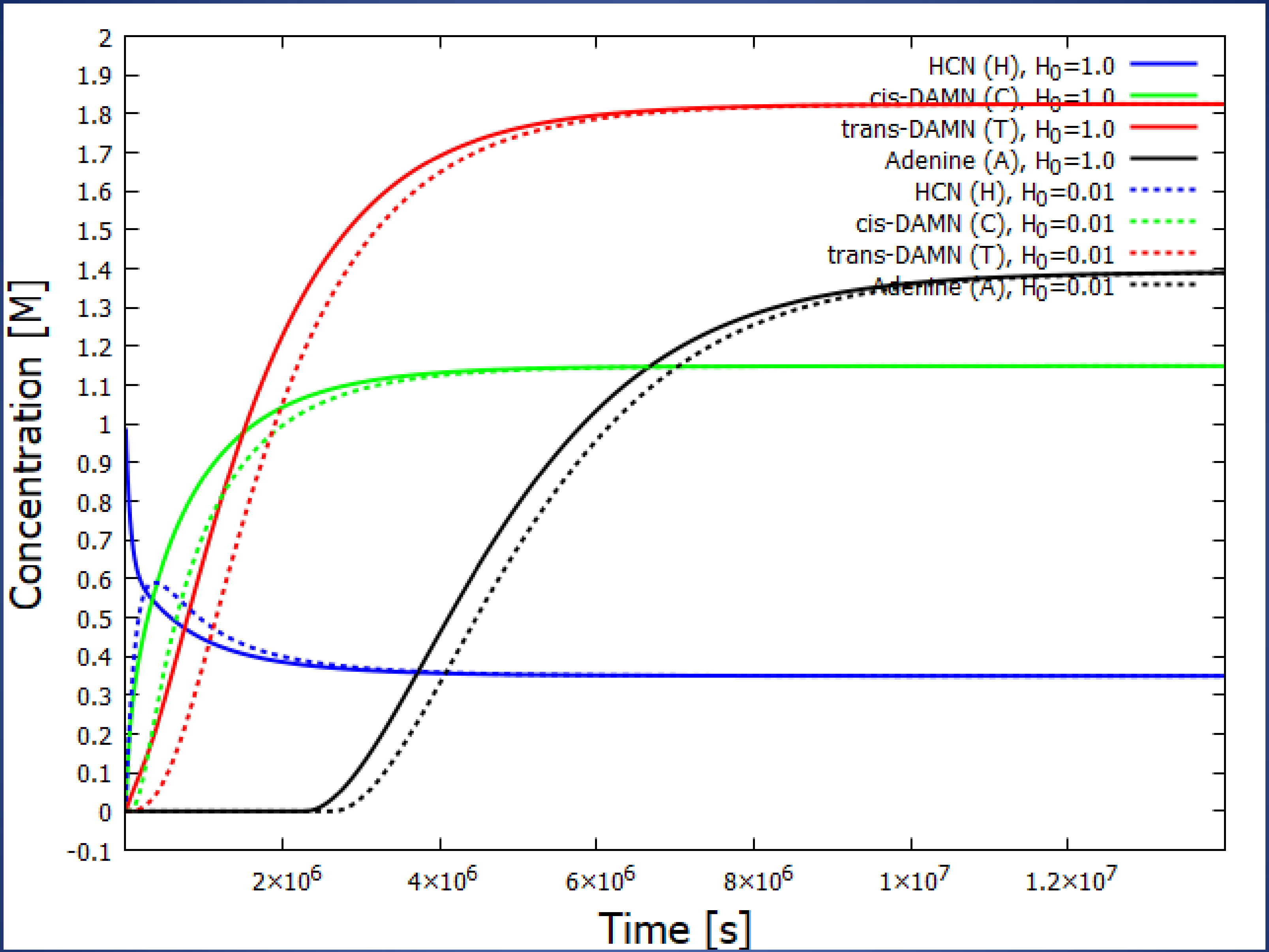
$$\frac{dJ^*}{dt} = \frac{I_{275}(1 - 10^{-x\epsilon_{275} I - x\alpha_{275}})}{x N_A} - k_{10} J^* - k_{11} J^* \qquad (34)$$

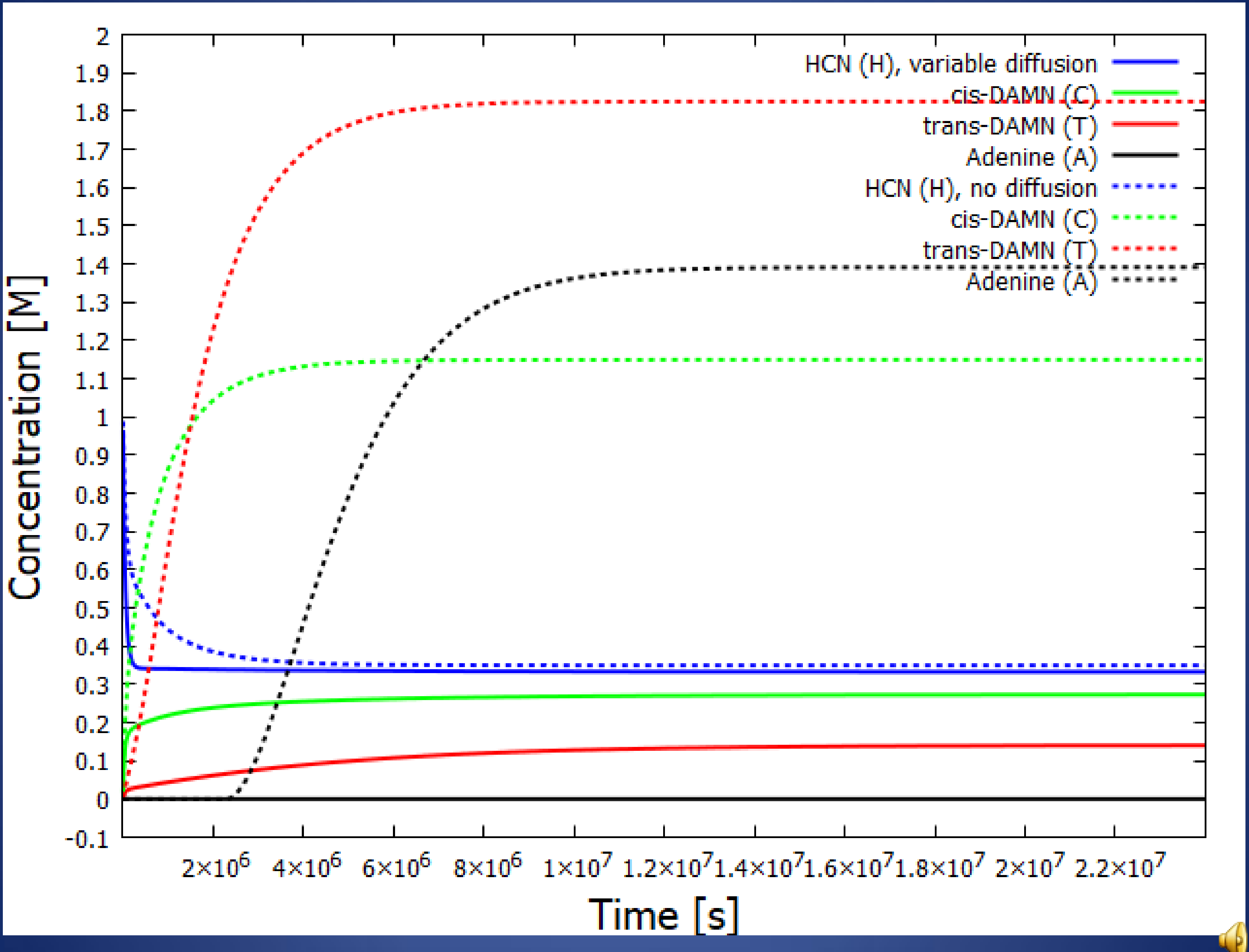
$$\frac{dI}{dt} = k_{11} J^* + k_{12} I^* - \frac{I_{250}(1 - 10^{-x\epsilon_{250} I - x\alpha_{250}})}{x N_A} - k_{13} I H \qquad (35)$$

$$\frac{dI^*}{dt} = \frac{I_{250}(1 - 10^{-x\epsilon_{250} I - x\alpha_{250}})}{x N_A} - k_{12} I^* \qquad (36)$$

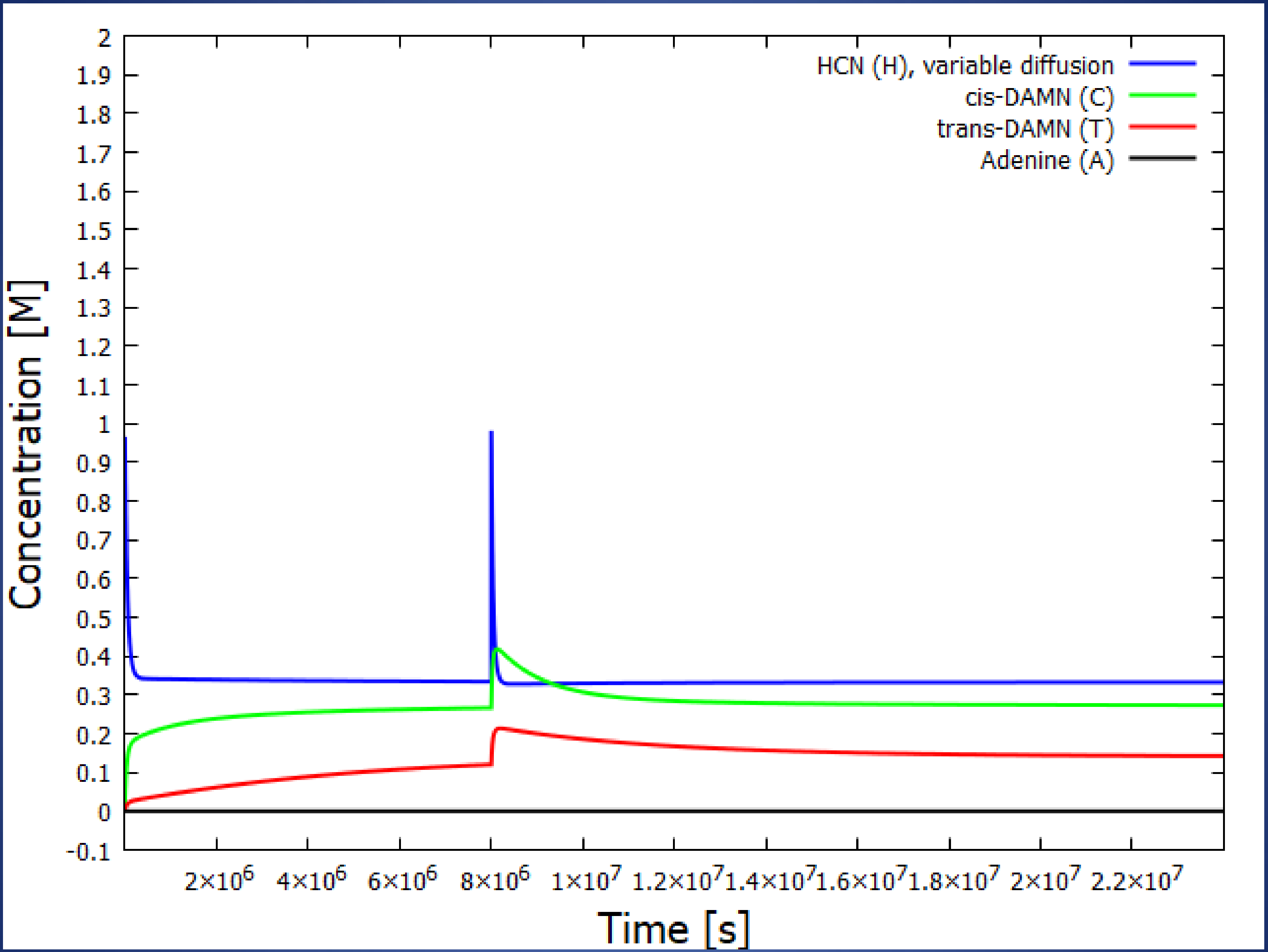
$$\frac{dA}{dt} = k_{13} I H + k_{14} A^* - \frac{I_{260}(1 - 10^{-x\epsilon_{260} A - x\alpha_{260}})}{x N_A} - D_A \frac{\partial^2 A}{\partial x^2} \qquad (37)$$

$$\frac{dA^*}{dt} = \frac{I_{260}(1 - 10^{-x\epsilon_{260} A - x\alpha_{260}})}{x N_A} - k_{14} A^* \qquad (38)$$

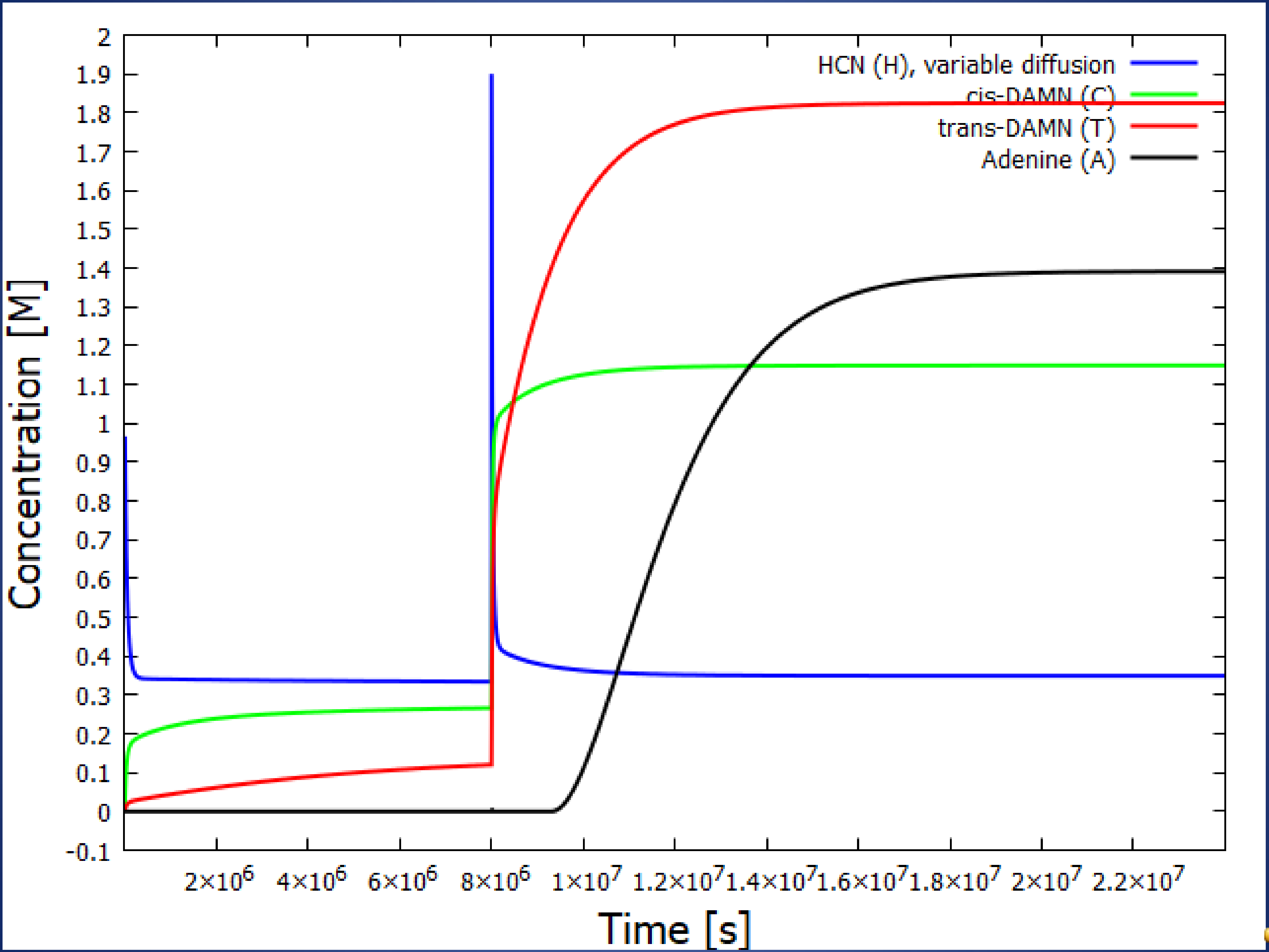

HCN (H), H0=1.0
cis-DAMN (C), H0=1.0
trans-DAMN (T), H0=1.0
Adenine (A), H0=1.0
HCN (H), H0=0.01
cis-DAMN (C), H0=0.01
trans-DAMN (T), H0=0.01
Adenine (A), H0=0.01
Concentration [M]
Time [s]
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
2×10^6
4×10^6
6×10^6
8×10^6
1×10^7
1.2×10^7

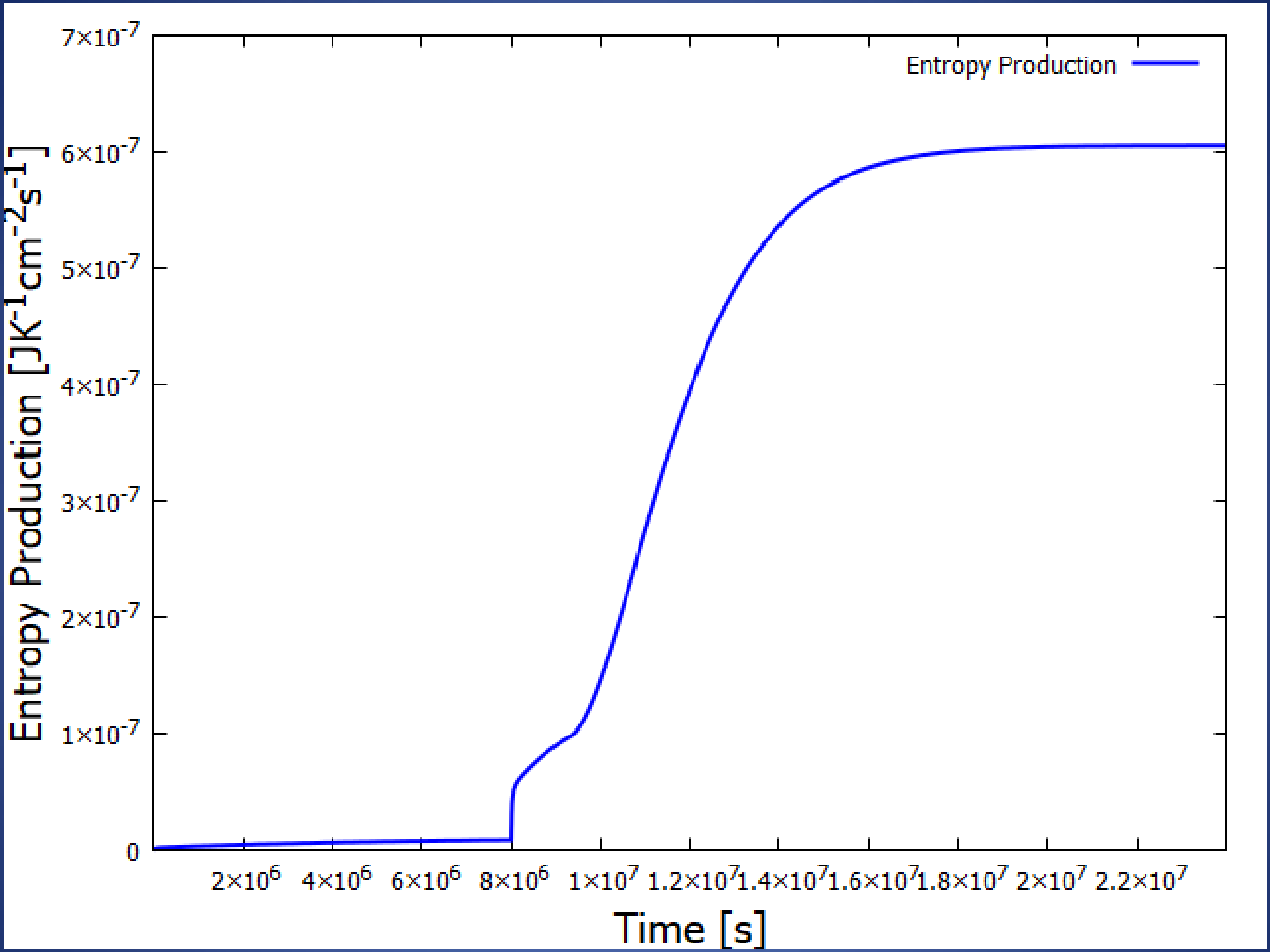


HCN (H), variable diffusion
cis-DAMN (C)
trans-DAMN (T)
Adenine (A)
HCN (H), no diffusion
cis-DAMN (C)
trans-DAMN (T)
Adenine (A)
Concentration [M]
Time [s]
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
2×10^6
4×10^6
6×10^6
8×10^6
1×10^7
1.2×10^7
1.4×10^7
1.6×10^7
1.8×10^7
2×10^7
2.2×10^7



HCN (H), variable diffusion
cis-DAMN (C)
trans-DAMN (T)
Adenine (A)
Concentration [M]
Time [s]
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
2×10^6 4×10^6 6×10^6 8×10^6 1×10^7 1.2×10^7 1.4×10^7 1.6×10^7 1.8×10^7 2×10^7 2.2×10^7


HCN (H), variable diffusion
cis-DAMN (C)
trans-DAMN (T)
Adenine (A)
Concentration [M]
Time [s]
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
2×10^6
4×10^6
6×10^6
8×10^6
1×10^7
1.2×10^7
1.4×10^7
1.6×10^7
1.8×10^7
2×10^7
2.2×10^7



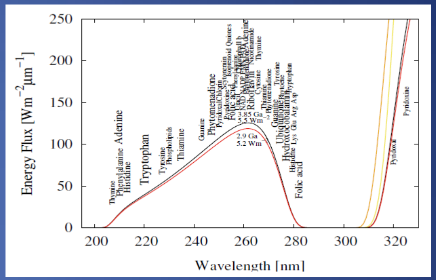
Entropy Production
Entropy Production [JK-1cm-2s-1]
Time [s]
0
1×10-7
2×10-7
3×10-7
4×10-7
5×10-7
6×10-7
7×10-7
2×10^6
4×10^6
6×10^6
8×10^6
1×10^7
1.2×10^7
1.4×10^7
1.6×10^7
1.8×10^7
2×10^7
2.2×10^7

Conclusions

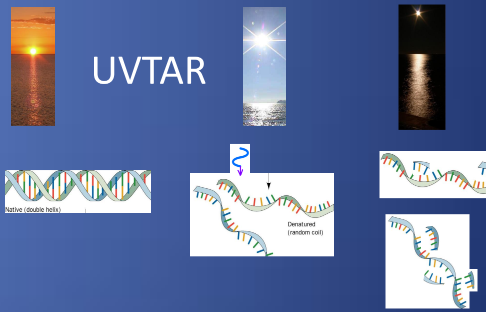
Life's function

Sunlight → Heat (dissipation)

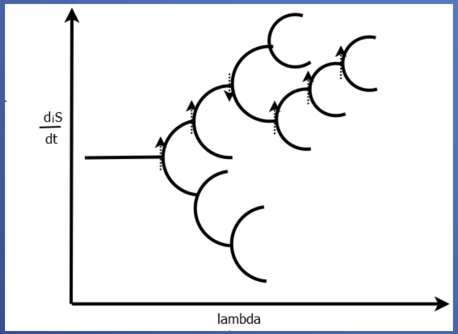
Dissipative Structuring

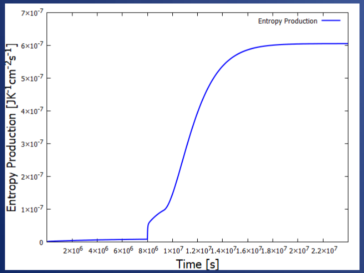


Dissipative Proliferation



Dissipative Selection





$$\frac{d_X P}{dt} \le 0 \Rightarrow \frac{dP}{dt} \ge 0.$$

Necessary and sufficient elements for explaining origin and evolution of life

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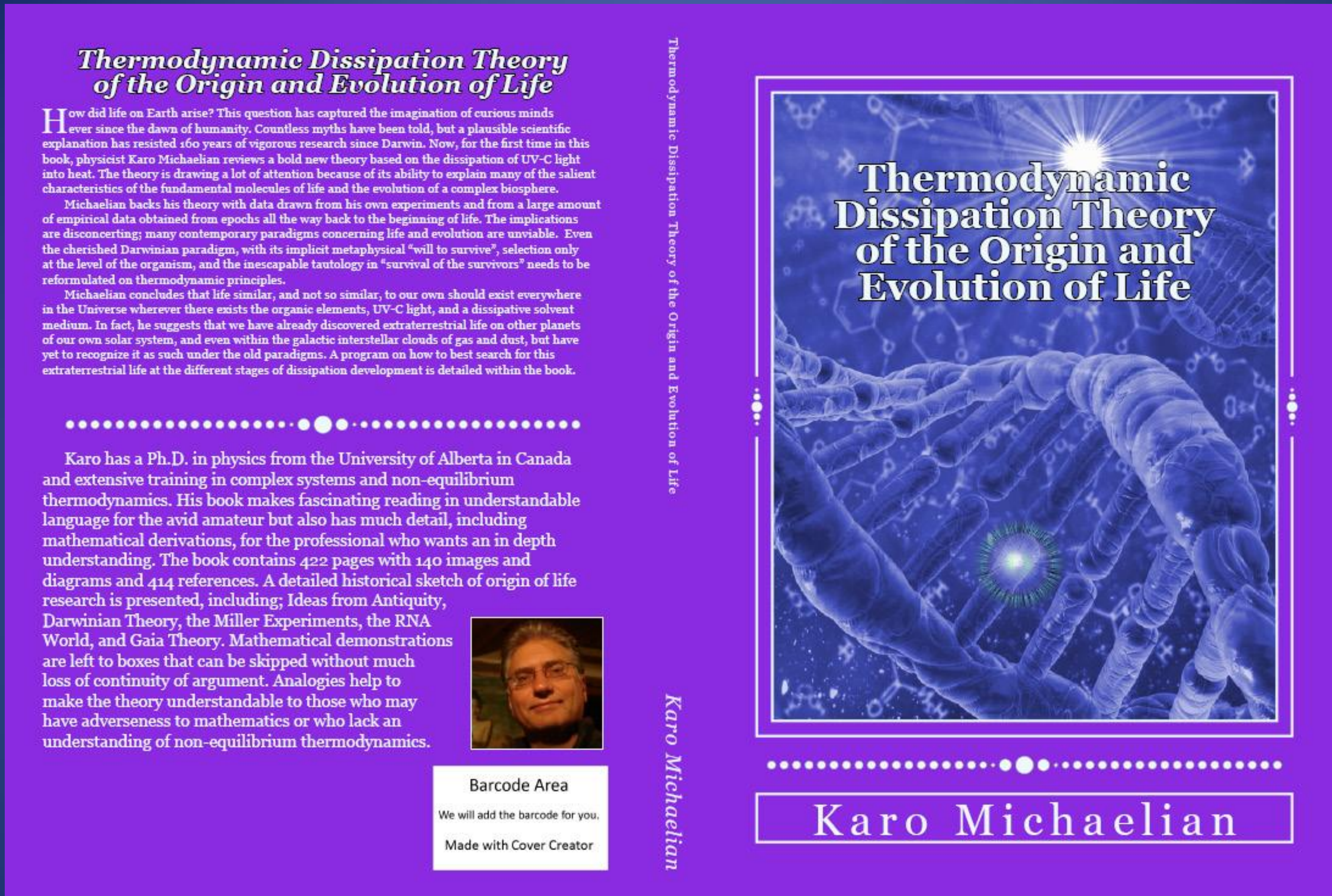
Projects DGAPA-PAPIIT

1. DGAPA-UNAM IN-118206, June, 2005.
2. DGAPA-UNAM IN-112809, January 2009.
3. DGAPA-UNAM IN-103113, January 2013.
4. DGAPA-UNAM IN-102316, January 2016.
5. DGAPA-UNAM IN-104920, January, 2020.

Book available;



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