

Methods and calculations of single electron capture and nuclear exchange in $H^+ + H_2$ collisions from high to low energies.

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● Ion-Molecule Collisions

● Inelastic Processes:

- VE without NE: $H^+ + H_2(X^1\Sigma_g^+, n = 0) \rightarrow H^+ + H_2(X^1\Sigma_g^+, n)$
- Dissociation: $H^+ + H_2(X^1\Sigma_g^+, n = 0) \rightarrow H^+ + H(1s) + H(1s)$
- EC without NE: $H^+ + H_2(X^1\Sigma_g^+, n = 0) \rightarrow H(1s) + H_2^+(X^2\Sigma)$
- Dissociative EC : $H^+ + H_2(X^1\Sigma_g^+, n = 0) \rightarrow H(1s) + H^+ + H(1s)$
- EC with NE: $H^{+C} + H_2^{AB}(X^1\Sigma_g^+, n = 0) \rightarrow H^{A,B}(1s) + H_2^{+BC,AC}(X^2\Sigma^+)$
- Elastic NE: $H_C^+ + H_2^{AB}(X^1\Sigma_g^+, n = 0) \rightarrow H_{A,B}^+ + H_2^{BC,AC}(X^1\Sigma_g^+, n)$

- **Energies and Methods**

- **Low energy:** Expansion in a basis of molecular wavefunctions with

- Quantal treatments ($E < 50$ eV/amu).

- * Vibronic Expansion.

- Semiclassical treatments.

- * Sudden approximation for rotation and vibration.

- * Franck-Condon approximation.

- **High Energy:** CTMC treatments.

- **Quantum Chemistry calculations.**
- Several **P**otential **E**nergy **S**urfaces needed.
- Multireference C.I. methods to calculate PES and couplings
 - Program MELDF. (E.R. Davidson, QCPE 580)
 - Calculation of dynamical couplings: $\langle \Phi_1 | \frac{d}{dX} | \Phi_2 \rangle$
- Sign determination by using the delayed overlap matrix.
- **C**onical **I**ntersections.

- **Vibro-rotational Sudden approach**(SEIKON).

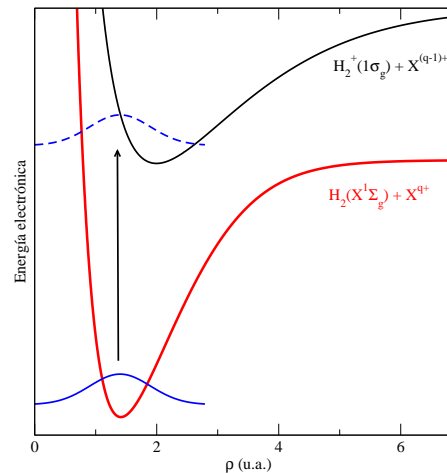
- Charge exchange with vibrational distribution ($100 \text{ eV/amu} \leq E \leq 50 \text{ keV/amu}$).

$v > 0.01 a.u.$ Projectile $\mathbf{R} = \mathbf{b} + \mathbf{v}t$. Electronic **quantal** treatment.

$$\left[T_\rho + H_{\text{el}}(\mathbf{r}, \mathbf{R}, \rho) - i \frac{\partial}{\partial t} \Big|_{\mathbf{r}, \rho} \right] \Psi(\mathbf{r}, \rho, t) = 0; \quad \Psi_{t \rightarrow -\infty} \sim \chi_0(\rho) Y_{JM}(\hat{\rho}) \Phi_i(\mathbf{r}, \rho) D^i(\mathbf{r}, t) e^{-iE_i t}$$

$$H_{\text{el}} = \sum_{i=1}^{\text{Nelec}} \left[-\frac{1}{2} \nabla_{r_i}^2 - \frac{Z_P}{r_{iP}} - \frac{1}{r_{iH_1}} - \frac{1}{r_{iH_2}} \right] + \frac{Z_P}{R_{PH_1}} + \frac{Z_P}{R_{PH_2}} + \frac{1}{\rho} + \sum_{i < j} \frac{1}{r_{ij}}$$

- $t_{\text{el}} (\approx 10^{-15} \text{ a } 100 \text{ eV}) \ll t_{\text{vib}} \approx 10^{-(13-14)} \text{ s} \ll t_{\text{rot}} \approx 10^{-12} \text{ s}$



Ψ_{nuclear} almost unchanged during electronic transitions

- $\Psi^{\text{sub}}(\mathbf{r}, \boldsymbol{\rho}, t) \approx \chi_0(\rho) Y_{JM}(\hat{\rho}) \Phi^{\text{sub}}(\mathbf{r}; \boldsymbol{\rho}, t)$

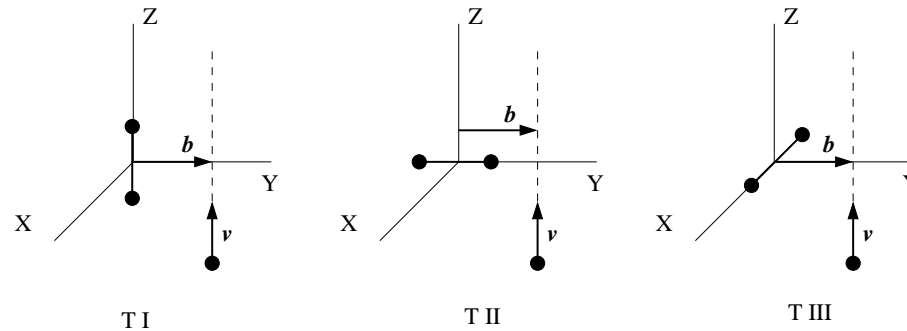
$$\Phi^{\text{sub}}(\mathbf{r}; \boldsymbol{\rho}, t) = e^{iU(\mathbf{r}, t)} \sum_k a_k(t, \boldsymbol{\rho}) \phi_k(\mathbf{r}; \mathbf{R}, \boldsymbol{\rho}) e^{\left[-i \int_0^t E_k dt'\right]}$$

$$H_{\text{el}} \phi_k = E_k \phi_k \rightarrow \{\phi_j(\mathbf{r}; \boldsymbol{\rho}, R), E_j(\boldsymbol{\rho}, R)\}$$

$$M_{jk} = \langle \phi_j e^{iU} | H_{\text{el}} - i \frac{\partial}{\partial t} | \phi_k e^{iU} \rangle; \quad \frac{\partial}{\partial t} = v_R \frac{\partial}{\partial R} + v_\alpha \frac{1}{R} \frac{\partial}{\partial \alpha};$$

$$\langle \phi_j | \frac{\partial}{\partial R} | \phi_k \rangle = \delta^{-1} \langle \phi_j(R) | \phi_k(R + \delta) \rangle$$

- Solving, para cada $\boldsymbol{\rho}$, $[H_i - i \frac{\partial}{\partial t}] \Psi^{\text{sub}} = 0 \rightarrow \{a_j(t, \boldsymbol{\rho})\}$



- **Electro-vibro-rotational transition probabilities**

$$P_{\nu'f}^{J'M'}(v, \mathbf{b}) = \lim_{t \rightarrow +\infty} \left| \left\langle \Psi_{\nu'f}^{J'M'} \mid \Psi^{\text{sud}} \right\rangle \right|^2$$

- **Vibronic transition probabilities** (No rotational distribution)

$$\overline{P_{\nu'f}}(v, \mathbf{b}) = \frac{1}{4\pi} \int d\hat{\rho} \left| \left\langle \chi_{\nu'} \Phi_f D^f \mid \chi_0 \Phi^{\text{sud}} \right\rangle \right|^2(\hat{\rho})$$

- **Electronic transition probabilities** ($\sum_{\nu'} |\chi_{\nu'}| > \chi_{\nu'} = I$)

$$P_f(\mathbf{b}, \mathbf{v}) = \int d\rho \chi_0^2 \left| \left\langle \Phi_f D^f \mid \Phi^{\text{sud}} \right\rangle_{\mathbf{r}} \right|^2 ; \sigma_f(\mathbf{v}) = \int d\rho \chi_0^2 \sigma_f^{el}(\rho, \mathbf{v})$$

- Franck-Condon:

$$\sigma_{\nu'f} \simeq \sigma_f^{el}(\rho_0) \left| \int d\rho \chi_0 \chi_{\nu'} \right|^2 \rightarrow \sigma_f = \sigma_f^{el}(\rho_0)$$

- Isotropic: $E_j(\alpha) \approx E_j(\alpha_0)$; $M_{jk}(\alpha) \approx M_{jk}(\alpha_0)$

- **Variational calculation of $\chi_{vib}^{H_2}, \chi_{vib}^{H_2^+}$** (GTOs, Bessel)

- H_3^+ : **Transitions at low impact velocities** ($\tau_{col} \sim \tau_{vib}$).

(a) $H^+ + H_2(\nu = 0) \rightarrow H^+ + H_2(\nu = 3 - 5)$, ($\rho \simeq 2.5$),

(b) resonant capture $H^+ + H_2(\nu \sim 4) \rightarrow H(1s) + H_2^+(\nu' = 0)$ ($R > 6$).

- Described by vibronic expansions

$$\Psi(\mathbf{r}, \boldsymbol{\rho}; R) = e^{iU(\mathbf{r}, \mathbf{R})} \sum_{i\nu} a_{i\nu}(t) \phi(\mathbf{r}; \boldsymbol{\rho}, \mathbf{R}) \chi_{i\nu}(\rho) e^{-i \left[\int_0^t dt' E_{i\nu}(t') + \epsilon_{i\nu} t \right]}$$

- **Conical intersections**

- Analysis of transitions in a.c.i. ($\nu \rightarrow 0$) $H^+ + H_2(X^1\Sigma_g^+)$ and $H(1s) + H_2^+(X^2\Sigma_g^+)$

($R \rightarrow \infty$ and $\rho \simeq 2.5$)(a.c.i.)

- L-E model in H_3^+ a.c.i. $H_{11} - H_{22} = a(\rho - \rho_0)$; $H_{12} = k(1 + R)e^{(-\beta R)}$

- $V^{Morse}(\rho) = D_e [e^{-2\alpha(\rho-\rho_m)} - 2e^{-\alpha(\rho-\rho_m)}]$;

$$E'_\nu = \omega_e \left[(\nu + 1/2) - \frac{\omega_e}{4D_e} (\nu + 1/2)^2 \right];$$

- **Divergent non-adiabatic couplings** \rightarrow regular states $\{\Psi_1^d, \Psi_2^d\}$

$(\frac{\partial \theta}{\partial R}, \frac{\partial \theta}{\partial \rho})$ eliminate divergent parts of couplings.

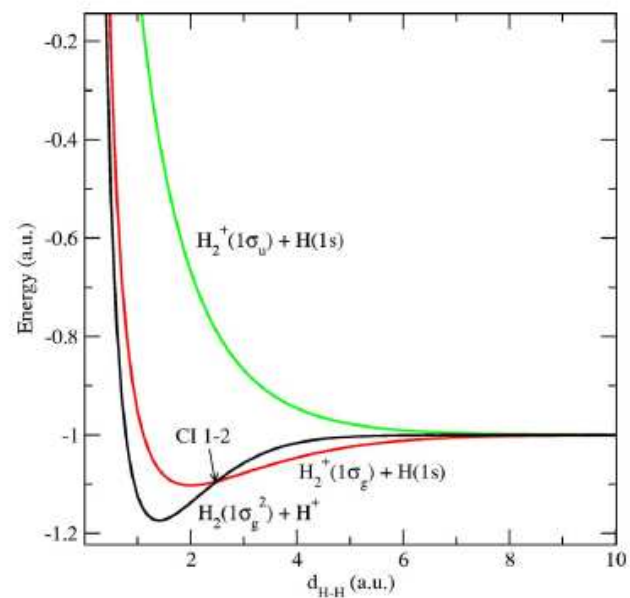


FIG. 4. (Color online) *Ab initio* diatomic energies used in the DIM calculations.

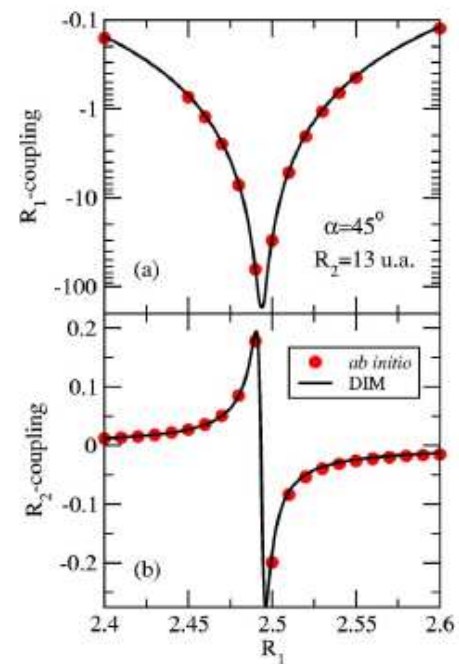


FIG. 2. (Color online) Cut along R_1 of the two nonadiabatic couplings between the first two singlet states of H_3^+ .

- Initial H₂ Morse vibrational distributions .

- Quantal

$$\varrho_\nu^{(q)}(\rho) = \left| F_\nu^{(q)}(\rho) \right|^2; \quad F_\nu^{(q)}(\rho) = \mathcal{N} e^{-x/2} x^\varepsilon Y_\nu(x);$$

$$x = \frac{\exp(-\alpha(\rho - \rho_m))}{c}, \quad c = \frac{\alpha}{\sqrt{8\mu D_e}}, \quad \varepsilon^2 = -\frac{2\mu E_\nu}{\alpha^2} \text{ and } Y_\nu(x) \text{ hypergeometric.}$$

- Classical Microcanonical, ($E_j = E_\nu$)

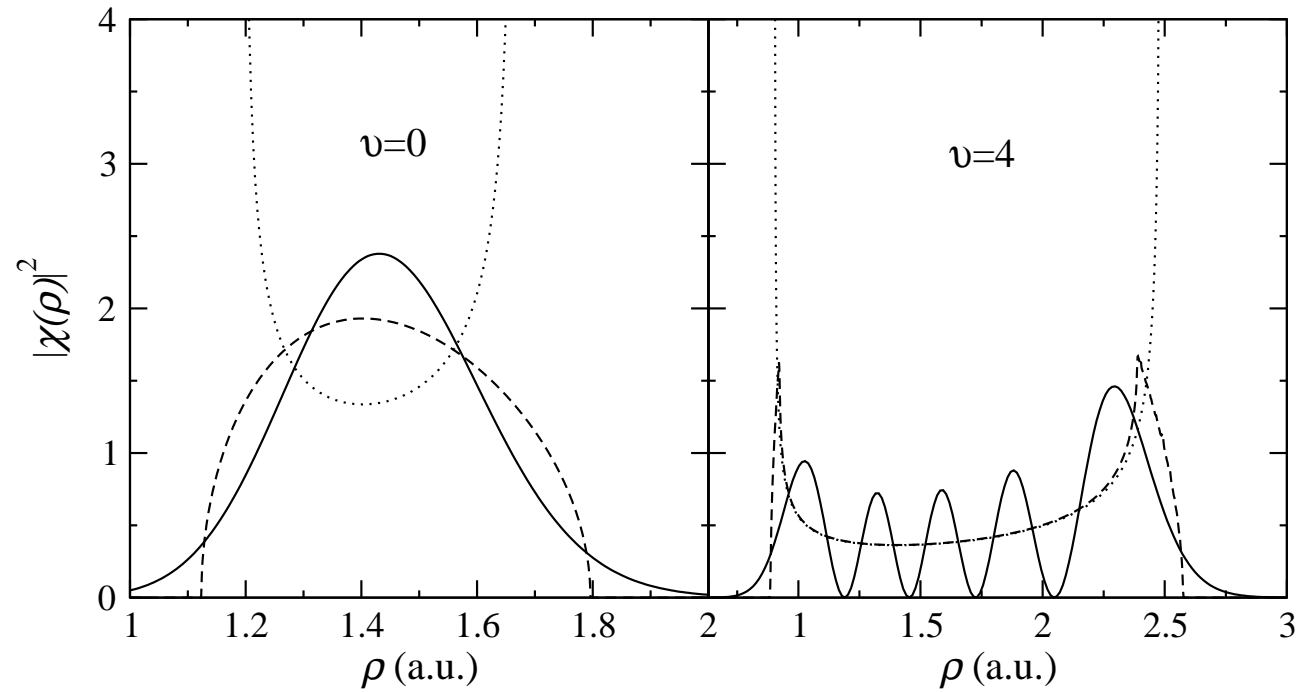
$$\varrho_\nu^{(m)}(\rho) = \frac{\alpha}{\pi} \left[\frac{V(\rho)}{E_\nu} - 1 \right]^{-1/2} \text{ diverges in } \rho_{min} \text{ and } \rho_{max} \text{ (} V(\rho) = E_\nu \text{)}$$

- Classical Continuous:

$$\varrho_\nu^{(c)}(\rho) = \frac{1}{E_\nu^+ - E_\nu^-} \int_{E_\nu^-}^{E_\nu^+} \varrho_\nu^{(m)}(E; \rho) dE = \frac{1}{2(E_\nu^+ - E_\nu^-)} [W(E_\nu^+; \rho) - W(E_\nu^-; \rho)]$$

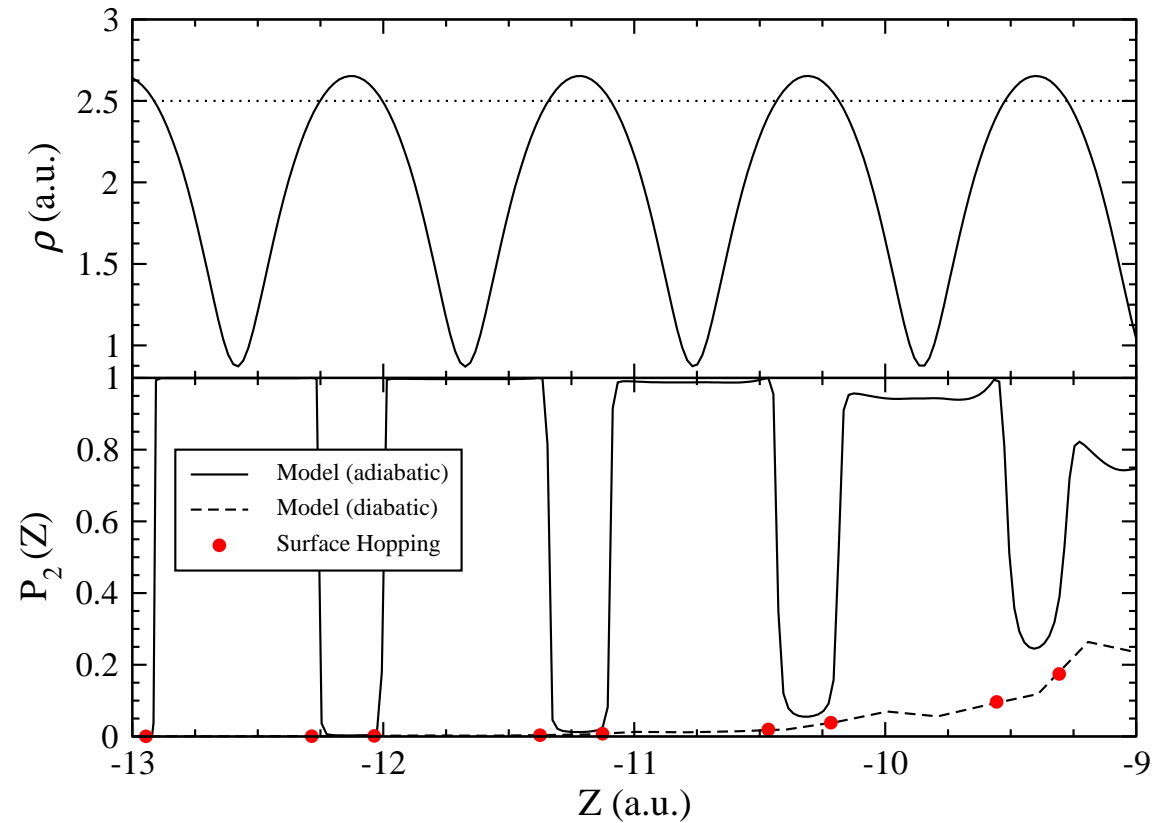
$$W(E, \rho) = \frac{2\alpha}{\pi} \mathcal{R}e \left\{ \sqrt{E(V(\rho) - E)} + V(\rho) \sin^{-1} \sqrt{\frac{E}{V(\rho)}} \right\}.$$

- Initial H₂ vibrational distributions

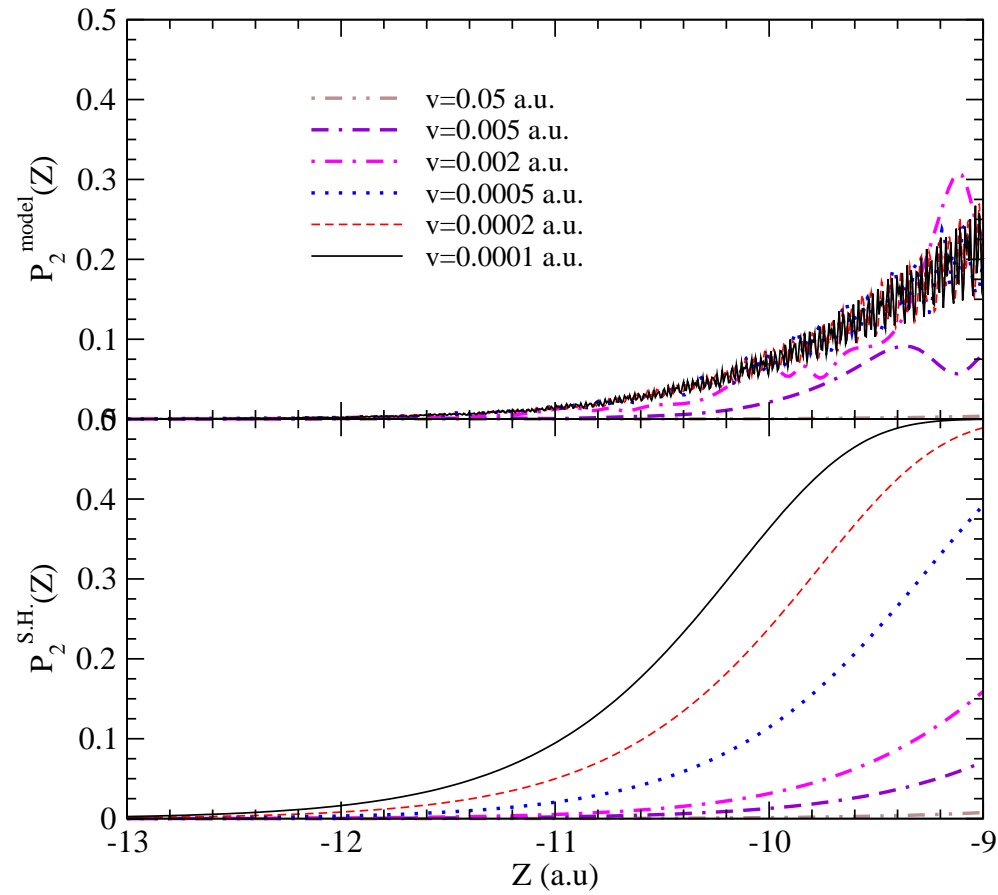


quantal (—), microcanonical (...), continuous (- - -)

- $\text{H}^+ + \text{H}_2(\nu = 5)$ results, ($v=0.002$, $b=1.0$, $\nu = 5$, $\phi = 180^\circ$.)
- Adiabatic representation: Sudden change $\rho(t)$ crosses ρ_c : $\Psi_1^d \leftrightarrow \Psi_2^d$.
- Diabatic representation smooth: Non-total diabatic transitions.

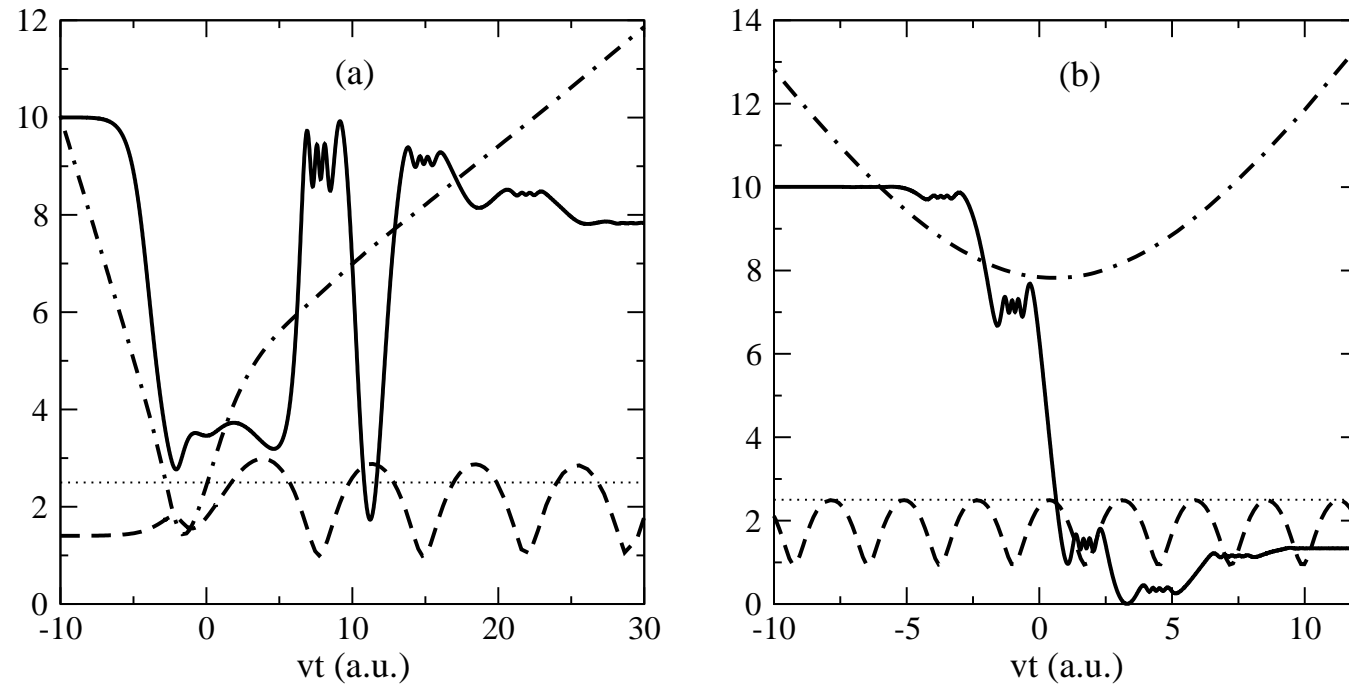


- **Low- v limit** P_2^d increases until saturation ~ 0.3 , $(\beta H_{12}(Z)/\delta)^2$
- $P_2^{SH}(Z_{in}, v, b) \xrightarrow{v \rightarrow 0} 1/2$, faster the smaller v .



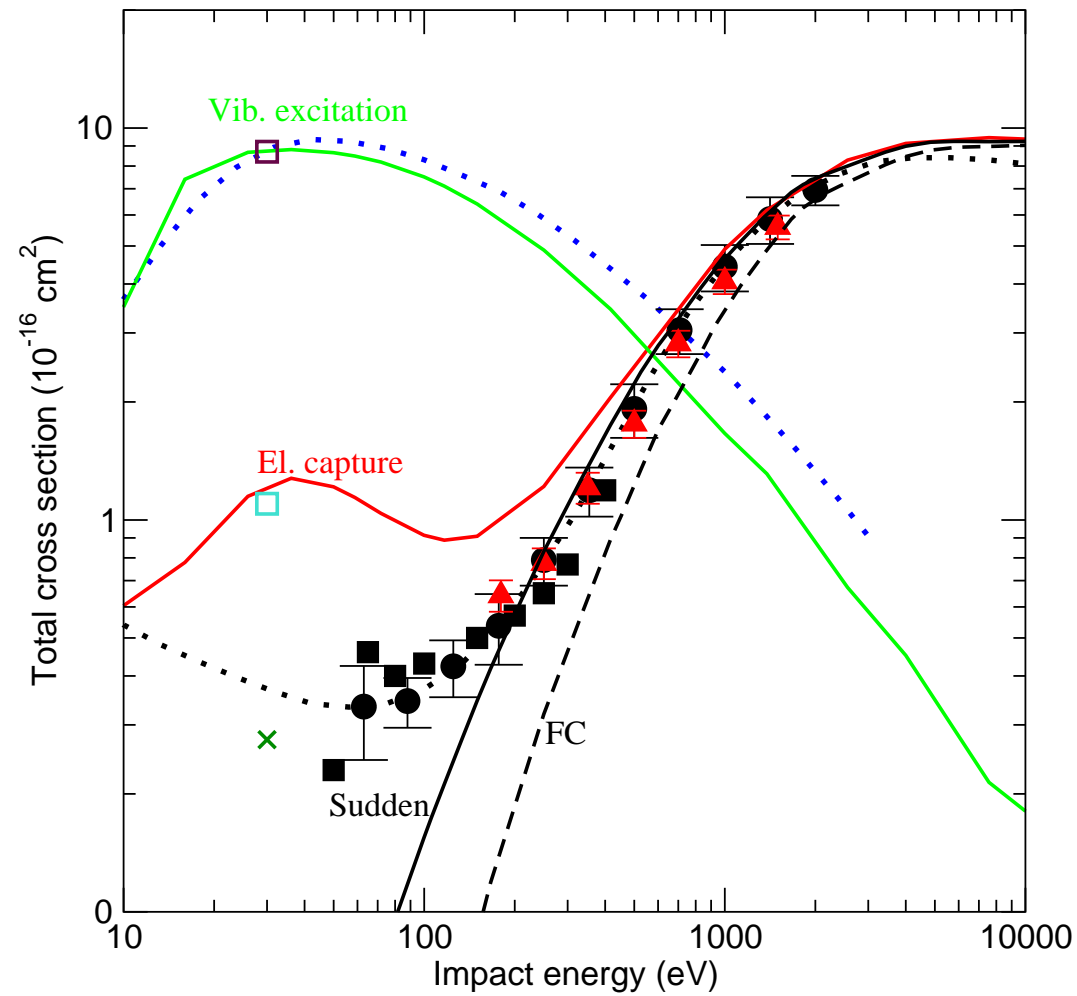
- Example of transitions in a.c.i.

- (a) $E= 5$ eV, $b= 0.8$, $E_\rho=0$; (b) $E= 1.05$ eV, $b= 8.0$, $\nu = 4$.



(—) $P_{el} \cdot 10$, (---) $\rho(t)$, (-.-) $R(t)$.

- F.C., Sudden and Vibronic SEC cross sections in $H^+ + H_2$
- VCC Sudden isotropic rotational approximation. N.E. no considered.



- CNDIM Method

- $H^+ + H_2$ collisions ($2 \leq E \leq 2000eV$).

- $\tau_{rot} \ll \tau_{col}$. H_2 not initial rotation.

- CTMC nuclear evolution ground PES $H_3^+ \rightarrow \{\mathbf{R}_{A,B,C}(t)\}$ (Giese and Gentry 1974)

$$\dot{\mathbf{R}}_j = \mathbf{P}_j; \quad \dot{\mathbf{P}}_j = -\nabla V$$

- Integrated until $vt_{max} \geq 300$ a.u. Electronic and nuclear transitions taken place.

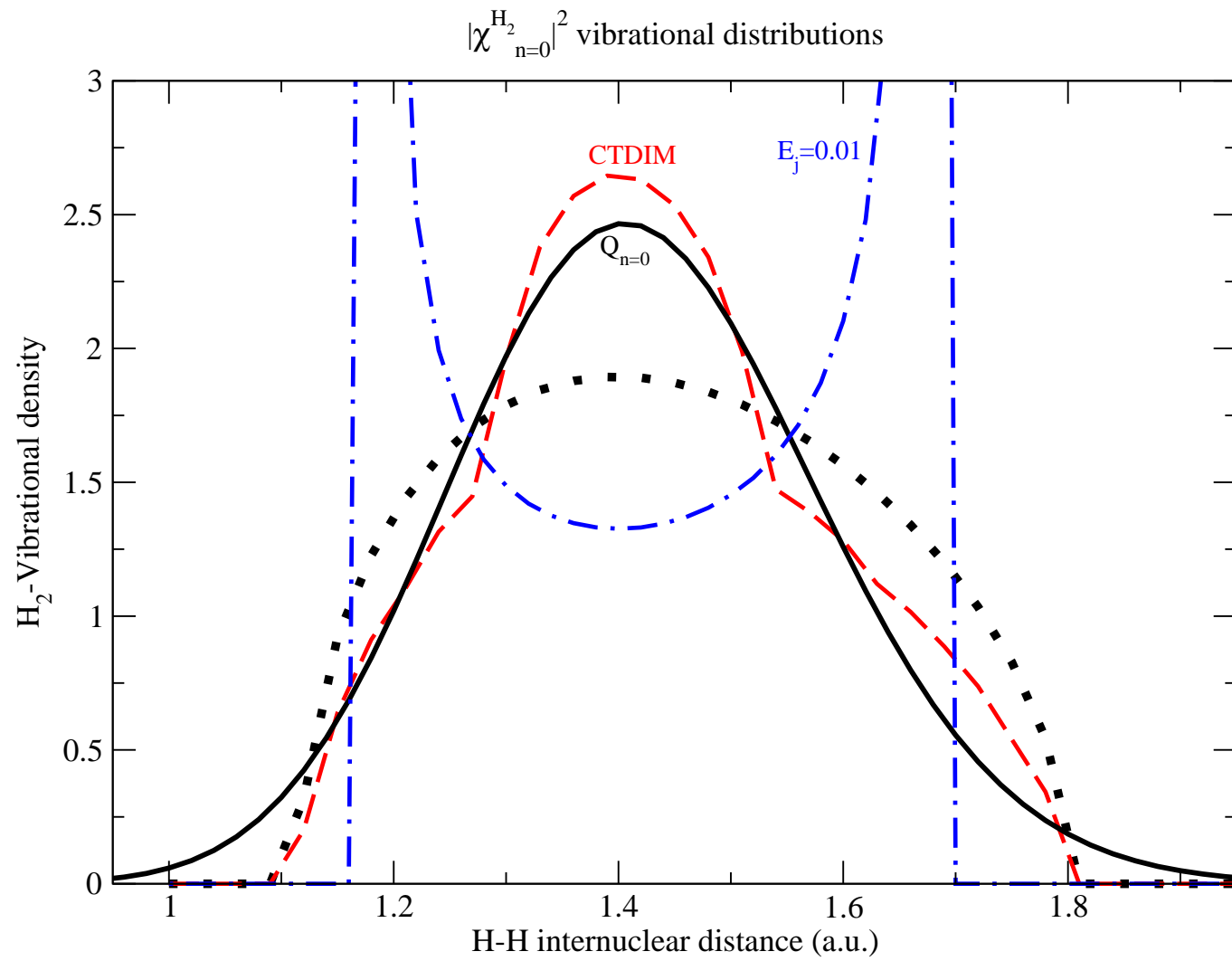
- Nuclear E and \mathbf{L} conserved with a minimum of eight figures.

- Diatoms In Molecules (DIM) electronic states.

- Electronic and nuclear exchange and rotational excitation allowed.

- $|\chi_n^{CNDIM}(\boldsymbol{\rho})|^2$
- $|\chi_n(\boldsymbol{\rho})|^2 = \int dE_k \int d\mathbf{p} \varrho_k^{cla}(\boldsymbol{\rho}) P_{nk}; E_k = \frac{p_k^2}{2\mu} + V^M(\boldsymbol{\rho})$
- $P_{n,k} = |a_{k,n}|^2 \simeq W_n^{Pr}(\boldsymbol{\rho}, \mathbf{p}) = |\chi_n(\boldsymbol{\rho})|^2 |\bar{\chi}_n(\mathbf{p}_k)|^2$
- $|\chi_n^{CNDIM}(\boldsymbol{\rho})|^2 \simeq \sum_{k=1}^5 \frac{P_{0k}}{E_k^{max} - E_k^{min}} \int_{E_k^{min}}^{E_k^{max}} \varrho_k^{cla}(\boldsymbol{\rho}, E_k) dE_k$

- CNDIM Distribution



- Identification final vibrational states

- 1.- $t = t_{max}$, diatom XY dissociated if $E_{vib} \geq D_0$. Bound if $E_{vib} \leq D_0$

- 2.- Bound final diatoms J= AB (1), AC (2) o BC (3):

$$\mathbf{L}_{cla,J} = \mu \boldsymbol{\rho}^J \wedge \mathbf{v}_\rho^J ; E_{rot,J}^{cla} = \frac{|\mathbf{L}_{cla,J}|^2}{2\mu\rho^2} (\mu \approx 918).$$

- 3.- $E_{vib}^{cla} = E_{diat}^{cla} - E_{rot}$.

- 4.- $E_{vib}^{cla} \in [E_n^- = \frac{E_n - E_{n-1}}{2}, E_n^+ = \frac{E_n - E_{n+1}}{2}] \rightarrow \mathbf{n}$.

- Elastic AB (J=1). N.E. (J=2+3). Dissoc. (J=4), ($c_4 = c_1$) nuclear contributions

- **Electronic evolution**

- D.I.M. states correctly describe electronic transitions in a.c.i.

- $\psi_1(\mathbf{r}; \mathbf{R}(t)) \sim H_C^+ + H_2(\text{AB});$

- $\psi_2(\mathbf{r}; \mathbf{R}_j(t)) \sim H_B^+ + H_2(\text{AC}),$

- $\psi_3(\mathbf{r}; \mathbf{R}_j(t)) \sim H_A^+ + H_2(\text{BC})$

- $\Psi^{DIM}(\mathbf{r}; R(t)) = \sum_{j=1}^3 c_j(t) \psi_j(\mathbf{r}; R(t)) e^{-i \int_{t_{in}}^t h_{jj}(t') dt'}$

- Schrödinger equation:

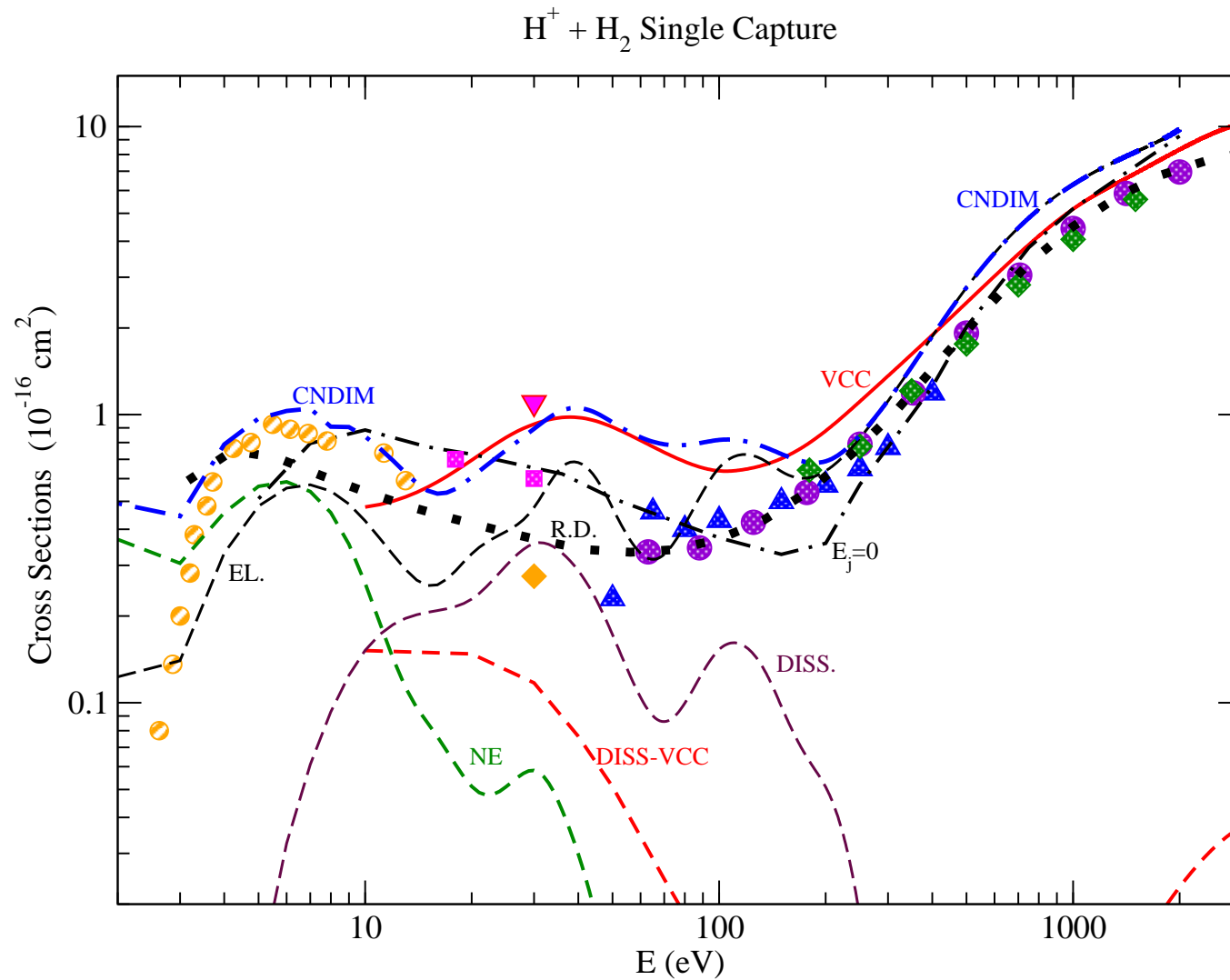
$$[H_{el} - i \frac{\partial}{\partial t}] \Psi(\mathbf{r}; R(t)) = 0; \rightarrow i \dot{c}_k(t) = \sum_{j \neq k} c_j h_{kj}(t) e^{-i \int_{t_{in}}^t (h_{jj} - h_{kk})(t') dt'}$$

- Transition amplitudes: From $c_j(t_{in}) = \delta_{j,1} e^{-ih_{11}(t_{in})},$

$$t_{i,m} = \lim_{t \rightarrow \infty} \langle \psi_m(\mathbf{r}, t) e^{-iE_m t} | \Psi(\mathbf{r}, t) \rangle = c_m(t_{max}) e^{-i \int_{t_{in}}^{t_{max}} (h_{mm}(t) - h_{mm}(t_{max})) dt}$$

- SEC cross sections

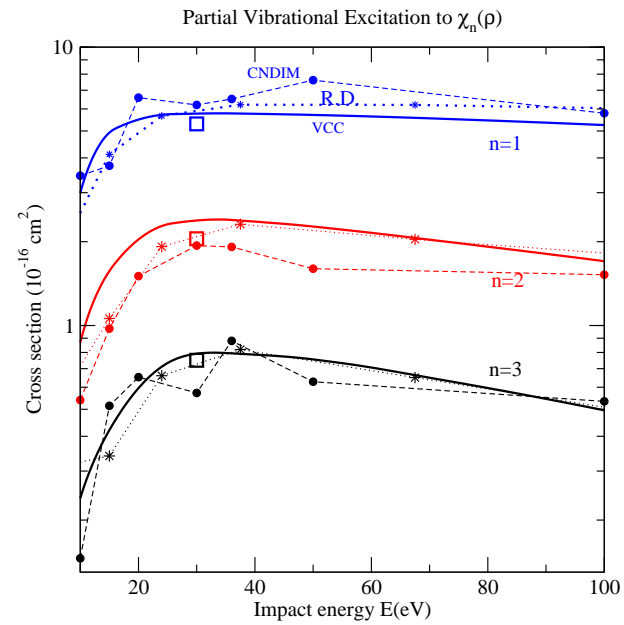
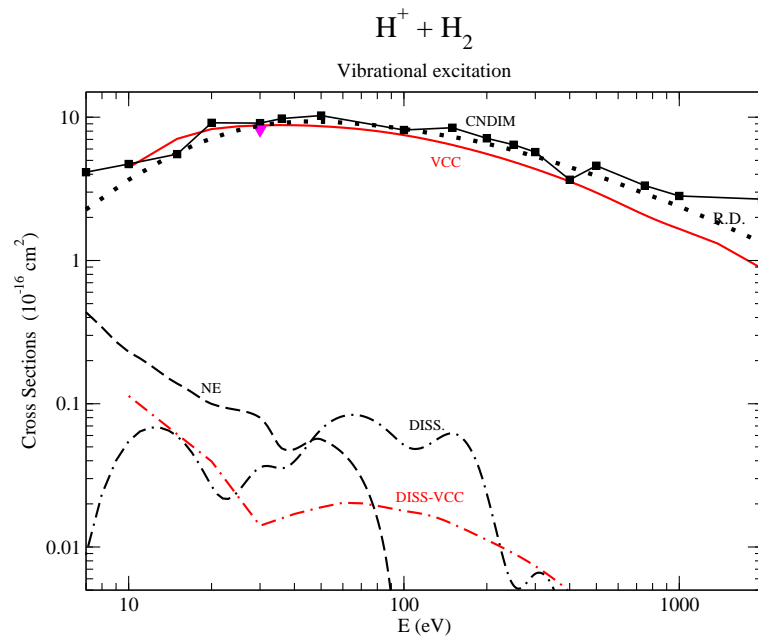
$$\sigma_J^{SC}(v) = \frac{2\pi}{N} \sum_{k=1}^{N_J} P_{0k} \int_0^{b_{max}} db b [1 - |c_{Jk}|^2](v, b); \rightarrow \sigma^{SC}(v) = \sum_{J=1}^4 \sigma_J^{SC}(v)$$



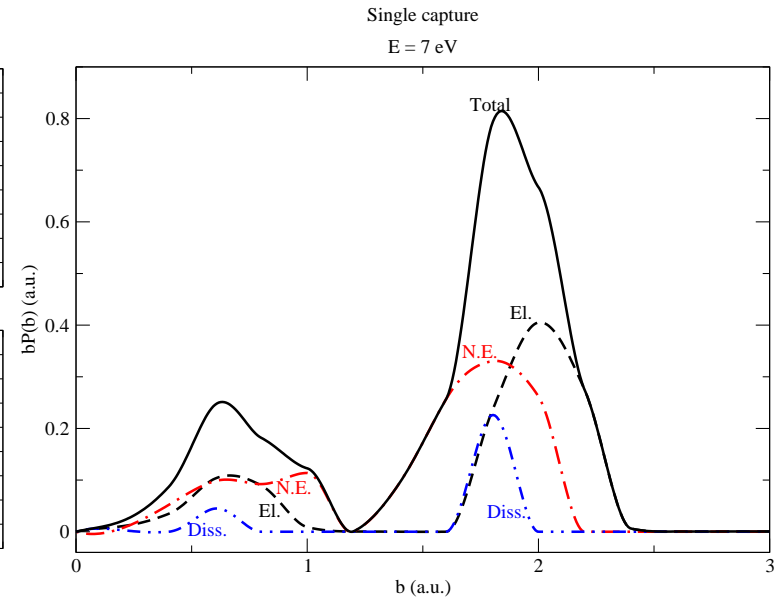
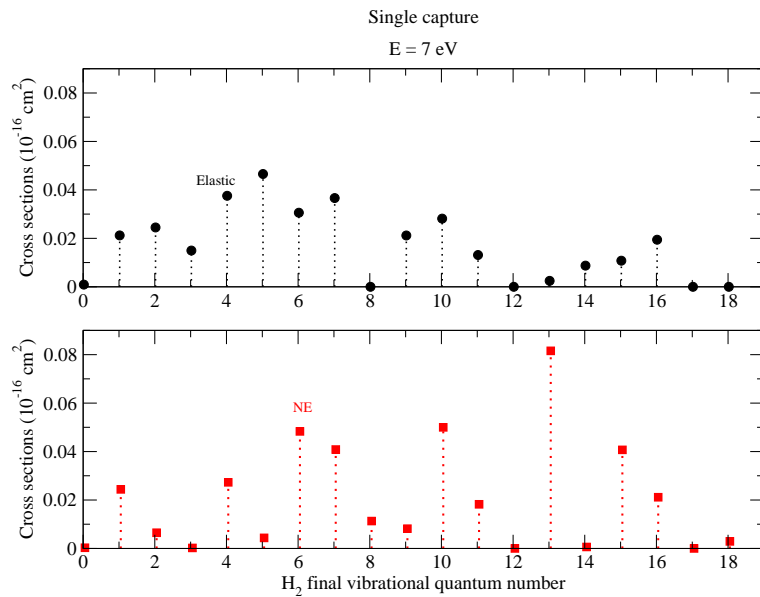
- VE cross sections

- Partial VE $\chi_0^{H_2} \rightarrow \chi_n^{H_2}$: $\sigma_{Jn}^{VE}(v) = 2\pi \sum_{I=1}^{N=51} P_{0I} \int_0^{b_{max}} db b \delta_{n,nI} \delta_{J,JI} |c_J(t_{max})|^2$

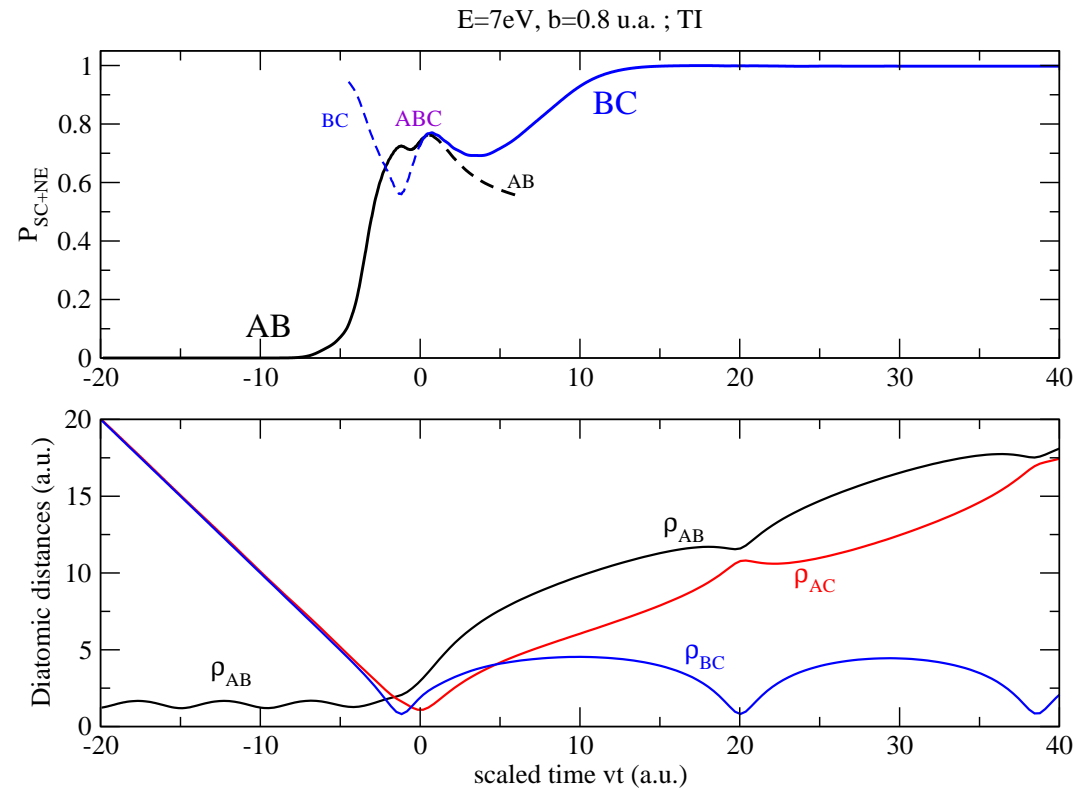
- Total VE $\sigma^{VE}(v) = \sum_{J=1}^4 \sum_{n \geq 1} \sigma_{Jn}^{VE}(v)$



- Mechanisms and illustrations ($E=7\text{eV}$).
- $\sigma^{SEC}(AB) \ n = 4 - 7$. First stage common to EV.
- Capture with N.E: Great dispersion, with very excited $n\text{-H}_2$.
- P^{SC} limited to $b \leq 2.5$. Similar contributions $J=1-4$.



- Electron capture with nuclear exchange: $AB \rightarrow BC$ ($n=13$)



- $P^{SC}(vt)$ from AB and BC show $A \leftrightarrow C$ molecular region (H_3^+).
- $P^{SC} H_C^+ + H_2(AB)$ and $P^{SC} H_A^+ + H_2(BC)$ smoothly joint. Unique collision history.

- **CNDIM conclusions**

- 1.- CTMC (nuclei) and DIM (electrons). SEC and VE in $H^+ + H_2$ $E = 2 - 2000$ eV, including N.E.
- 2.- SEC CNDIM and VCC similar values in $20 < E < 500$ eV. Maximum $E \sim 30$ eV, not plotted by experiments and R.D.
- 3.- At $E \leq 10$ eV, CNDIM-SEC merge Linder 1995 measurements.
- 4.- **Limitación:** Nuclear evolution ground H_3^+ PES. Lack of H_2^+ vibrational states.
 - Results with $E_j = 0$, similar to R.D. Phelps, and TSH Janev 2001.
- 5.- New method with simultaneous nuclear and electronic evolution under average or different PES (project).

- Capture and ionization in $H^+ + H_2O$. (Preliminar)
- H_2O prototype multi-electronic and polyatomic molecules.
- Secondary ions and electrons may fragment DNA.
- New CTMC and *ab-initio* methods.

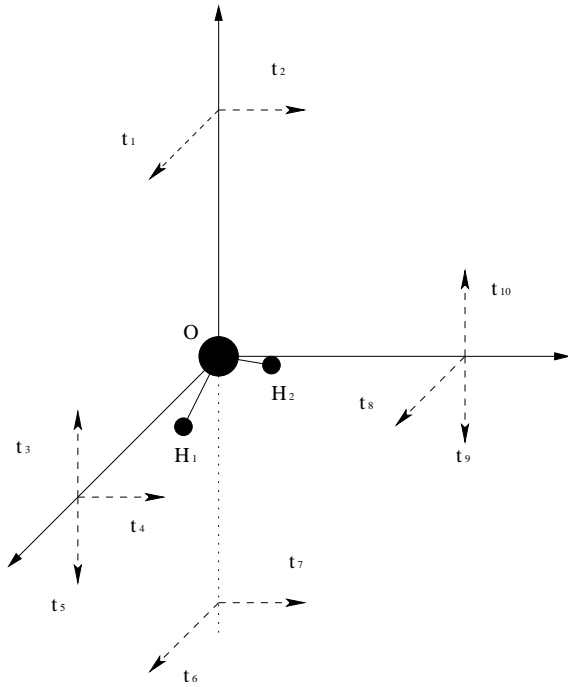
(A) CTMC-IPM study of ionizing processes.

(B) IPM-Asymptotic molecular orbitals (a.m.o.)

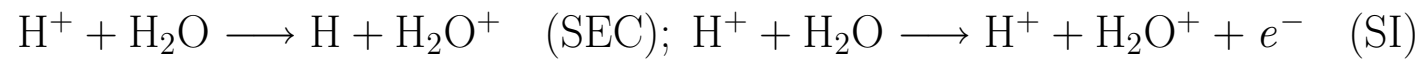
(C) IPM-SEC Asymptotic states (a.s.)

- three-center $e - H_2O^+$ pseudo-potencial calculations

$$\left(H - i \frac{\partial}{\partial t} \Big|_{\mathbf{r}} \right); \Psi(\mathbf{r}, t) = 0; H(\mathbf{r}; \mathbf{R}) = -\frac{1}{2} \nabla^2 + V_{H_2O^+} - \frac{1}{r_{H_3}}$$



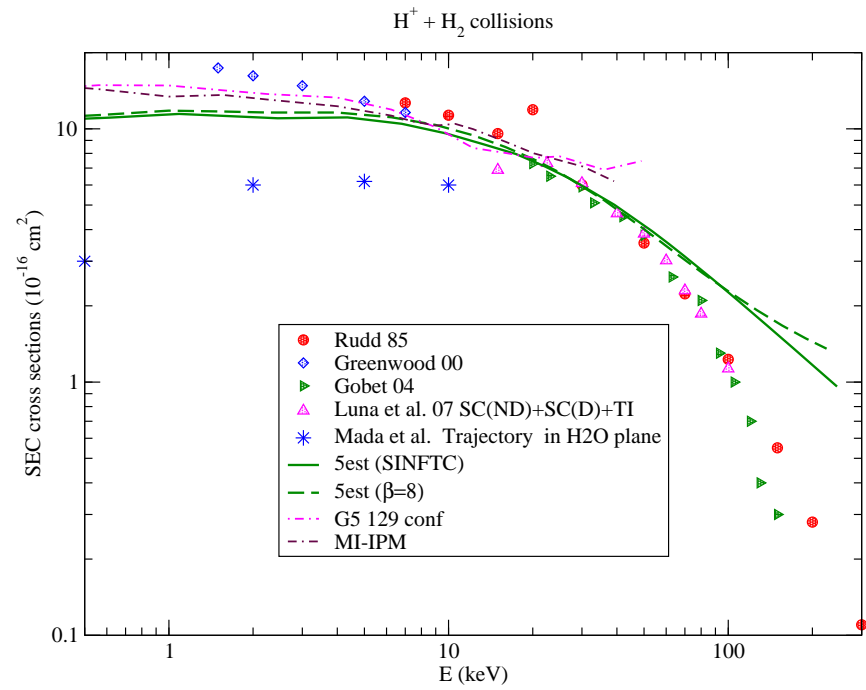
- Equilibrium H₂O geometry (F.C.). Simulation Sudden approach other geometries.



- H₂O not spherical. 10 projectile trajectory types.

- Results

- $\bar{\sigma}^{SC}$ include trajectories along Y-axis. Larger P^{SEC} . from H₂O HOMO.



- Projects

1.- New methods at low energy in $H^+ + H_2$.

- Simultaneous electronic and nuclear evolutions (SE).
- Classical vibronic expansions (CVE).

2.- New methods to study collisions of ions with intermediate molecules.

- Study of electronic and nuclear processes including fragmentation.
- Evaluation of D.I.M. hamiltonian matrices in H_3O^+ . CNDIM.

- Members of group

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