

Ionization and fragmentation of water molecules in ion-H₂O collisions.

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- 1 Introduction
- 2 Previous calculations
- 3 Fragmentation of H_2O^+ .
- 4 Calculation of PES
- 5 Dynamics
- 6 Final Remarks

Motivation

- Primary processes in **IBCT**.
- Production of electrons and ions.
- Atomic data (cross sections) needed in simulations.

Proton – molecule collisions

Primary processes

- **Single Electron Capture (SEC):** $\text{H}^+ + \text{M} \rightarrow \text{H} + \text{M}^+$
- **Single Ionization (SI):** $\text{H}^+ + \text{M} \rightarrow \text{H}^+ + \text{M}^+ + \text{e}^-$
- **Transfer Ionization (TI):** $\text{H}^+ + \text{M} \rightarrow \text{H} + \text{M}^{2+} + \text{e}^-$
- **Double Ionization (DI):** $\text{H}^+ + \text{M} \rightarrow \text{H}^+ + \text{M}^{2+} + 2\text{e}^-$

Molecular fragmentation

The cations M^+ and M^{2+} formed in capture and ionization reactions can dissociate; e.g., the ions:



are detected in ion- H_2O collision experiments.

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Eikonal CTMC method

We consider ion-water collisions (see Illescas *et al.*, Phys. Rev. A **83** (2011))

- Franck- Condon approximation.
- The projectile follows **straight-line trajectories**: $\mathbf{R} = \mathbf{b} + \mathbf{v}t$.
- Independent electron approximation.
- Use of a three-centre model potential to describe the electron – H_2O^+ interaction.
- Electronic motion described by a **classical distribution function** $\rho(\mathbf{r}, \mathbf{p}, t)$.
- Orientation-averaged cross sections.

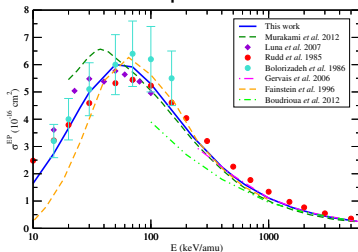
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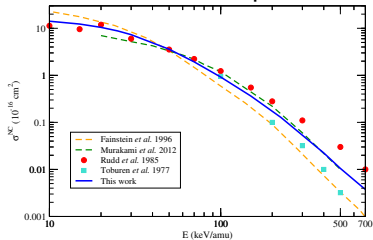
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$H^+ + H_2O$ collisions. Total cross sections

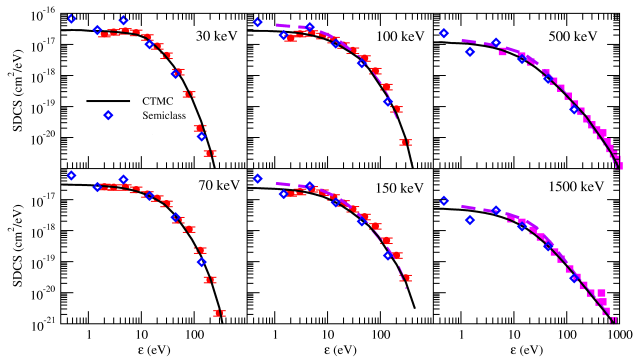
Electron production



Net electron capture



SDCS



- Our calculations: Errea et al. PRA 87, 032709.
- Experiments: Toburen and Wilson, JCP 66, 5202; Rudd et al. PRA, 31, 492.
- Other Calculations: Boudrioua et al. PRA 75, 022720.

Fragmentation cross sections.

Tan et al. CP 29, 299

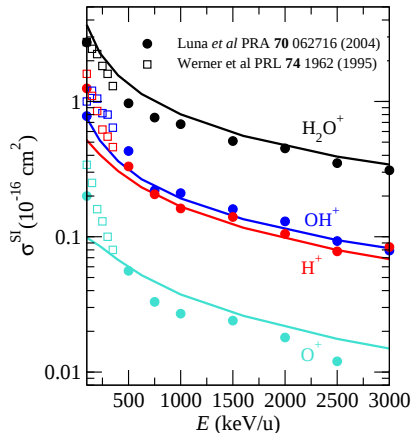
$$\sigma^{\text{H}_2\text{O}^+} = 1.0 \sigma(1b_1) + 1.0 \sigma(3a_1)$$

$$+ 0.08 \sigma(1b_2)$$

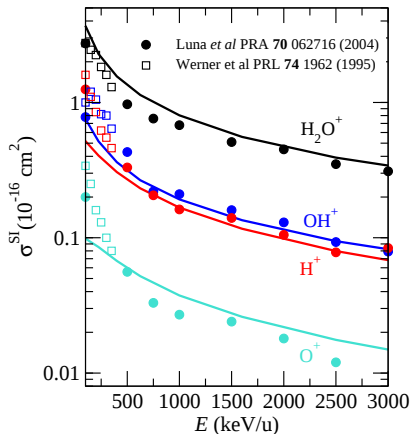
$$\sigma^{\text{OH}^+} = 0.7 \sigma(1b_2)$$

$$\sigma^{\text{H}^+} = 0.22 \sigma(1b_2) + 0.74 \sigma(2a_1)$$

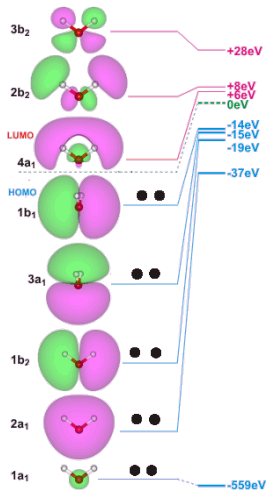
$$\sigma^{\text{O}^+} = 0.26 \sigma(2a_1)$$

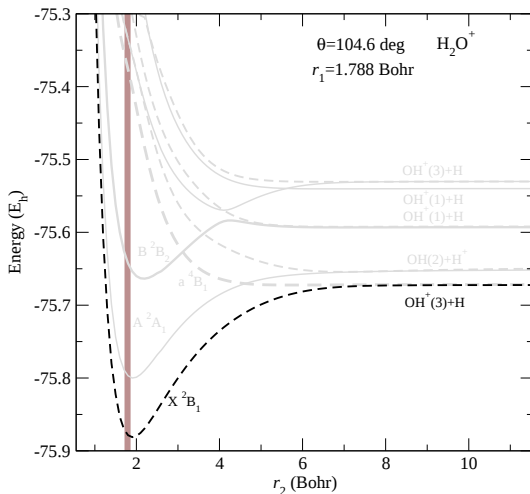
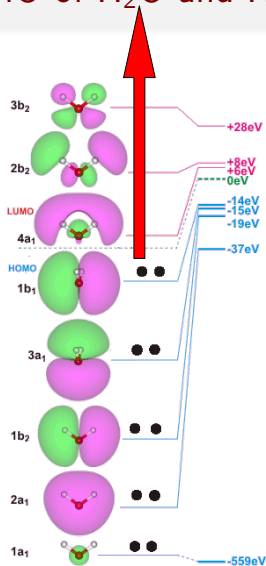


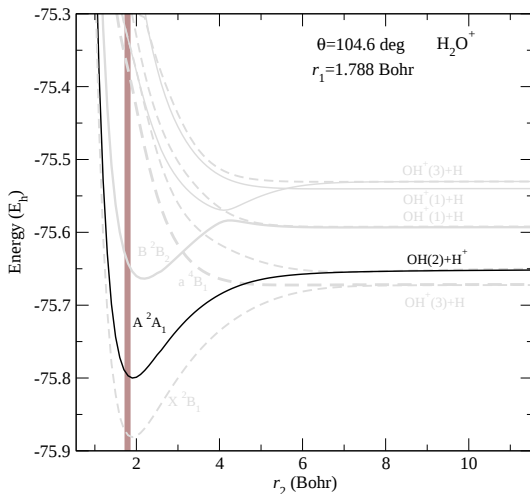
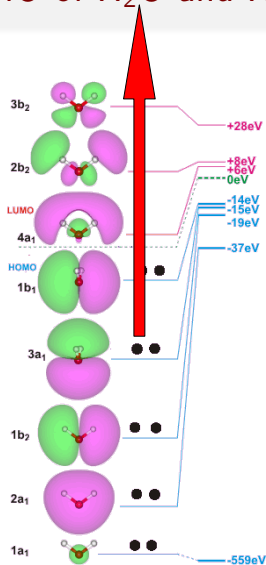
Fragmentation cross sections.

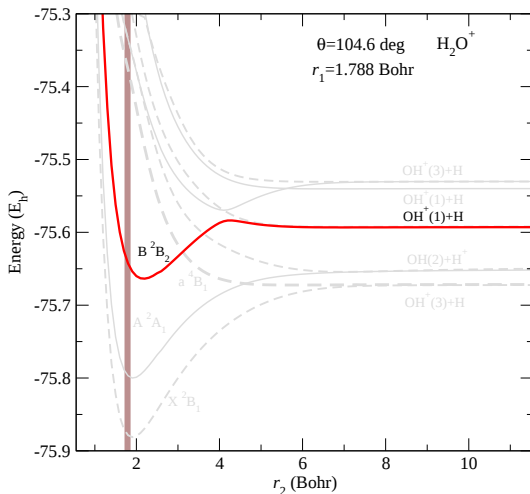
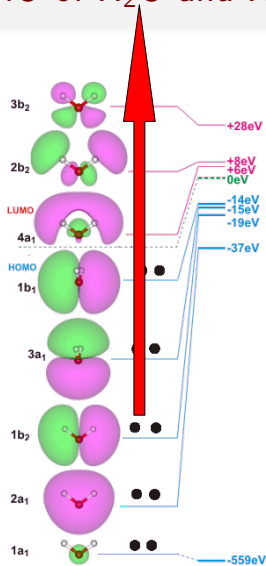


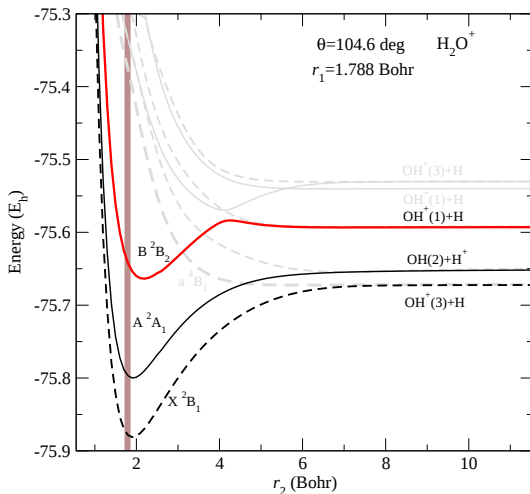
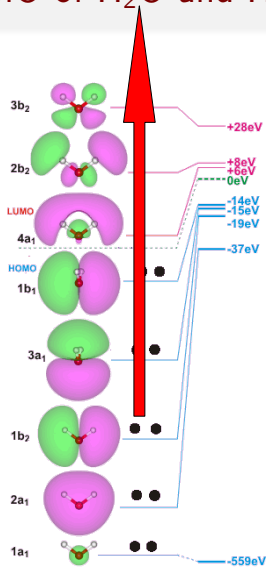
- The dissociation of H_2O^+ is a postcollisional process.
- There is not an *ab initio* study of the H_2O^+ breakdown reaction.

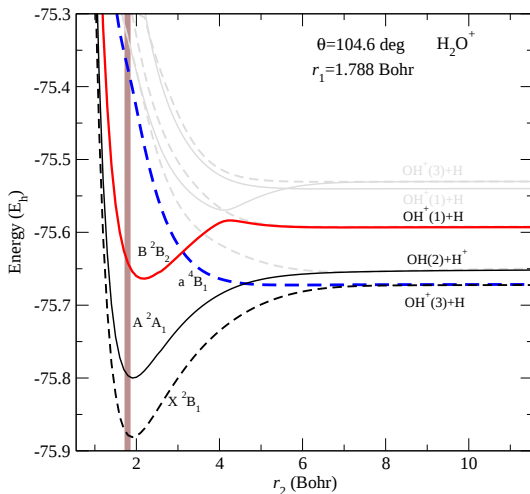
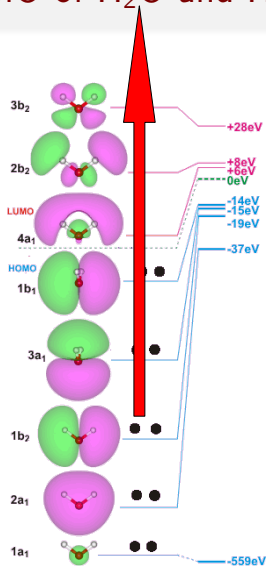
MO of H_2O and H_2O^+ PEC

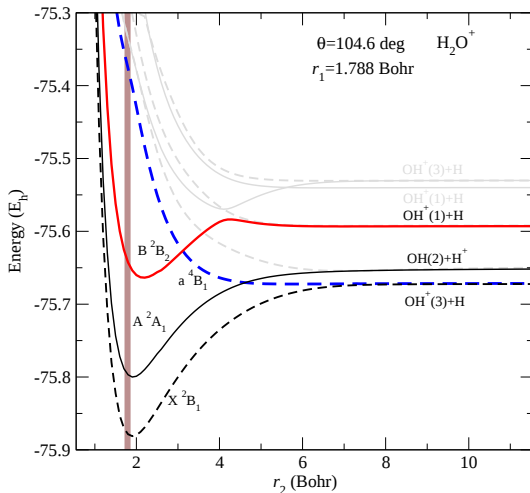
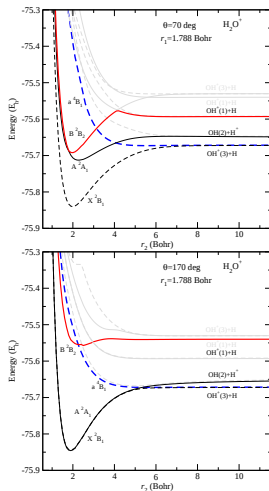
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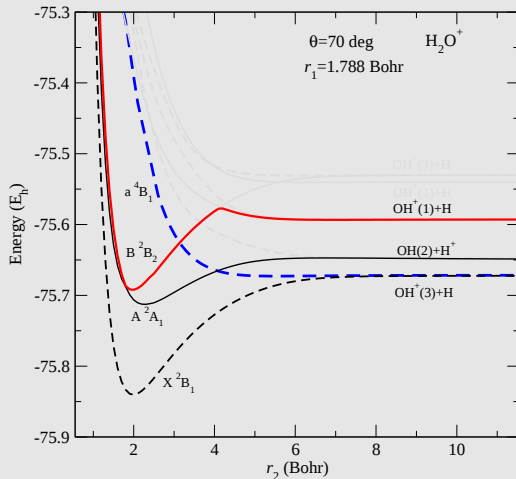
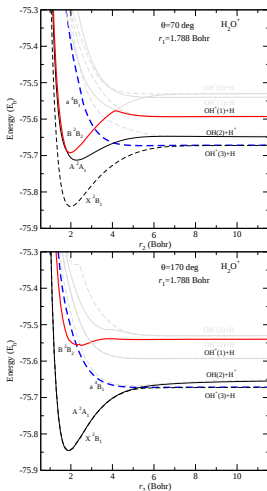
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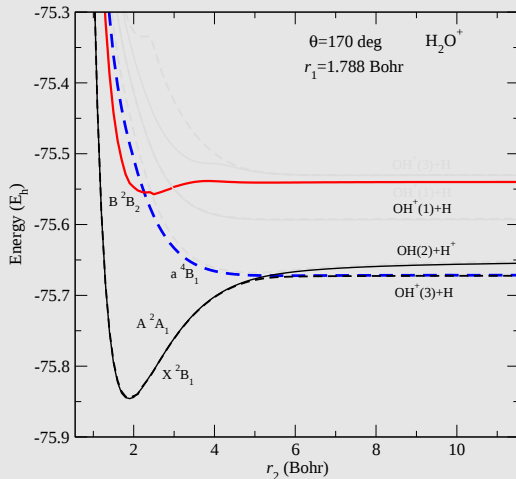
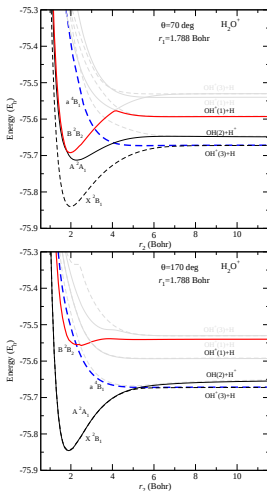
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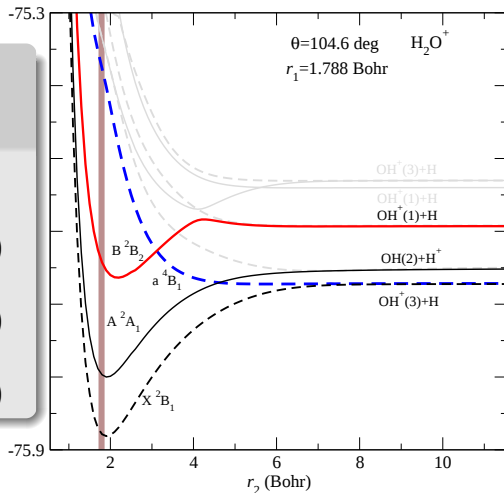
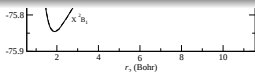
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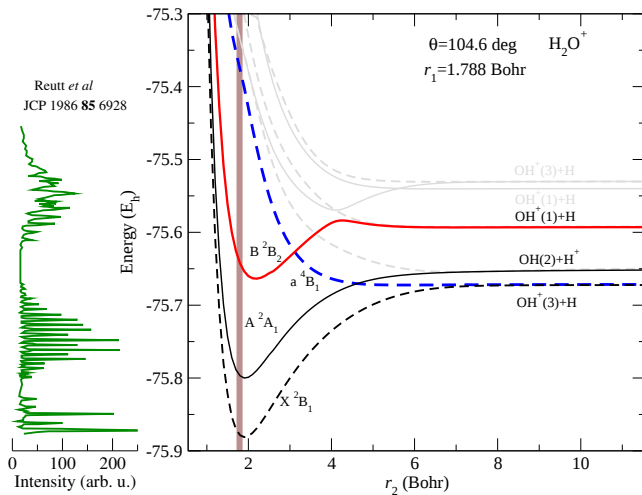
1b₂: Tan *et al* CP 29 299
(1978)

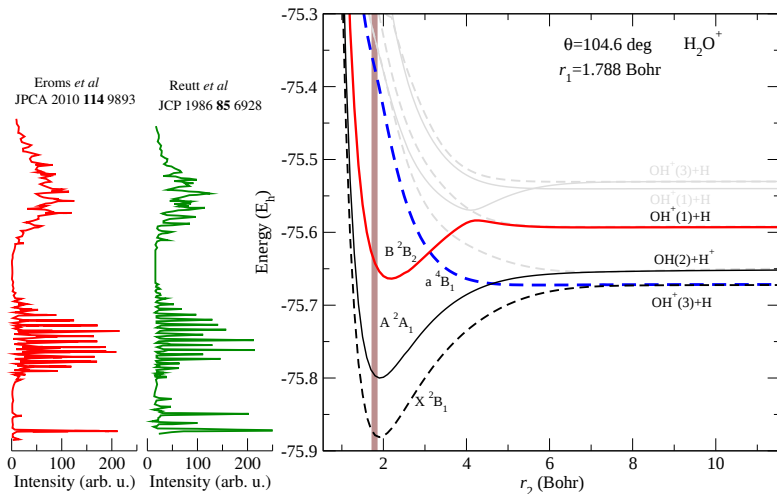
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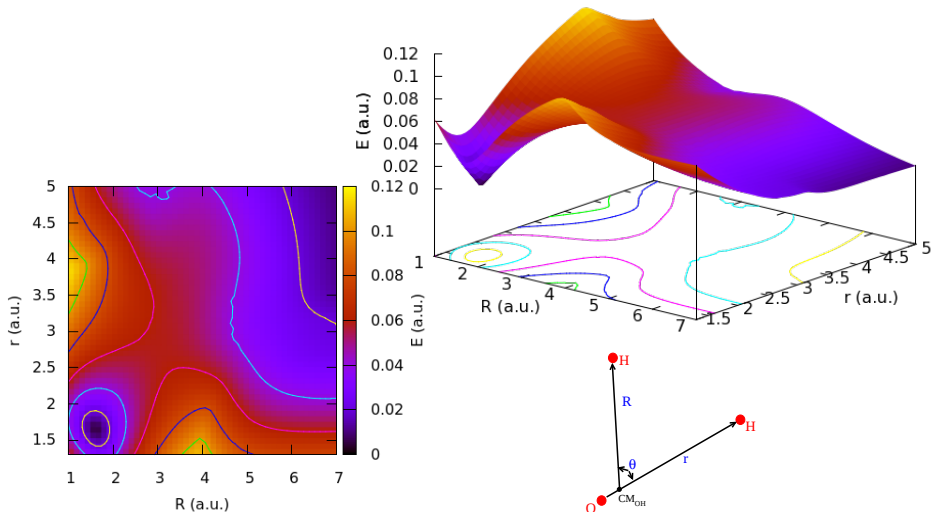
MO of H_2O and H_2O^+ PEC

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PES details

- MOLPRO: MRCI wave functions.
- Basis: (O, aug-cc-pvqz; H, aug-cc-pvtz).
- 1.8 million uncontracted configurations ($^2A'$ symmetry).
- $50 \times 50 \times 31 = 77500$ points in (r, R, θ) Jacobi coordinates.
- Slightly smaller calculations for symmetries $^2A''$ and $^4A''$ PES.
- Calculation of non-adiabatic couplings near the CI.

$$\tilde{A} \ ^2A_1 - \tilde{B} \ ^2B_2 \text{ CI } (\theta = 70^\circ)$$



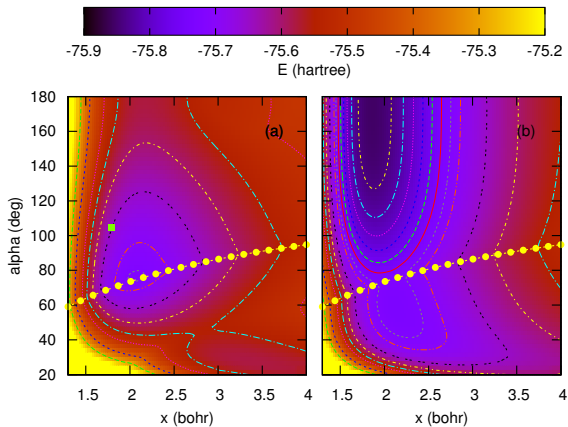
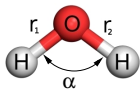
$\tilde{A} \ ^2A_1 - \tilde{B} \ ^2B_2 \text{ Cl}$

Symmetry

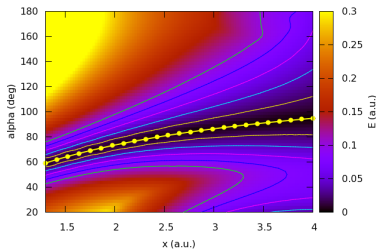
coordinates

$$x = \frac{r_1 + r_2}{2} ;$$

$$y = \frac{r_1 - r_2}{2}$$

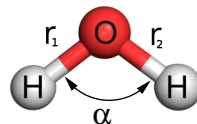


Regularization of $\tilde{B}^2B_2 - \tilde{A}^2A_1\text{Cl}$

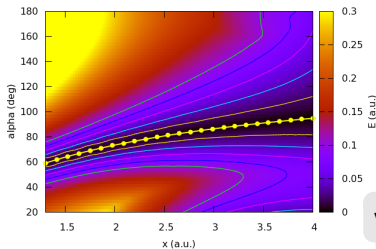


$$x = \frac{r_1 + r_2}{2} ; y = \frac{r_1 - r_2}{2}$$

$$\alpha_{\text{Cl}}(x) = \frac{81.75x}{1 + 0.61x}$$



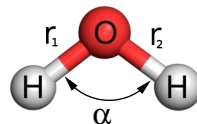
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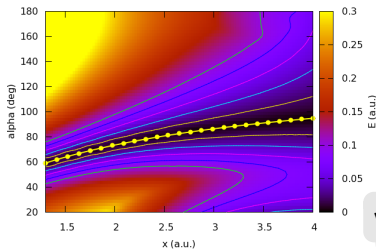
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$$V^d = S^\dagger V S$$



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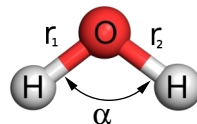


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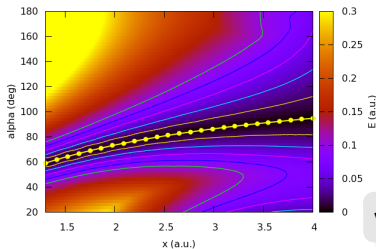
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$$\mathbf{S} = \begin{pmatrix} \cos \Theta & -\sin \Theta \\ \sin \Theta & \cos \Theta \end{pmatrix}$$



Regularization of $\tilde{B}^2B_2 - \tilde{A}^2A_1\text{Cl}$



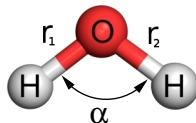
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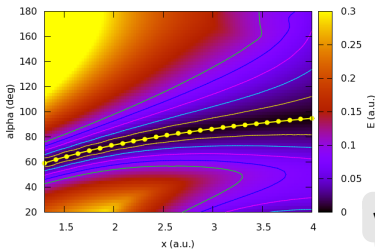
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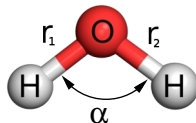
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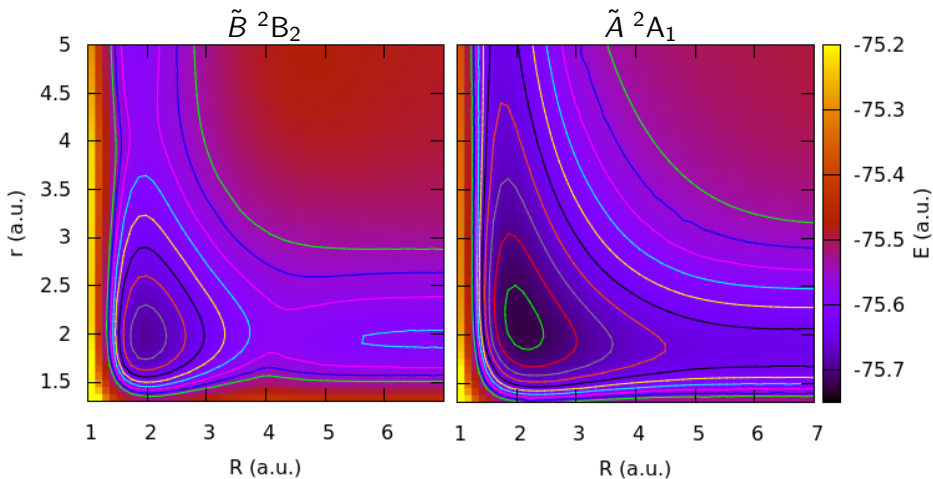
$$\Theta = \frac{1}{2} \arctan \left(\frac{2V_{12}^d}{\Delta V^d} \right)$$

$$\Delta V^d(\alpha, x) = (\alpha - \alpha_{\text{Cl}}) \sin(\pi/2 - \alpha'_{\text{Cl}}) \approx d(p, \text{Cl})$$

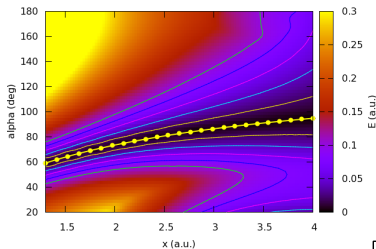
$$V_{12}^d(\alpha, y) = 0.18y + 0.77 - 0.050\alpha + 6.75 \times 10^{-4}\alpha^2$$



H_2O^+ Diabatic PES: $\theta = 70^\circ$



H₂O⁺ PES: C_{2v} symmetry

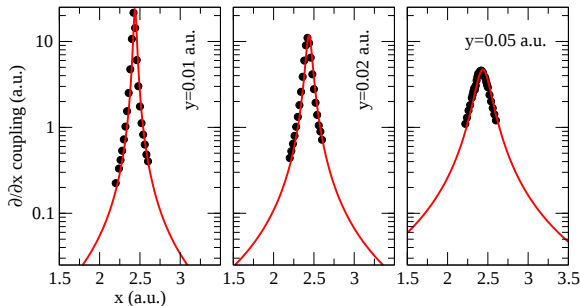


$$x = \frac{r_1 + r_2}{2} ; y = \frac{r_1 - r_2}{2}$$

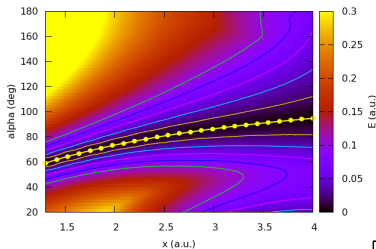
$$\alpha_{\text{Cl}}(x) = \frac{81.75x}{1 + 0.61x}$$

$$A_x = \left\langle \psi_1 \left| \frac{\partial \psi_2}{\partial x} \right. \right\rangle$$

$$A_x = \frac{\partial \Theta}{\partial x}$$



H₂O⁺ PES: C_{2v} symmetry

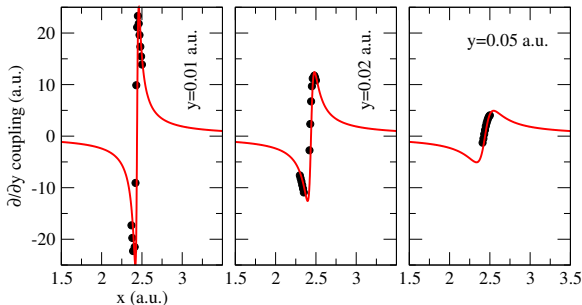


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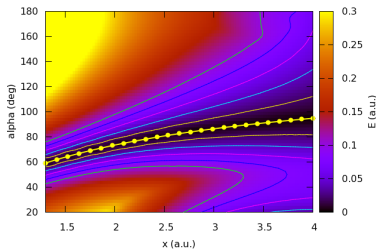
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H₂O⁺ PES: C_{2v} symmetry

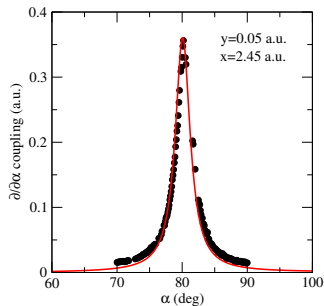


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$$A_\alpha = \left\langle \Psi_1 \left| \frac{\partial \Psi_2}{\partial \alpha} \right. \right\rangle$$

$$A_\alpha = \frac{\partial \Theta}{\partial \alpha}$$



Renner-Teller coupling ($\tilde{X}^2B_1 - \tilde{A}^2A_1$)

In the $C_{\infty v}$ limit, the angular momentum operators:

$$\left. \begin{array}{lll} \text{total:} & \hat{J}_z & \longrightarrow K \\ \text{elect:} & \hat{l}_z & \longrightarrow \Lambda \\ \text{nuclear:} & \hat{j}_z & \longrightarrow k \end{array} \right\} \quad \boxed{k = K - \Lambda}$$

In the limit $\theta \rightarrow 180^\circ$ $\tilde{A}^2A_1$ and $\tilde{X}^2B_1$ correlate with the two components of $^2\Pi_u$ ($|\Lambda| = \pm 1$).

$$\begin{pmatrix} \psi_+ \\ \psi_- \end{pmatrix} = \begin{pmatrix} 1 & i \\ 1 & -i \end{pmatrix} \begin{pmatrix} \psi_A \\ \psi_X \end{pmatrix} \quad \begin{array}{l} (k = K - 1) \\ (k = K + 1) \end{array}$$

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Renner-Teller coupling ($\tilde{X}^2B_1 - \tilde{A}^2A_1$)

Introducing the **rotation out-of-plane** term:

$$\begin{aligned} \mathbf{H}_J = & -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} \\ & -\frac{1}{2} \left(\frac{1}{\mu_R R^2} + \frac{1}{\mu_r r^2} \right) \left(\frac{\hbar^2}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} - \frac{\hat{j}_z^2}{\sin^2 \theta} \right) \\ & + V(R, r, \theta) \end{aligned}$$

In the low $\mathbf{J}^2$ limit, we can neglect the Coriolis coupling.

Renner-Teller coupling ($\tilde{X}^2B_1 - \tilde{A}^2A_1$)

Introducing the **rotation out-of-plane** term:

$$\begin{aligned}
 \mathbf{H}_J \approx & -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} \\
 & -\frac{\hbar^2}{2} \left(\frac{1}{\mu_R R^2} + \frac{1}{\mu_r r^2} \right) \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} - \frac{\mathbf{k}^2}{\sin^2 \theta} \right) \\
 & + V(R, r, \theta)
 \end{aligned}$$

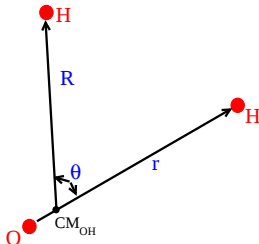
Since $\mathbf{k} = \mathbf{K} \pm 1$ Including **Renner-Teller** transitions involves calculations with different values of K

(Haxton et al. PRA 75, 01271)

Kinetic energy operator

In **Jacobi coordinates** (R, r, θ) and $J = 0$:

$$\mathbf{T} = -\frac{\hbar^2}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2} \left(\frac{1}{\mu_R R^2} + \frac{1}{\mu_r r^2} \right) \left(\frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right)$$



Evaluation of $\mathbf{H}\Psi$

$$\mathbf{H}\Psi = \mathbf{T}\Psi + \mathbf{V}\Psi$$

$$V(x_1, \dots, x_{N_d}) \implies \text{Diagonal matrix elements}$$

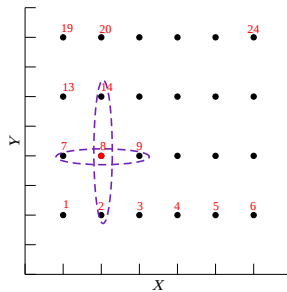
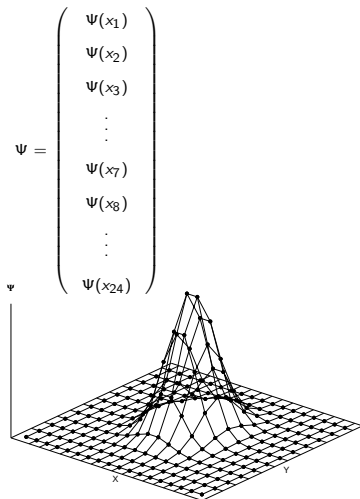
$$T = \sum_i -\frac{\hbar^2}{2m_i} \partial_i^2 \implies \text{Non-diagonal matrix elements}$$

Finite differences method (Program Grid-TDSE, Suarez et al. CPC 180, 2025)

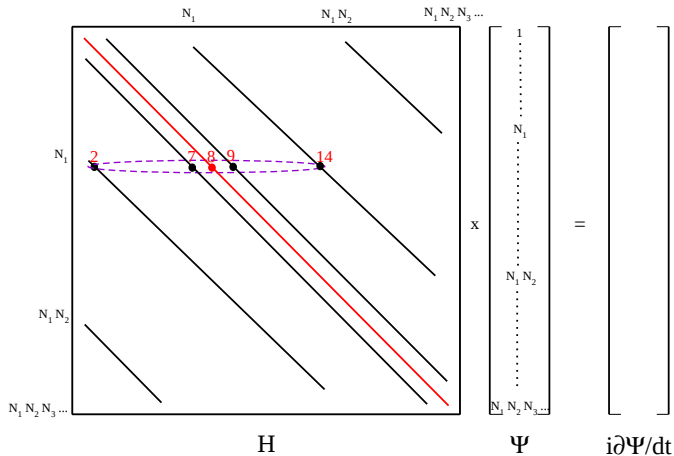
$\mathbf{T}$ is approximated considering only n_s neighboring grid points:

$$\Psi(x) \approx \Psi_N(x) = \sum_k \Psi(x_k) L_k(x) \Rightarrow (\nabla^2 \Psi)_k \approx \sum_{j=1}^{n_s} b_{kj}^2 \Psi_N(x_j)$$

Discretization of Ψ



Evaluation of $\mathbf{H}\Psi$



Propagation in time of $\Psi(t)$

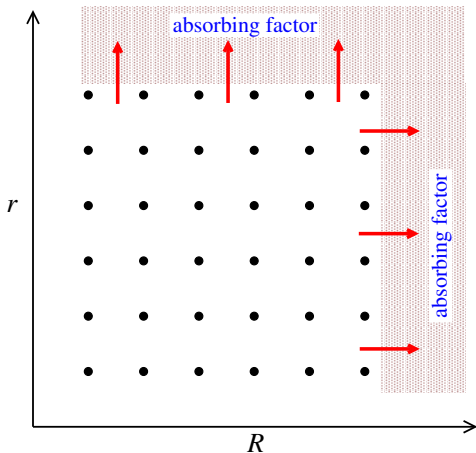
Second order difference method (SOD):

$$\Psi(t + \Delta) = e^{-i\mathbf{H}\Delta/\hbar}\Psi(t) \approx \Psi(t - \Delta) - 2i\Delta\mathbf{H}\Psi(t)$$

- Recursive method.
- Two previous points needed.
- Norm and energy conserved.
- Accuracy $O(\Delta)^2$.

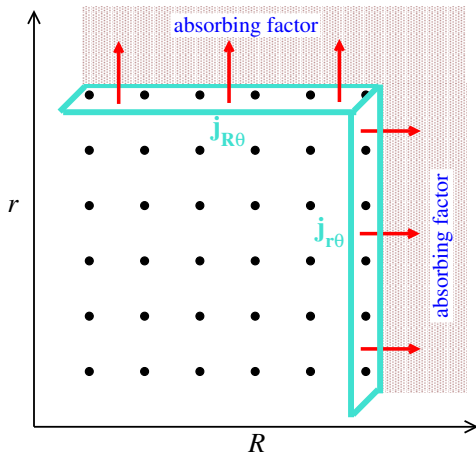
Absorbing boundary conditions

Dumping factor to avoid reflections at borders



Absorbing boundary conditions

Dumping factor to avoid reflections at borders



Flux:

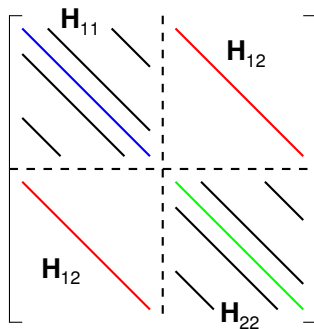
$$\vec{j}(\vec{r}, t) = \frac{\hbar}{m} \text{Im} \{ \Psi^* (\nabla \Psi) \}$$

Continuity Equation:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{j} = 0$$

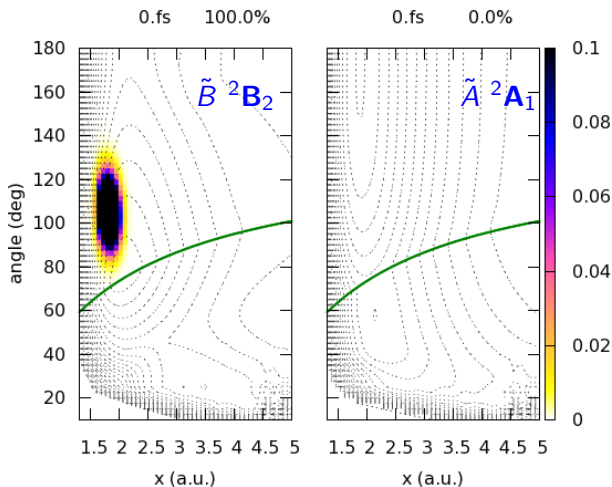
Two-state matrix hamiltonian

$$\begin{pmatrix} \mathbf{H}_{11}^d & \mathbf{H}_{12}^d \\ \mathbf{H}_{12}^d & \mathbf{H}_{22}^d \end{pmatrix} \begin{pmatrix} \psi_1 \\ \psi_2 \end{pmatrix} = i\hbar \begin{pmatrix} \dot{\psi}_1 \\ \dot{\psi}_2 \end{pmatrix}$$

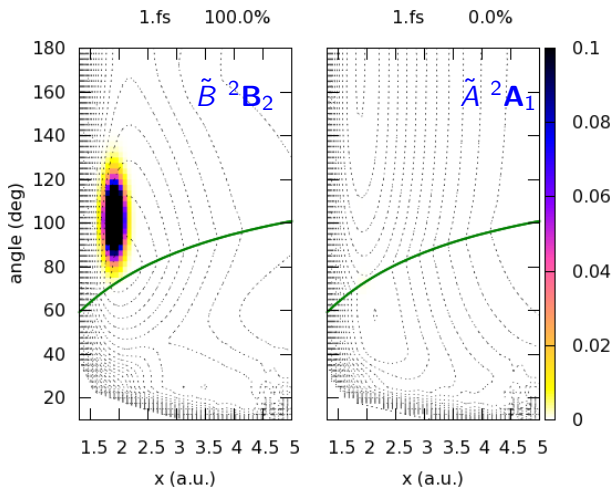


WP in H_2O^+ ($\tilde{B} \ ^2\text{B}_2$ and $\tilde{A} \ ^2\text{A}_1$)

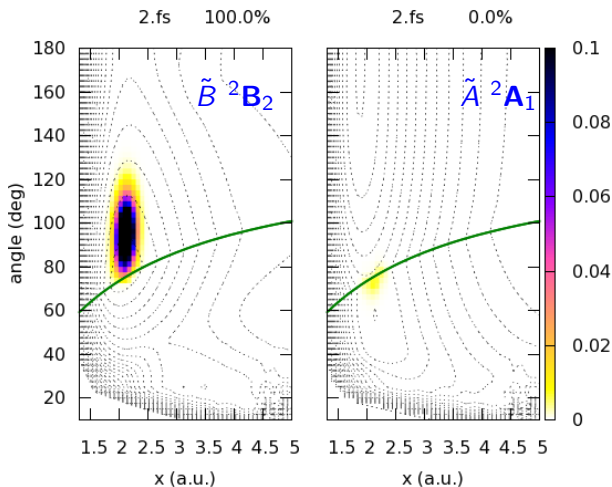
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



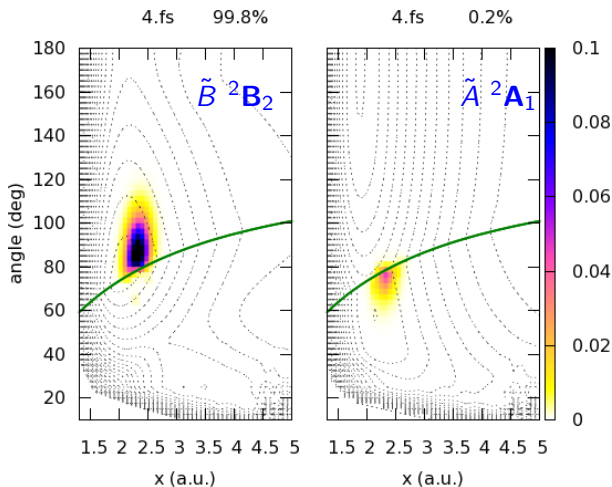
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



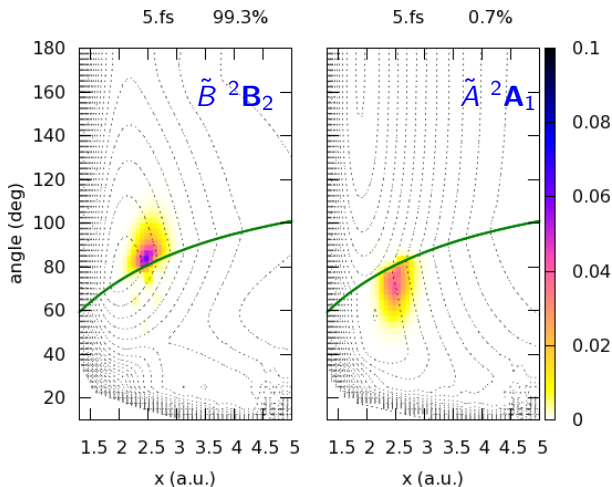
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



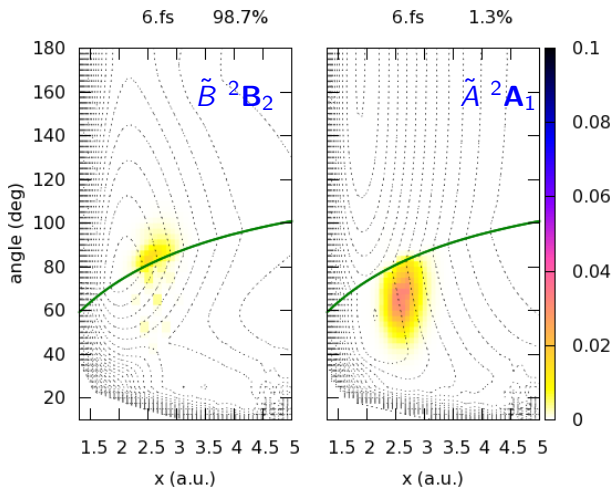
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



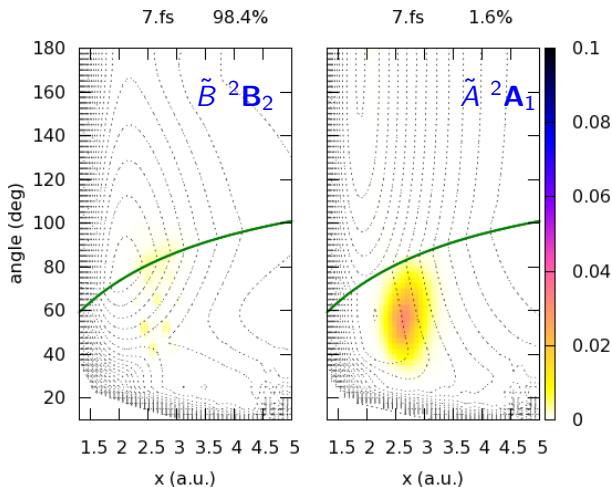
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



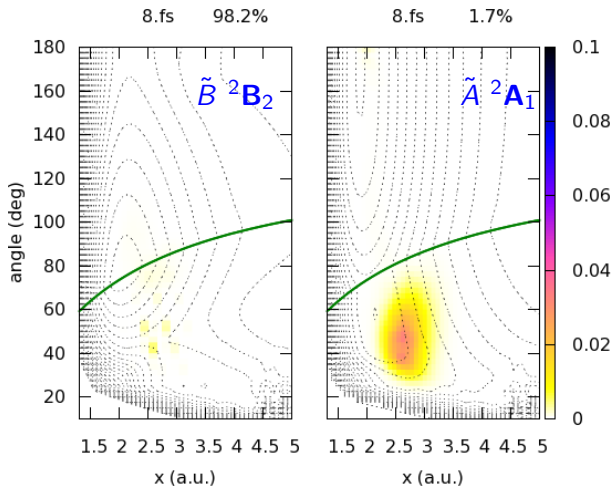
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



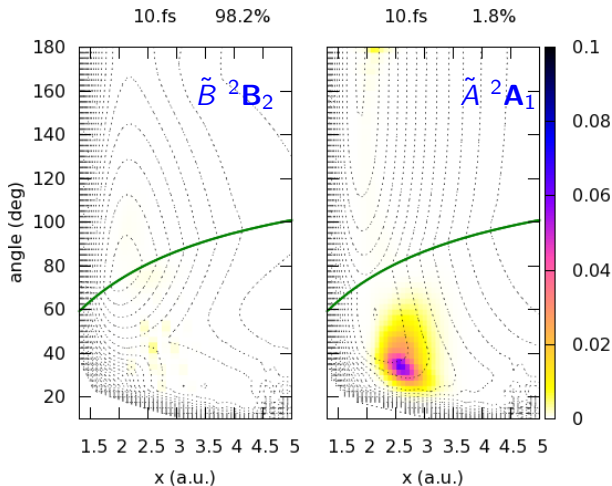
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



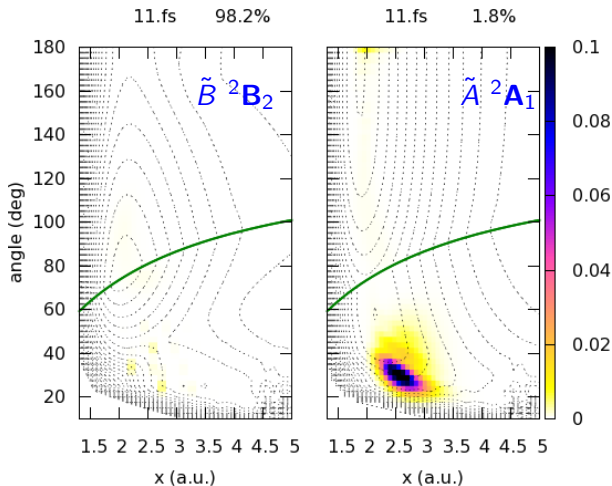
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



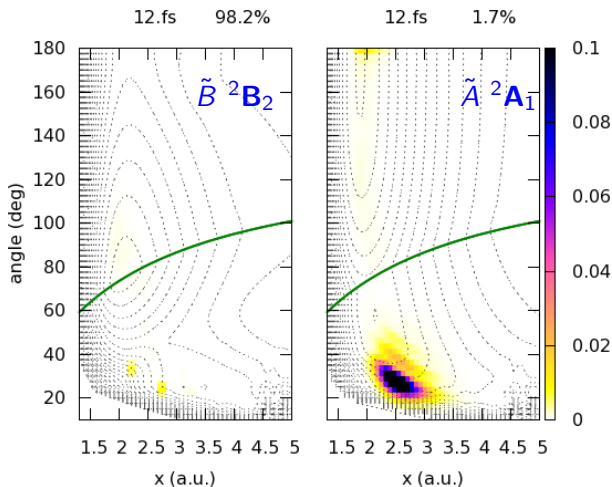
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



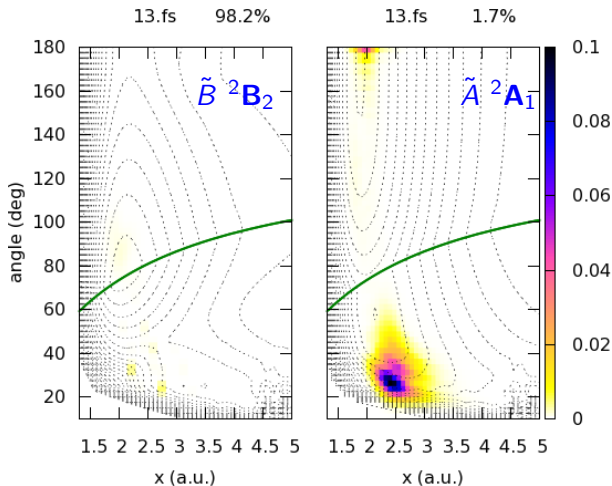
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



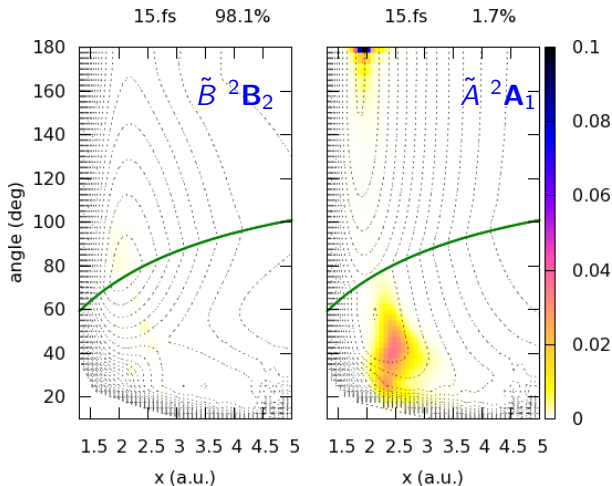
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



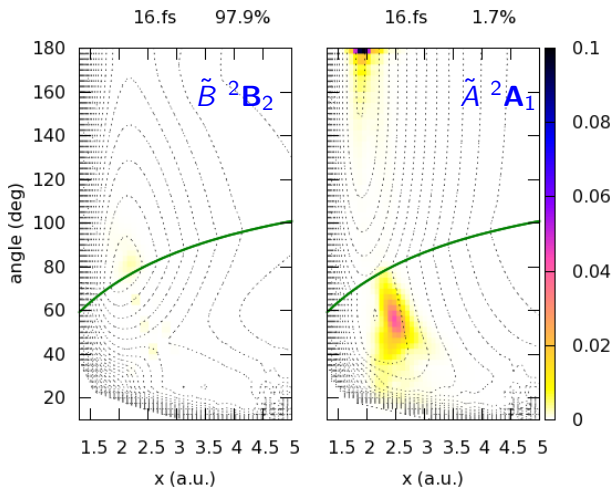
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



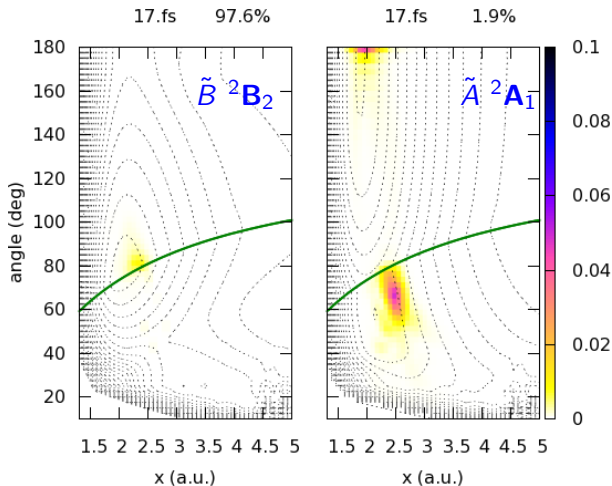
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



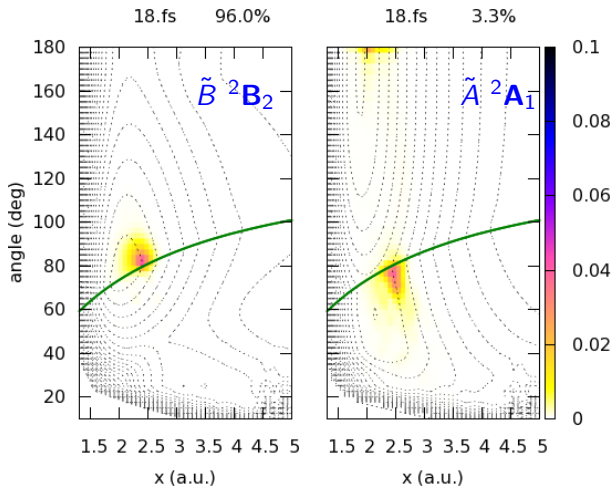
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



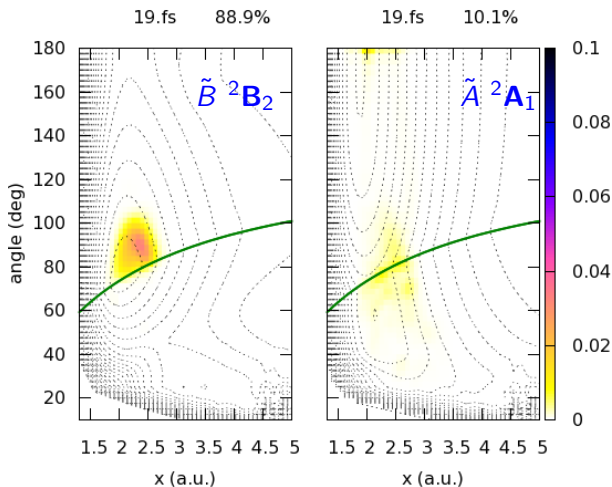
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



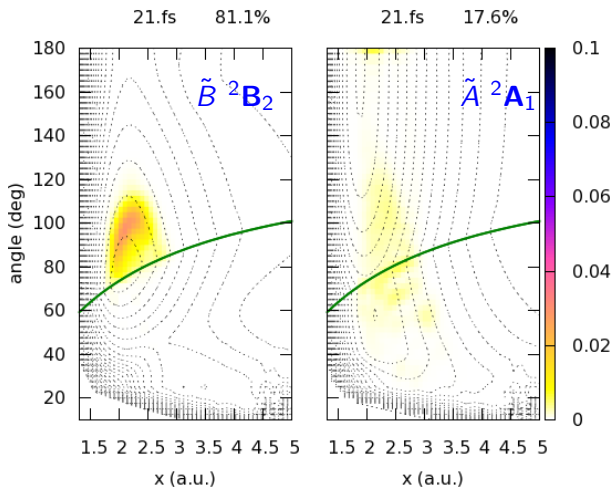
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



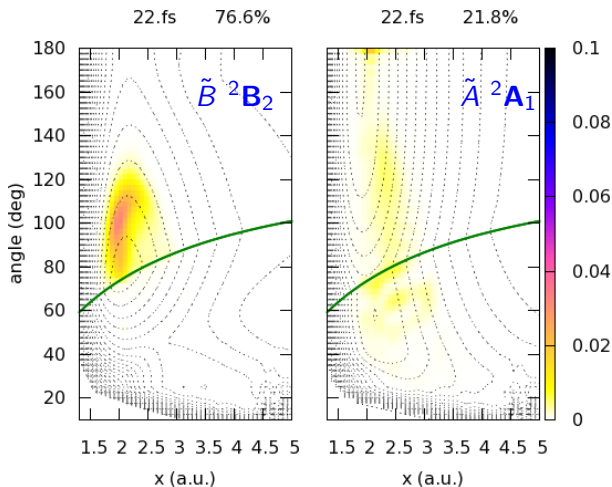
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



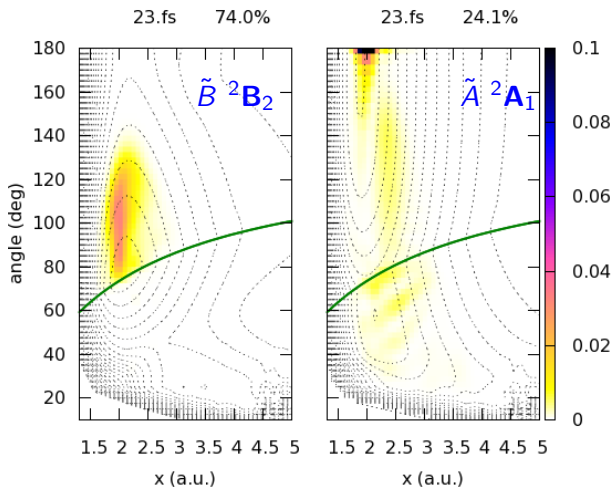
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



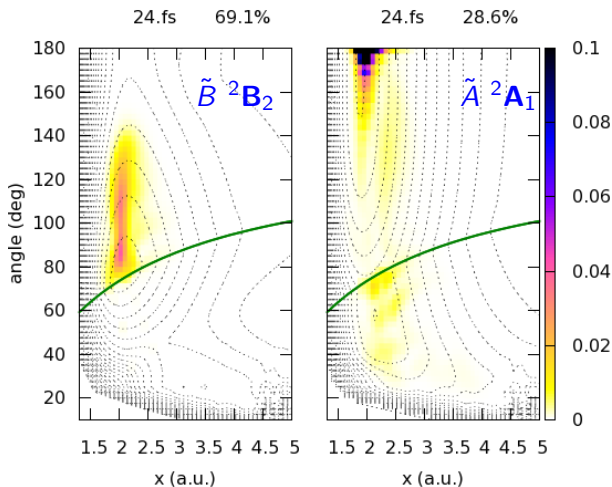
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



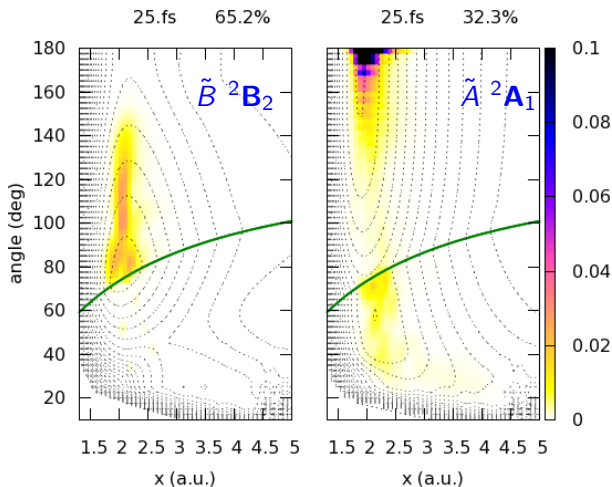
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



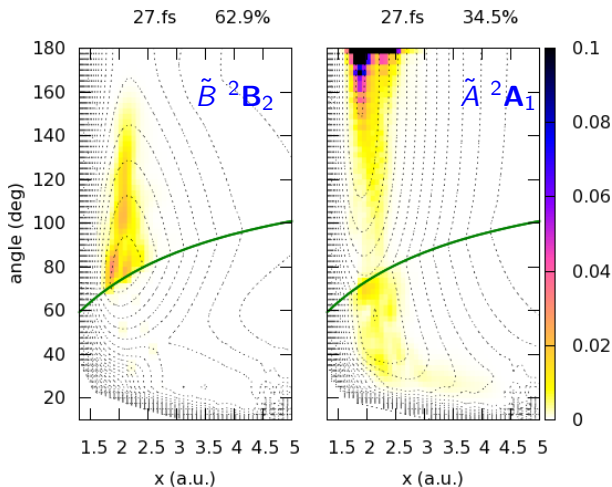
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



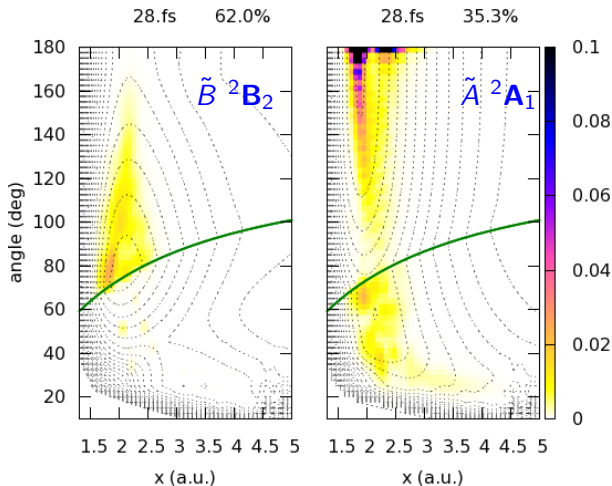
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



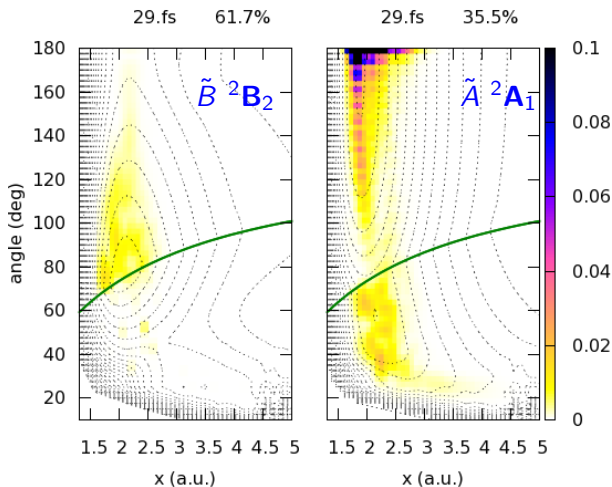
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



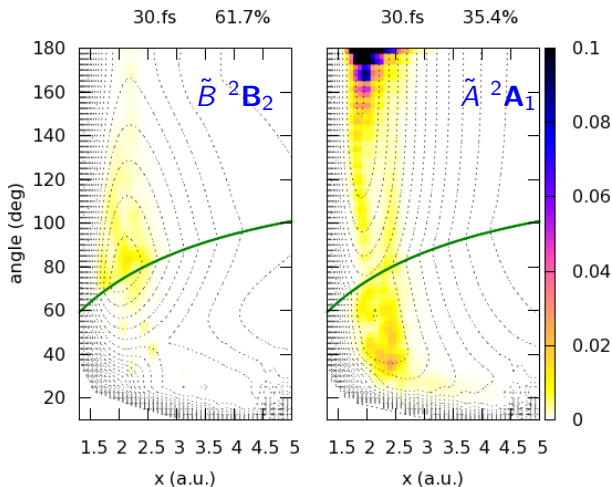
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



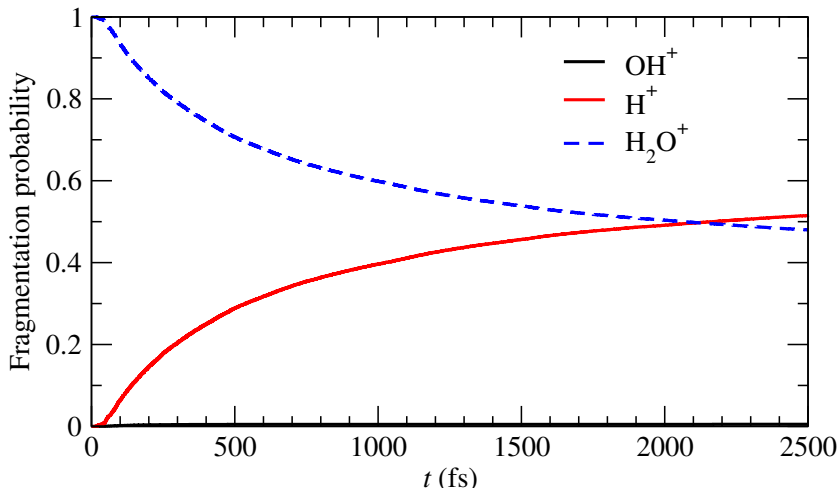
WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



WP in H_2O^+ ($\tilde{B}^2B_2$ and $\tilde{A}^2A_1$)



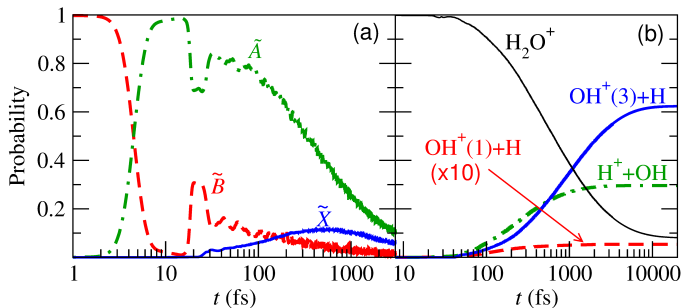
Fragmentation probability with only CI: $\tilde{B}^2B_2$ and $\tilde{A}^2A_1$

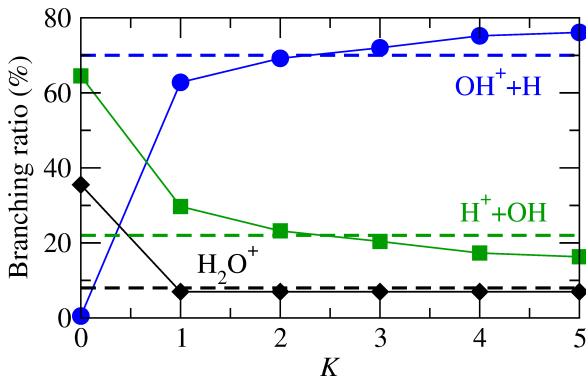


WP in H_2O^+ ($\tilde{B} \ ^2\text{B}_2$, $\tilde{A} \ ^2\text{A}_1$, $\tilde{X} \ ^2\text{B}_1$; $K = 1$)

(wavepacket-animation)

WP in H_2O^+ ($\tilde{B}^2\text{B}_2$, $\tilde{A}^2\text{A}_1$, $\tilde{X}^2\text{B}_1$; $K=1$)



Fragmentation probabilities ($\tilde{B}^2B_2$, $\tilde{A}^2A_1$, $\tilde{X}^2B_1$)

The dashed lines are the experimental branching ratios of Tan et al.

Summary

- Calculation of four PESs of H_2O^+ : $\tilde{B}^2\text{B}_2$, $\tilde{A}^2\text{A}_1$, $\tilde{a}^4\text{B}_1$ and $\tilde{X}^2\text{B}_1$.
- Regularization of the CI between $\tilde{B}^2\text{B}_2$, $\tilde{A}^2\text{A}_1$ PESs.
- Inclusion of the Renner-Teller coupling between $\tilde{X}^2\text{B}_1$ and $\tilde{A}^2\text{A}_1$.
- Modification of the Grid-TDSE code to treat non-adiabatic transitions.
- Unimportant SO transitions $\tilde{B}^2\text{B}_2 \rightarrow \tilde{a}^4\text{B}_1$.
- The mechanism $\tilde{B}^2\text{B}_2 \rightarrow \tilde{A}^2\text{A}_1 \rightarrow \tilde{X}^2\text{B}_1$ leads to a breakdown scheme that agrees with the experiments.

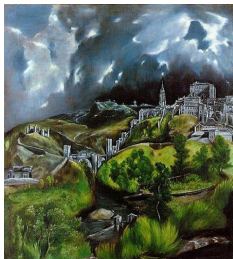
Coworkers



- [TCAM](#) group : Luis Errea, Clara Illescas, Alba Jorge, **Ismanuel Rabadán, Jaime Suárez.**







Thank you for your attention!

