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Introdução à Física Atômica e Molecular

**Acoplamentos Diabáticos
(Não Born-Oppenheimer)**

Aproximação Born-Oppenheimer

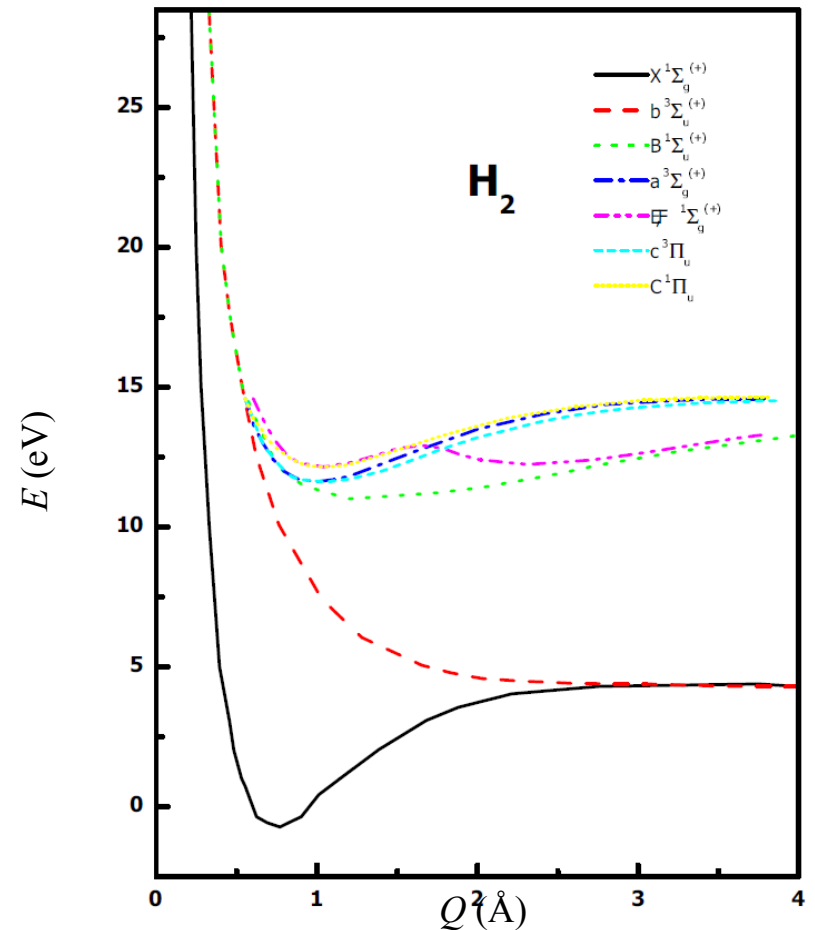
$$\left[-\frac{\nabla_Q^2}{2\mu} - \frac{(\nabla_Q^2)_{ll}}{2\mu} + (H_{\text{ele}})_{ll} - E \right] \chi_l(Q) = \sum_{k \neq l} \left[\frac{(\nabla_Q^2)_{lk}}{2\mu} + \frac{(\nabla_Q)_{lk} \cdot \nabla_Q}{\mu} \right] \chi_k(Q)$$

$$\left[-\frac{\nabla_Q^2}{2\mu} + U_l(Q) \right] \chi_l(Q) = E \chi_l(Q)$$

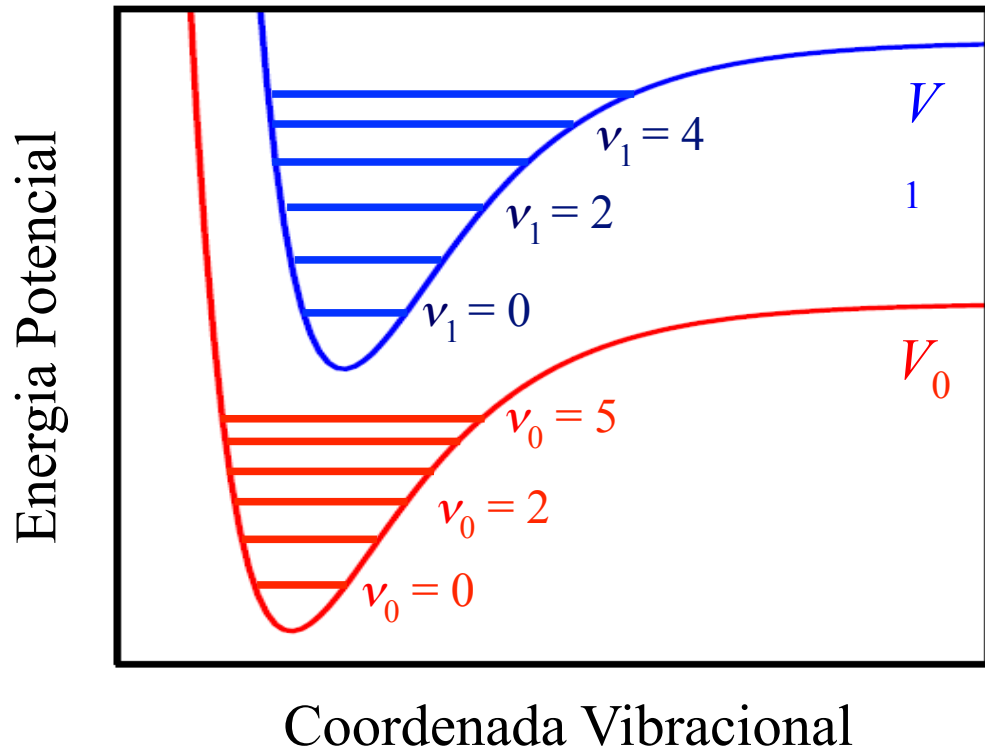
$$\begin{aligned} U_l(Q) &= -\frac{(\nabla_Q^2)_{ll}}{2\mu} + (H_{\text{ele}})_{ll} \\ &= -\frac{(\nabla_Q^2)_{ll}}{2\mu} + V_l(Q) \end{aligned}$$

Validade:

$$(\nabla_Q)_{lk} = \frac{\langle \psi_l | \nabla_Q H_{\text{ele}} | \psi_k \rangle}{U_k(Q) - U_l(Q)}$$



Acoplamentos Não Born-Oppenheimer



Como visto anteriormente, a aproximação Born-Oppenheimer (BO) desacopla os estados eletrônicos, definindo problemas vibracionais independentes em cada curva de energia potencial. Assim, um estado vibracional que esteja inicialmente em uma dada curva de potencial permanecerá sempre nessa curva (desprezando a possibilidade de emissão espontânea).

$$H_0 = T_Q + V_0(Q)$$

$$H_1 = T_Q + V_1(Q)$$

$$i\hbar \frac{\partial}{\partial t} \chi_0(Q, t) = [T_Q + V_0] \chi_0(Q, t)$$

$$i\hbar \frac{\partial}{\partial t} \chi_1(Q, t) = [T_Q + V_1] \chi_1(Q, t)$$

Acoplamentos Não Born-Oppenheimer

Caso haja acoplamentos não BO apreciáveis (por simplicidade, entre dois estados eletrônicos), as equações de Schrödinger vibracionais não poderão ser desacopladas (v_{ij} denota os acoplamentos não BO):

$$[T_Q + V_0(Q) - E]\chi_0(Q) = v_{01}\chi_1(Q) \quad [T_Q + V_1(Q) - E]\chi_1(Q) = v_{10}\chi_0(Q)$$

Poderemos escrever as equações de Schrödinger (dependente do tempo) para ambas as situações discutidas em forma matricial:

1) Aproximação BO válida:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \chi_0(Q, t) \\ \chi_1(Q, t) \end{pmatrix} = \begin{bmatrix} T_Q + V_0(Q) & 0 \\ 0 & T_Q + V_1(Q) \end{bmatrix} \begin{pmatrix} \chi_0(Q, t) \\ \chi_1(Q, t) \end{pmatrix}$$

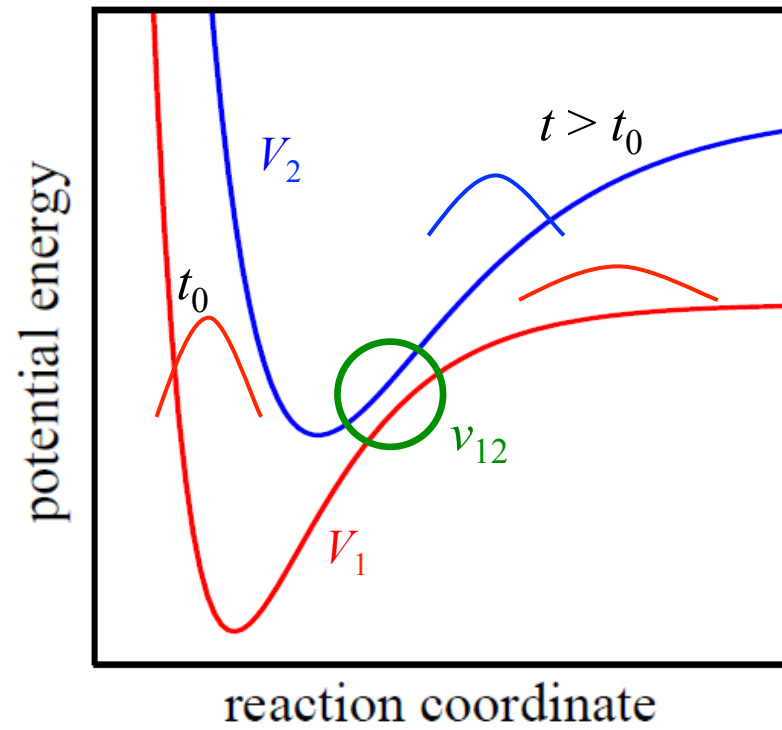
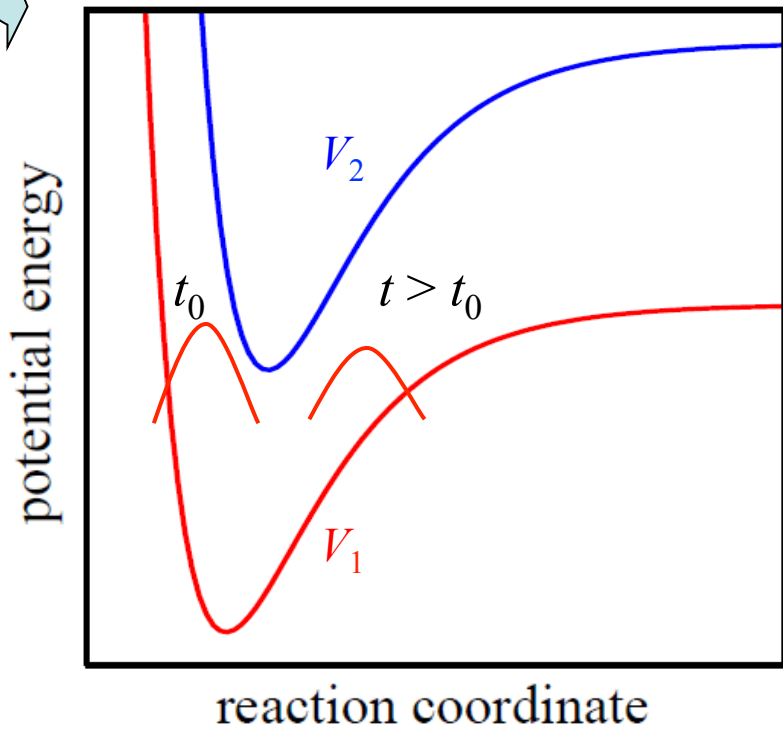
2) Acoplamentos não BO:

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \chi_0(Q, t) \\ \chi_1(Q, t) \end{pmatrix} = \begin{bmatrix} T_Q + V_0(Q) & v_{01}(Q) \\ v_{10}(Q) & T_Q + V_1(Q) \end{bmatrix} \begin{pmatrix} \chi_0(Q, t) \\ \chi_1(Q, t) \end{pmatrix}$$

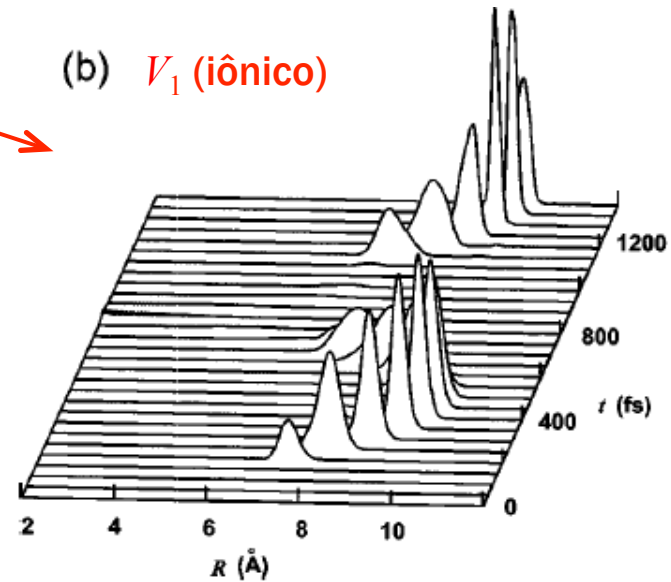
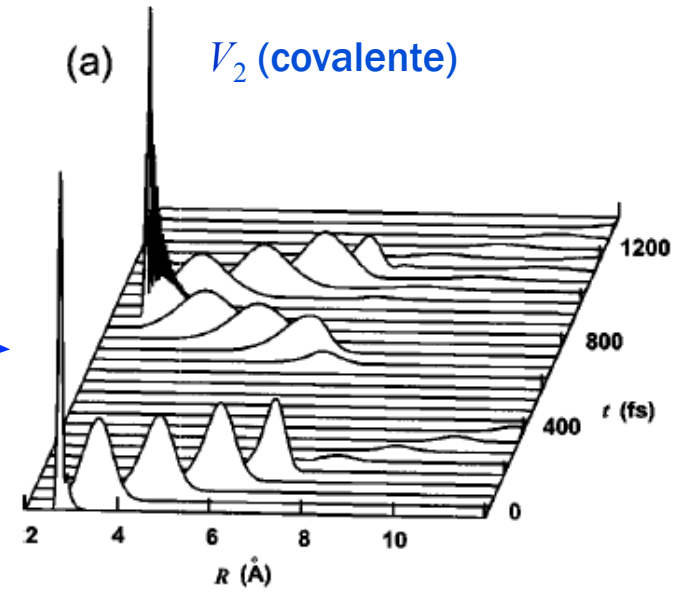
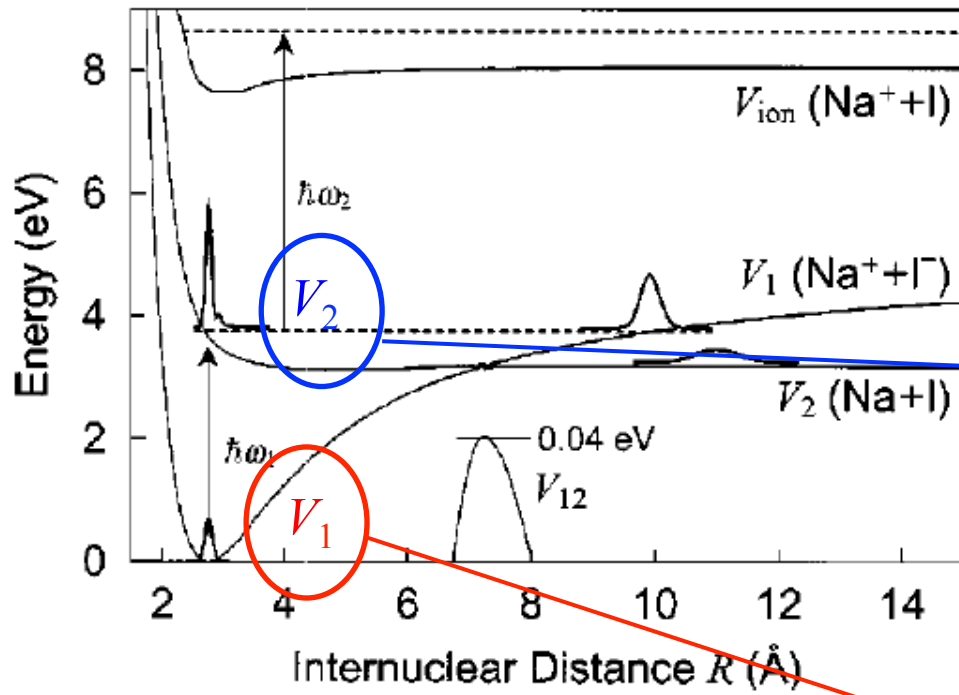


Acoplamentos Não Born-Oppenheimer

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \chi_0(Q, t) \\ \chi_1(Q, t) \end{pmatrix} = \begin{bmatrix} T_Q + V_0(Q) & 0 \\ 0 & T_Q + V_1(Q) \end{bmatrix} \begin{pmatrix} \chi_0(Q, t) \\ \chi_1(Q, t) \end{pmatrix}$$



$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \chi_0(Q, t) \\ \chi_1(Q, t) \end{pmatrix} = \begin{bmatrix} T_Q + V_0(Q) & v_{01}(Q) \\ v_{10}(Q) & T_Q + V_1(Q) \end{bmatrix} \begin{pmatrix} \chi_0(Q, t) \\ \chi_1(Q, t) \end{pmatrix}$$



$t = 0$: Foto-excitação, $V_1 \rightarrow V_2$

$t \approx 150$ fs: Bifurcação, $V_2 \rightarrow V_1, V_2$

$t \approx 400$ fs: Reflexão em V_1
Dissociação em V_2

$t \approx 650$ fs: Decaimento não radiativo, $V_1 \rightarrow V_2$

$t \approx 900$ fs: Reflexão em V_2

$t \approx 1100$ fs: Bifurcação, $V_2 \rightarrow V_1, V_2$

Arasaki et al., J. Chem. Phys. **119**, 7913 (2003)

Estados Diabáticos

A Hamiltoniana nuclear resulta de elementos de matriz calculados a partir dos estados eletrônicos (ψ_1, ψ_2). Essa representação não é única, sendo possível obter outra base ortonormal por meio da transformação:

$$\begin{pmatrix} \psi'_1(\mathbf{r}_e) \\ \psi'_2(\mathbf{r}_e) \end{pmatrix} = \begin{bmatrix} \cos \Omega(\mathbf{Q}) & -\text{sen} \Omega(\mathbf{Q}) \\ \text{sen} \Omega(\mathbf{Q}) & \cos \Omega(\mathbf{Q}) \end{bmatrix} \begin{pmatrix} \psi_1(\mathbf{r}_e) \\ \psi_2(\mathbf{r}_e) \end{pmatrix}$$

Se a transformação for escolhida de modo a eliminar os acoplamentos não adiabáticos (fora da diagonal) a nova base de estados eletrônicos será dita *diabática*.

$$\hat{U} \hat{\Lambda} \hat{U}^\dagger = \hat{D}$$

As condições que garantem a existência, analiticidade e unicidade dessa transformação são tema de debate. Aqui vamos assumir essa possibilidade, seguindo o espírito prático de Köppel et al., Adv. Chem. Phys. **57**, 59 (1984): “the following heuristic definition emerges: a basis is considered diabatic if the condition is fulfilled to a sufficiently good approximation”.

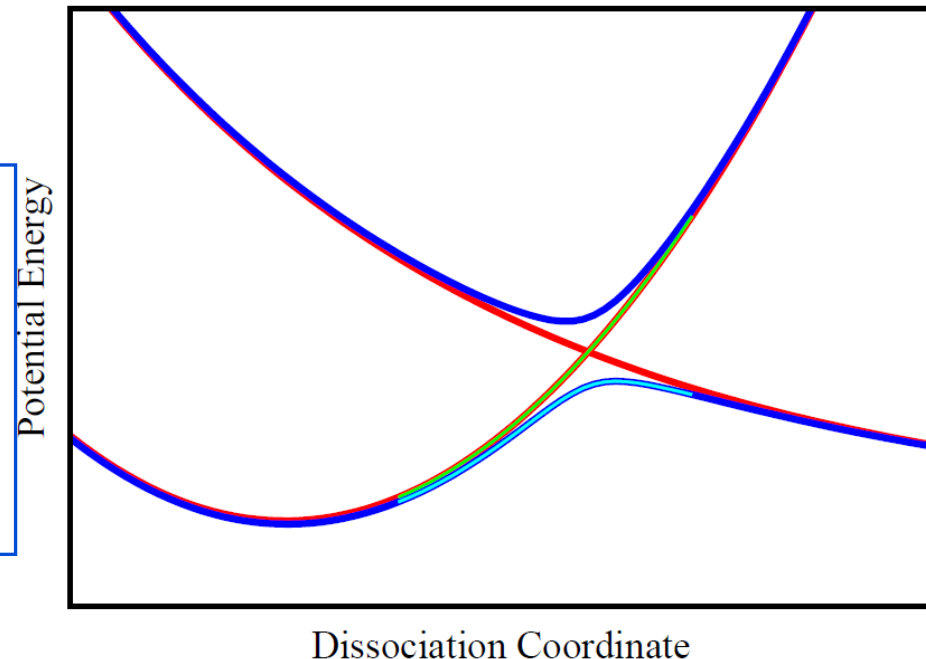
Estados Diabáticos

Por definição, a Hamiltoniana eletrônica é diagonal na base adiabática. Em um sentido prático (não rigoroso), a base diabática diagonaliza a representação do operador nuclear de energia cinética

$$H_{ij} = \delta_{ij} T_N + \langle \psi_i | T_N | \psi_j \rangle_{\mathbf{r}_e} + \delta_{ij} V_i(\mathbf{Q})$$

$$H_{ij}^d = \delta_{ij} T_N + V_{ij}(\mathbf{Q})$$

Superfícies de potencial adiabáticas obedecem à *Regra do Não Cruzamento* (RNC): superfícies M -dimensionais de mesma simetria e spin podem se cruzar em $(M-2)$ dimensões. Caso tenham simetria ou spin diferentes, podem se cruzar em $(M-1)$ dimensões.



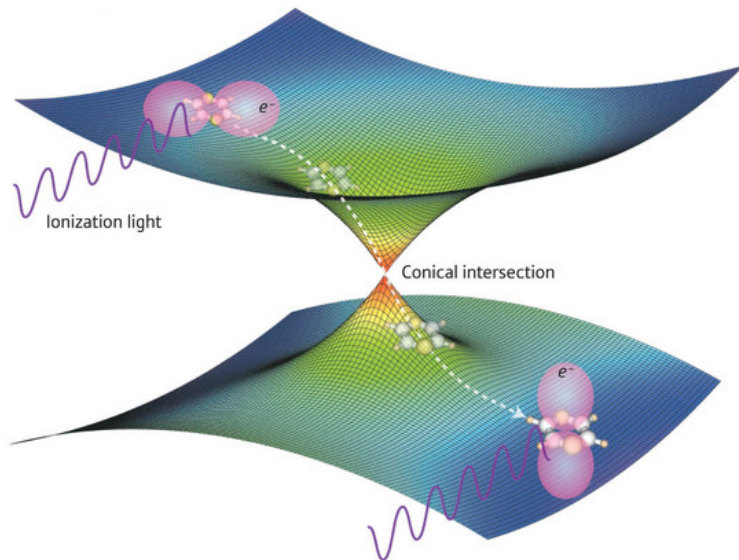
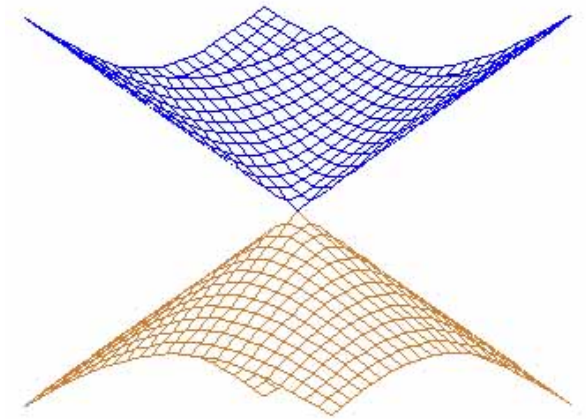
O enunciado da RNC acima é controverso [ver, por exemplo: Yarkony, *Rev. Mod. Phys.* **68**, 985 (1996); Shi *et al.*, *J. Chem. Phys.* **114**, 9697 (2001)]. Vale observar que essa regra não é uma lei física, e sim uma propriedade (espúria) da aproximação adiabática.

Interseções Cônicas

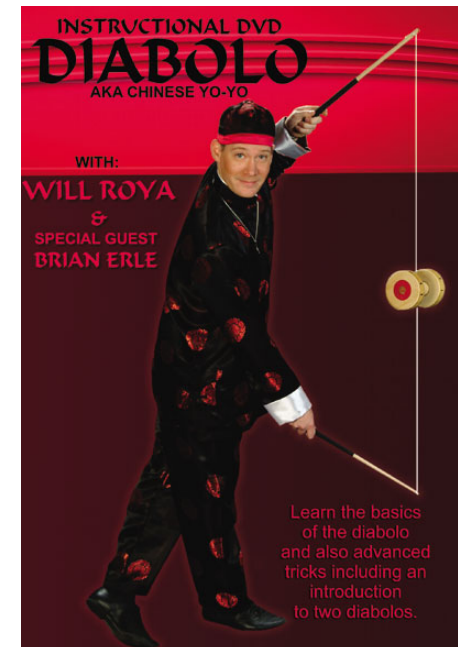
Uma interseção cônica é um ponto de degenerescência entre duas superfícies de potencial (adiabáticas). Mais precisamente

[Yakorny, Rev. Mod. Phys. 68, 985 (1996)]:

A point of conical intersection is a point in nuclear coordinate space at the confluence of two Born-Oppenheimer potential-energy surfaces. The local topology of the potential-energy surfaces at this point is that of a double cone, a diabolo (Berry and Wilkinson, 1984). Thus points of conical intersection are sometimes referred to, quite aptly we will argue, as diabolical points



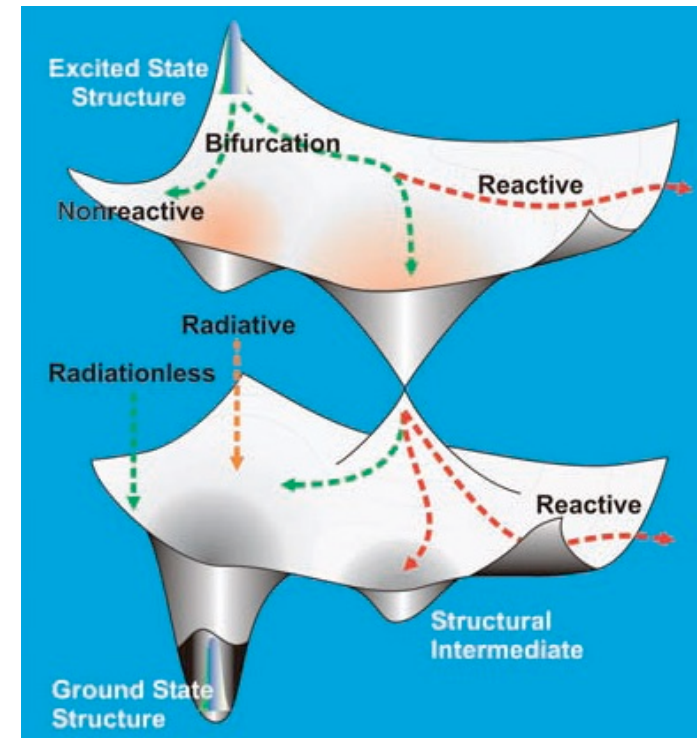
Horio, et al., JACS 131, 10392 (2009).



Interseções Cônicas

Interseções cônicas (em geral, acoplamentos não adiabáticos) permitem transições não radiativas entre estados eletrônicos.

Radiationless transitions abound in chemical, physical, and biological systems, yielding such diverse phenomena as the conversion of radiation to heat and the photodamage and photocarcinogenesis of DNA (1–5). After light absorption, a molecule can undergo radiationless processes of two general types: photochemical, involving bond fragmentation or isomerization; and photophysical, involving transitions between electronic states while either conserving spin (internal conversion) or altering spin (intersystem crossing).



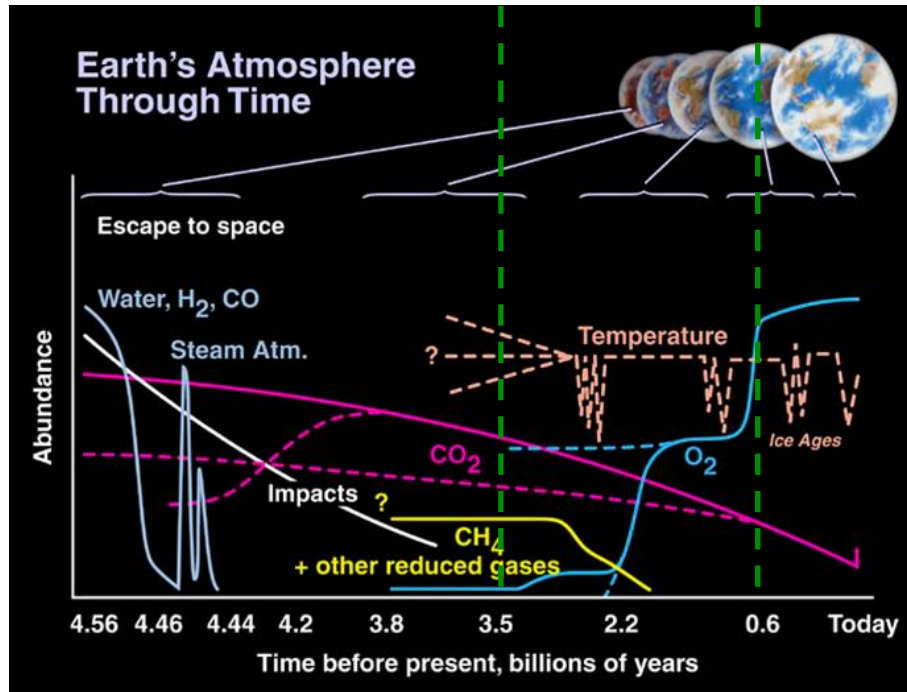
Dark Structures in Molecular Radiationless Transitions Determined by Ultrafast Diffraction

Ramesh Srinivasan, Jonathan S. Feenstra, Sang Tae Park, Shoujun Xu,* Ahmed H. Zewail†

Science **307**, 558 (2005)

Algas: $\sim 3.5 \times 10^9$ anos

Escudo UV: $\sim 0.6 \times 10^9$ anos



Radiação UV ($\lambda \sim 250\text{nm}$) causaria dano irreversível aos componentes do DNA (decomposição dos estados foto-excitados, muito reativos).

Fonte: R. Townsend

<http://www.astro.wisc.edu/~townsend>

A manutenção do código genético ao longo da evolução – particularmente nos primeiros estágios – exigiu um eficiente mecanismo de foto-proteção das biomoléculas...



“(...) extreme evolution pressure for UV protection”

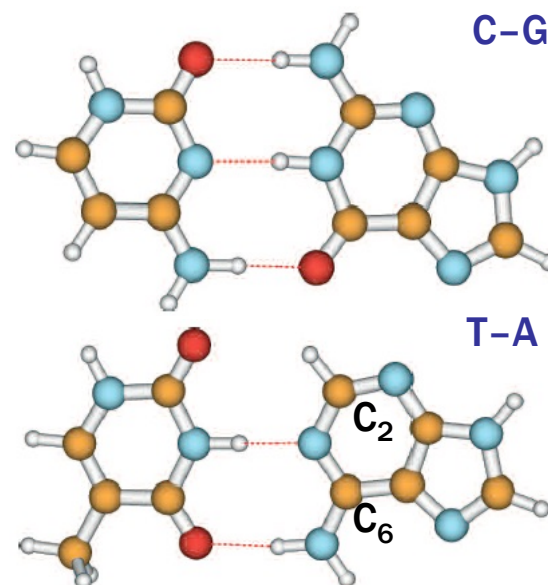
Carl Sagan, J. Theor. Biol. 39, 195 (1973)

The chemical physics of the photostability of life

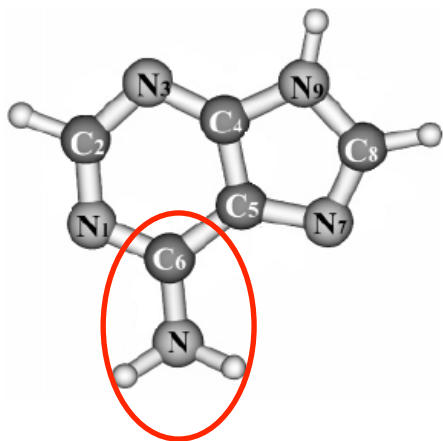
Andrzej L. Sobolewski¹ and Wolfgang Domcke²

euromphysicsnews 20 • volume 37 • number 4

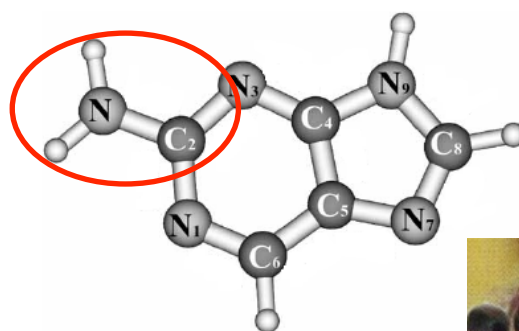
Organic molecules are not stable under persistent irradiation with ultraviolet (UV) light. UV photons can break covalent bonds and thus can induce a great variety of chemical transformations (isomerizations or fragmentations). In view of this, it is amazing that life can thrive under full exposition to sunlight. Moreover, biogenesis took place long before the formation of the stratospheric ozone layer (which today filters out the most dangerous UV components of sunlight) and thus under conditions of extremely intense short-wavelength UV radiation. As pointed out by Sagan, this must have resulted in an extreme selection pressure for UV protection [1]. These considerations suggest that photostability may have been the decisive selection criterion which has determined the molecular architecture of life at the beginning of the biological evolution.



Adenina



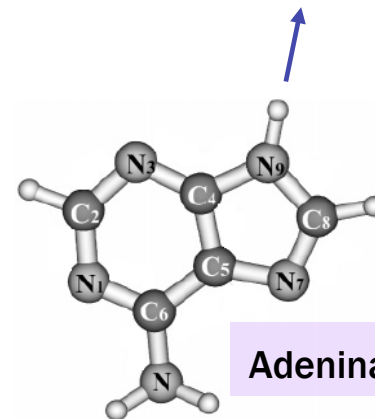
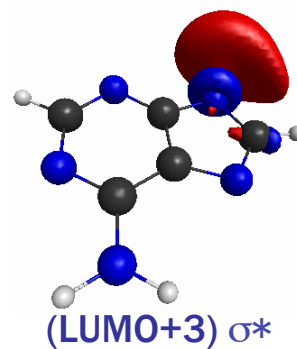
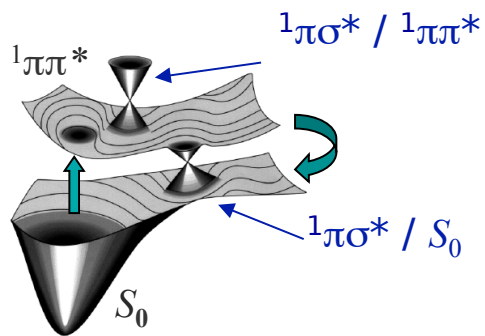
2-Aminopurina



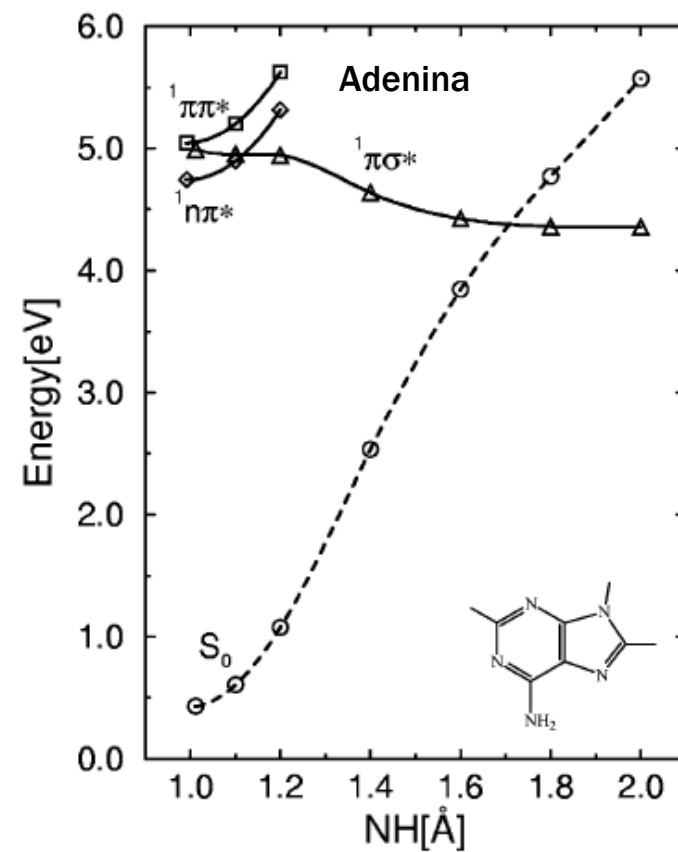
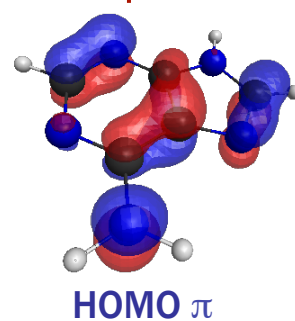
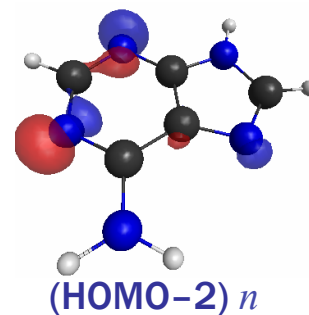
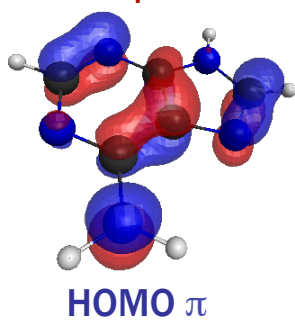
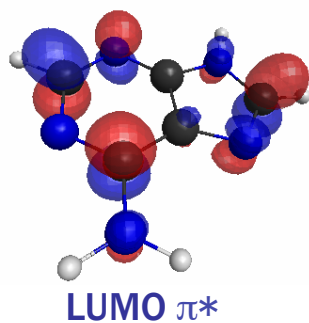
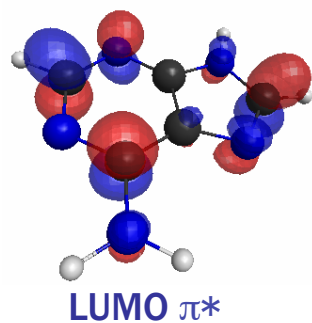
O decaimento por emissão de fótons (fluorescência) é 1000 vezes maior na 2-aminopurina que na adenina!



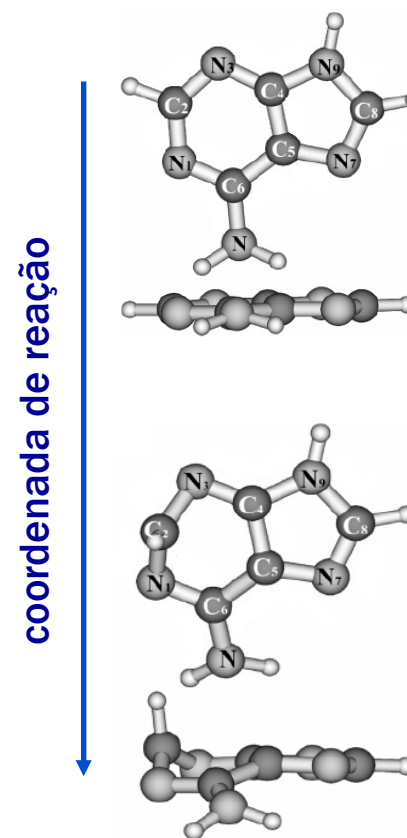
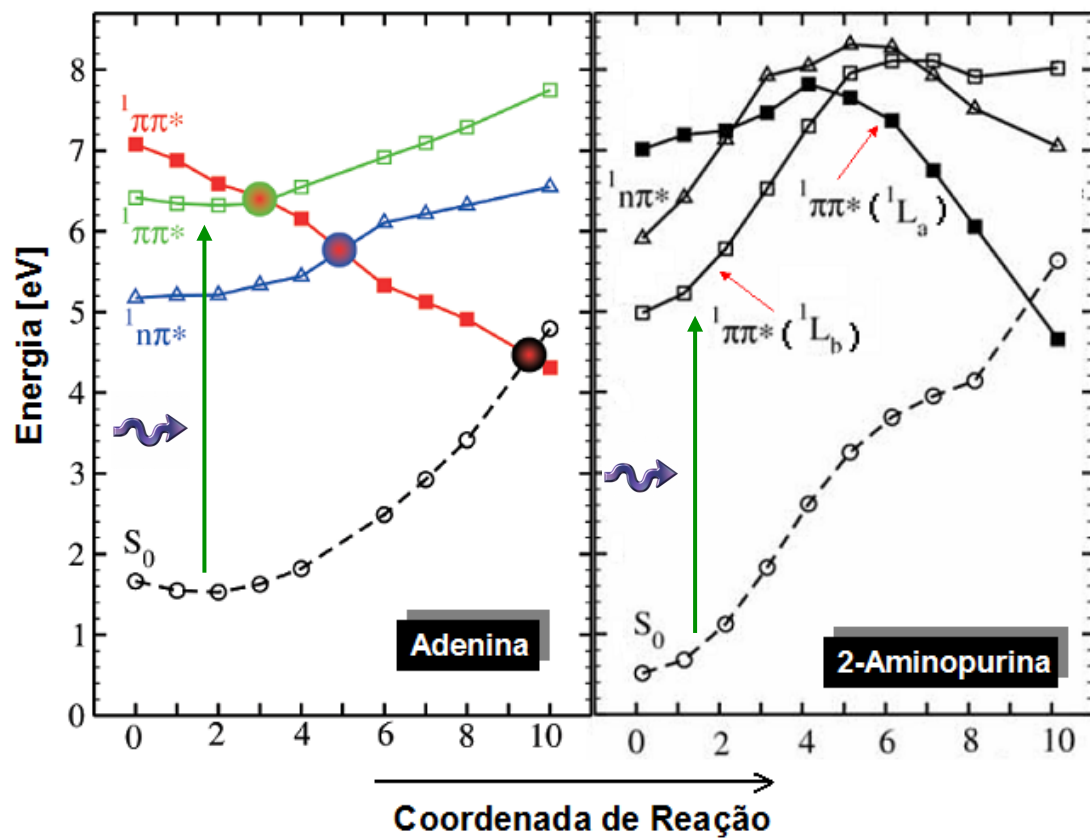
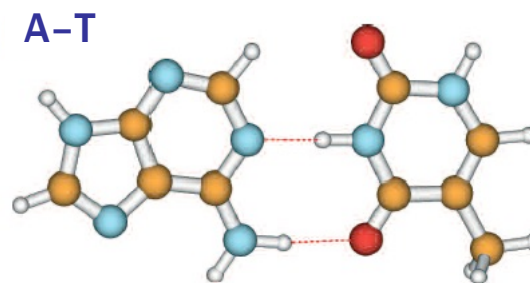
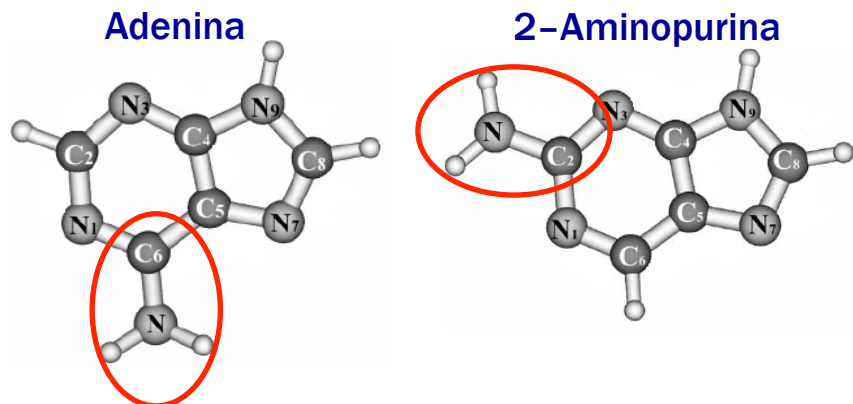
Perun *et al.*, *Mol. Phys.* **104**, 1113 (2006)



Adenina



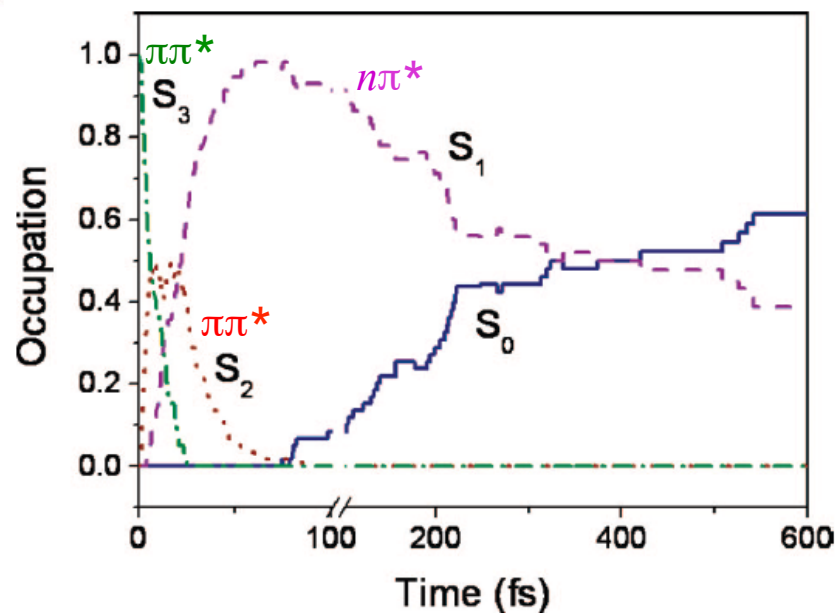
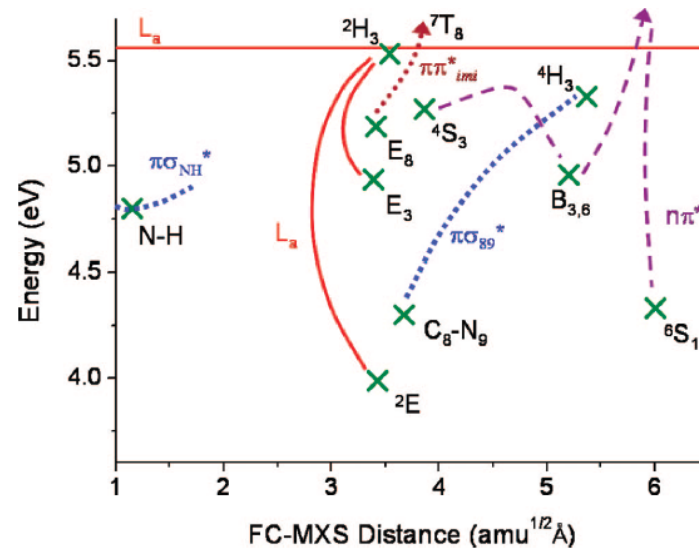
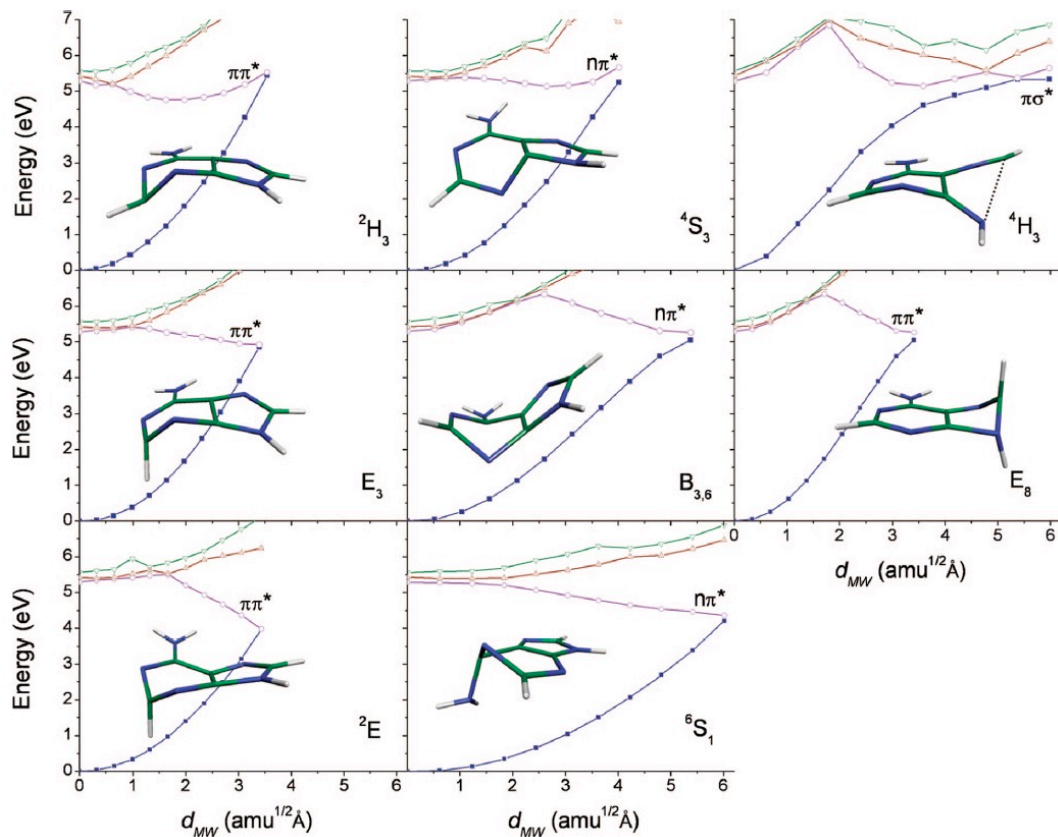
Sobolewski *et al.*, PCCP 4 1093 (2002)



Perun et al., JACS 127, 6257 (2005); Mol. Phys. 104, 1113 (2006)

Nonadiabatic Deactivation of 9H-Adenine: A Comprehensive Picture Based on Mixed Quantum–Classical Dynamics

Mario Barbatti* and Hans Lischka*



J|A|C|S

Life in the light: nucleic acid photoproperties as a legacy of chemical evolution

Ashley A. Beckstead,^a Yuyuan Zhang,^a Mattanjah S. de Vries*^b and Bern Kohler*^a

Phys. Chem. Chem. Phys., 2016, **18**, 24228–24238

