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 Potential Energy Surfaces 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.

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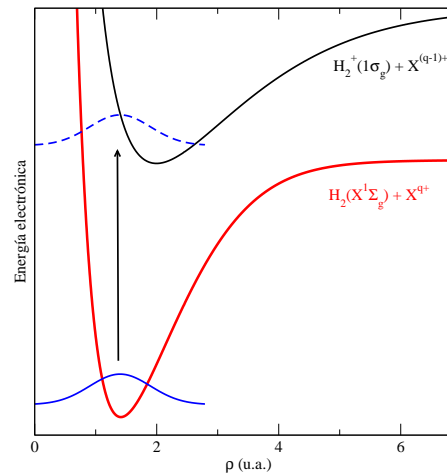
- **Vibro-rotational Sudden approach**(SEIKON).

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

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

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

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

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

$\Psi_{nuclear}$ almost unchanged during electronic transitions

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

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

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

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

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

- Solving, para cada $\boldsymbol{\rho}$, $\left[H_{\mathrm{i}} - \mathrm{i}\frac{\partial}{\partial t}\right]\Psi^{\mathbf{sub}} = 0 \rightarrow \{a_j(t, \boldsymbol{\rho})\}$

T I   T II   T III
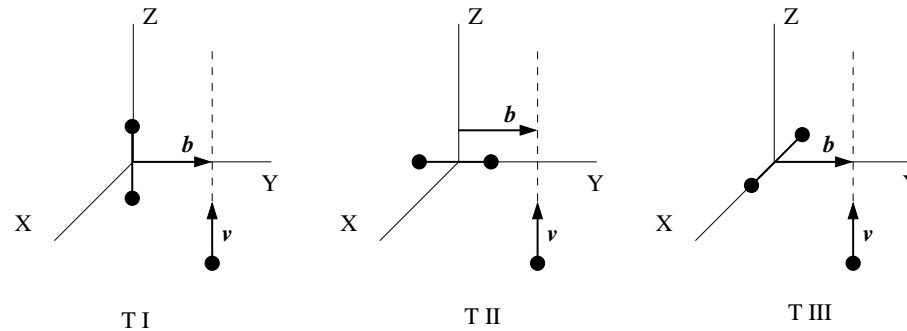
- **Electro-vibro-rotactional transition probabilities**

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

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

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

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

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

- Franck-Condon:

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

- Isotropic: $\mathrm{E}_j(\alpha) \approx \mathrm{E}_j(\alpha_0); \; \mathrm{M}_{jk}(\alpha) \approx \mathrm{M}_{jk}(\alpha_0)$

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

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

  (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

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

- **Conical intersections**

- Analysis of transitions in a.c.i. $(v \rightarrow 0)$ $H^+ + H_2(X\ ^1\Sigma_g^+)$ 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. $H_{11} - H_{22} = a(\rho - \rho_0);\ \ H_{12} = k(1 + R)e^{(-\beta R)}$

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

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

- 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.
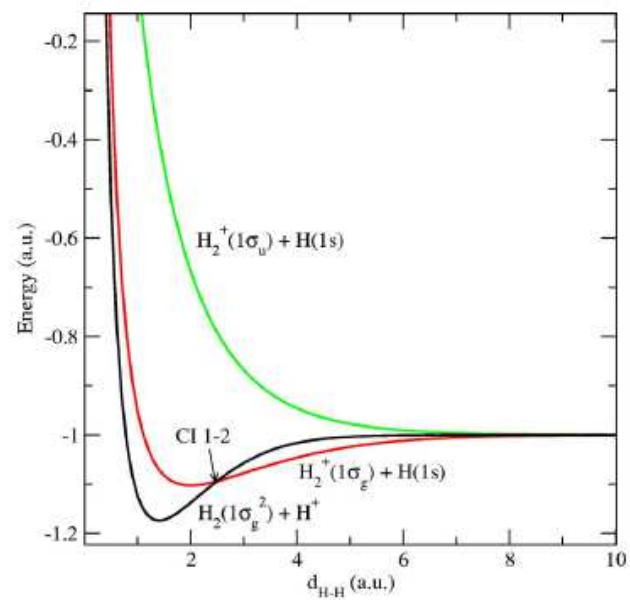
FIG. 4. (Color online) *Ab initio* diatomic energies used in the DIM calculations.
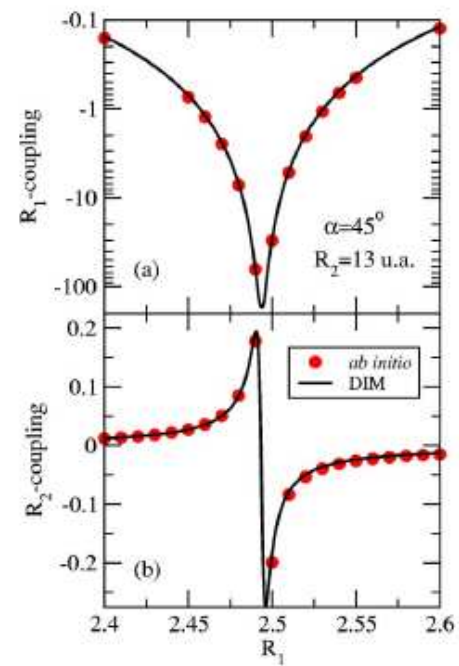
FIG. 2. (Color online) Cut along R_1 of the two nonadiabatic couplings between the first two singlet states of H_3^+.

- Initial H_2 Morse vibrational distributions .

- Quantal

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

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

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

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

  - Classical Continuous:

$$\varrho_\nu^{(c)}(\rho) = \frac{1}{E_\nu^+ - E_\nu^-} \int_{E_\nu^-}^{E_\nu^+} \varrho_\nu^{(m)}(E; \rho) \mathrm{d}E = \frac{1}{2(E_\nu^+ - E_\nu^-)} \left[W \left(E_\nu^+; \rho \right) - W \left(E_\nu^-; \rho \right) \right]$$
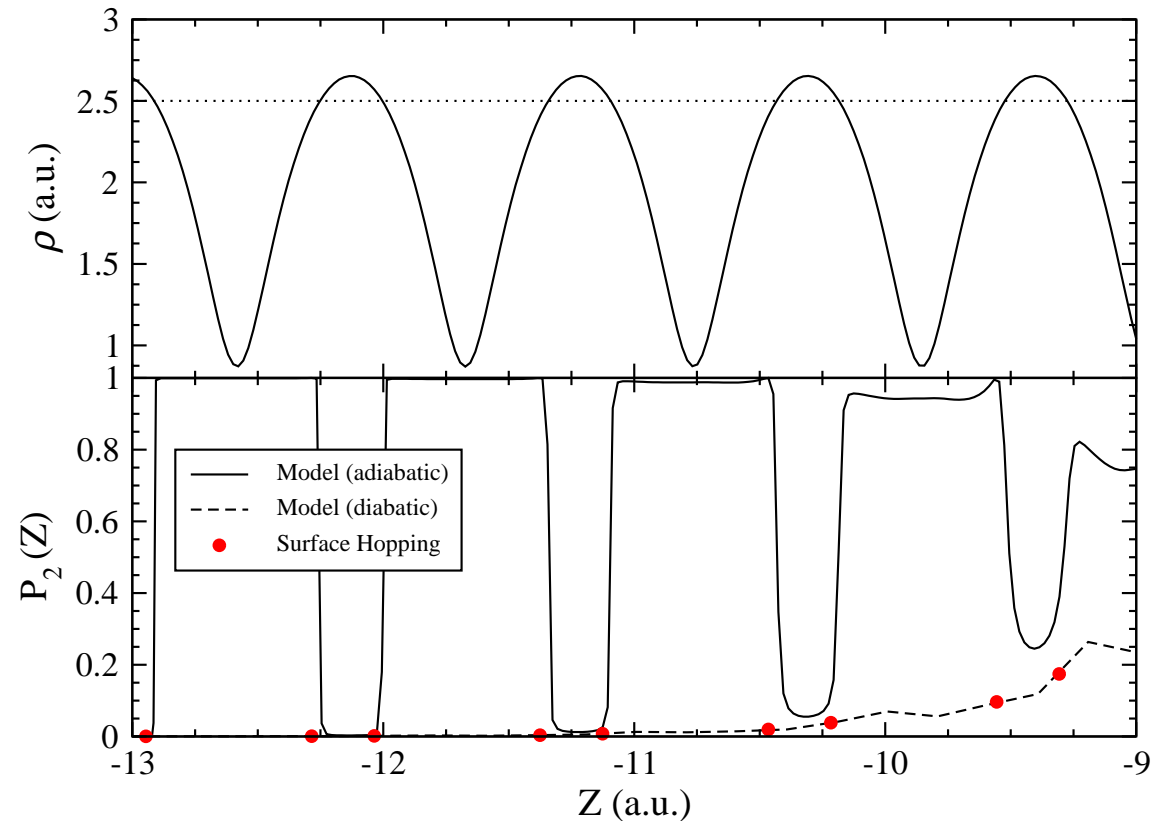
$$W(E, \rho) = \frac{2\alpha}{\pi} \mathcal{R}e \left\{ \sqrt{E(V(\rho) - E)} + V(\rho) \sin^{-1} \sqrt{\frac{E}{V(\rho)}} \right\} .$$
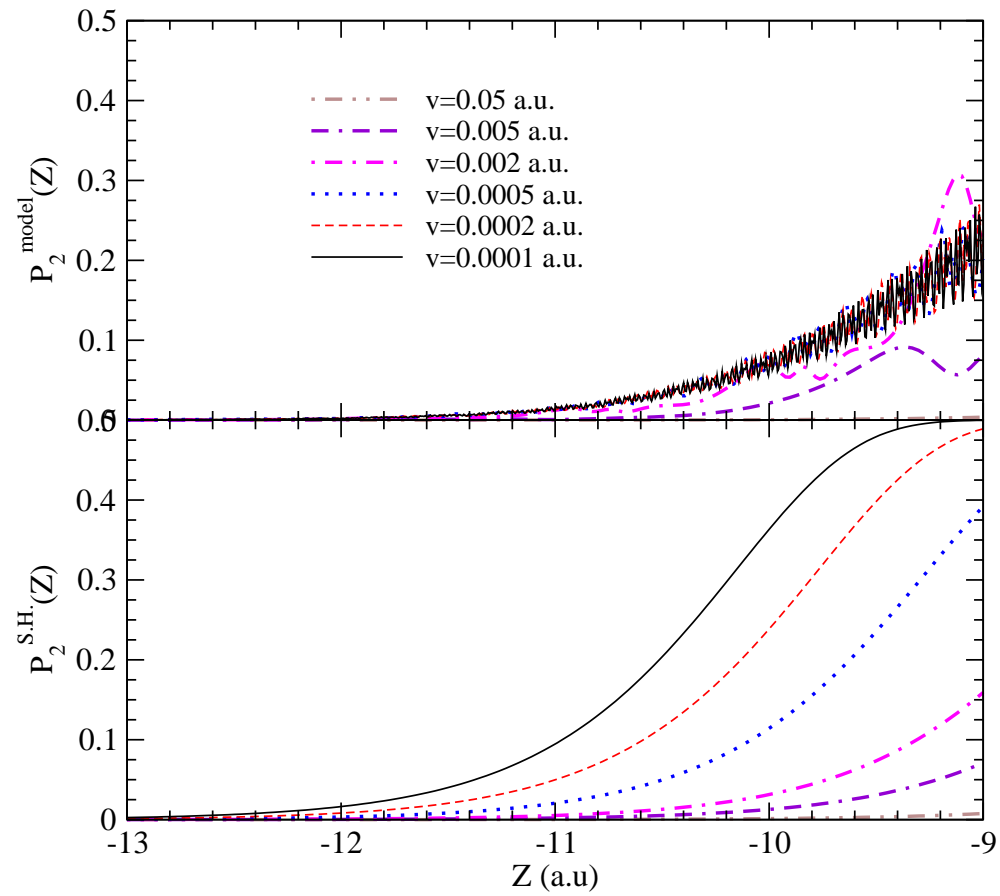
- Initial H_2 vibrational distributions
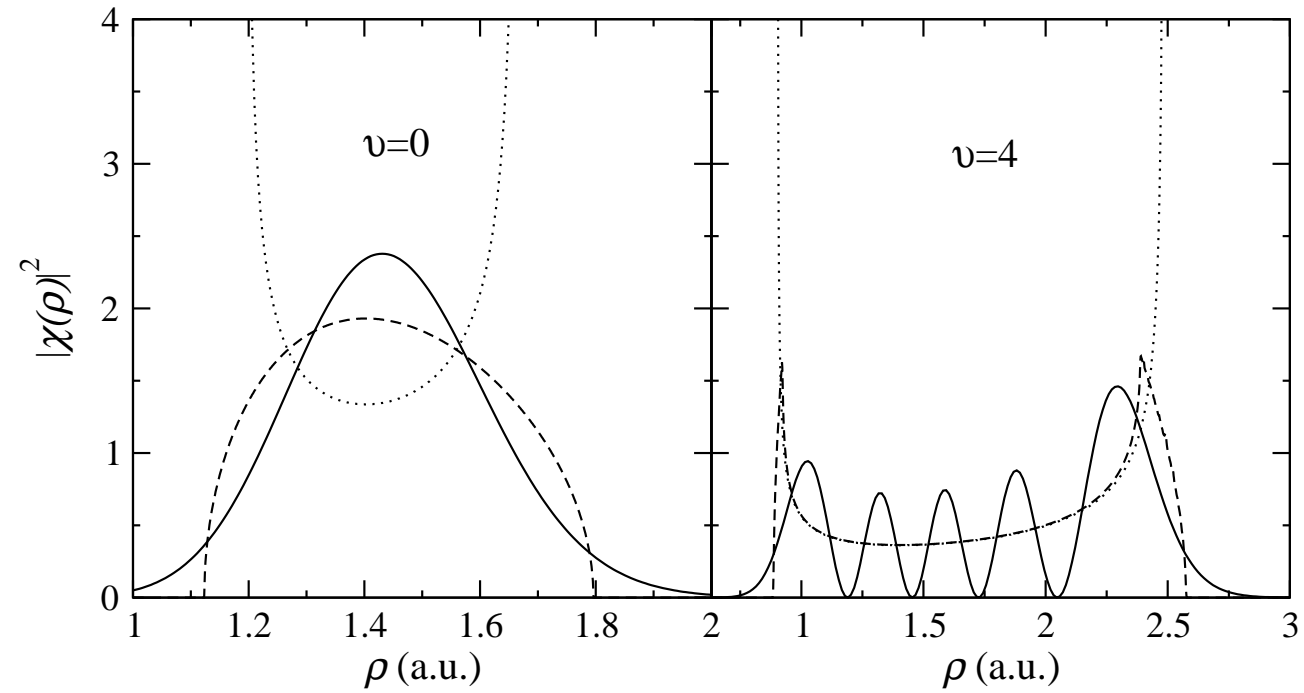
quantal (—), microcanonical (....), continuous (- - -)

- $H^+ + H_2(\nu = 5)$ results, (v=0.002, b=1.0, $\nu = 5$, $\phi = 180^o$.)

- Adiabatic representation: Sudden change $\rho(t)$ crosses ρ_c: $\Psi_1^d \leftrightarrow \Psi_2^d$.

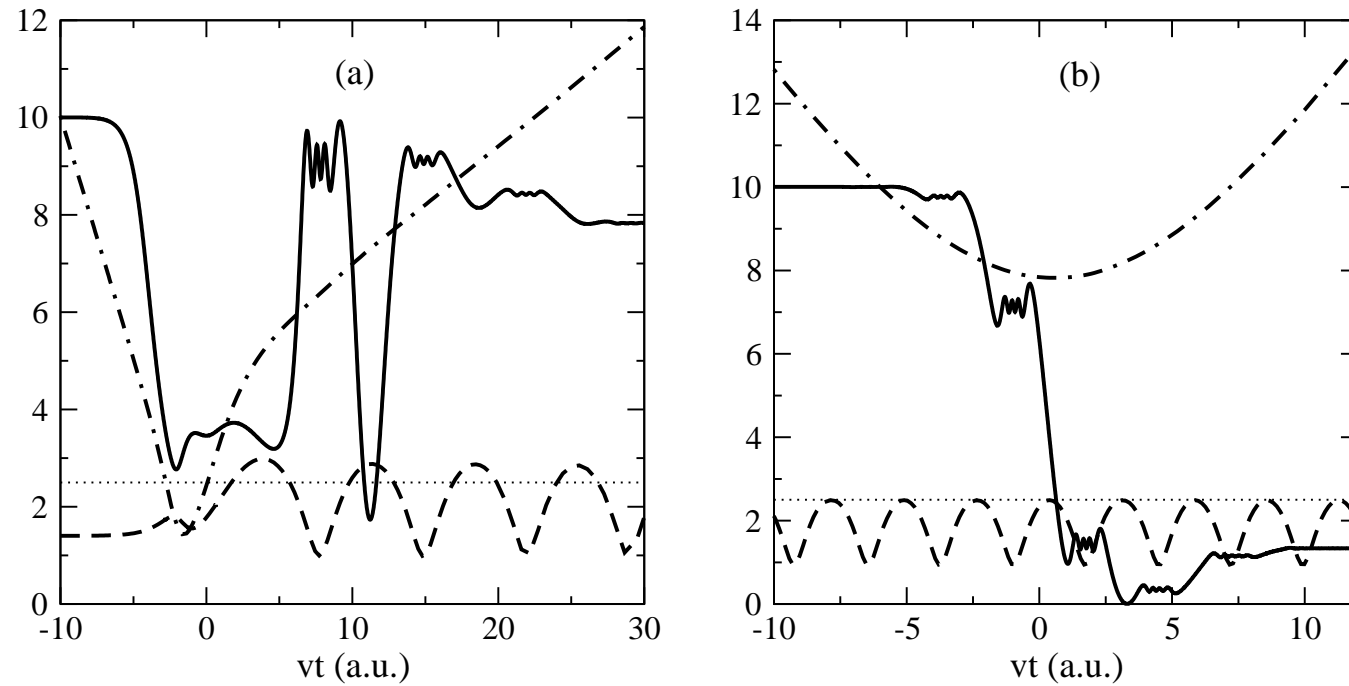- Diabatic representation smooth: Non-total diabatic transitions.

- Low-v limit $\quad P_2^d$ increases until saturation ~ 0.3, $(\beta H_{12}(Z)/\delta)^2$

- $P_2^{SH}(Z_{in}, v, b) \xrightarrow[v \to 0]{} 1/2$, faster the smaller v.

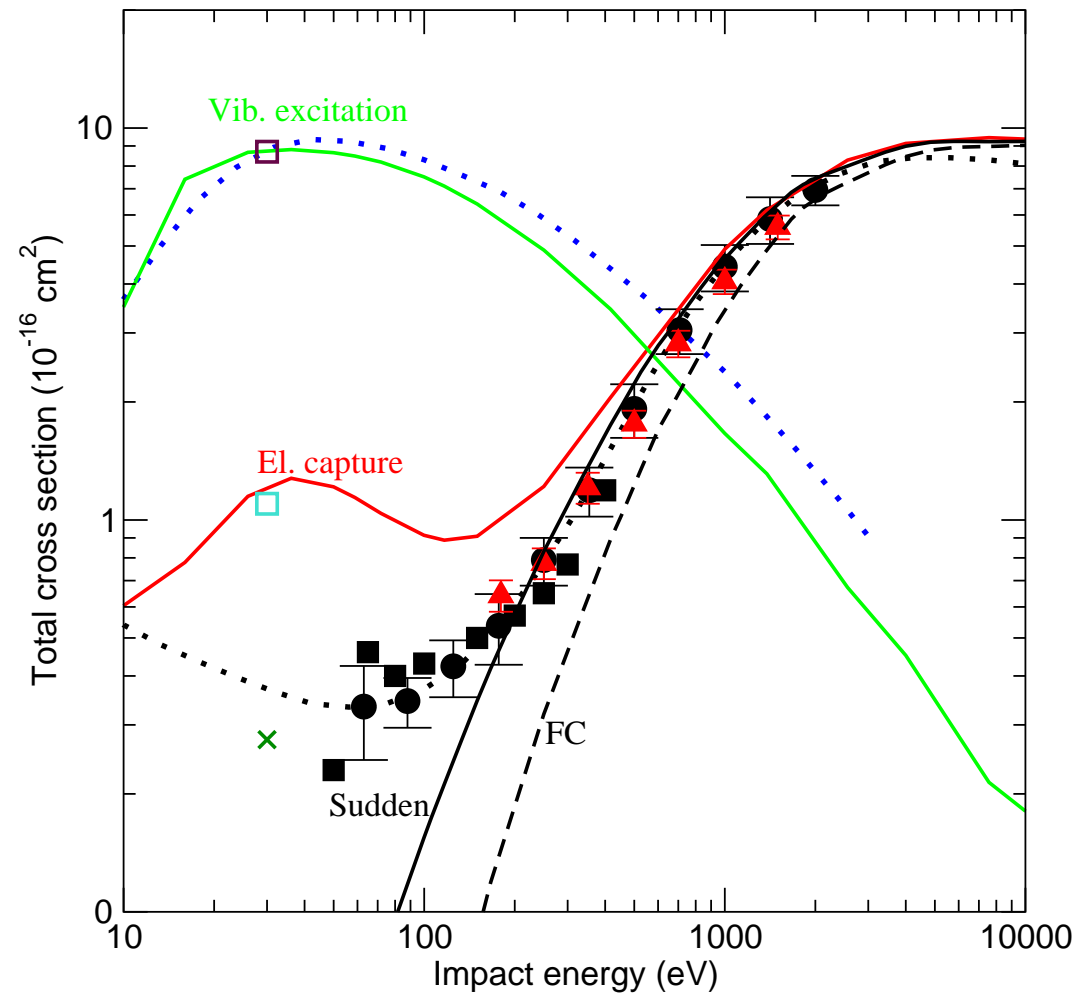- Example of transitions in a.c.i.

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

(—) P_{el}*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 $(2 \leq E \leq 2000 eV)$.

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

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

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

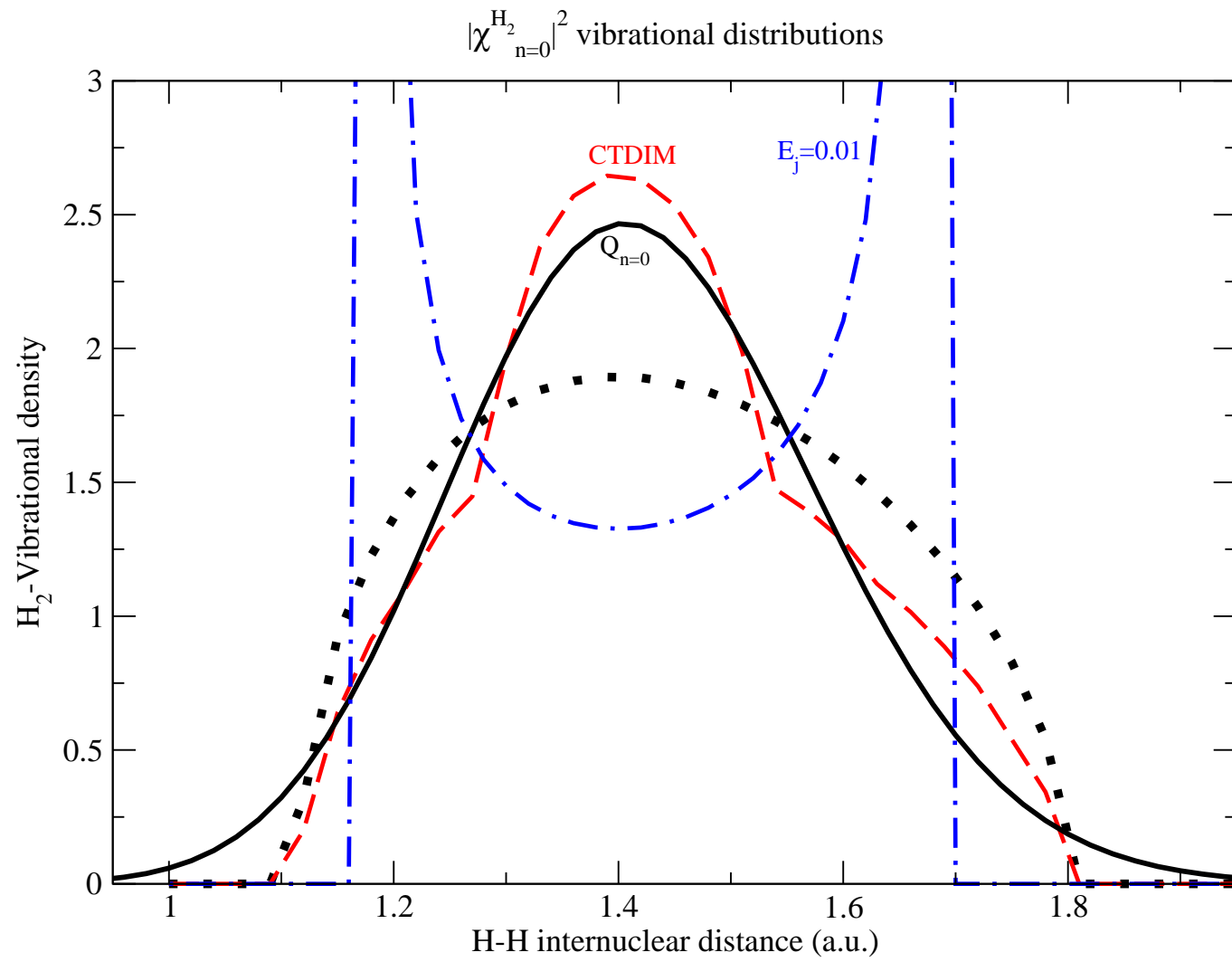- Integrated until $vt_{max} \geq 300$ a.u. Electronic and nuclear transitions taken place.

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

- Diatoms In Molecules (DIM) electronic states.

- Electronic and nuclear exchange and rotational excitation allowed.

- $\mid \chi_{\mathrm{n}}^{CNDIM}(\boldsymbol{\rho}) \mid^2$

- $\mid \chi_{\mathrm{n}}(\boldsymbol{\rho}) \mid^2 = \int dE_k \int d\boldsymbol{p}\varrho_k^{cla}(\boldsymbol{\rho})P_{nk}$; $\mathrm{E}_k = \frac{p_k^2}{2\mu} + V^M(\boldsymbol{\rho})$

- $P_{n,k} = \mid a_{k,\mathrm{n}} \mid^2 \simeq W_{\mathrm{n}}^{Pr}(\boldsymbol{\rho}, \boldsymbol{p}) = \mid \chi_{\mathrm{n}}(\boldsymbol{\rho}) \mid^2 \mid \bar{\chi}_{\mathrm{n}}(\boldsymbol{p}_k) \mid^2$

- $\mid \chi_{\mathrm{n}}^{CNDIM}(\boldsymbol{\rho}) \mid^2 \simeq \sum_{k=1}^{5} \frac{P_{0k}}{E_k^{max} - E_k^{min}} \int_{E_k^{min}}^{E_k^{max}} \varrho^{cla}(\rho, E_k)dE_k$

- CNDIM Distribution

$|\chi^{H_2}_{n=0}|^2$ vibrational distributions

CTDIM

$E_j=0.01$

$Q_{n=0}$

H_2-Vibrational density

H-H internuclear distance (a.u.)

- 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):

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

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

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

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

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

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

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

- Schrödinger equation:

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

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

$$t_{i,m} = \lim_{t \to \infty} < \psi_m(\boldsymbol{r}, t)e^{-iE_m t} \mid \Psi(\boldsymbol{r}, t) >= c_m(t_{max})e^{-i\int_{t_{in}}^{t_{max}}(h_{mm}(t)-h_{mm}(t_{max}))dt}$$
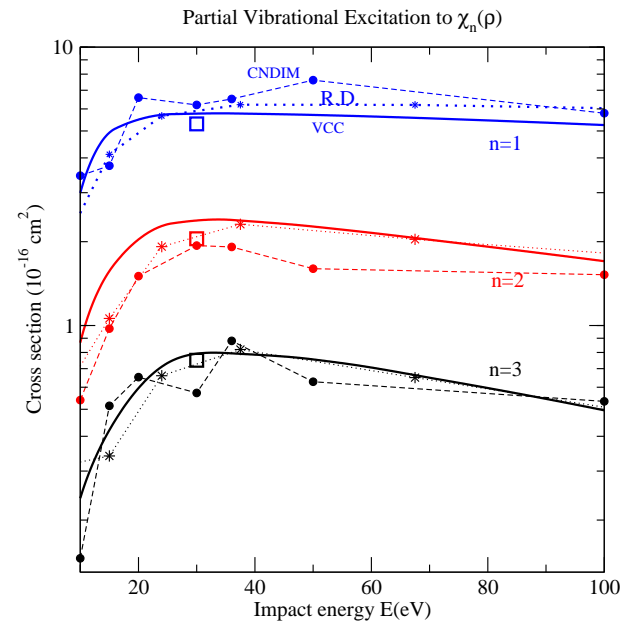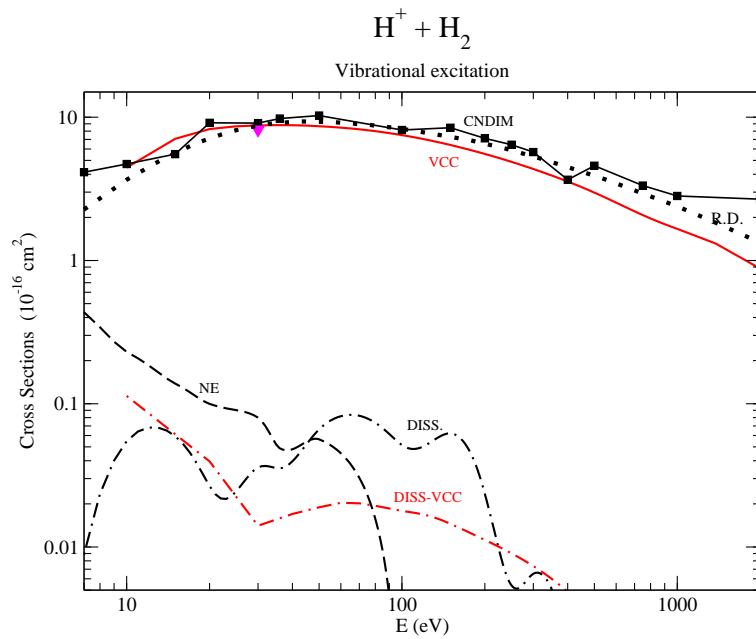
- SEC cross sections

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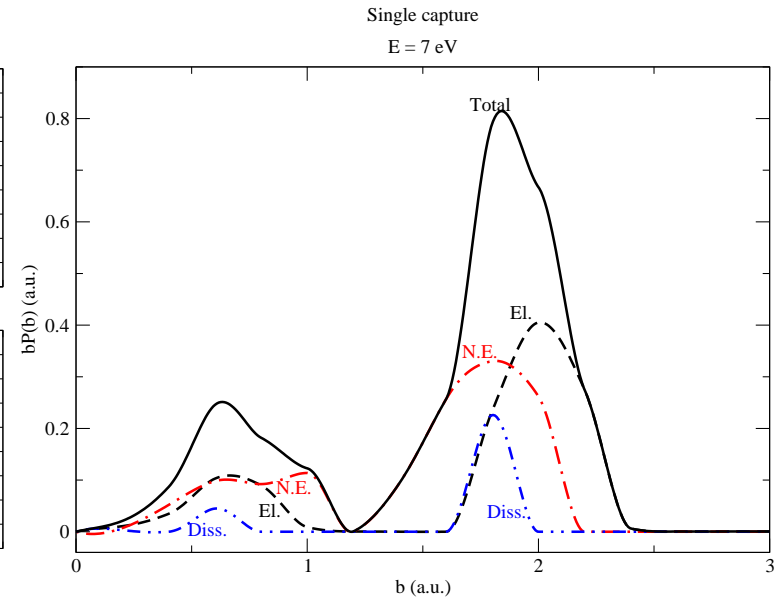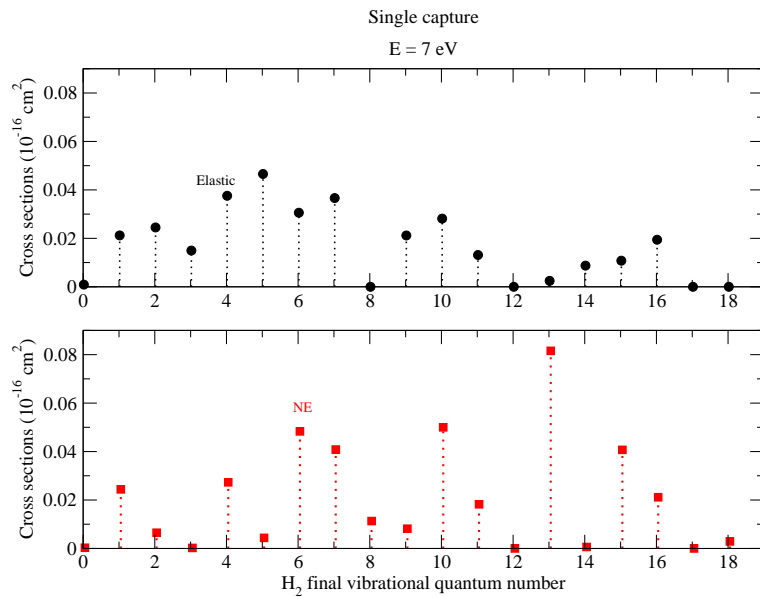

$H^+ + H_2$ Single Capture
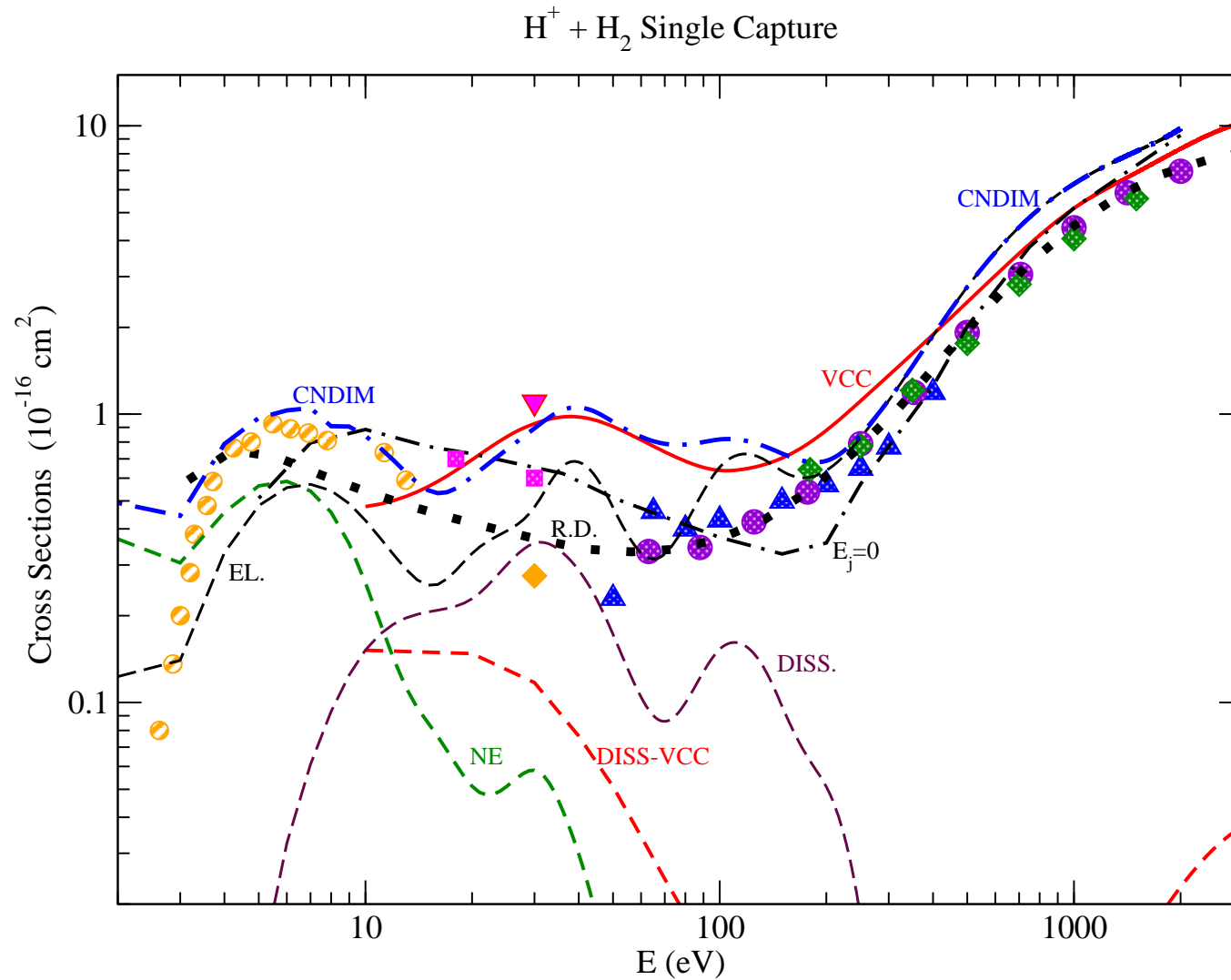
- VE cross sections

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

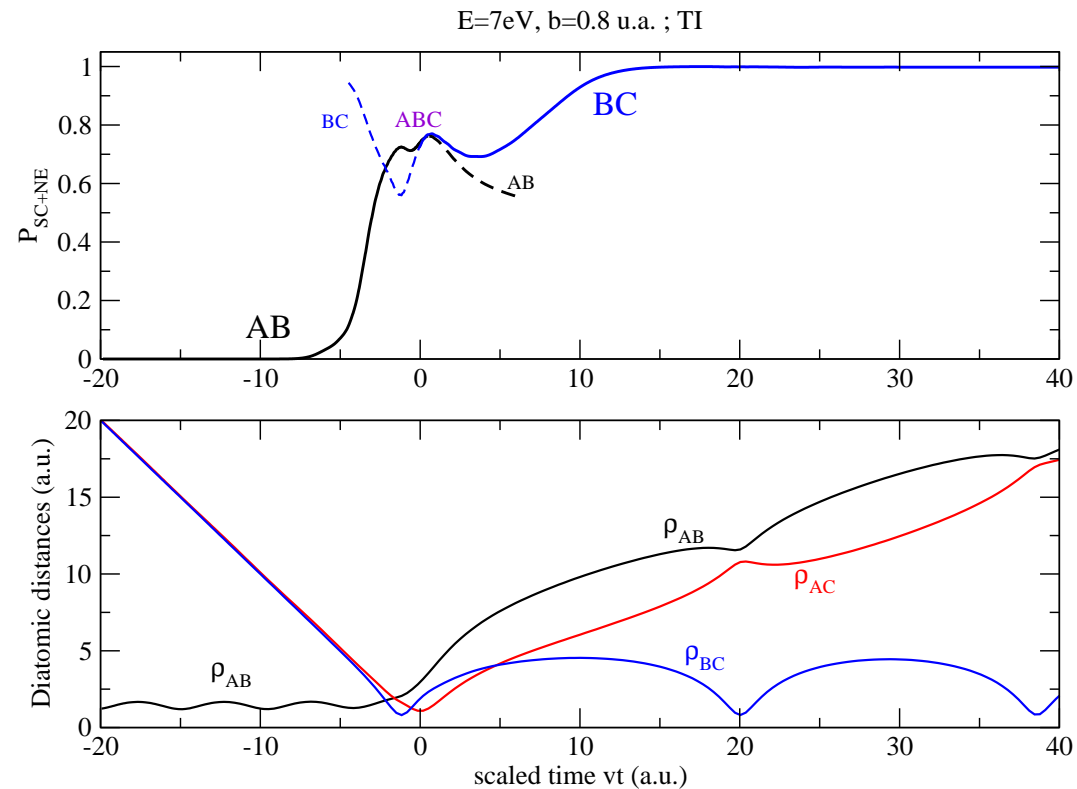- Total VE $\sigma^{VE}(v) = \sum_{J=1}^{4} \sum_{n \geq 1} \sigma_{Jn}^{VE}(v)$

- Mechanisms and illustrations (E=7eV).

- $\sigma^{SEC}(AB)$ $n = 4 - 7$. First stage common to EV.

- Capture with N.E: Great dispersion, with very excited n-H_2.

- P^{SC} limited to b$\leq$ 2.5. Similar contributions J=1-4.

- Electron capture with nuclear exchange:AB→ BC(n=13)

E=7eV, b=0.8 u.a. ; TI

- $P^{SC}(vt)$ 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~ 30 eV, not plotted by experiments and R.D.

3.- At E$\leq$ 10eV, 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.

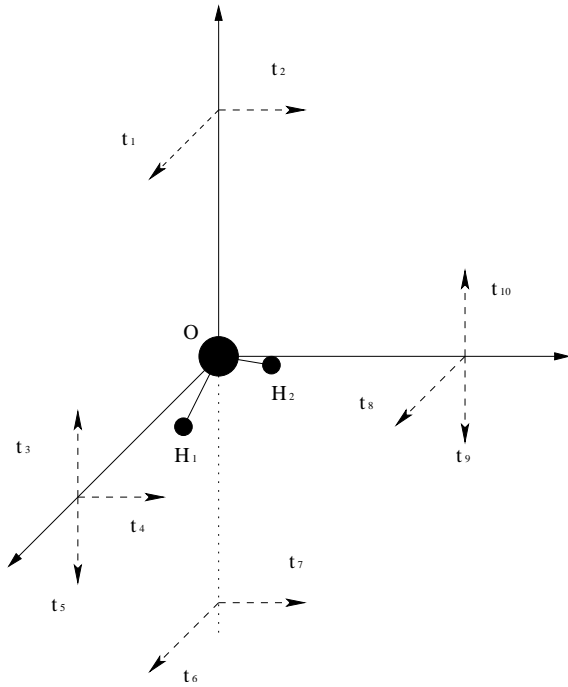- New CTMC and *ab-initio* methods.

(A) CTMC-IPM study of ionizing processes.

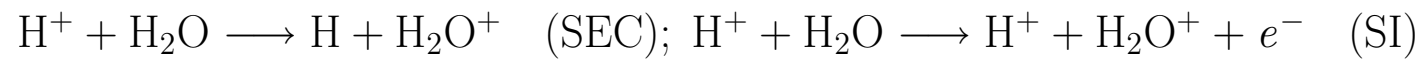(B) IPM-Asymptotic molecular orbitals (a.m.o.)

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

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

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

- Equilibrium H_2O geometry (F.C.). Simulation Sudden approach other geometries.

$$H^+ + H_2O \longrightarrow H + H_2O^+ \quad \text{(SEC)}; \ H^+ + H_2O \longrightarrow H^+ + H_2O^+ + e^- \quad \text{(SI)}$$

- H_2O not spherical. 10 projectile trajectory types.

- Results

- $\bar{\sigma}^{SC}$ include trajectories along Y-axix. Larger P^{SEC}. from H_2O HOMO.
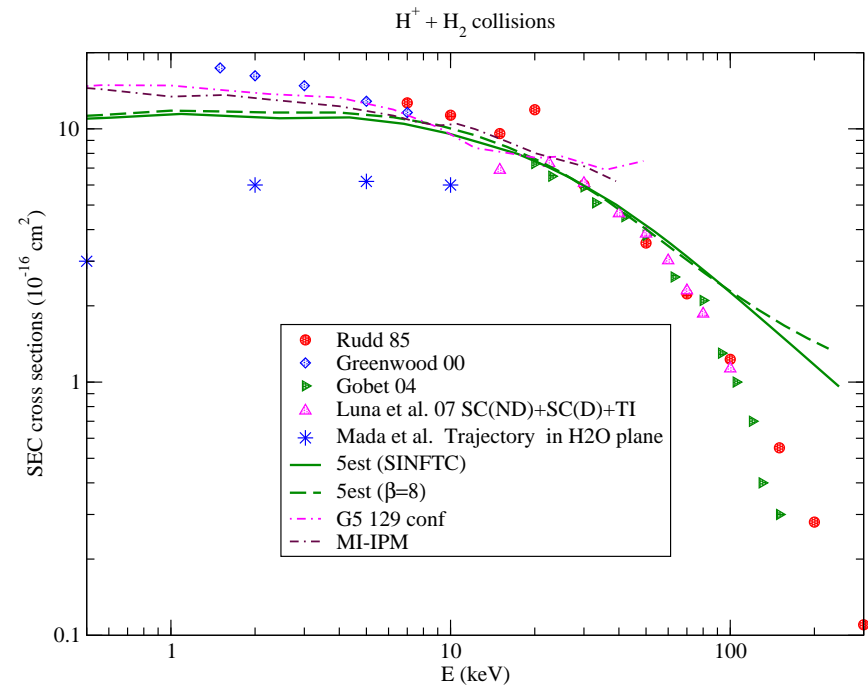
$H^+ + H_2$ collisions

- **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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