Photochemical Dynamics in the Truhlar Group

Developing new methods for studying photochemical and other non-Born-Oppenheimer processes

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NH$_3$ has two low-lying electronic states; the higher one (excited state) is planar. Experimentalists found that the excitation of a particular vibration of the planar structure leads to the adiabatic dissociation of NH$_3$ into H + NH$_2$*, where * denotes an excited electronic state, while exciting other vibrations leads to amino radical in the ground electronic state.

We are using computational methods to understand why.

The first step of our study consists in building a multi-dimensional surface.
Dynamical study of NH$_3$ molecules

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<th>Methods</th>
<th>Quantum methods</th>
<th>Mixed quantum-classical methods</th>
<th>Classical adiabatic methods</th>
<th>Statistical methods</th>
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<tr>
<td>Number of surfaces</td>
<td>$N_{\text{surf}} \leq 5$-$10$</td>
<td>$N_{\text{surf}} \leq 50$-$100$</td>
<td>$N_{\text{surf}} = 1$</td>
<td>No</td>
</tr>
<tr>
<td>Number of atoms</td>
<td>$N_{\text{at}} \leq 4$</td>
<td>$N_{\text{at}} \leq 20$</td>
<td>$N_{\text{at}} \leq \text{a few}$-$100$</td>
<td>$N_{\text{at}} \geq 100$</td>
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<td>Simulation time</td>
<td>$t_{\text{end}} \leq 100$ fs</td>
<td>$t_{\text{end}} \leq 100$ ps</td>
<td>$t_{\text{end}} \leq 10$ ns</td>
<td>$t_{\text{end}} \leq 1$ ms - 1 s</td>
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Photofragmentation of NH$_3$ Molecules

Mixed quantum-classical method:

- Nuclei are treated classically by following classical equation of motion in Cartesian coordinates
- The electronic part is treated quantum mechanically (wave function)
- The existence of two surfaces is taken into account by allowing for hops between surfaces (surface hopping techniques) or generating an average surface (mean field techniques)

Results:

- Following the fragmentation process as a function of time (energies, distances, electronic state populations, mode populations,...) → top figure
- Determining speed and kinetic energy distributions of departing H atoms (comparison to experiments) → bottom figure
- Testing the reliability of mean field and surface hopping techniques in diabatic and adiabatic representations
Bromoacetyl chloride photochemistry:
Using electronic structure calculations to explain experiments

Experimental (puzzling) fact:
• C-Cl has a higher barrier than C-Br but scission is easier for C-Cl! Why?

Theoretical interpretation:
• The C-Cl rupture is adiabatic: the molecule goes over the barrier
• The C-Br rupture is diabatic: the molecule goes to excited products
• C-Cl scission (right-hand side of figure) now needs less energy than C-Br scission (left-hand side of figure)!

Laser excites nonbonding electron of oxygen to C-O antibonding orbital
Electronic excitation redistributes to break the C-Cl and C-Br bonds

π*(C-O)

CO bond weakens and starts vibrating

Energy ends up in C-Cl and C-Br bonds

π*(C-O)

Energy (eV)

trans-C_s MIN
0.00
gauche MIN
0.03

gauche-to-trans-TS
0.08
gauche MIN S_1
4.81

h? = 5 eV

C-Br

C-Cl

MIN2
3.87
C-Br TS6
3.93
C-Cl TS4
4.03

4.23
4.86
3.35
2.67

h? = 5 eV

MIN2
3.87
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h? = 5 eV
A simple model to include spin-orbit effects in photochemistry

Spin-orbit interaction has two very important effects

1) Fine-structure splitting

\[
\begin{align*}
\text{Br}^{(2P)} & \quad \text{Br}^{(2P_{1/2})} \\
\text{Br}^{(2P)} & \quad \text{Br}^{(2P_{3/2})}
\end{align*}
\]

2) Singlet-triplet interaction and mixing. Example: HBr molecule

Formulation of the model

(a) Express the energy of triplet states in terms of the energy of singlet states

(b) Assume spin-orbit coupling does not depend on internuclear distances

(c) With these two approximations compute potential energy curves

The model does a good job of generating a set of approximate potential curves with spin-orbit coupling included
Reactive quenching of the excited $\tilde{A}$ state of OH by hydrogen and deuterium molecules

This project involves
- obtaining diabatic molecular orbitals by the fourfold way
- obtaining diabatic potential energy surfaces by configurational uniformity
- fitting the surfaces and couplings by multi-configuration molecular mechanics
- calculating the non-Born-Oppenheimer dynamics and product energy distributions by decay of mixing with coherent switches

Todd, Anderson, and Lester, *JPC A*, 2001