Semiclassical Study of the Photodissociation Dynamics of Vibrationally Excited NH$_3$(Å) Molecules

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Principle of the experiments
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- **Excitation of NH\(_3\) molecules**
  - Photo-excitation of NH\(_3\) to a vibrational state of its first excited electronic state.
  - 6 modes with positive frequencies at the equilibrium geometry of the first excited electronic state well: \(\nu_1\) (symmetric stretch), \(\nu_2\) (out-of-plane bend or “umbrella” mode), \(\nu_3(2)\) (antisymmetric stretch), \(\nu_4(2)\) (bend).
### Excess energies

Denoting $E_{exc}$ the quantum energy available for fragmentation, also called excess energy, the NH$_2$ internal energy is given by

$$E_{int}(NH_2) = E_{exc} - E_{rel}(H)$$

with $E_{rel}(H) = \frac{\mu_{red}}{2} V^2_R$

with $\mu_{red} = \frac{m(NH_2)m(H)}{m(NH_3)}$, $\vec{V}_R = \vec{v}(H) - \vec{v}_{com}(NH_2)$.

<table>
<thead>
<tr>
<th>$n_2$</th>
<th>$E_{exc}$ (theory)</th>
<th>$E_{exc}$ (exp.1)</th>
<th>$E_{exc}$ (exp.2)</th>
<th>$E_{exc}$ (exp.3)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Biesner et al., 1989)</td>
<td>(Bach et al., 2003)</td>
<td>(Hause et al., 2006)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.16</td>
<td>1.08</td>
<td>1.13</td>
<td>1.12</td>
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<tr>
<td>1</td>
<td>1.27</td>
<td>1.19</td>
<td>1.23</td>
<td>n.a.</td>
</tr>
<tr>
<td>2</td>
<td>1.38</td>
<td>1.30</td>
<td>1.34</td>
<td>n.a.</td>
</tr>
<tr>
<td>3</td>
<td>1.49</td>
<td>1.41</td>
<td>1.46</td>
<td>n.a.</td>
</tr>
<tr>
<td>4</td>
<td>1.60</td>
<td>1.53</td>
<td>1.57</td>
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</tr>
<tr>
<td>5</td>
<td>1.71</td>
<td>1.64</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>6</td>
<td>1.82</td>
<td>1.76</td>
<td>n.a.</td>
<td>n.a.</td>
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</table>
Semiclassical methods (I)

- A mean-field approach, the CSDM (Coherent Switching with Decay of Mixing) method:

  - The dynamics of nuclei is performed on an average potential-energy surface.
  - The average surface decays toward an adiabatic surface, the decay proceeding faster as the system gets farther from a region of strong coupling.
  - First-order decay time used to control the demixing of the average surface to a quantized state:

\[
\tau = \frac{\hbar}{\Delta V} \left( c + \frac{E_0}{T_s} \right)
\]

\(\Delta V\) is the difference between the adiabatic electronic energies, \(c\) and \(E_0\) are two parameters, \(T_s\) is the kinetic energy associated with the component of the momentum where energy is being added or removed as the trajectory demixes.

Semiclassical methods (II)

- A trajectory surface-hopping method, the FSTU (Fewest Switches with Time Uncertainty) and FSTU/SD (FSTU with Stochastic Decay) methods:
  - The dynamics of nuclei is performed on one adiabatic surface at a time.
  - Electronic nonadiabatic transitions ("hops") between surfaces \( j \) and \( k \) are governed by a hopping probability \( g_{jk} = f(\dot{\mathbf{R}} \cdot \mathbf{d}_{jk}, c_j, c_k) \).
  - Hopping event: Kinetic energy needs to be adjusted, some hops may be "frustrated", i.e., classically forbidden.
  - Improvements of FSTU: it looks backward \((t_h < t_0)\) and forward \((t_h > t_0)\) in time for a possible hopping time \( t_h \) that is different from \( t_0 \). The electronic transition is allowed at \( t_h \neq t_0 \) if a hopping point is reachable within the Heisenberg interval of time uncertainty, that is when
    \[
    |t_0 - t_h| \leq \frac{\hbar}{2\Delta E}
    \]
    \( \Delta E \) is the energy that would need to be borrowed at \( t_0 \) to allow a hop.
  - Improvements of FSTU/SD: some decoherence is included (phenomenological decay of the off-diagonal elements of the electronic density matrix).
NH₂ internal energy

\[ n_2 = 0 \quad \text{and} \quad n_2 > 0 \]

1a: Experiment of Biesner et al. (1989)

1b: Experiment of Hause et al. (2006)

2: FSTU/SD simulations
TRAjectory Projection onto Zero-point energy orbit (TRAPZ)

• Classical trajectories must not cross the orbits $E_i = E_{i,ZPE}$ for each mode $i$.
  - If $E_i > E_{i,ZPE}$ then nothing to do.
  - If $E_i < E_{i,ZPE}$ then adjusting $p_i$ to maintain ZPE.

Main features of TRAPZ (I)

- Preliminary conditions:
  - Working in the center-of-mass frame.
  - Mass weighted Cartesian coordinates

\[ x = [M]^{1/2} x_c \text{ et } p = [M]^{-1/2} p_c \]
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- **Harmonic analysis:**
  - Calculation of the projected Hessian \([K^P]\) at time \(t_0\) by removing the 6 infinitesimal rotations and translations from the Hessian \([K]\)


  - Diagonalization of \([K^P]\): normal modes, \(L_k(t_0)\), and frequencies, \(\Omega_k(t_0)\)
  - Calculation of the instantaneous vibrational energy of mode \(k\) at time \(t_0\)

\[ E_k(t_0) = \frac{1}{2\mu} \left[ P_k^2 + \left( \frac{D_k(t_0)}{\Omega_k(t_0)} \right)^2 \right] \]
Main features of TRAPZ (II)

- Comparison to the ZPE of each mode: \( E_{ZPE,k}(t_0) = \frac{1}{2} \hbar \Omega_k(t_0) \)?
- If \( E_k(t_0) < E_{ZPE,k}(t_0) \) then

\[
P'_k = \text{sign}(P_k) \sqrt{\mu \hbar \Omega_k(t_0) - \left( \frac{D_k(t_0)}{\Omega_k(t_0)} \right)^2}
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- Different TRAPZ-like methods:
  
  **TRAPZ criterion:** 
  \[ E_k(t_0) \leq E_{ZPE,k}(t_0) \]

  **mTRAPZ criterion:** 
  \[ \sum_{k=1}^{3N-q(t_0)} E_k(t_0) \leq \sum_{k=1}^{3N-q(t_0)} E_{ZPE,k}(t_0) \]

  **mTRAPZ* criterion (less general):** 
  \[ \sum_{k=1}^{3N-q(t_0)} E_k(t_0) \leq E_{ZPE,NH_2}(t_0) \]

**NH$_2$ internal energy (mTRAPZ)**

\[ n_2 > 0 \]

\[ n_2 = 0 \]

1a: Experiment of Biesner et al. (1989)

1b: Experiment of Hause et al. (2006)

2: FSTU/SD simulations

3a: FSTU/SD+mTRAPZ simulations
### Partitioning of energy

<table>
<thead>
<tr>
<th>$n_2$</th>
<th>mTRAPZ</th>
<th>mTRAPZ*</th>
<th>Experiment</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Internal</td>
<td>Translational</td>
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</tr>
<tr>
<td>6</td>
<td>71</td>
<td>29</td>
<td>71</td>
</tr>
</tbody>
</table>

- **Comparison between methods:**
  - mTRAPZ and mTRAPZ* are equivalent.
  - The partitioning is much better when considering mTRAPZ or mTRAPZ* rather than TRAPZ (highly vibrationally excited NH$_2$ molecules, very cold H atoms for all the $n_2$ values) or no TRAPZ-like method (hot H atoms).
Conclusion

- The mixed quantum/classical methods tested here (CSDM, FSTU, FSTU/SD)
  - lead to similar results,
  - qualitatively reproduce experimental results,
  - but the ZPE maintenance is not ensured,
  - and the dynamics is found mainly nonadiabatic whatever \( n_2 \) whereas the experiment finds that the percentage of adiabatic dissociation steadily increases with \( n_2 \) for \( n_2 \geq 3 \).

- The mTRAPZ and mTRAPZ* methods
  - allows to ensure ZPE throughout the dynamics,
  - improve the partitioning of energy (compared to FSTU/SD or FSTU/SD+TRAPZ),
  - but the dynamics is found more nonadiabatic.

- Future work:
  - Studying the effect of exciting the symmetric and antisymmetric stretch of \( \text{NH}_3 \).
  - Modifying conditions at hopping events to favor adiabaticity!
Acknowledgements

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