Photochemistry: adiabatic and nonadiabatic molecular dynamics with multireference ab initio methods

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COLUMBUS in BANGKOK (3-TS₂C₂)
Apr. 2 - 5, 2006
Burapha University, Bang Saen, Thailand
Outline

First Lecture: An introduction to molecular dynamics
1. Dynamics, why?
2. Overview of the available approaches

Second Lecture: Towards an implementation of surface hopping dynamics
1. The NEWTON-X program
2. Practical aspects to be addressed

Third Lecture: Some applications: theory and experiment
1. On the ambiguity of the experimental raw data
2. On how the initial surface can make difference
3. Intersection? Which of them?
4. Readressing the DNA/RNA bases problem
Part III

Some applications: theory and experiment

Cândido Portinari, Futebol, 1935
On the ambiguity of the experimental raw data
Experimental: pump-probe

Analysis of the experimental results

The lifetime of ethylene

Barbatti, Granucci, Persico and Lischka, CPL 401, 276 (2005)
### Survey of theoretical and experimental predictions

<table>
<thead>
<tr>
<th>Method</th>
<th>Lifetime (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTSH [1]</td>
<td>( S_1 \rightarrow S_2, S_0 )</td>
</tr>
<tr>
<td>DTSH [1]</td>
<td>( S_1, S_2 \rightarrow S_0 )</td>
</tr>
<tr>
<td>DTSH [2]</td>
<td>( S_1 \rightarrow S_2, S_0 )</td>
</tr>
<tr>
<td>AIMS [3]</td>
<td>( S_1 \rightarrow S_2, S_0 )</td>
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<tr>
<td>AIMS [4]</td>
<td></td>
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<tr>
<td>MCDTH [5]</td>
<td></td>
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<tr>
<td>Experimental [6]</td>
<td></td>
</tr>
<tr>
<td>Experimental [7]</td>
<td></td>
</tr>
<tr>
<td>Experimental (( \tau_1 + \tau_2 )) [8]</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) \( E_v^{(a)} = 6.2 \pm 0.3 \) eV.
\(^b\) \( E_v^{(b)} = 7.4 \pm 0.15 \) eV.

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The time-window question

Radloff has a rather distinct explanation!
On how the initial surface can make difference
Basic scenery expected:
Torsion + decay at twisted MXS

Large momentum along CN stretch is acquired in the $S_2$-$S_1$ transition.

Stretching + pyramidalization dominate
If $S_1 (\sigma\pi^*)$ is directly populated, the torsion should dominate the dynamics.

This and other movies are available at: [homepage.univie.ac.at/mario.barbatti](http://homepage.univie.ac.at/mario.barbatti)
Intersection?
Which of them?
The $S_0/S_1$ crossing seam

Barbatti, Paier and Lischka, JCP 121, 11614 (2004).

Ohmine 1985
Freund and Klessinger 1998
Ben-Nun and Martinez 1998
Laino and Passerone 2004
First $S_1 \rightarrow S_0$ hopping.
Conical intersections in ethylene

Barbatti, Ruckenbauer and Lischka, JCP 122, 174307 (2005)
Readressing the DNA/RNA bases problem
Why RNA and DNA are composed by only 5 bases?

Ultrafast deactivation might have played a role in natural selection of them.

Ultrafast deactivation means more stability against photoinduced damage.

\[ \text{In water } \tau = 0.72 \text{ ps} \]

\[ \text{In water } \tau = 1.1 \text{ ps} \]

\[ \text{In water } \tau = 73 \text{ ps} \]

\[ \text{In water } \tau = 30 \text{ ps} \]

Blancafort et al. JPCA 109, 4431 (2005)  
Canuel et al. JCP 122, 074316 (2005)

Is the ultrafast deactivation important for the photostability of DNA/RNA?
In this model, proton transfer along the nitrogen bonds between bases is responsible for internal conversion.

In this other model, base-stack interactions lead to ultrafast formation of excimers.

The defects stay localized in the excimers and can be fixed by using the second strand as a template.

Base–pairs and base stack models depend on the presence of a second strand to explain the photostability.

But RNA is normally single-stranded. Therefore, both models doesn't explain it completely.

Moreover, RNA appeared in Nature before DNA. So some molecular processes promoting photostability must be based on single-stranded systems and, maybe, isolated bases.

Probably, the photostability of NAs is due to several levels of mechanisms, since ultrafast deactivation of isolated bases to enzymatic repair.

“[Darwinism] is a breathtaking cascade of levels upon levels upon levels, with new principles of explanation, new phenomena appearing at each level, forever revealing that the fond hope of explaining ‘everything’ at some one lower level is misguided.”

Daniel Dennett, Darwin’s Dangerous Idea, p. 195
The adenine`s deactivation:
aminopyrimidine as a model for adenine
Experimental lifetimes of the excited state of DNA/RNA bases: \(~ 1\ \text{ps}\)

What has theory to say?

For adenine

- The decay can be due to $\pi\sigma^*/S_0$ crossing ($N_9$-H stretching)
- Or maybe due to the $\pi\pi^*/S_0$ crossing ($C_2$-H puckering)
- Or $n\pi^*/S_0$ crossing, who knows ($NH_2$ out-of-plane)?
- Maybe, there’s no crossing at all!
Adenine is still too big to be studied by adequate ab initio dynamics methods.

The 6-aminopyrimidine (6AMP) may help to understand the nature and efficiency of the C\textsubscript{2}H puckering and out-of-plane NH\textsubscript{2}.

Some partial information about the role of the imidazole group can be added to the model by isotopic substitutions at H\textsubscript{4} and H\textsubscript{5}.
The reaction paths

The basic features of adenine`s PES are present in 6AMP.
The dynamics of 6AMP: preferential path
Preliminary results show a substantial increase in the lifetime of substituted 6AMP in comparison to normal 6AMP.
The dynamics of 6AMP

[Diagram showing a graph with energy (eV) on the y-axis and time (fs) on the x-axis. The graph includes a molecule structure labeled as the current state.]

- Energy (eV)
  - 0
  - 1
  - 2
  - 3
  - 4
  - 5
  - 6
  - 7
  - 8
  - 9

- Time (fs)
  - 0
  - 200
  - 400
  - 600
  - 800
  - 1000

- Current state
The dynamics of 6AMP

• NH$_2$ out-of-plane path is never activated

• In normal 6AMP, C$_4$H-puckering is the dominant path. S$_1$ lifetime is 400 fs.

• In the substituted species, out-of-plane deformations involving C$_6$H and N3 are the preferential path. S$_1$ lifetime is 800 fs.

We expect a similar scenario in the case of adenine: Out-of-plane deformation of C$_2$H and N$_3$ sites and no contribution of the out-of-plane NH$_2$ conical intersections.
Conclusions
Conclusions

Dynamics, Why?
- Ab initio dynamics can be used to characterize lifetimes, and relaxation paths in the ground and excited state, occurring in the time scale of sub-picosecond.
- Dynamics reveal features that are not easily found by static methods.
- Dynamics can be used to locate the important regions of the crossing seam.

Dynamics, what kind?
- **Semiclassical dynamics:**
  - Cheap.
  - Good results if nuclear non-local phenomena are not important.
  - No information about quantization of rotational and vibrational modes.
- **Wave packet:**
  - Expensive.
  - Full and reliable quantum results.
  - Limited to few degrees of freedom.
Conclusions

Excited-state dynamics around the world (a very incomplete and biased inventory…)

• Semiclassical dynamics:
  Tully; Jasper and Thrular; Robb, Olivucci and Buss; Barbatti and Lischka; Marx and Doltsinis (Car-Parrinello); Granucci and Persico (local diabatization); Martinez-Nuñez; Pittner and Bonačič-Koutecký; Neufeld.

• Multiple spawning
  Ben-Nun and Martínez

• Wave packet
  Gonzalez and Manz; Manthe and Cederbaum; Viel, Eisfeld and Domcke; Jacubtz; de Vivie-Riedle and Hofmann; Schinke; Köppel.
Our contribution

Towards an implementation of surface hopping dynamics
- **NEWTON-X**: new implementation of on-the-fly surface hopping dynamics.
- Energies, gradients and nonadiabatic coupling vectors can be read from any quantum chemical package.
- For MRCI and CASSCF dynamics, COLUMBUS has been used.
- For TD-DFT and RI-CC2, TURBOMOLE.

Where are we going now?
- QM/MM: investigation of the influence of the environment on the relaxation paths, lifetimes and efficiency of the crossing seam (COLUMBUS + TINKER).
Collaborators

Vienna:
Hans Lischka
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Pisa:
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Prague:
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Zagreb:
Mario Vazdar
This work has been funded by:

- Austrian Science Fund within the Special Research Program F16 (Advanced Light Sources)
- COST-Chemistry, Project No. D26-0006-02.
- Calculations have been partially performed at Schroedinger III cluster of University of Vienna.
- MB also thanks for financial support of the Brazilian agency CNPq.