

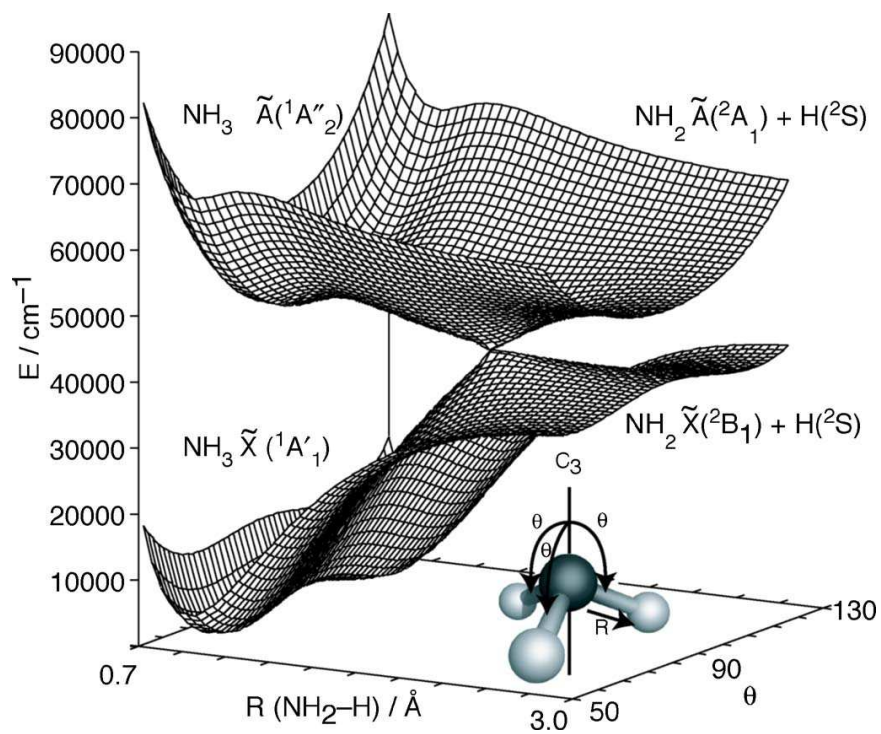


Semiclassical Study of the Photodissociation Dynamics of Vibrationally Excited $\text{NH}_3(\tilde{A})$ Molecules

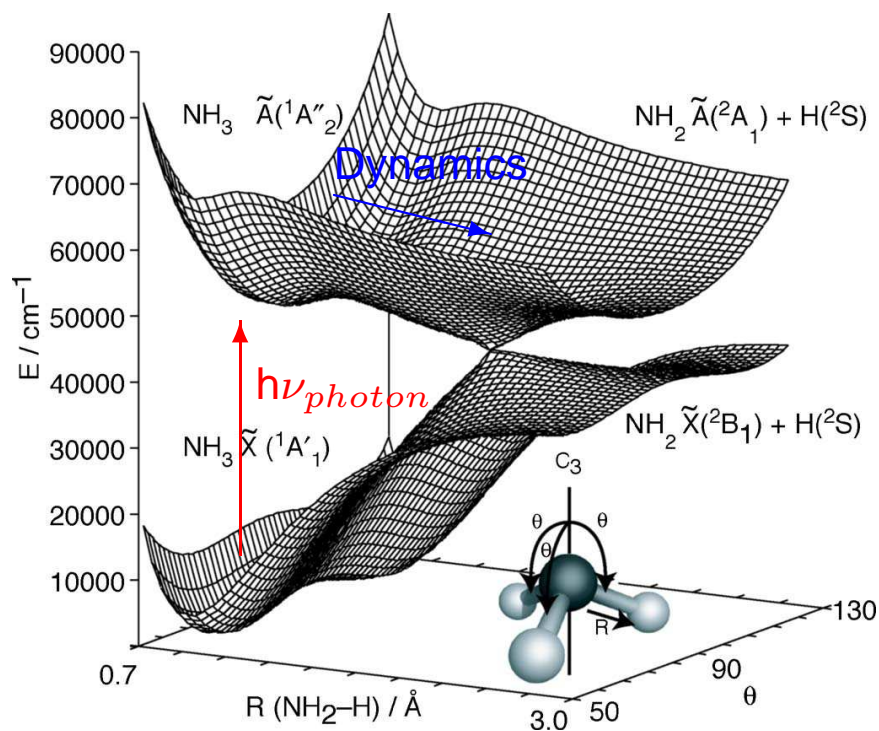
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Principle of the experiments



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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: ν_1 (symmetric stretch), ν_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

$$E_{int}(NH_2) = E_{exc} - E_{rel}(H) \text{ with } E_{rel}(H) = \frac{\mu_{red}}{2} V_R^2$$

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

n_2	E_{exc} (theory)	E_{exc} (exp.1) (Biesner et al., 1989)	E_{exc} (exp.2) (Bach et al., 2003)	E_{exc} (exp.3) (Hause et al., 2006)
0	1.16	1.08	1.13	1.12
1	1.27	1.19	1.23	n.a.
2	1.38	1.30	1.34	n.a.
3	1.49	1.41	1.46	n.a.
4	1.60	1.53	1.57	n.a.
5	1.71	1.64	n.a.	n.a.
6	1.82	1.76	n.a.	n.a.

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:

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

ΔV 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.

Ref (CSDM): C. Zhu et al., J. Chem. Phys., **121**, 7658 (2004).

Ref (FSTU): A. W. Jasper et al., J. Chem. Phys., **116**, 5424 (2002).

Ref (FSTU/SD): A. W. Jasper et al., J. Chem. Phys., **127**, 194306 (2007).

Semiclassical methods (II)

- A trajectory surface-hopping method, the FSTU (Fewest Switches with Time Uncertainty) and FSTU/SD (FSTU with Stochastic Decay) methods:

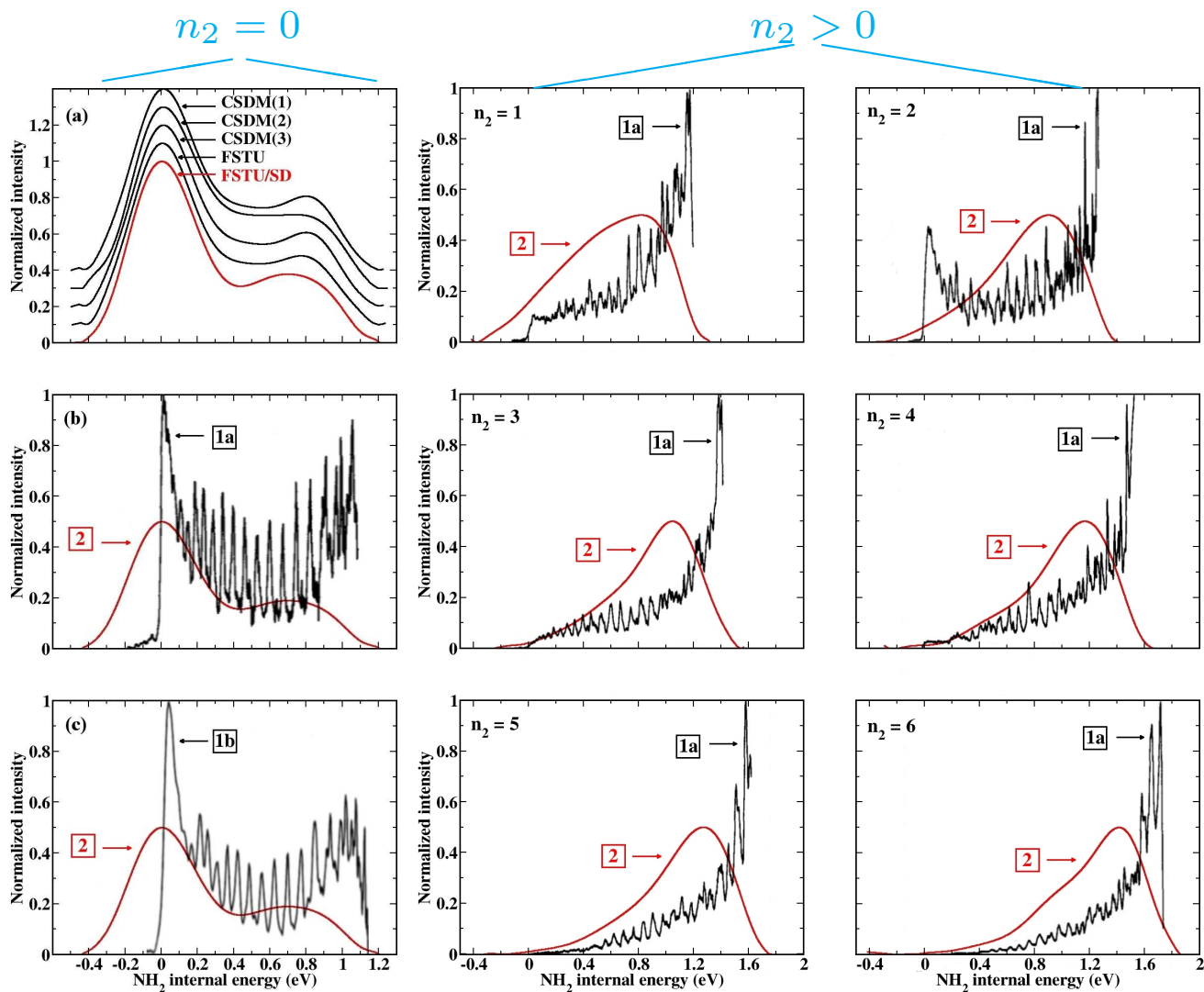
- ★ The dynamics of nuclei is performed on one adiabatic surface at a time.
- ★ Electronic nonadiabatic transitions (“hops”) between surfaces j and k are governed by a hopping probability $g_{jk} = f(\dot{\mathbf{R}} \cdot \mathbf{d}_{jk}, c_j, c_k)$.
- ★ Hopping event: Kinetic energy needs to be adjusted, some hops may be “frustrated”, ie 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

$$|t_0 - t_h| \leq \frac{\hbar}{2\Delta E}$$

ΔE 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

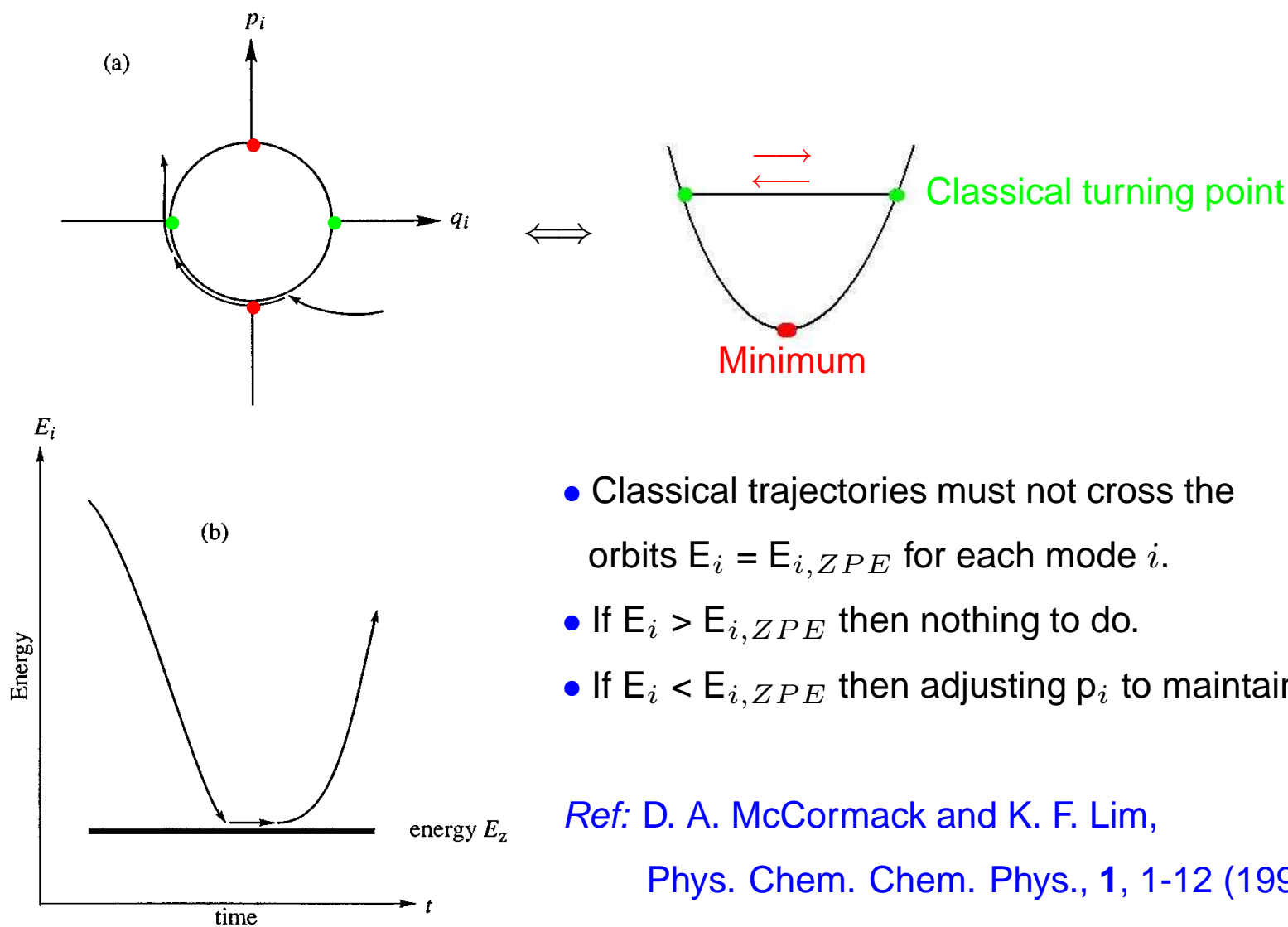


1a: Experiment of Biesner et al. (1989)

2: FSTU/SD simulations

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

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.

Ref: D. A. McCormack and K. F. Lim,
Phys. Chem. Chem. Phys., **1**, 1-12 (1999).

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 $[K]$

$$[K^P] = ([I] - [\mathcal{P}])[K]([I] - [\mathcal{P}])$$

- ★ 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: $E_{\text{ZPE},k}(t_0) = \frac{1}{2} \hbar \Omega_k(t_0)$?
- If $E_k(t_0) < E_{\text{ZPE},k}(t_0)$ 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:

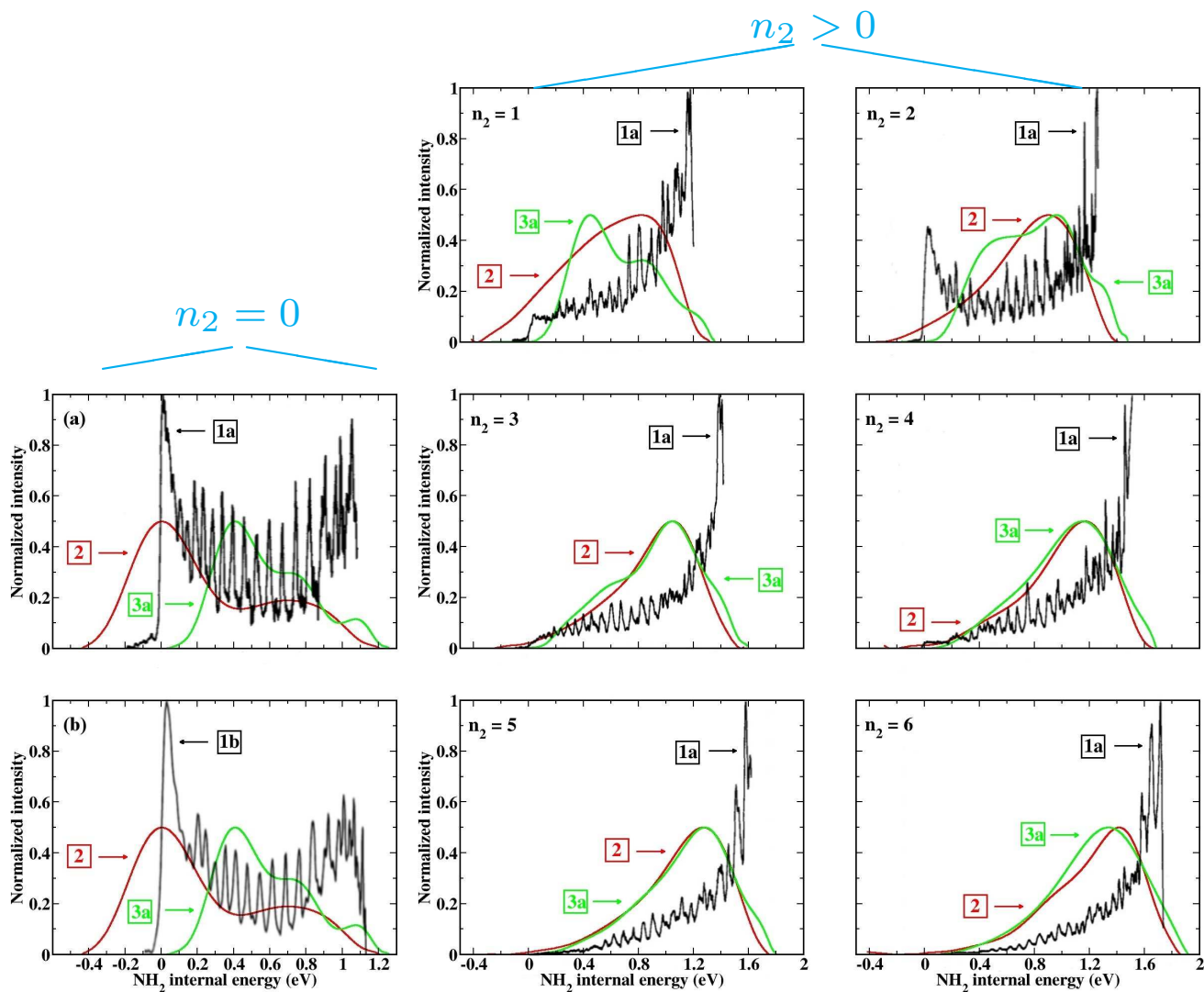
TRAPZ criterion: $E_k(t_0) \leq E_{\text{ZPE},k}(t_0)$

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

mTRAPZ* criterion (less general): $\sum_{k=1}^{3N-q(t_0)} E_k(t_0) \leq E_{\text{ZPE,NH}_2}(t_0)$

Ref: D. Bonhommeau, and D. G. Truhlar, J. Chem. Phys., accepted (2008).

NH₂ internal energy (mTRAPZ)



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

2: FSTU/SD simulations

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

3a: FSTU/SD+mTRAPZ simulations

Partitioning of energy

n_2	mTRAPZ		mTRAPZ*		Experiment	
	Internal	Translational	Internal	Translational	Internal	Translational
0	51	49	50	50	47 ± 2	53 ± 2
1	54	46	54	46	67 ± 2	33 ± 2
2	60	40	61	39	53 ± 2	47 ± 2
3	64	36	65	35	71 ± 2	29 ± 2
4	67	33	68	32	73 ± 2	27 ± 2
5	69	31	70	30	77 ± 2	23 ± 2
6	71	29	71	29	80 ± 2	20 ± 2

- **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 NH_3 .
 - ★ Modifying conditions at hopping events to favor adiabaticity !

Acknowledgements

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