



Theoretical Vibrational-excitation Cross Sections for PIC Based Negative Ion Plasma Computations"

Vincenzo Laporta

Istituto di Scienza e Tecnologia dei Plasmi (ISTP) - CNR, Italy

10th International symposium on Negative Ions, Beams and Sources - NIBS'26

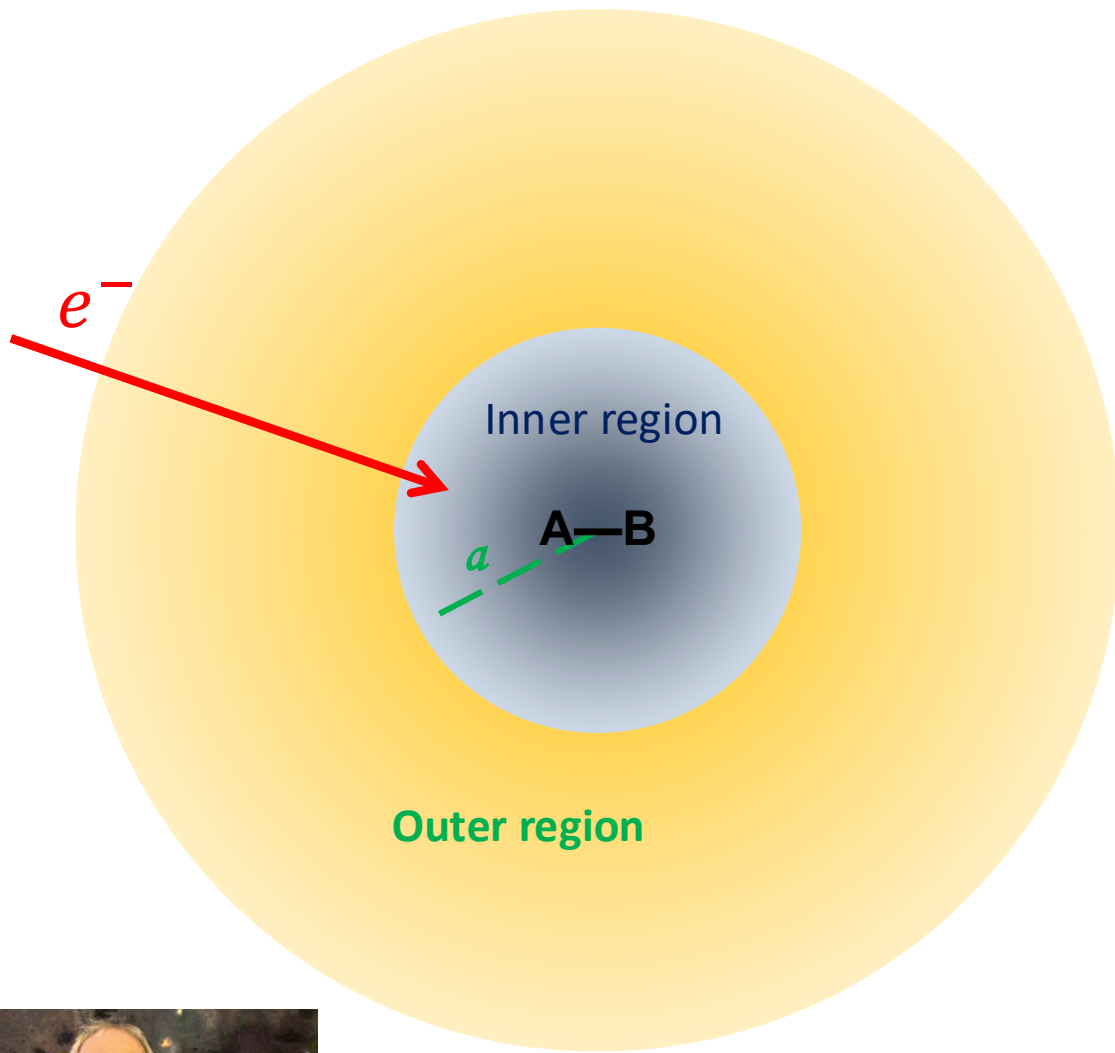
20-September 25, 2026

Nelson, BC, Canada

Plan of the presentation:

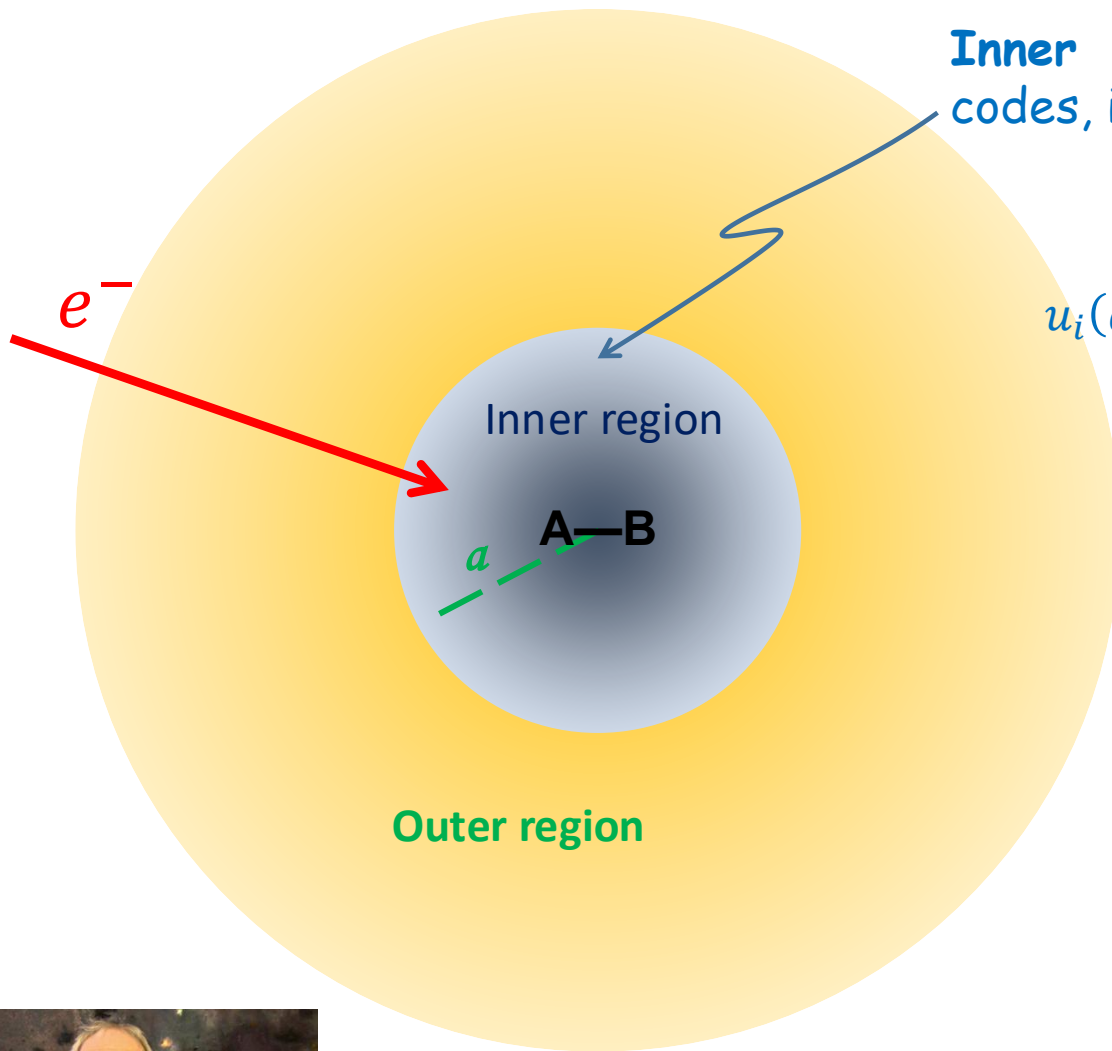
1. Theoretical approaches for vibrationally resolved electron-molecule scattering
 - *R*-matrix method
 - Local-Complex-Potential model
 - Multichannel Quantum Defect Theory
2. *ab-initio* state-resolved cross sections and vibrational relaxation time:
 - electron-D₂ cross sections
 - D₂ vibrational relaxation time
 - electron-O₂ cross sections
 - electron-H₂⁺ cross sections

The R-matrix method



J. Tennyson, Phys. Rep., **491**, 29 (2010)

The R-matrix method



Inner region: N+1 electrons; *ab-initio* quantum chemistry codes, including exchange correlations; continuum orbitals

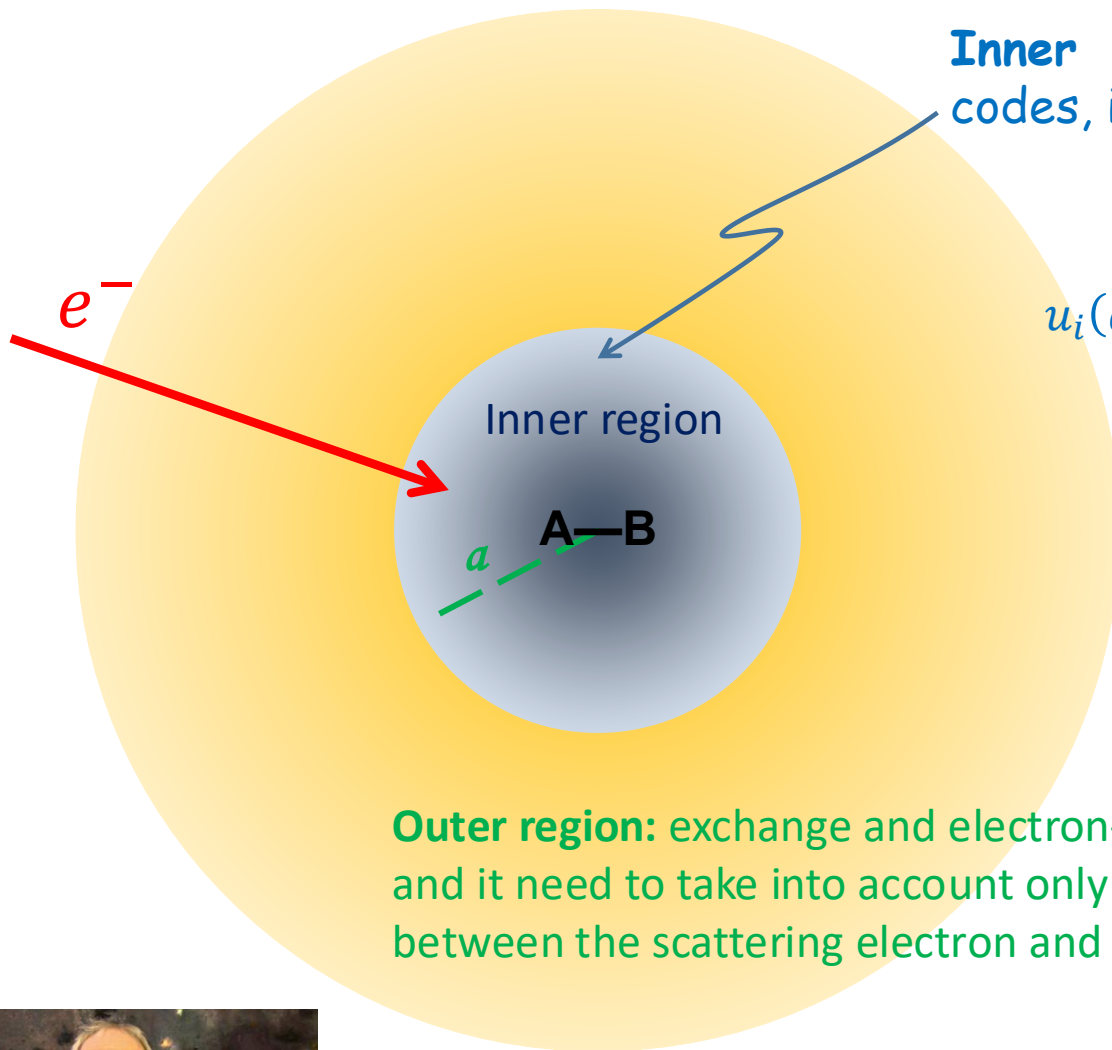
$$\Psi_k = \mathcal{A} \sum_{i,j} a_{i,j,k} \phi_i^N \eta_{i,j} + \sum_i b_{j,k} \phi_j^{N+1}$$

$$u_i(a) = \sum_j R_{ij}(a, E) [r u_j' - b u_j]_{r=a}$$

$$R_l(a, E) = \frac{1}{2} \sum_{\lambda} \frac{w_{\lambda l}(a)^2}{E_{\lambda} - E}$$



The R-matrix method



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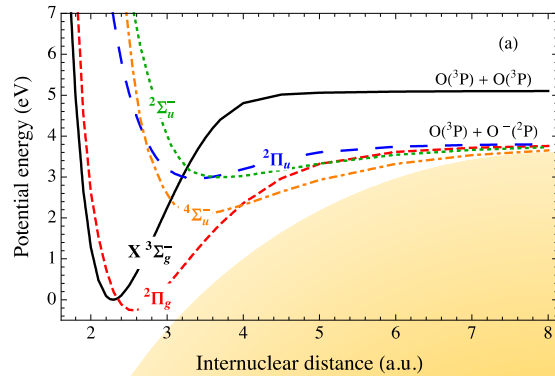
$$R_l(a, E) = \frac{1}{2} \sum_{\lambda} \frac{w_{\lambda l}(a)^2}{E_{\lambda} - E}$$

Outer region: exchange and electron-electron correlations are neglected and it need to take into account only long-range multi-polar interactions between the scattering electron and the target

$$u_l(r) \sim \frac{1}{\sqrt{k}} (\sin \varphi_l + \cos \varphi_l K_l)$$



The R-matrix method



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Inner region

A—B

a

Boundary

$$K_l = e^{-2i\varphi_l} \frac{1 - R_l(L^* - b)}{1 - R_l(L - b)}, \quad \Rightarrow \quad T_l = \frac{2iK_l}{1 - iK_l}$$

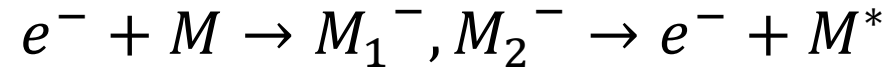
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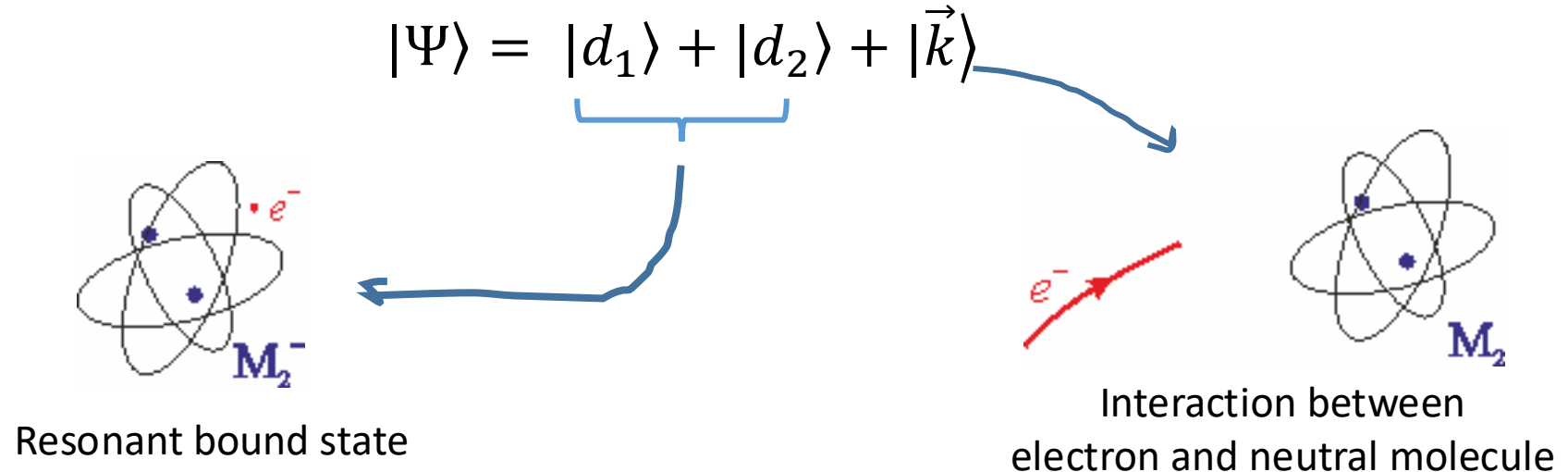


Local Complex Potential model

Let's consider electron-molecule scattering with the presence of **two** interacting resonances:



The process can be described by two **discrete** electronic states, $|d_1\rangle$ and $|d_2\rangle$, *embedded-in* and *interacting-with* a single electronic **continuum** $|\vec{k}\rangle$



The electron-molecule effective Hamiltonian

$$\mathbf{H} = \mathbf{H}_0 + \mathbf{U} + \mathbf{V}$$

$$H_0 = |d_1\rangle(T_N + V_0 + \epsilon_1)\langle d_1| + |d_2\rangle(T_N + V_0 + \epsilon_2)\langle d_2| + \int d\vec{k} |\vec{k}\rangle(T_N + V_0 + \epsilon_{\vec{k}})\langle \vec{k}|$$

$$U = |d_1\rangle U_{12} \langle d_2| + \text{h.c.}$$

$$V = \int d\vec{k} |d_1\rangle V_{1k} \langle \vec{k}| + |d_2\rangle V_{2k} \langle \vec{k}| + \text{h.c.}$$

- V_0 is the neutral molecule potential
- $\epsilon_{1,2}$ are the resonance energies respect to V_0
- U describes the coupling between the discrete states
- V couples the discrete states with the continuum states

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- U describes the coupling between the discrete states
- V couples the discrete states with the continuum states

Local Complex Potential model

$$H |\Psi\rangle = E |\Psi\rangle$$

$$H = H_0 + V$$

$$|\Psi\rangle = |d_1\rangle + |d_2\rangle + |\vec{k}\rangle$$

$E = \text{total energy}$

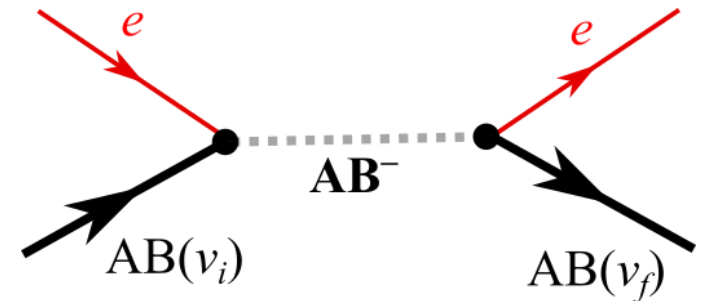


$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_r^-(R) - \frac{i}{2} \Gamma_r(R) - E \right] \xi_{s,v}^r(R) = -\mathcal{V}_r^s(R) \chi_v^s(R), \quad r \in \mathcal{R},$$

$$\mathcal{V}_r^{s2} = \frac{\hbar}{2\pi} \frac{\Gamma_r^s}{k}, \quad \Gamma_r = \sum_{s \in \mathcal{S}} \Gamma_r^s, \quad r \in \mathcal{R}.$$

coupling

resonance widths



Local Complex Potential model

$$H |\Psi\rangle = E |\Psi\rangle$$

$$H = H_0 + V$$

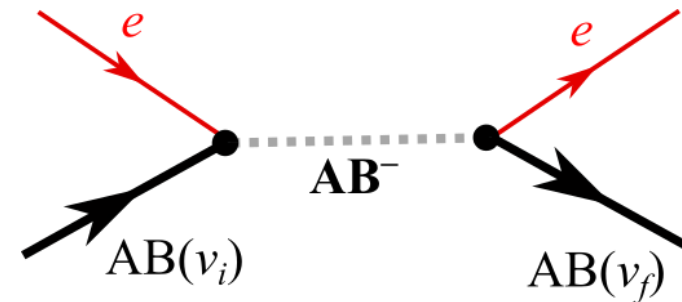
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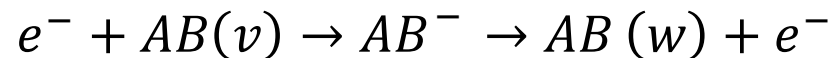
$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + \underbrace{V_r^-(R) - \frac{i}{2}\Gamma_r(R)}_{\text{complex potential resonant state}} - E \right] \underbrace{\xi_{s,v}^r(R)}_{\text{resonant nuclear wave function}} = -\underbrace{\mathcal{V}_r^s(R)}_{\text{coupling}} \underbrace{\chi_v^s(R)}_{\text{initial molecular nuclear wave function}}, \quad r \in \mathcal{R},$$

$$\underbrace{\mathcal{V}_r^{s2}}_{\text{coupling}} = \frac{\hbar}{2\pi} \frac{\Gamma_r^s}{k}, \quad \Gamma_r = \sum_{s \in \mathcal{S}} \Gamma_r^s, \quad r \in \mathcal{R}. \quad \underbrace{\hspace{10em}}_{\text{resonance widths}}$$

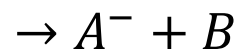


Local Complex Potential model

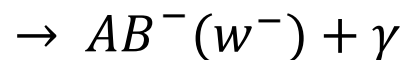
Processes occurring for vibrationally resolved resonant electron-molecule scattering:



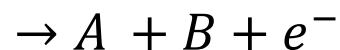
Vibrational Excitation



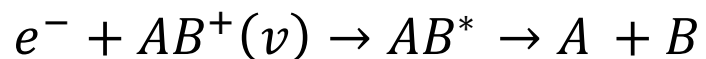
Dissociative electron Attachment



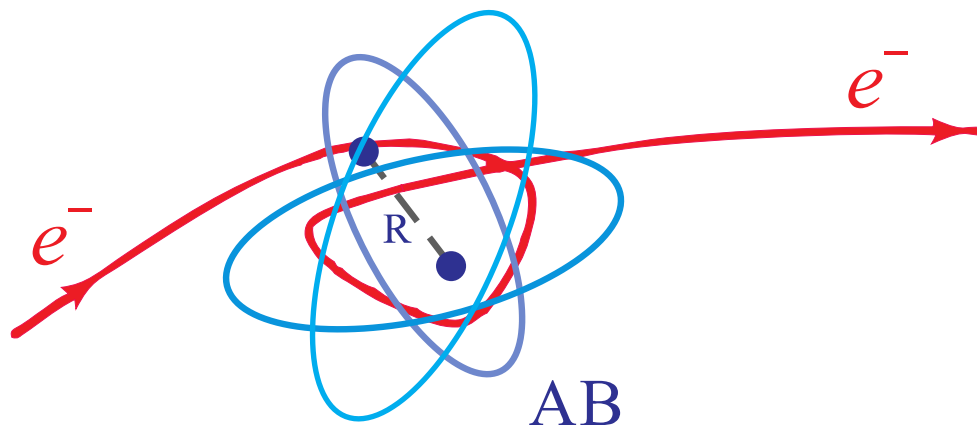
Radiative electron Attachment



Dissociative Excitation

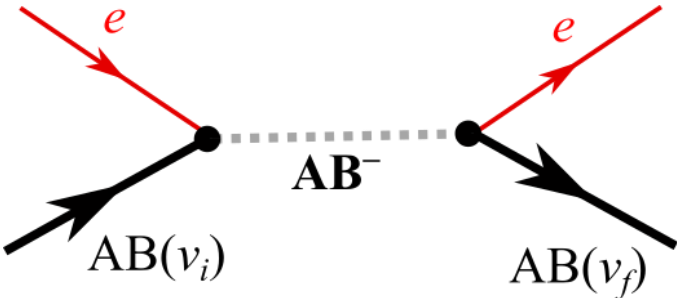


Dissociative Recombination

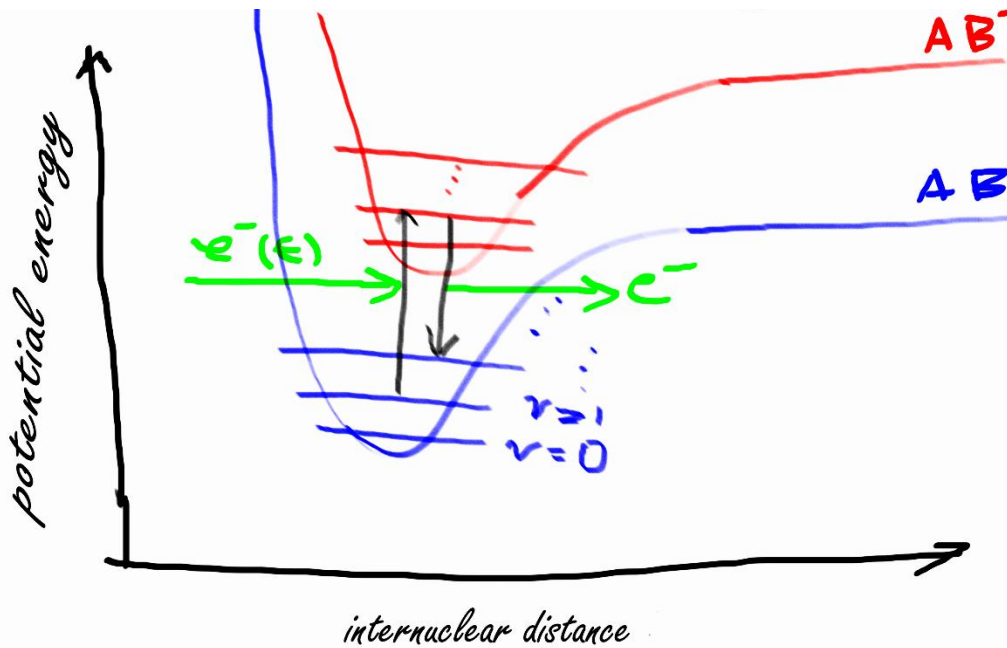
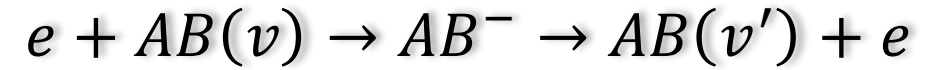


$$\begin{aligned}\sigma_{s,v\rightarrow s',v'}^{\rm VE}(\epsilon) &= \sum_{r\in\mathcal{R}} \frac{2S_r+1}{(2S_s+1)} \frac{g_r}{2} \frac{64\pi^5 m^2}{\hbar^4} \frac{k'}{k} \left| \langle \chi_{v'}^{s'} | \mathcal{V}_r^{s'} | \xi_{s,v}^r \rangle \right|^2, \qquad s,s'\in\mathcal{S}, \\ \sigma_{s,v}^{\rm DA}(\epsilon) &= \sum_{r\in\mathcal{R}} \frac{2S_r+1}{(2S_s+1)} \frac{g_r}{2} 2\pi^2 \frac{K}{\mu} \frac{m}{k} \lim_{R\rightarrow\infty} \left| \xi_{s,v}^r(R) \right|^2, \qquad s\in\mathcal{S}, \\ \sigma_{s,v}^{\rm DE}(\epsilon) &= \sum_{r\in\mathcal{R}} \frac{2S_r+1}{(2S_s+1)} \frac{g_r}{2} \frac{64\pi^5 m^2}{\hbar^4} \int_{\epsilon^{th}}^{\epsilon^{max}} d\epsilon_c \frac{k'}{k} \left| \langle \chi_c^{s'} | \mathcal{V}_r^{s'} | \xi_{s,v}^r \rangle \right|^2, \qquad s,s'\in\mathcal{S},\end{aligned}$$

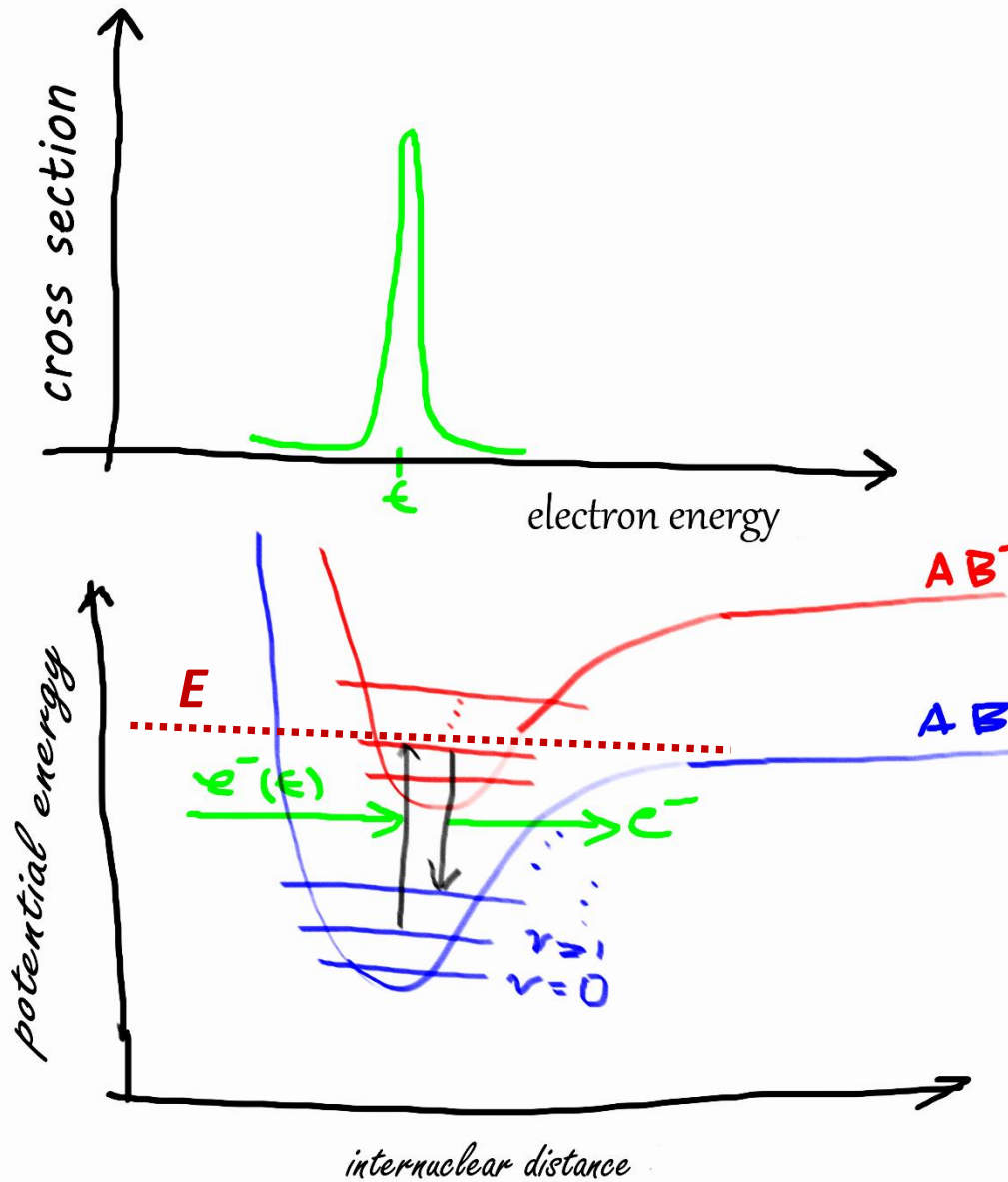
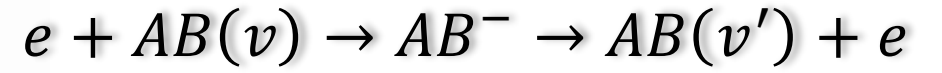
$$\begin{aligned}\mathcal{S} &= \{X^1\Sigma_g^+, b^3\Sigma_u^+, B^1\Sigma_u^+\} = \{X, b, B\} \\ \mathcal{R} &= \{X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+\} = \{X^-, B^-, C^-\}\end{aligned}$$

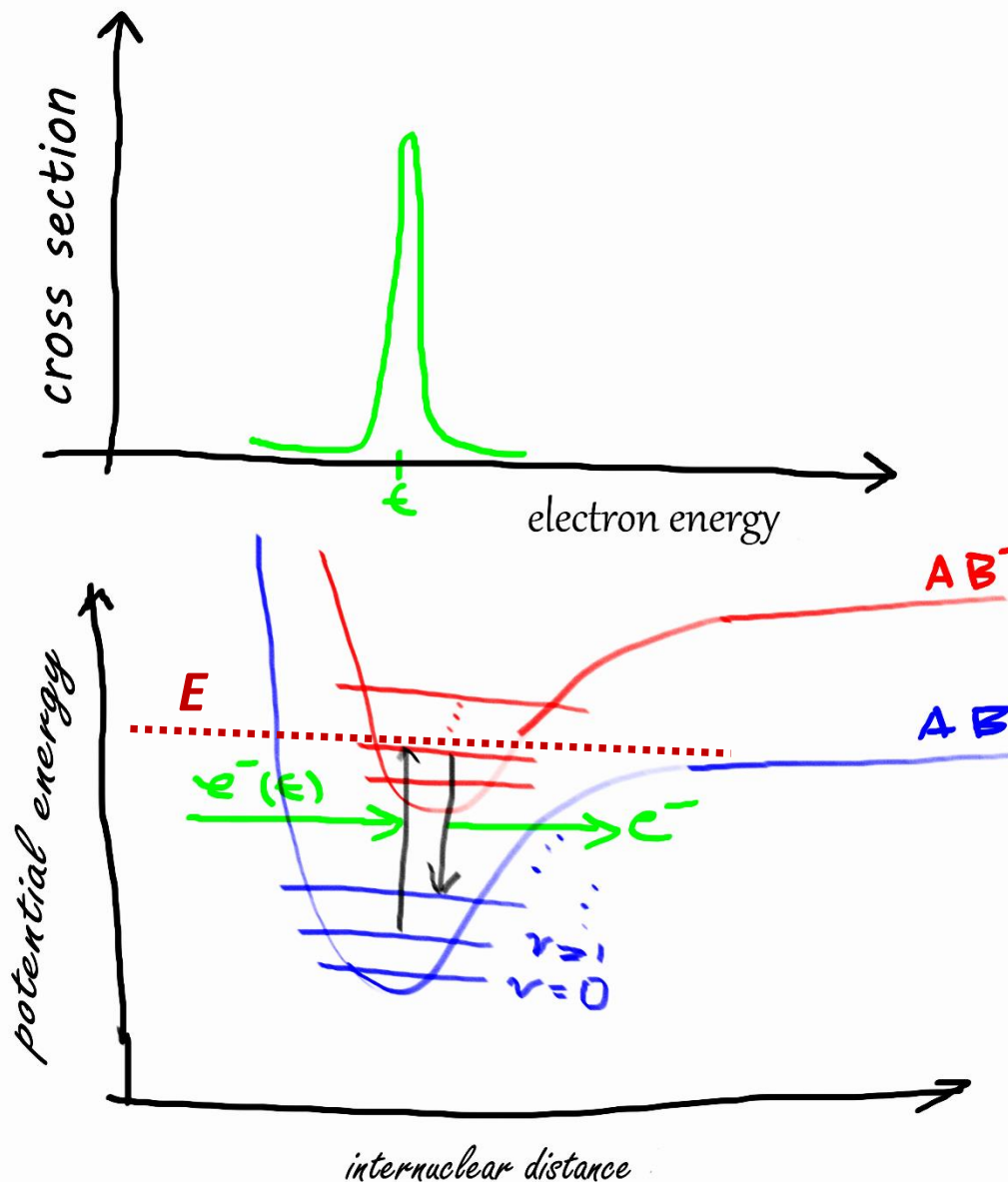


Resonant
Vibrational-excitation
cross section

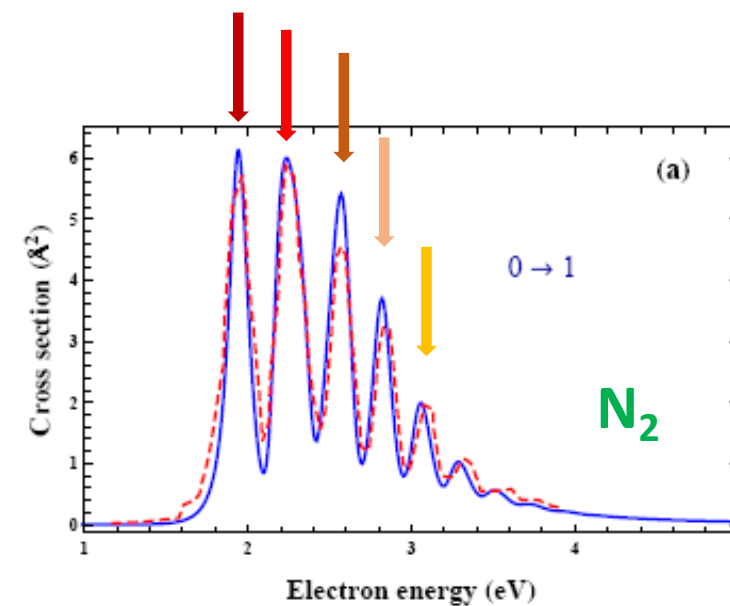


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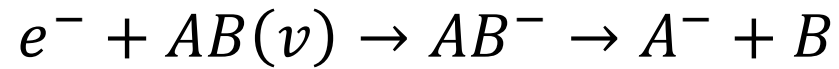


Resonant Vibrational-excitation cross section

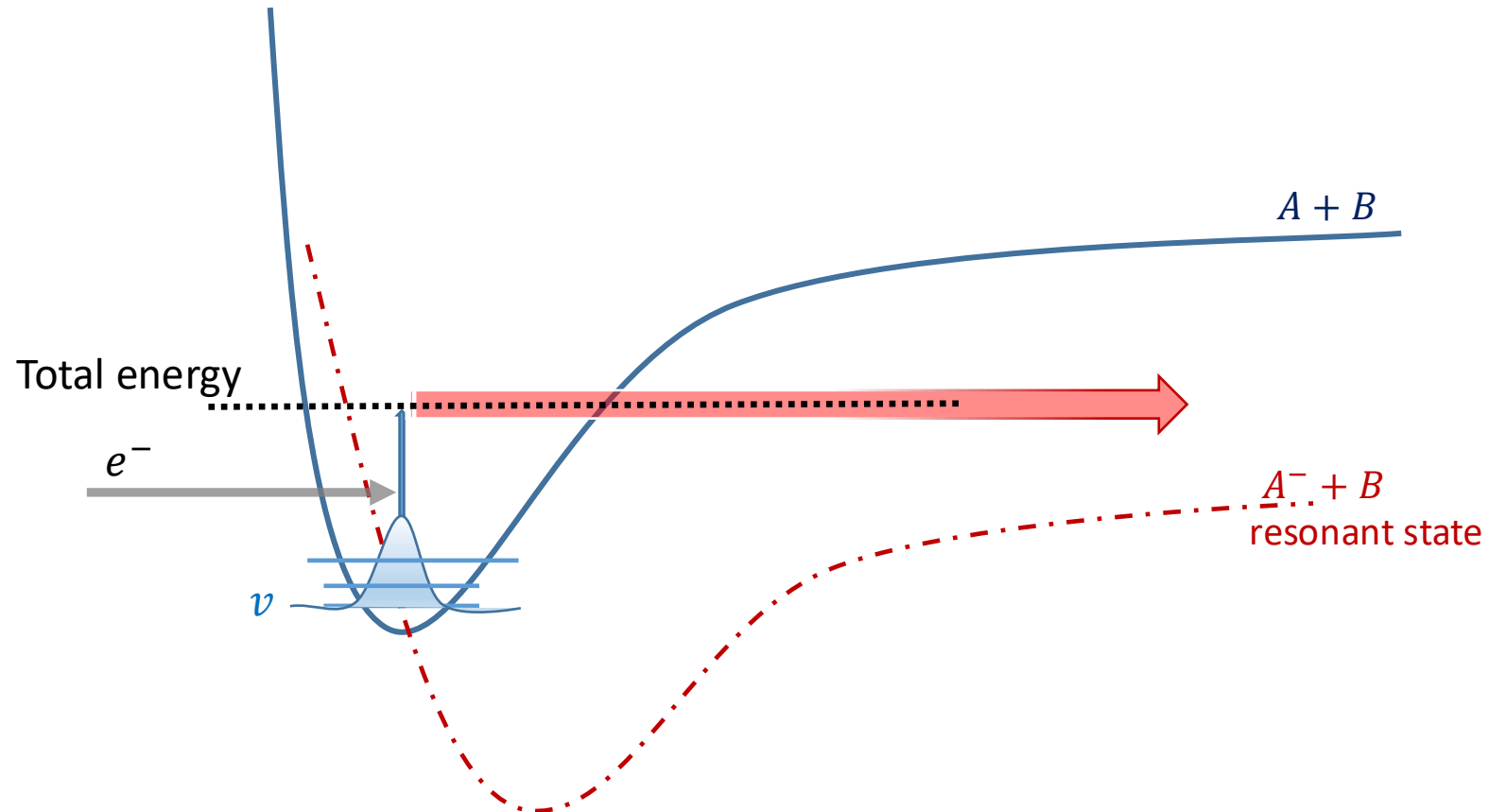
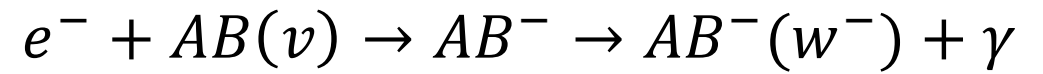


Production of negative ions

Dissociative electron Attachment

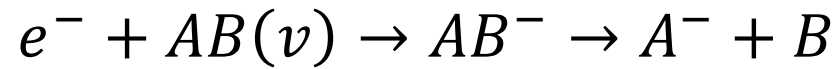


Radiative electron Attachment

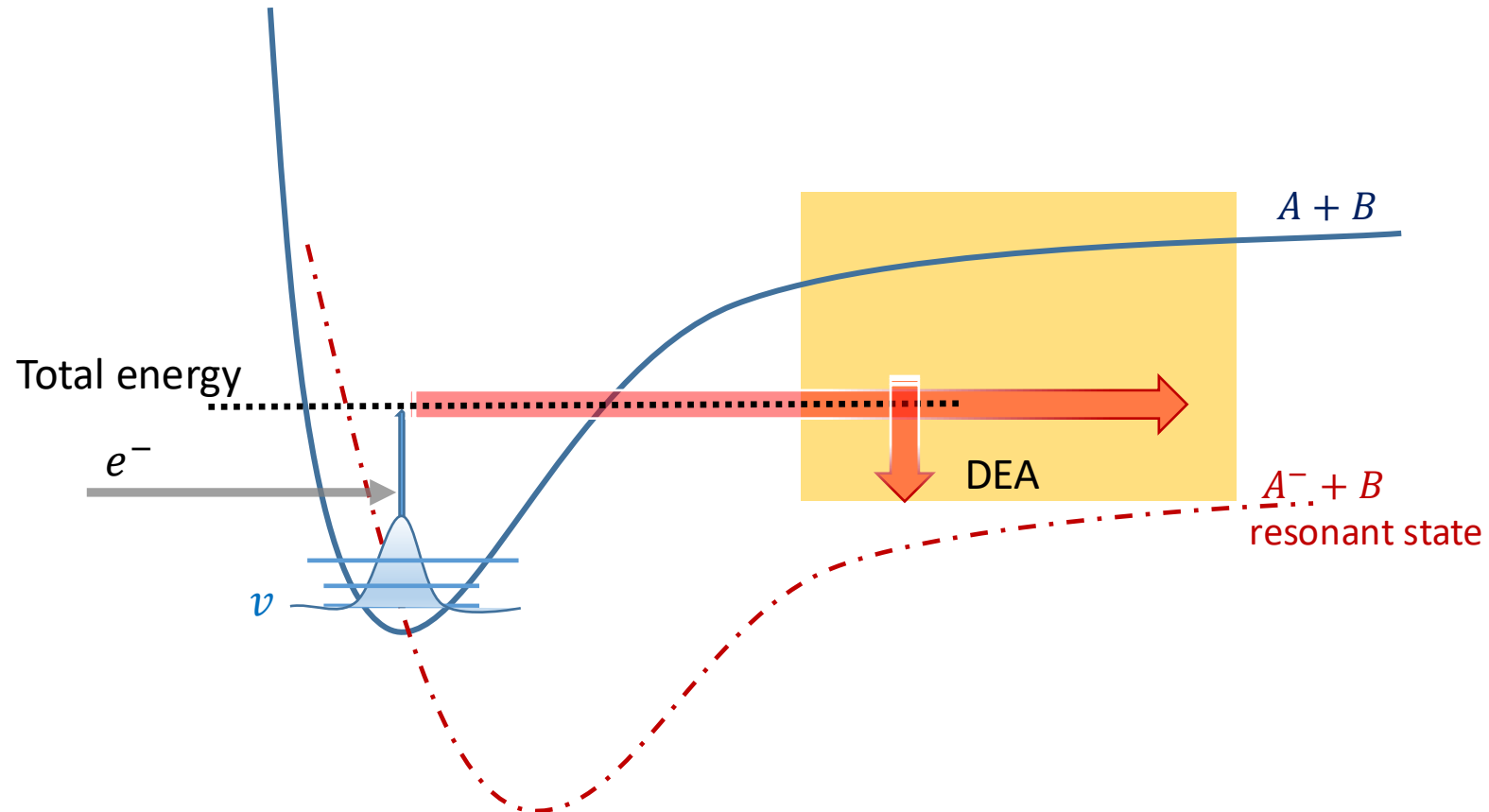
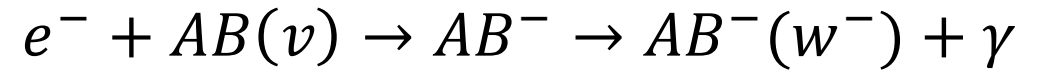


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Dissociative electron Attachment

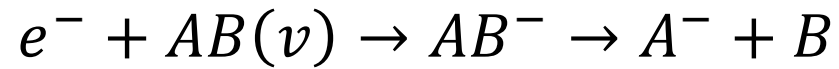


Radiative electron Attachment

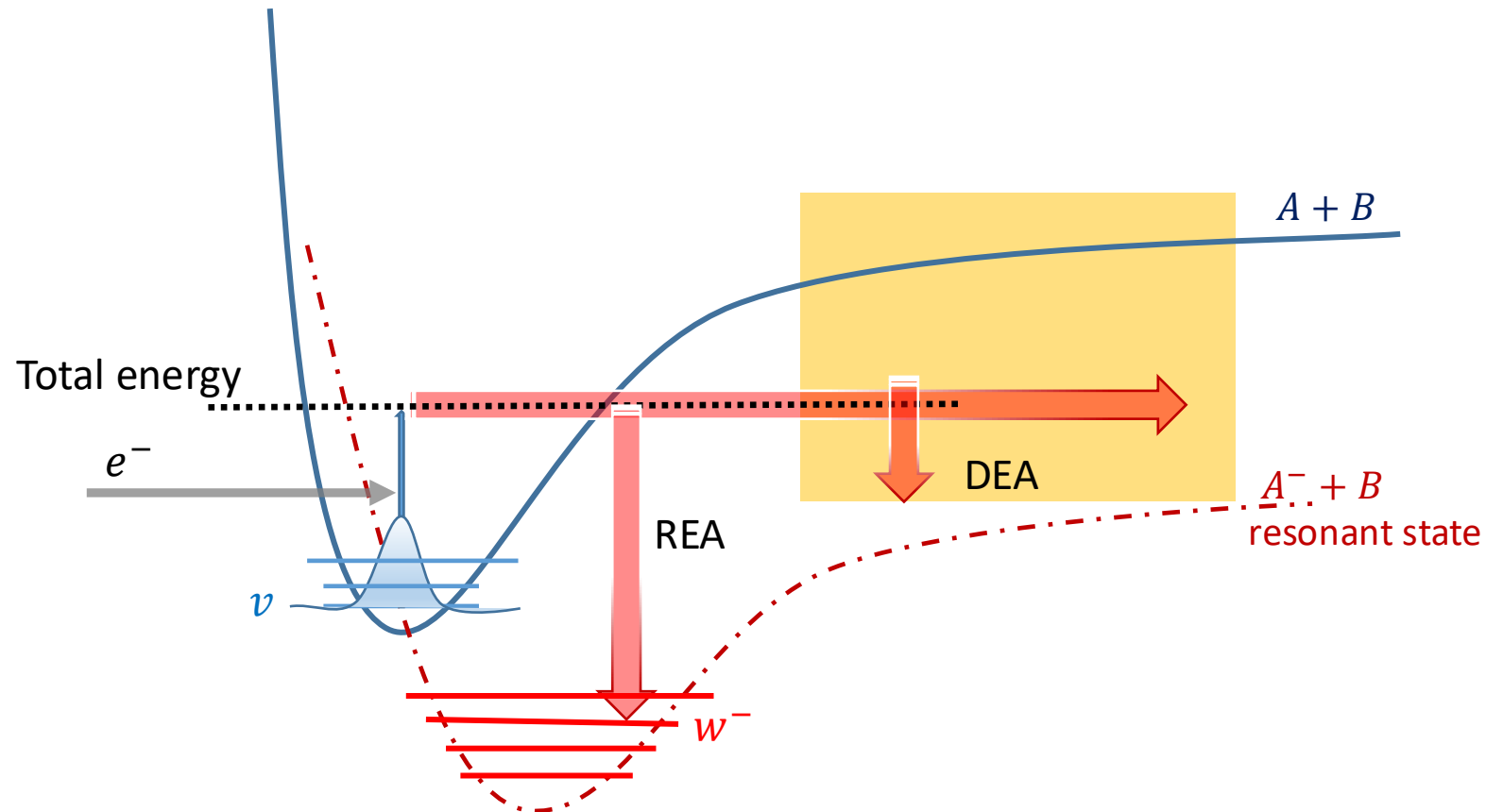
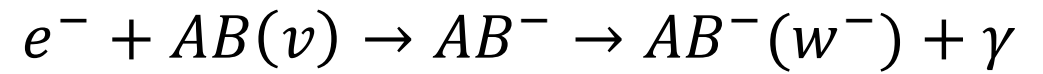


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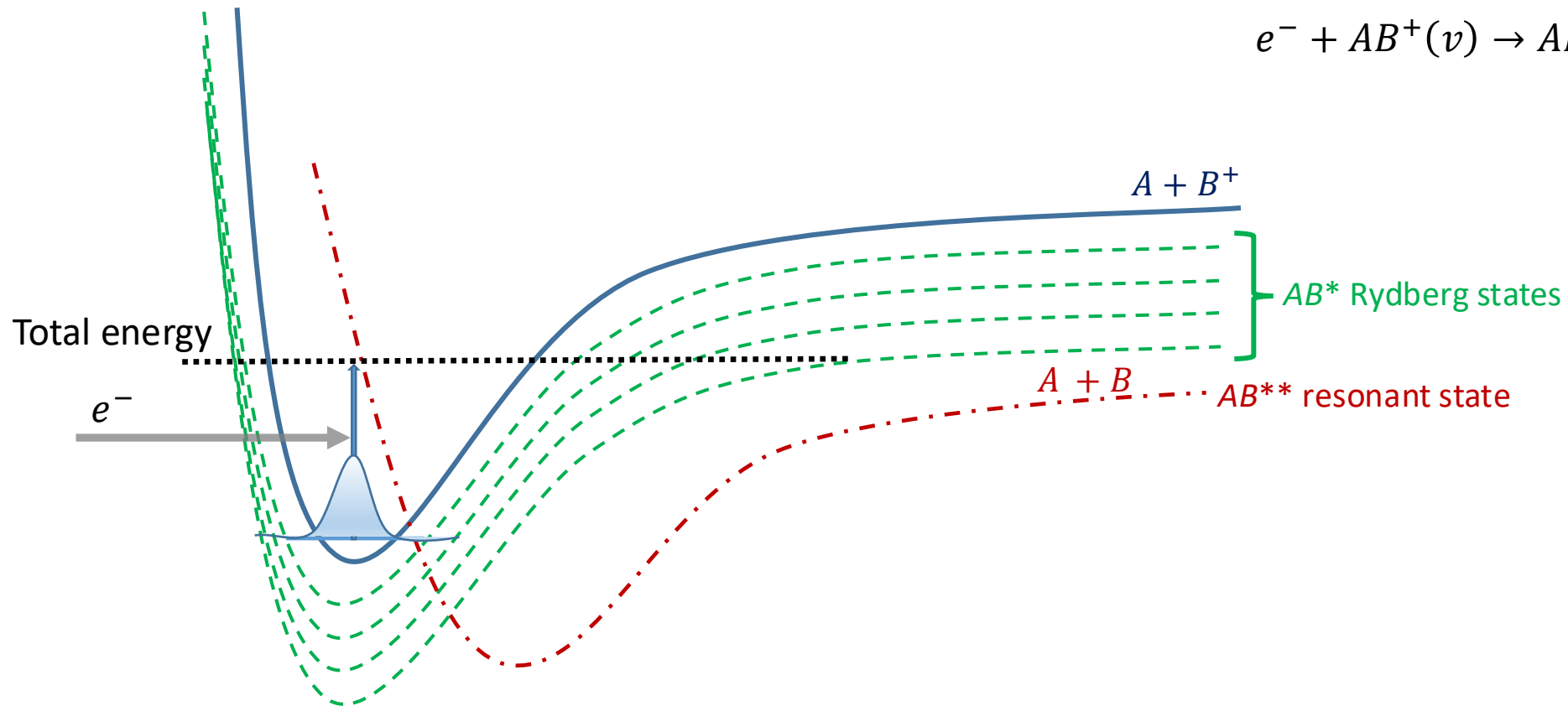


Radiative electron Attachment



electron-molecular ion cross sections

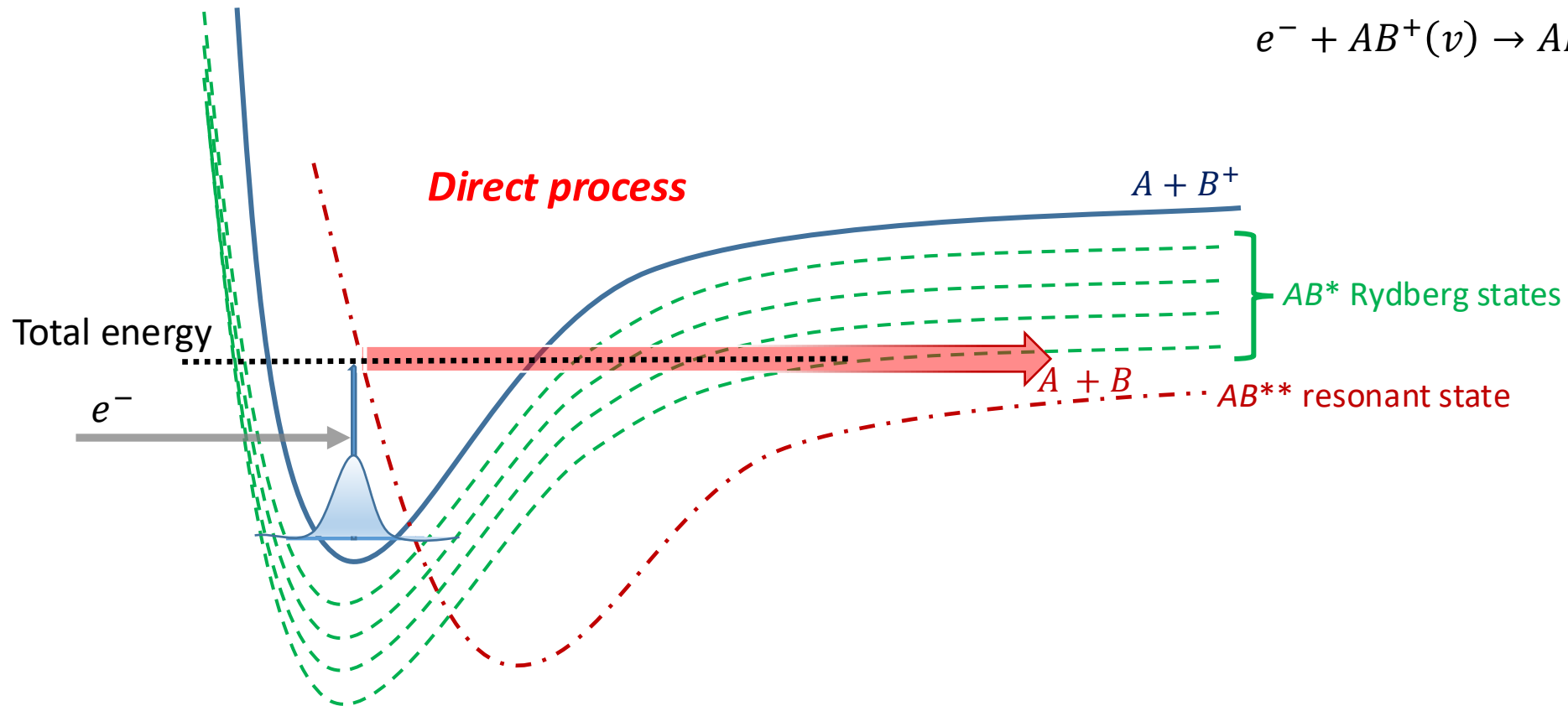
Dissociative recombination



Multichannel Quantum Defect Theory

electron-molecular ion cross sections

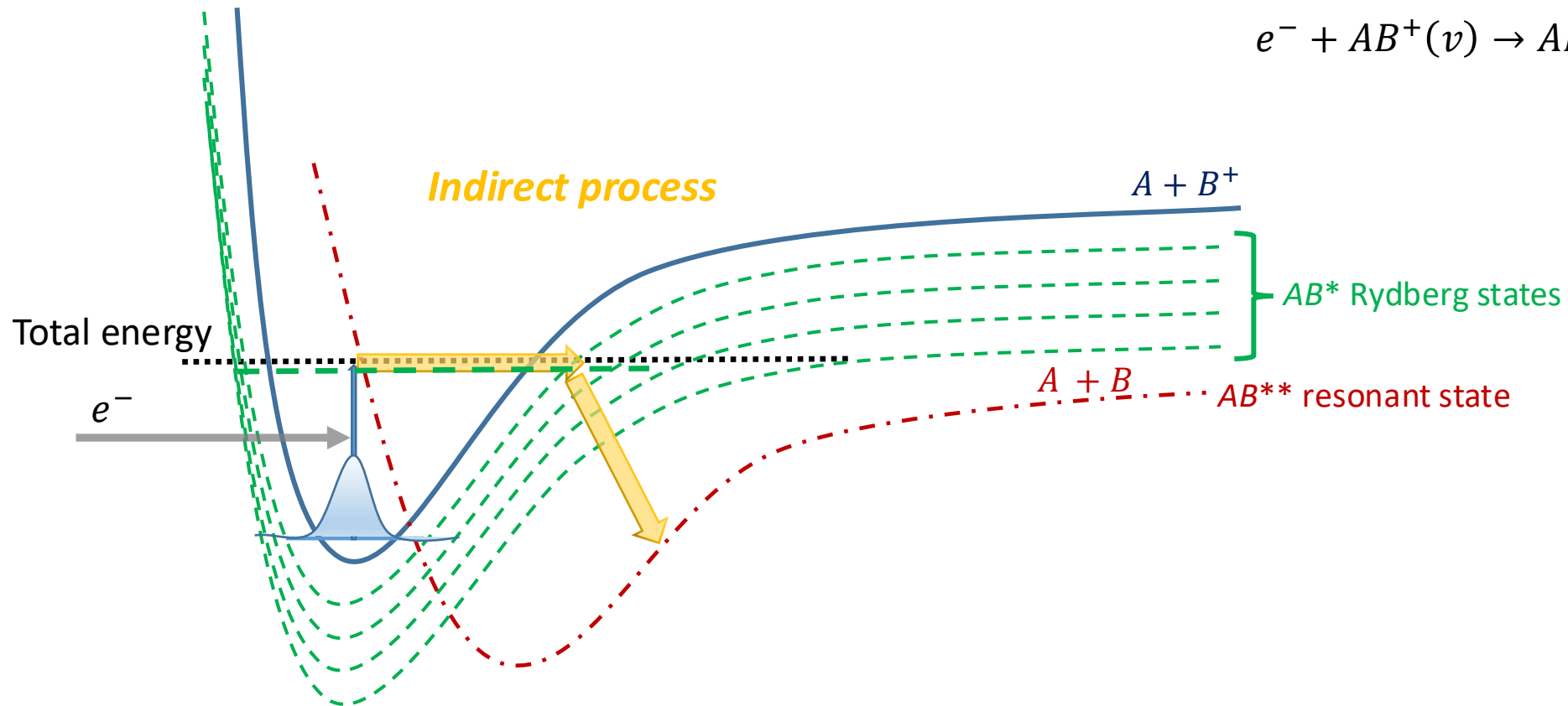
Dissociative recombination



Multichannel Quantum Defect Theory

electron-molecular ion cross sections

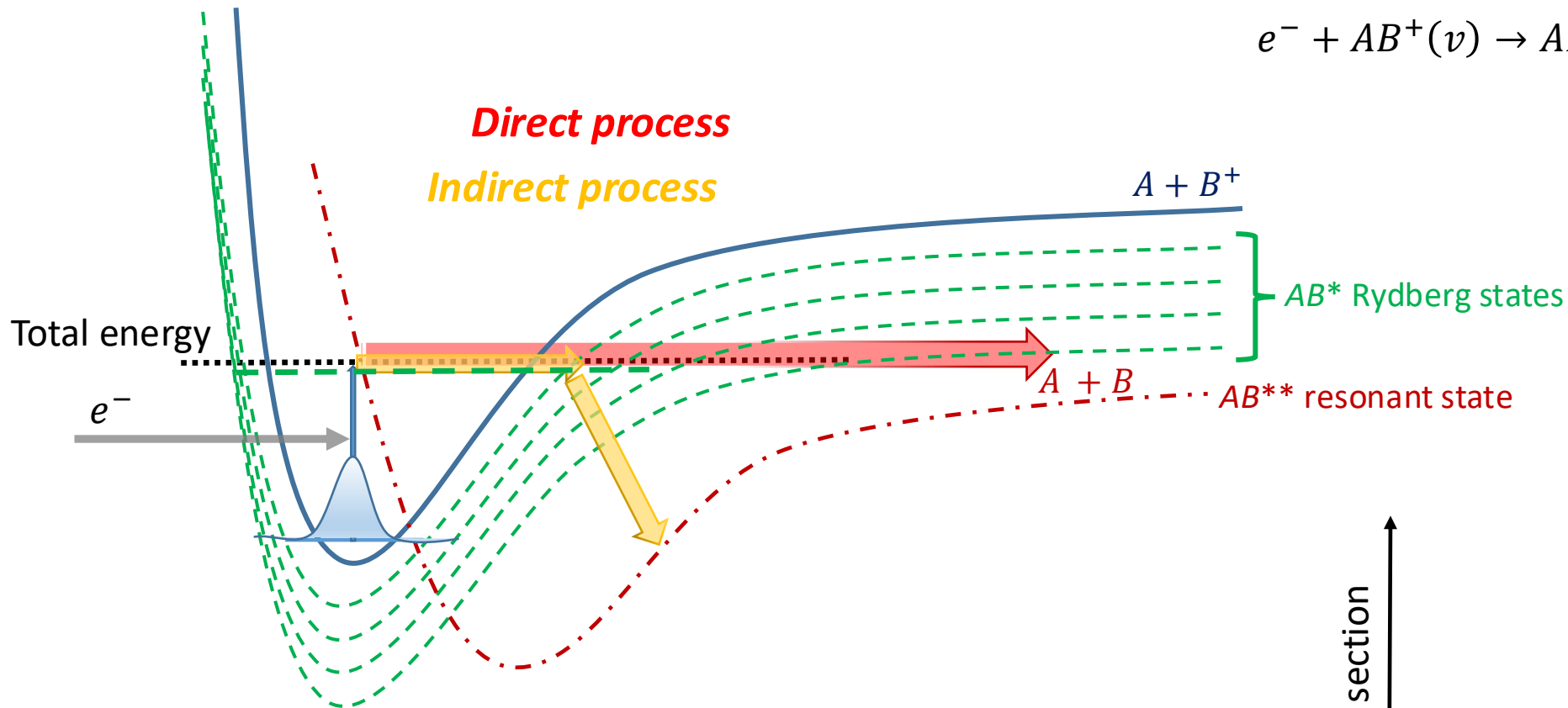
Dissociative recombination



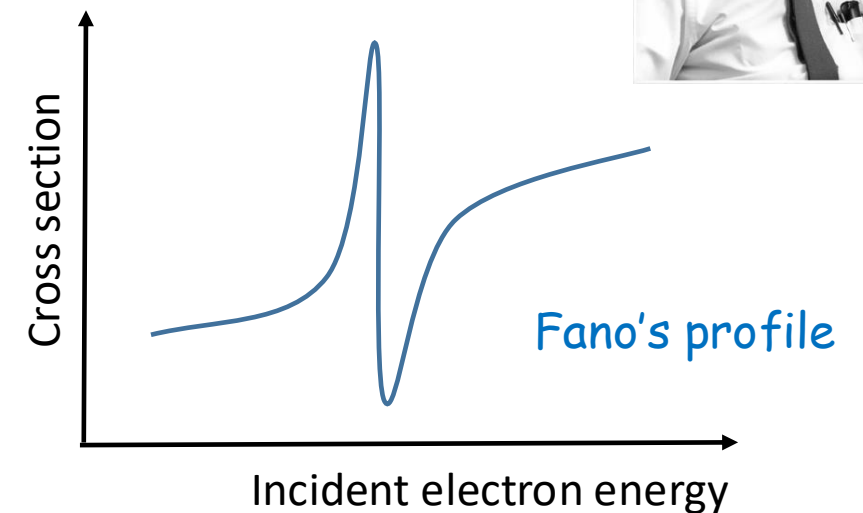
Multichannel Quantum Defect Theory

electron-molecular ion cross sections

Dissociative recombination



Multichannel Quantum Defect Theory



electron- D_2 cross sections

$$\mathbf{D}_2 = \{X^1\Sigma_g^+, b^3\Sigma_u^+, B^1\Sigma_u^+\} = \{X, b, B\}$$

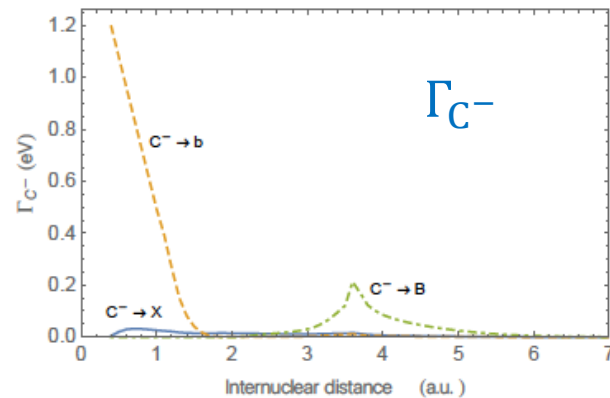
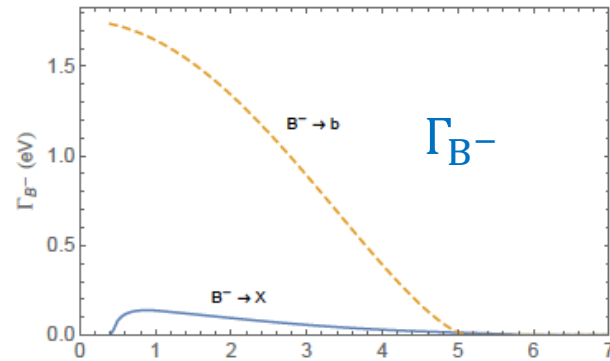
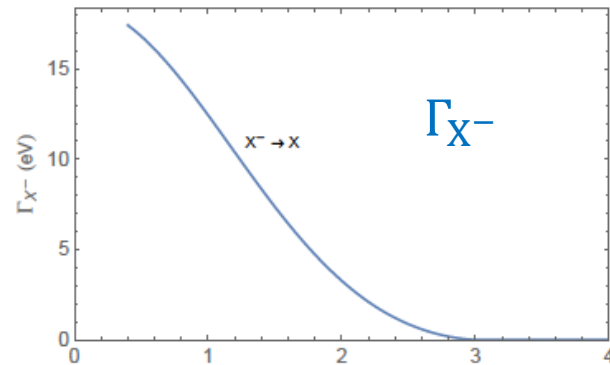
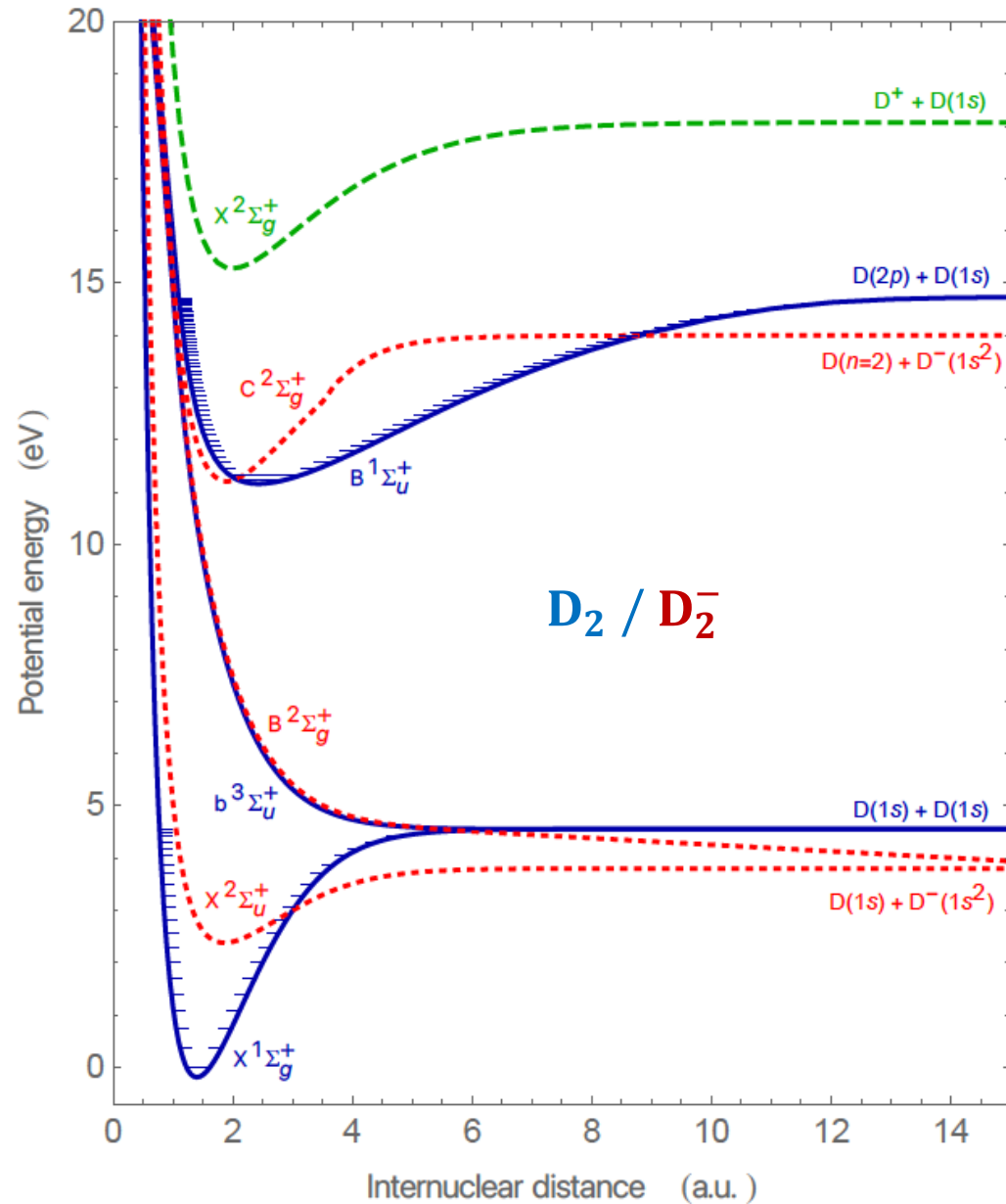
$$\mathbf{D}_2^- = \{X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+\} = \{X^-, B^-, C^-\}$$

Local Complex Potential Model

*First time (in my knowledge) of using this approach to calculate
vibrationally-electronically-excited collisions*

V. Laporta, R. Agnello, G. Fubiani, I. Furno, C. Hill, D. Reiter, and F. Taccogna, *Plasma Phys. Control. Fusion* 63, 085006 (2021)

Potentials and couplings for D_2/D_2^-

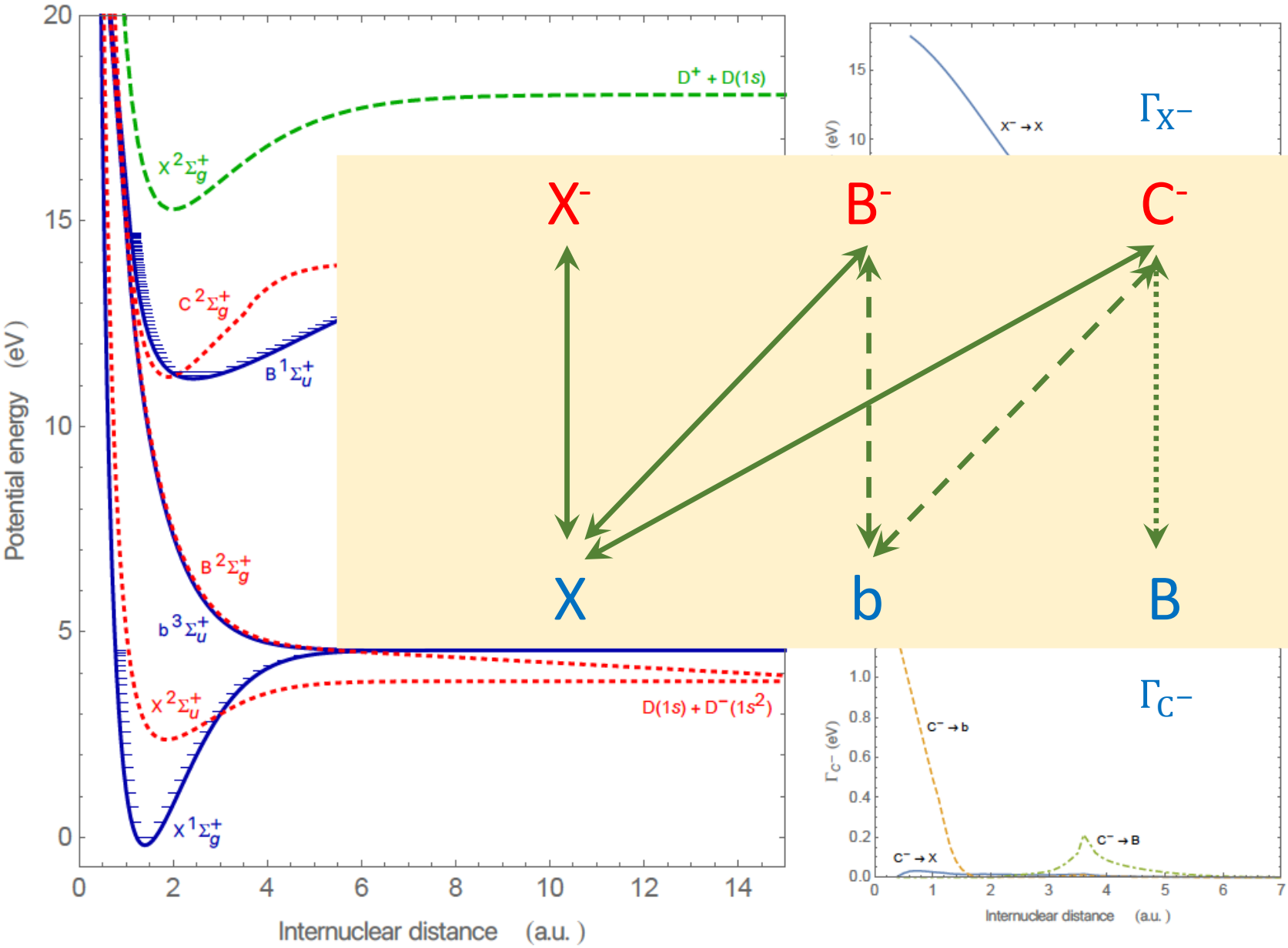


$$\Psi_k = \mathcal{A} \sum_{i,j} a_{i,j,k} \phi_i^N \eta_{i,j} + \sum_i b_{j,k} \phi_j^{N+1}$$

$$R_{ij}(x, E) = \frac{1}{2} \sum_k \frac{u_{ik}(x) u_{jk}(x)}{E_k - E}$$

**R-matrix
calculations**

Potentials and couplings for D₂/D₂⁻



$$\mathcal{A} \sum_{i,j} a_{i,j,k} \phi_i^N \eta_{i,j} + \sum_i b_{j,k} \phi_j^{N+1}$$

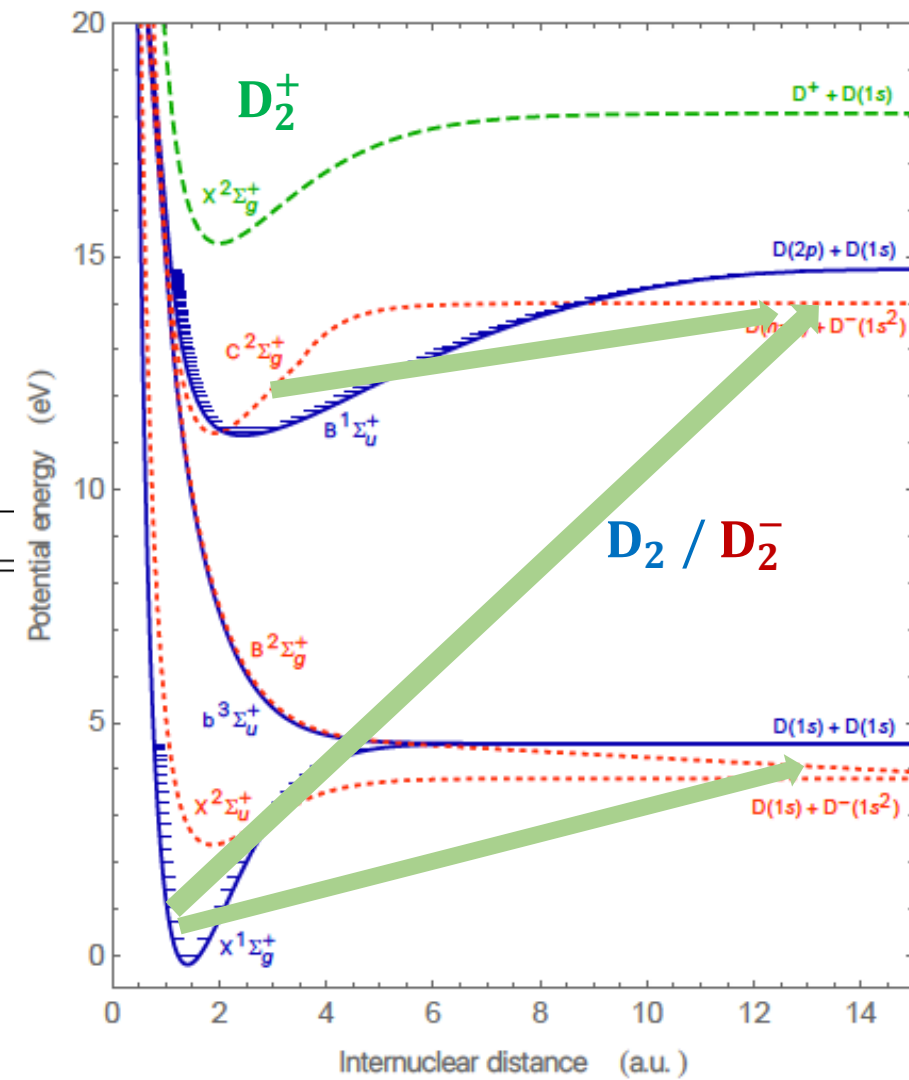
$$R_{ij}(x, E) = \frac{1}{2} \sum_k \frac{u_{ik}(x) u_{jk}(x)}{E_k - E}$$

R-matrix
calculations

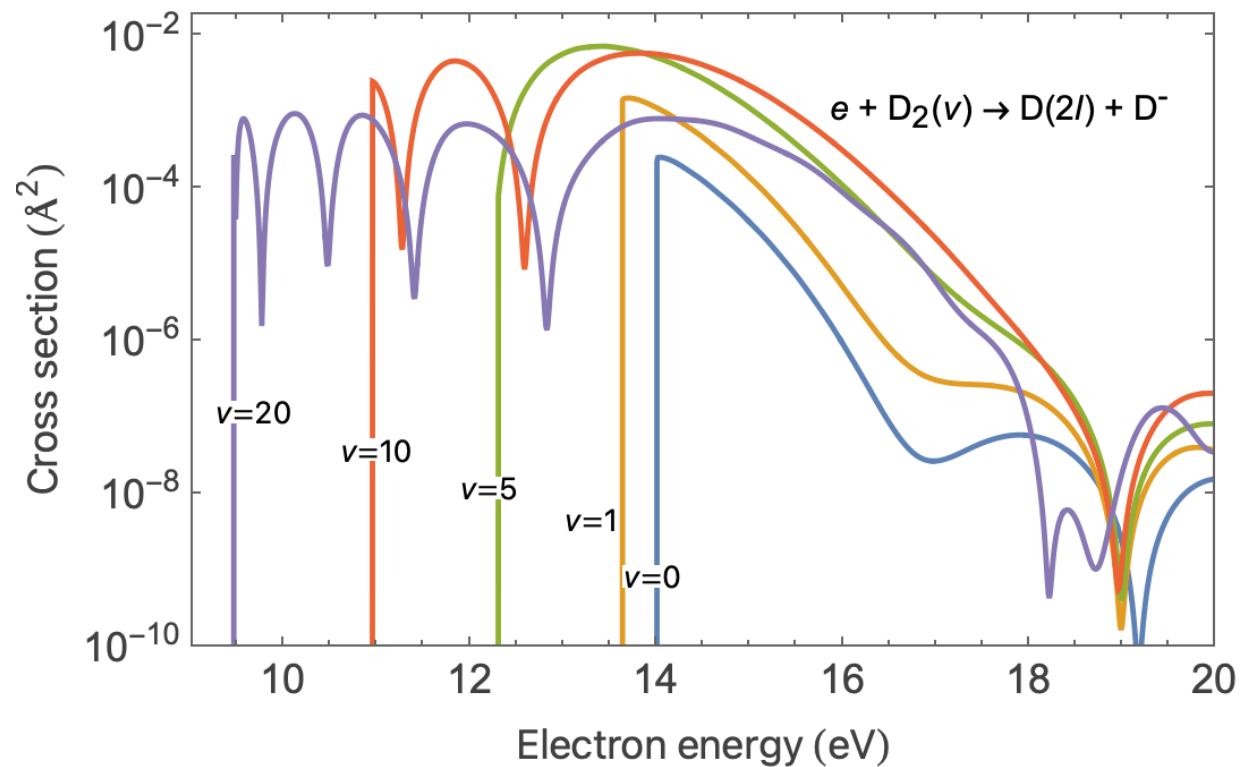
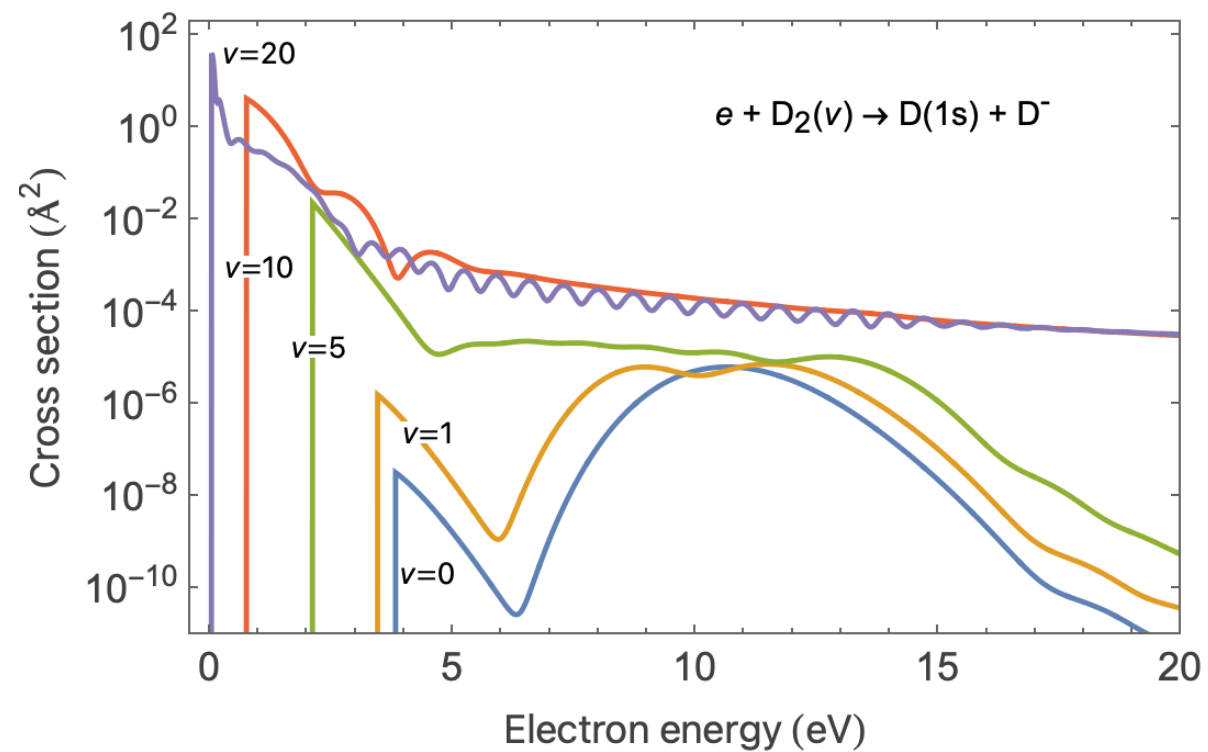
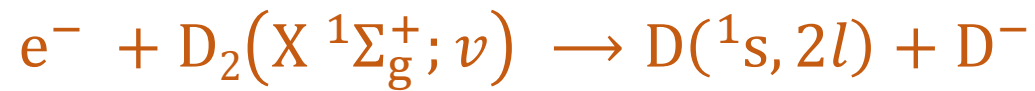
$$\mathbf{D}_2 = \{X^1\Sigma_g^+, b^3\Sigma_u^+, B^1\Sigma_u^+\} = \{X, b, B\}$$

$$\mathbf{D}_2^- = \{X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+\} = \{X^-, B^-, C^-\}$$

Label	Reaction
<i>Vibrational excitation</i>	
VE1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; v')$
VE2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; v')$
VE3	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; v')$
<i>Dissociative electron attachment</i>	
DA1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+) \rightarrow D(1s) + D^-(1s^2)$
DA2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow D(n=2) + D^-(1s^2)$
DA3	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow D(n=2) + D^-(1s^2)$
<i>Dissociative excitation</i>	
DE1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(b^3\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE3	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(2p) + D(1s)$
DE4	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(2p) + D(1s)$
DE5	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(b^3\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE6	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$



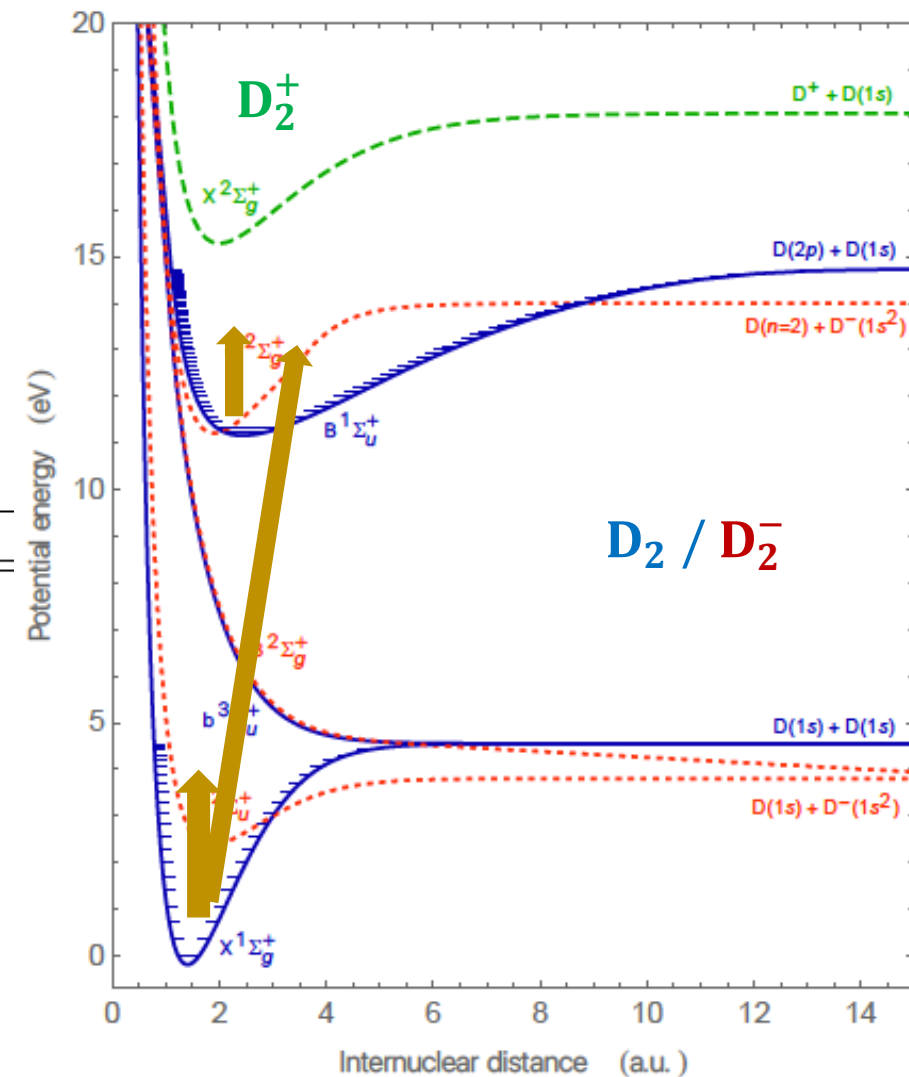
Vibrationally resolved *dissociative electron attachment* cross sections



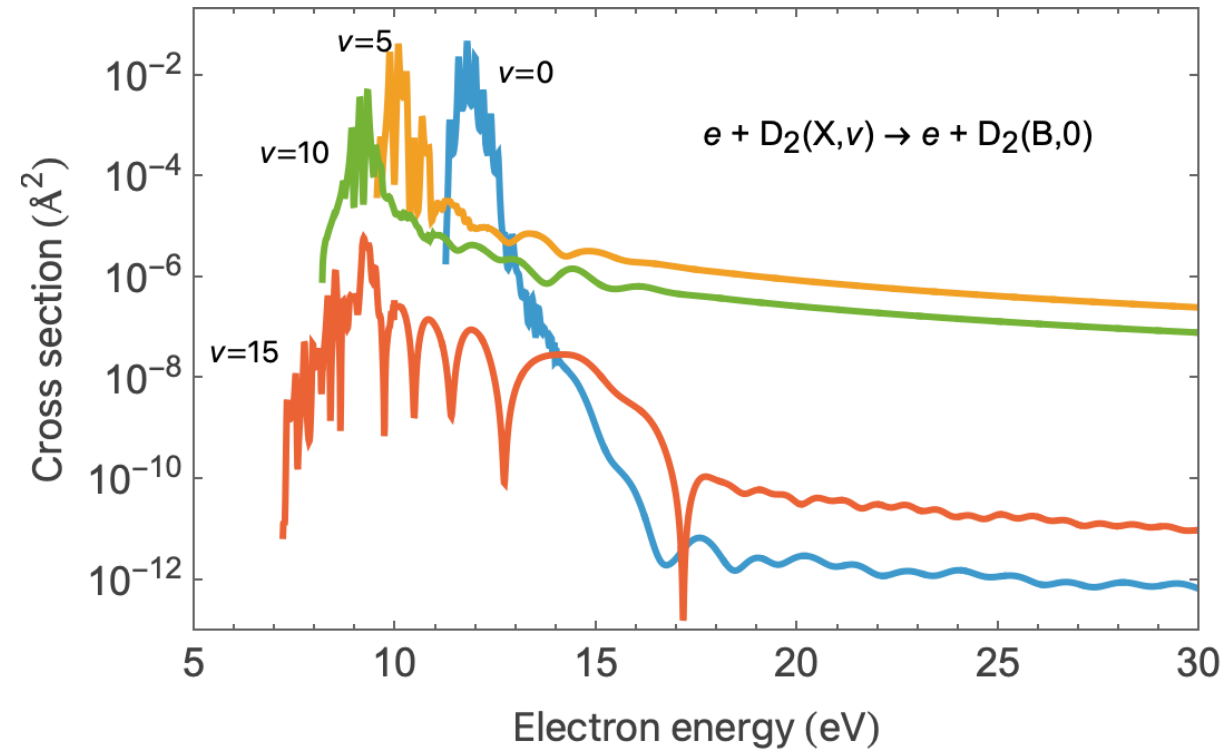
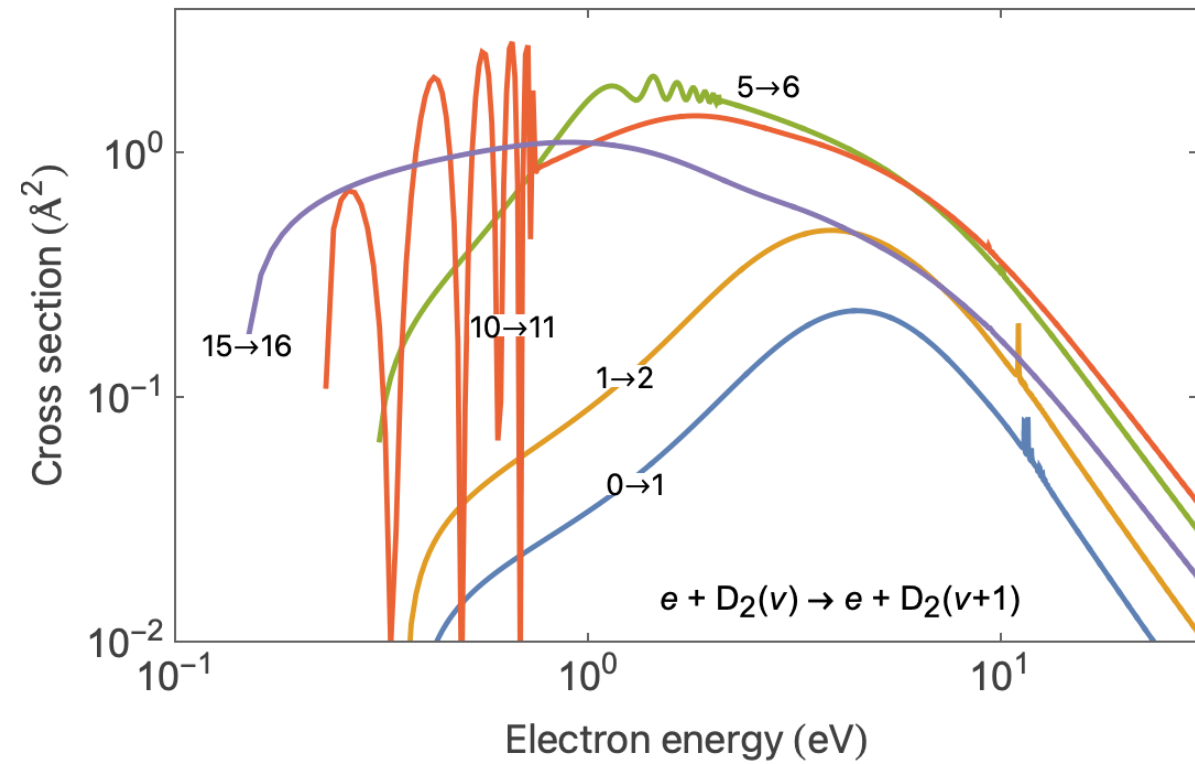
$$\mathbf{D}_2 = \{X^1\Sigma_g^+, b^3\Sigma_u^+, B^1\Sigma_u^+\} = \{X, b, B\}$$

$$\mathbf{D}_2^- = \{X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+\} = \{X^-, B^-, C^-\}$$

Label	Reaction
<i>Vibrational excitation</i>	
VE1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; v')$
VE2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; v')$
VE3	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; v')$
<i>Dissociative electron attachment</i>	
DA1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+) \rightarrow D(1s) + D^-(1s^2)$
DA2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow D(n=2) + D^-(1s^2)$
DA3	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow D(n=2) + D^-(1s^2)$
<i>Dissociative excitation</i>	
DE1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(b^3\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE3	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(2p) + D(1s)$
DE4	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(2p) + D(1s)$
DE5	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(b^3\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE6	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$



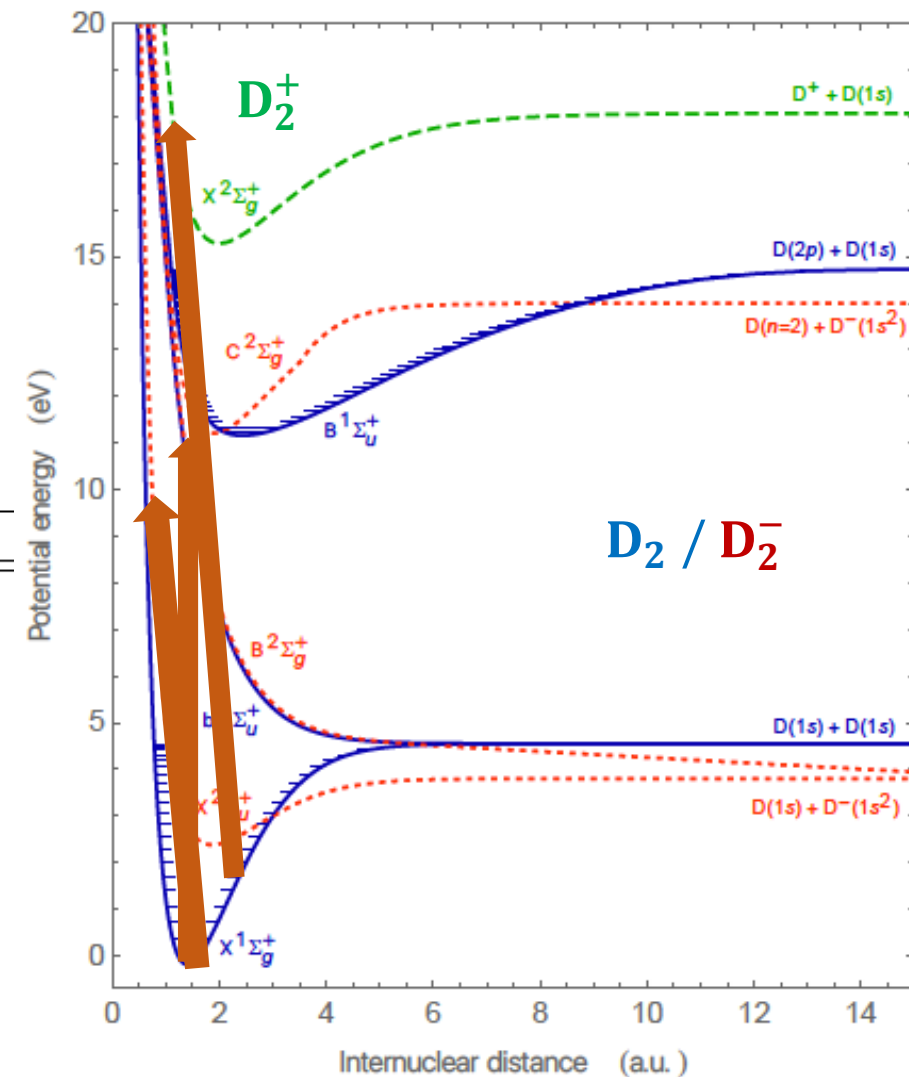
vibrational excitation cross sections



$$\mathbf{D}_2 = \{X^1\Sigma_g^+, b^3\Sigma_u^+, B^1\Sigma_u^+\} = \{X, b, B\}$$

$$\mathbf{D}_2^- = \{X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+\} = \{X^-, B^-, C^-\}$$

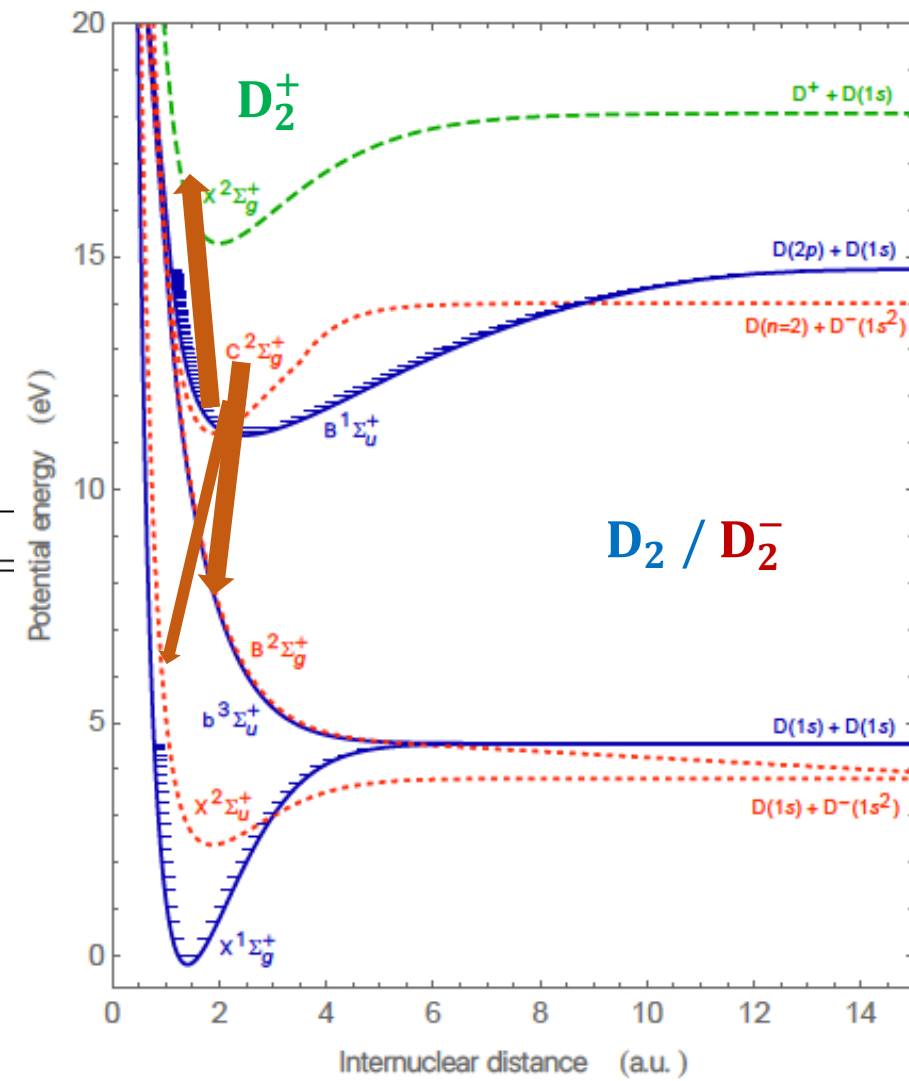
Label	Reaction
<i>Vibrational excitation</i>	
VE1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; v')$
VE2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; v')$
VE3	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; v')$
<i>Dissociative electron attachment</i>	
DA1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+) \rightarrow D(1s) + D^-(1s^2)$
DA2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow D(n=2) + D^-(1s^2)$
DA3	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow D(n=2) + D^-(1s^2)$
<i>Dissociative excitation</i>	
DE1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(b^3\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE3	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(2p) + D(1s)$
DE4	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(2p) + D(1s)$
DE5	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(b^3\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE6	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$



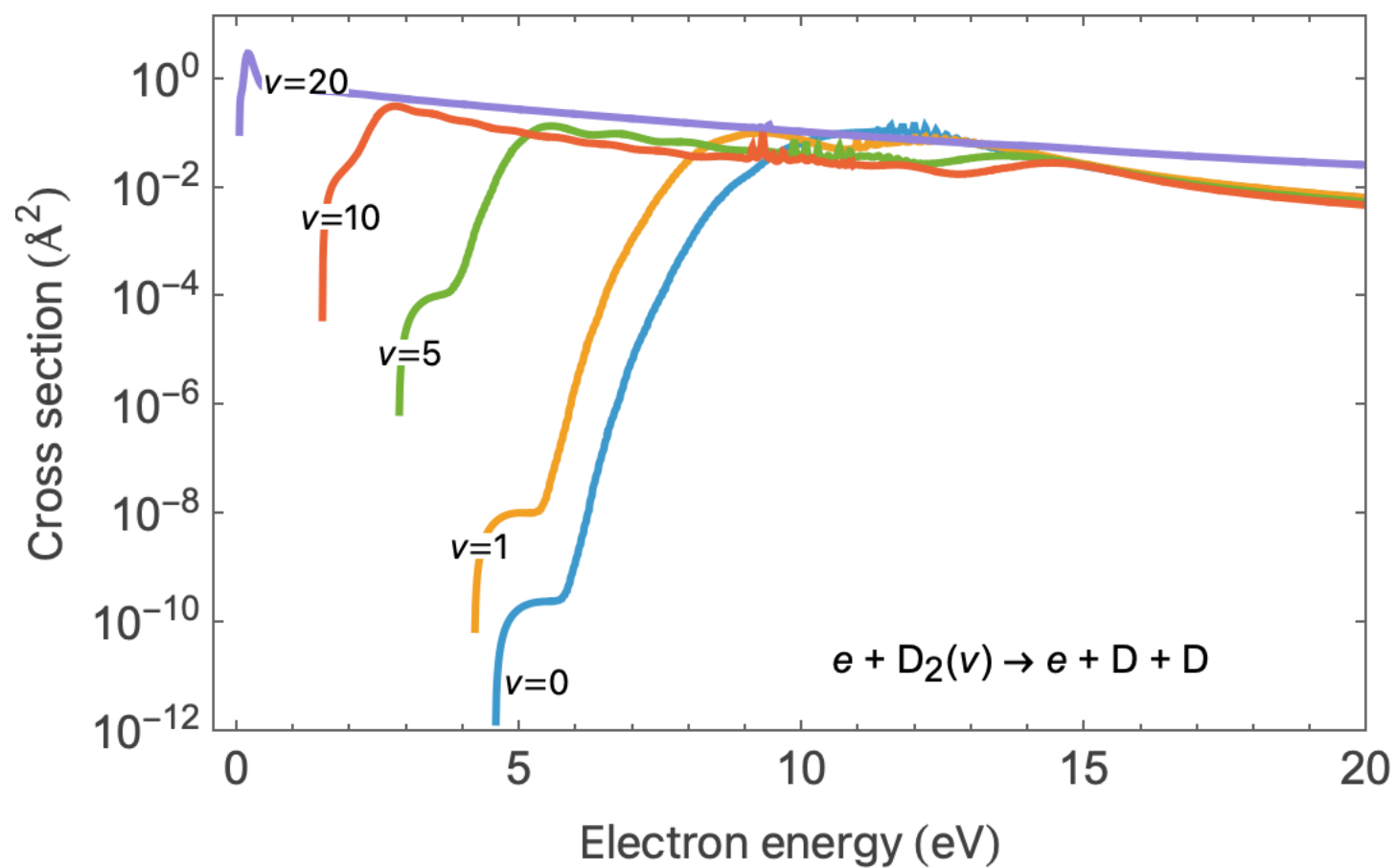
$$\mathbf{D}_2 = \{X^1\Sigma_g^+, b^3\Sigma_u^+, B^1\Sigma_u^+\} = \{X, b, B\}$$

$$\mathbf{D}_2^- = \{X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+\} = \{X^-, B^-, C^-\}$$

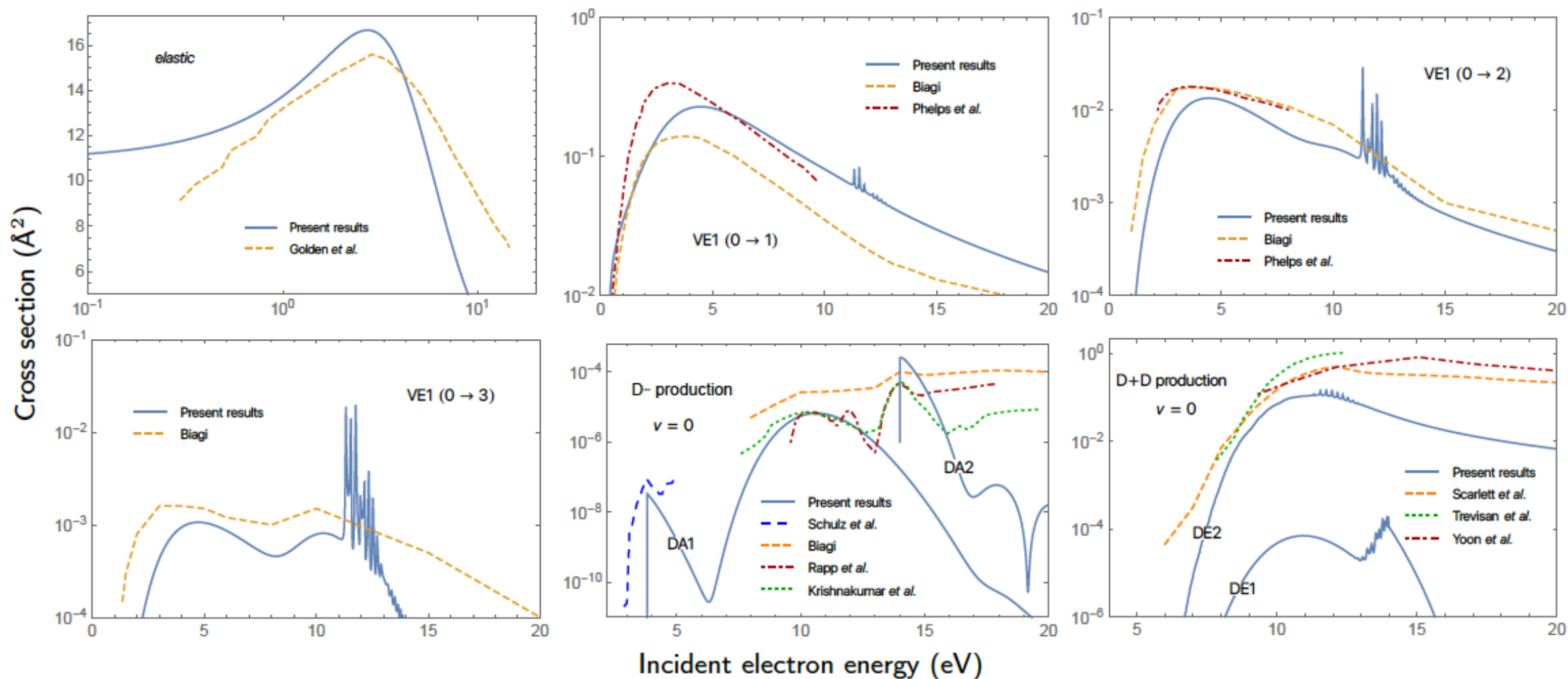
Label	Reaction
<i>Vibrational excitation</i>	
VE1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; v')$
VE2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; v')$
VE3	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; v')$
<i>Dissociative electron attachment</i>	
DA1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+) \rightarrow D(1s) + D^-(1s^2)$
DA2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow D(n=2) + D^-(1s^2)$
DA3	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow D(n=2) + D^-(1s^2)$
<i>Dissociative excitation</i>	
DE1	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(X^2\Sigma_u^+, B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE2	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(B^2\Sigma_g^+, C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(b^3\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE3	$e(\epsilon) + D_2(X^1\Sigma_g^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(2p) + D(1s)$
DE4	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(B^1\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(2p) + D(1s)$
DE5	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(b^3\Sigma_u^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$
DE6	$e(\epsilon) + D_2(B^1\Sigma_u^+; v) \rightarrow D_2^-(C^2\Sigma_g^+) \rightarrow e(\epsilon') + D_2(X^1\Sigma_g^+; \epsilon_c) \rightarrow e(\epsilon') + D(1s) + D(1s)$



*Vibrationally resolved **dissociation** cross sections*

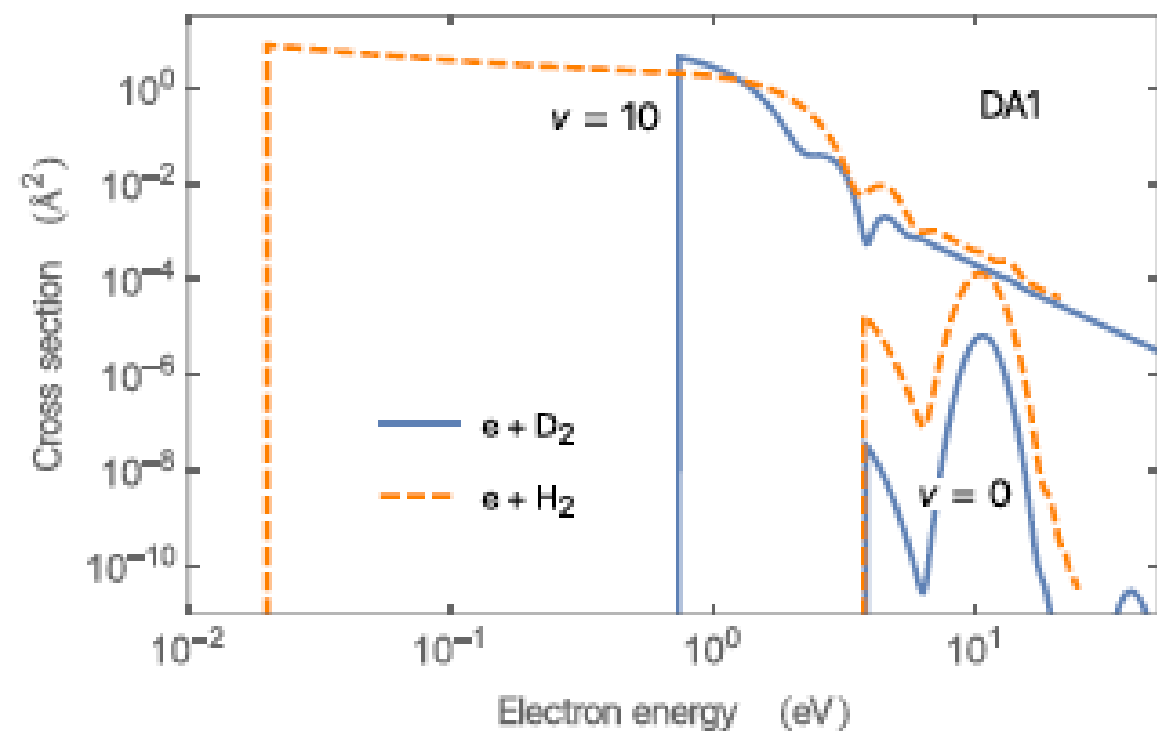


Comparison with data in literature

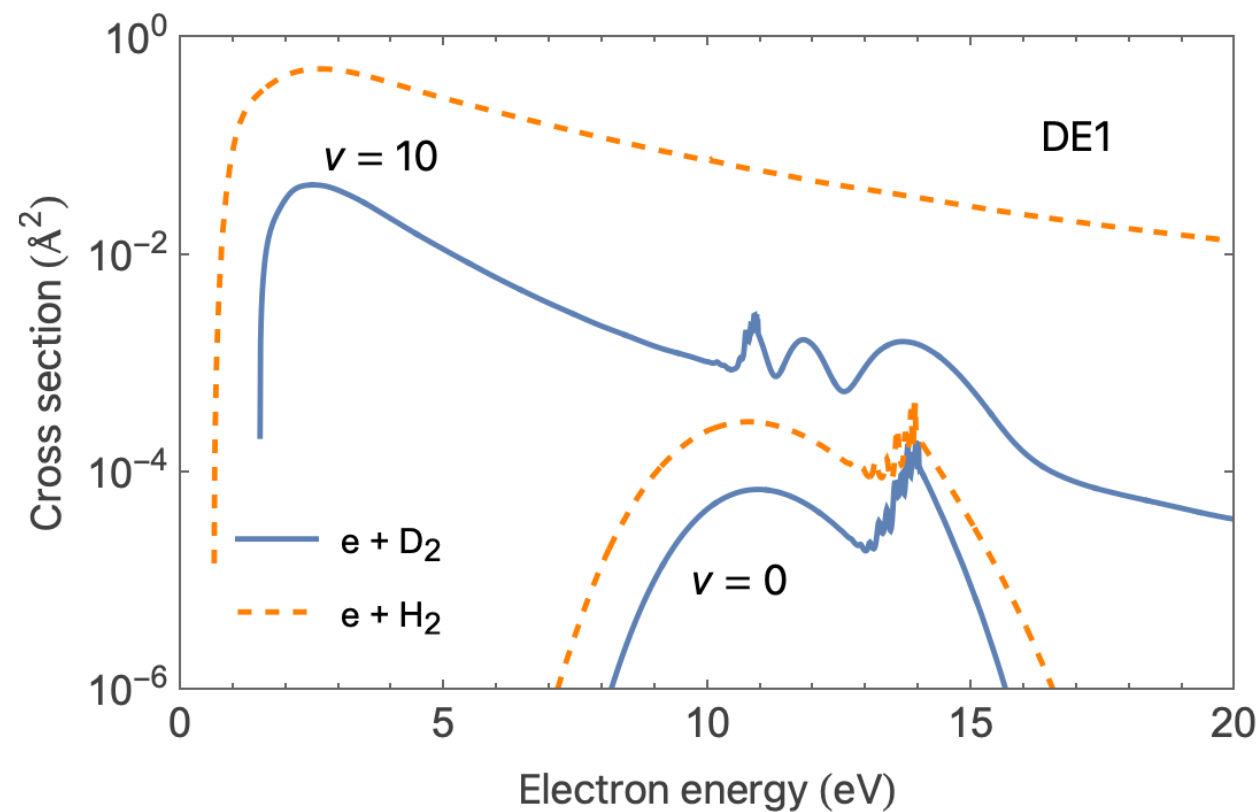


Isotopic effect for D₂ and H₂

dissociative electron attachment

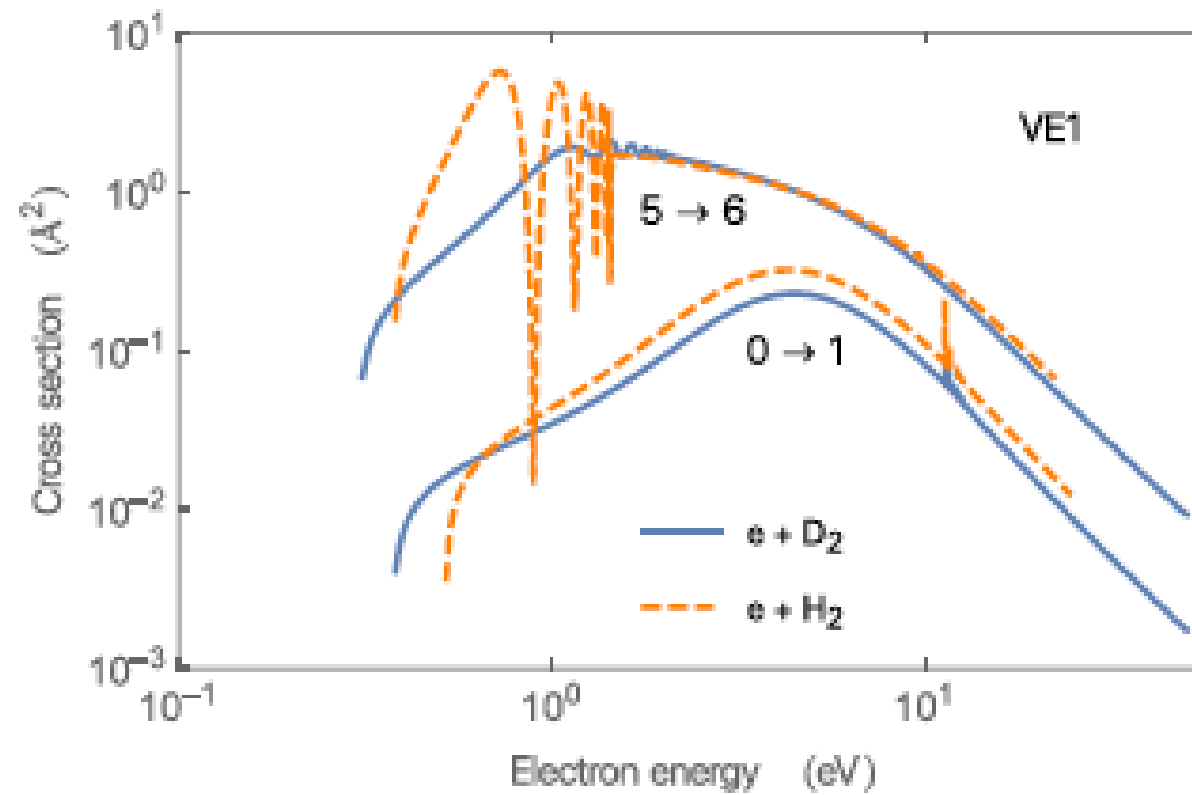


Dissociative excitation



Isotopic effect for D₂ and H₂

vibrational excitation



$e + D_2(X, v) \rightarrow e + D_2(X, w)$ elastic, VE1

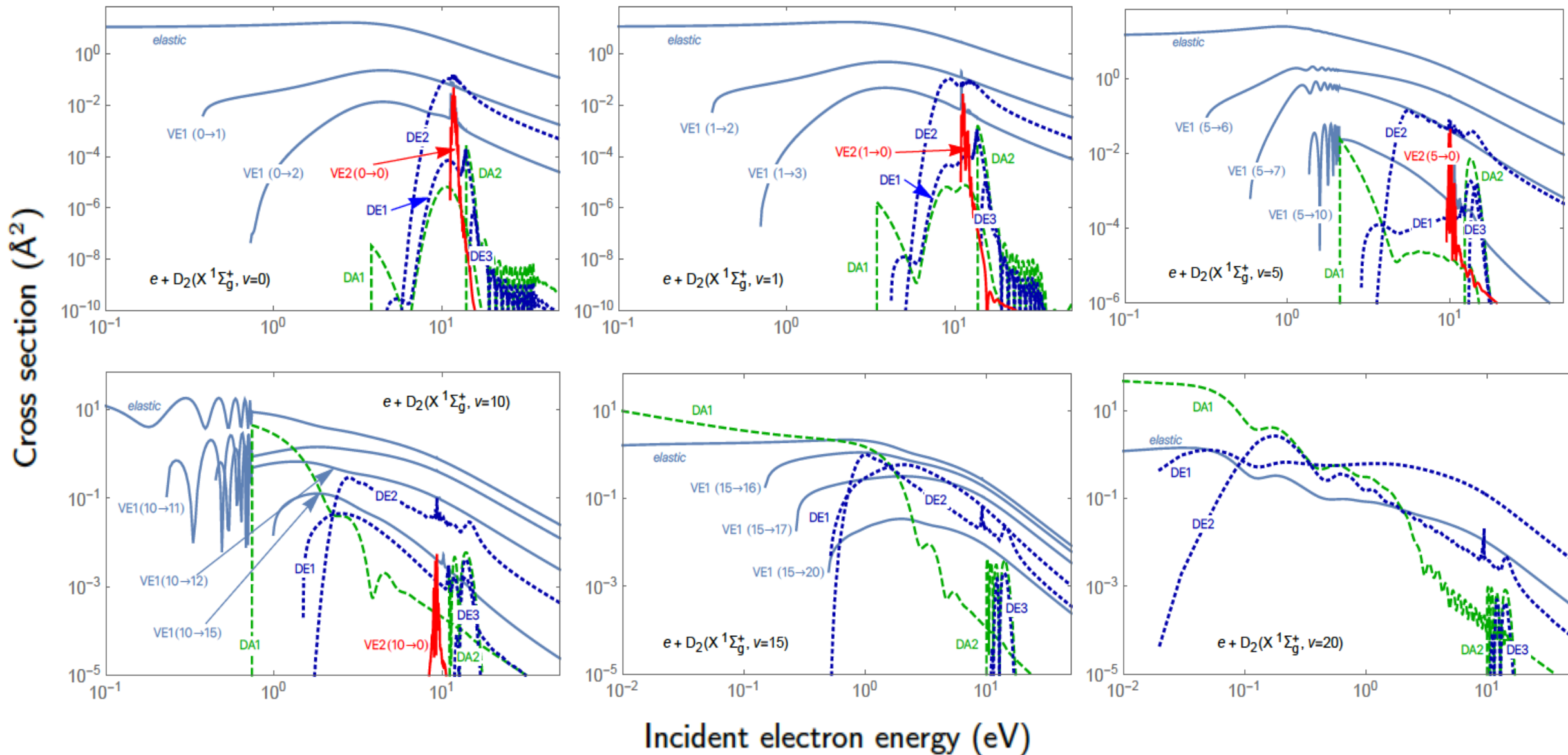
$e + D_2(X, v) \rightarrow D(1s) + D^-(1s^2)$ DA1

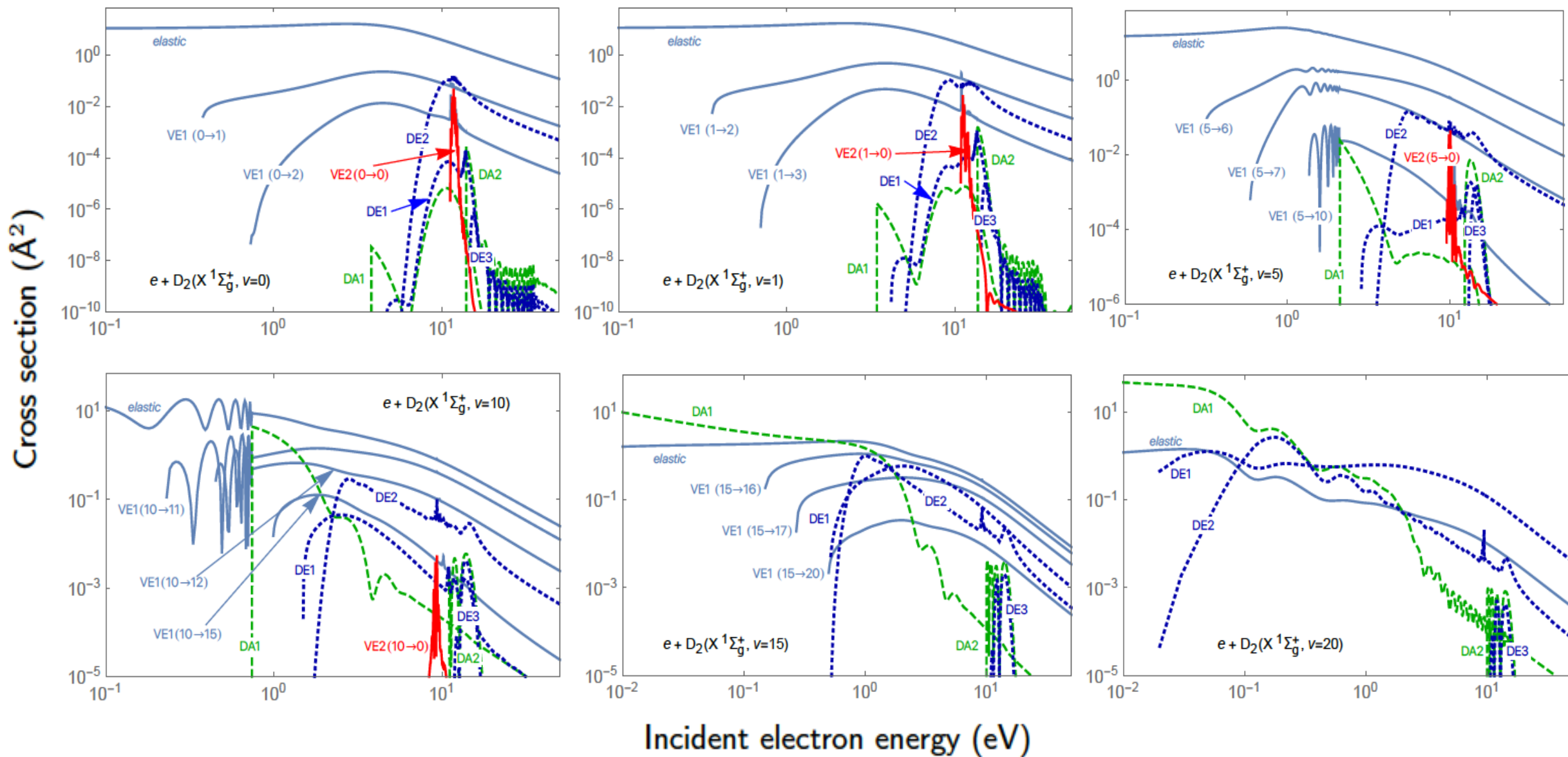
$e + D_2(X, v) \rightarrow D(n=2) + D^-(1s^2)$ DA2

$e + D_2(X, v) \rightarrow e + D(1s) + D(1s)$ DE1

$e + D_2(X, v) \rightarrow e + D(1s) + D(1s)$ DE2

$e + D_2(X, v) \rightarrow e + D(2p) + D(1s)$ DE3





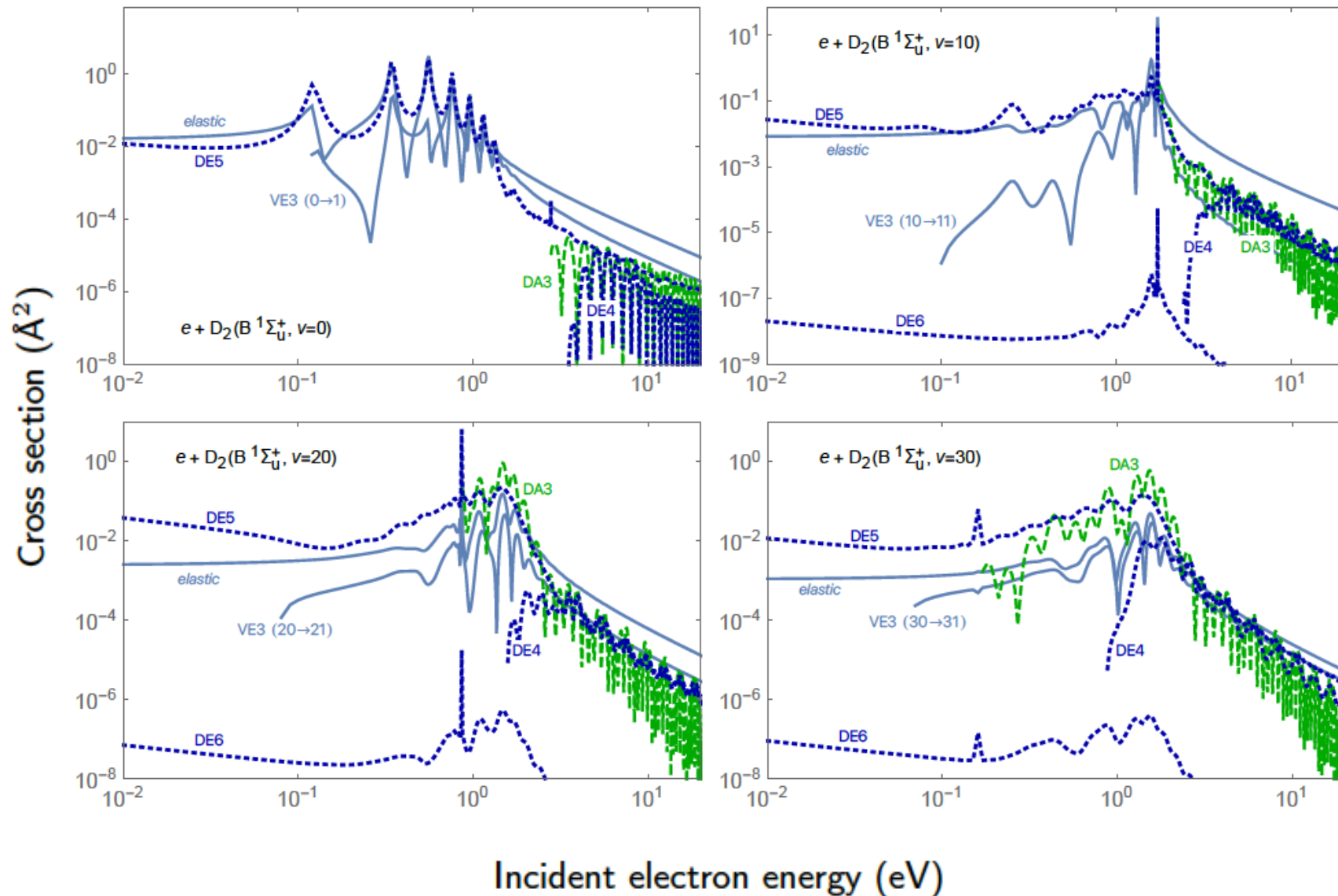
$$e + D_2(B, v) \rightarrow e + D_2(B, w) \quad \text{elastic, VE3}$$

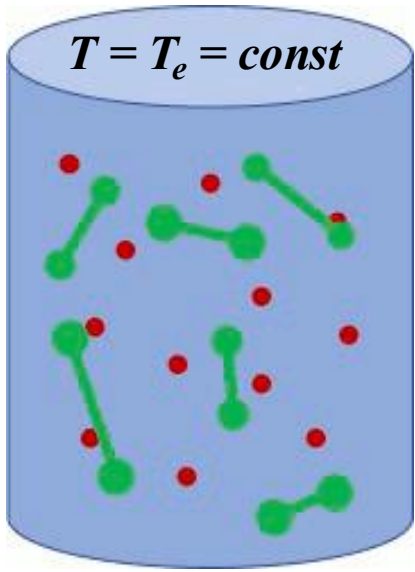
$$e + D_2(B, v) \rightarrow D(n=2) + D^-(1s^2) \quad \text{DA3}$$

$$e + D_2(B, v) \rightarrow e + D(2p) + D(1s) \quad \text{DE4}$$

$$e + D_2(B, v) \rightarrow e + D(1s) + D(1s) \quad \text{DE5}$$

$$e + D_2(B, v) \rightarrow e + D(1s) + D(1s) \quad \text{DE6}$$



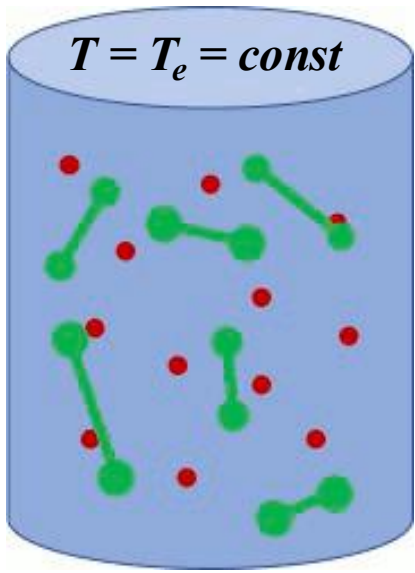


Electron-vibration energy exchange

State-to-State kinetics for electron-D₂ collisions

Master equation approach

$$\frac{dn_v}{dt} = n_e \sum_{w=0}^{20} [k_{w,v} n_w - k_{v,w} n_v] , \quad v = 0, \dots, 20 ,$$

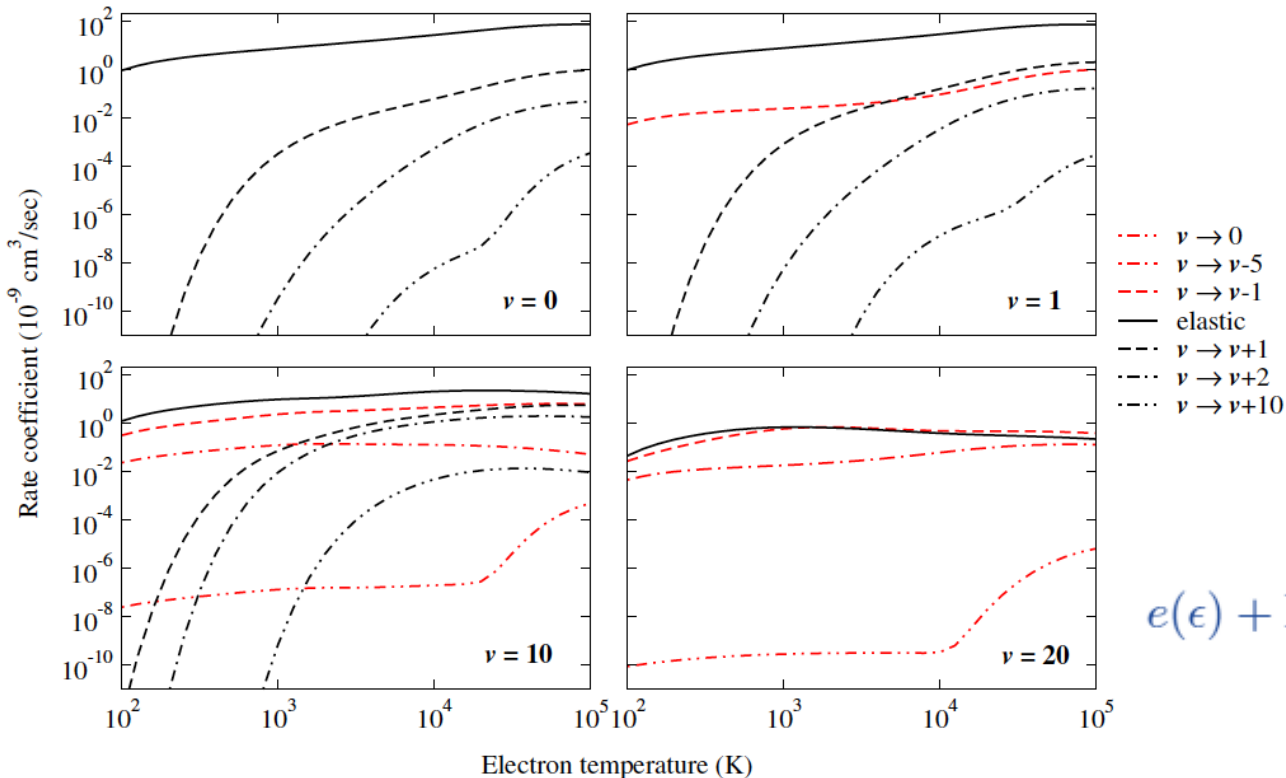


Electron-vibration energy exchange

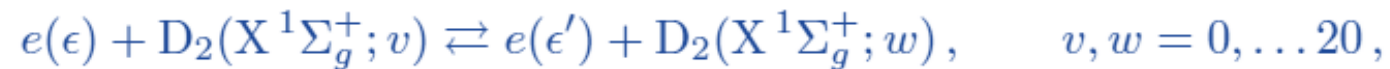
State-to-State kinetics for electron-D₂ collisions

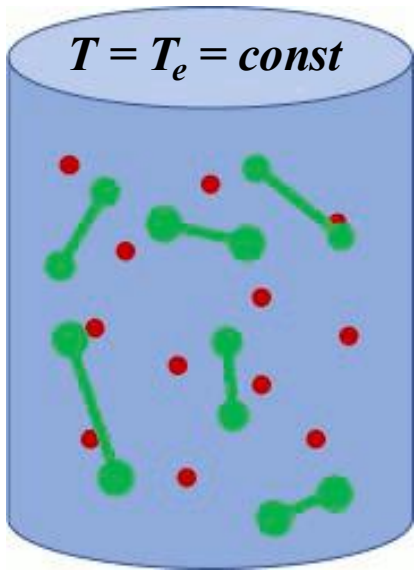
$$\frac{dn_v}{dt} = n_e \sum_{w=0}^{20} [k_{w,v} n_w - k_{v,w} n_v] , \quad v = 0, \dots, 20 ,$$

Master equation approach



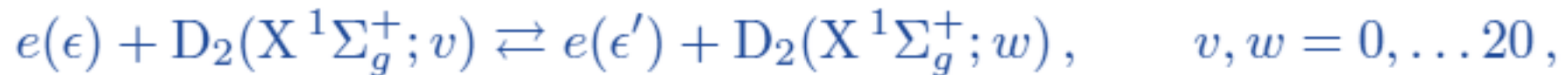
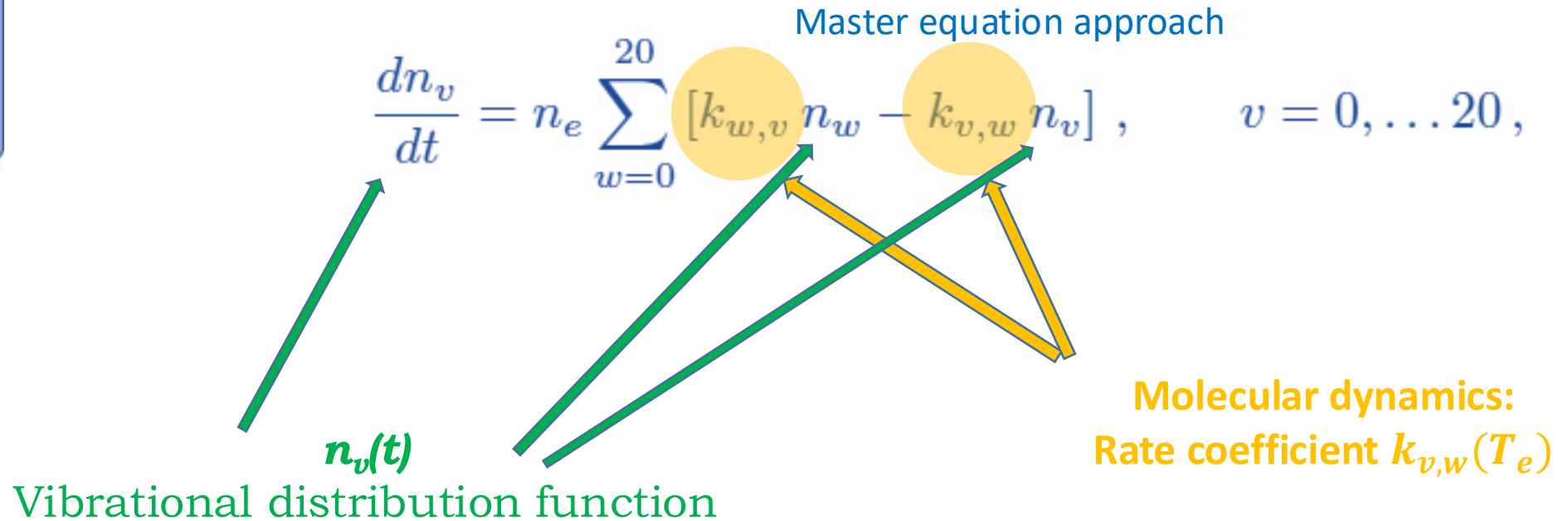
Molecular dynamics:
Rate coefficient $k_{v,w}(T_e)$

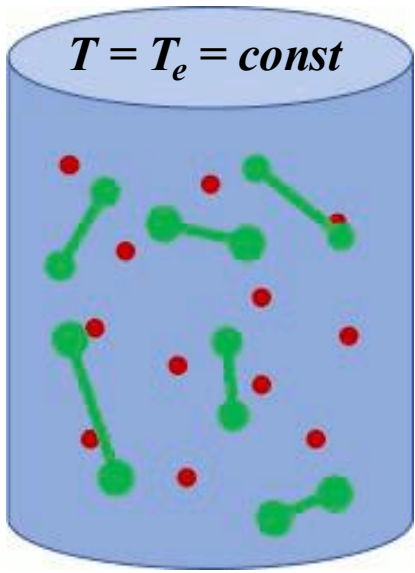




Electron-vibration energy exchange

State-to-State kinetics for electron-D₂ collisions



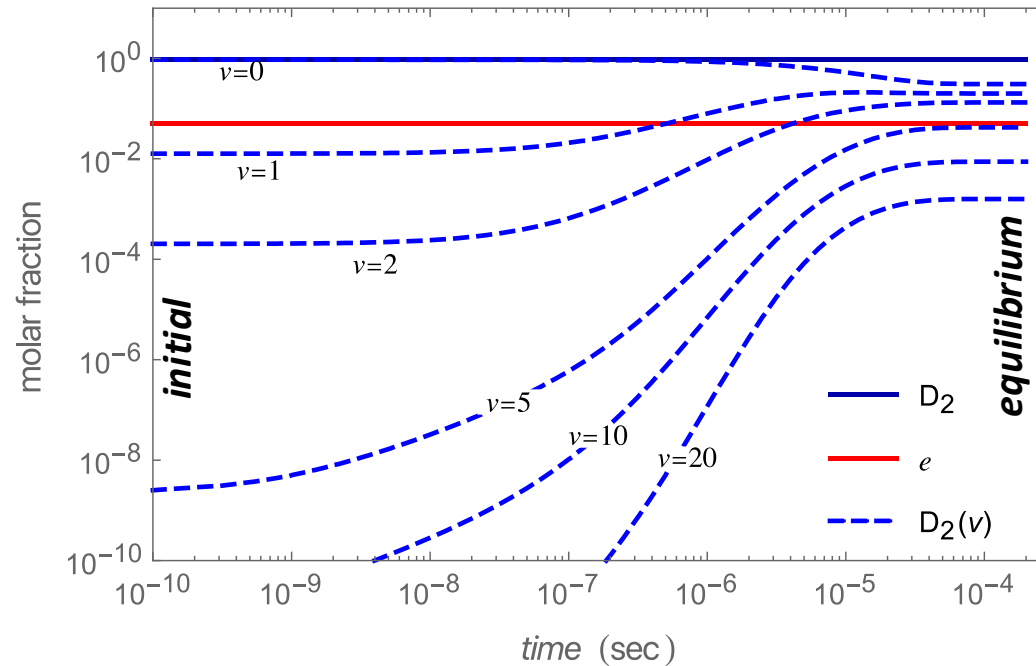


Electron-vibration energy exchange

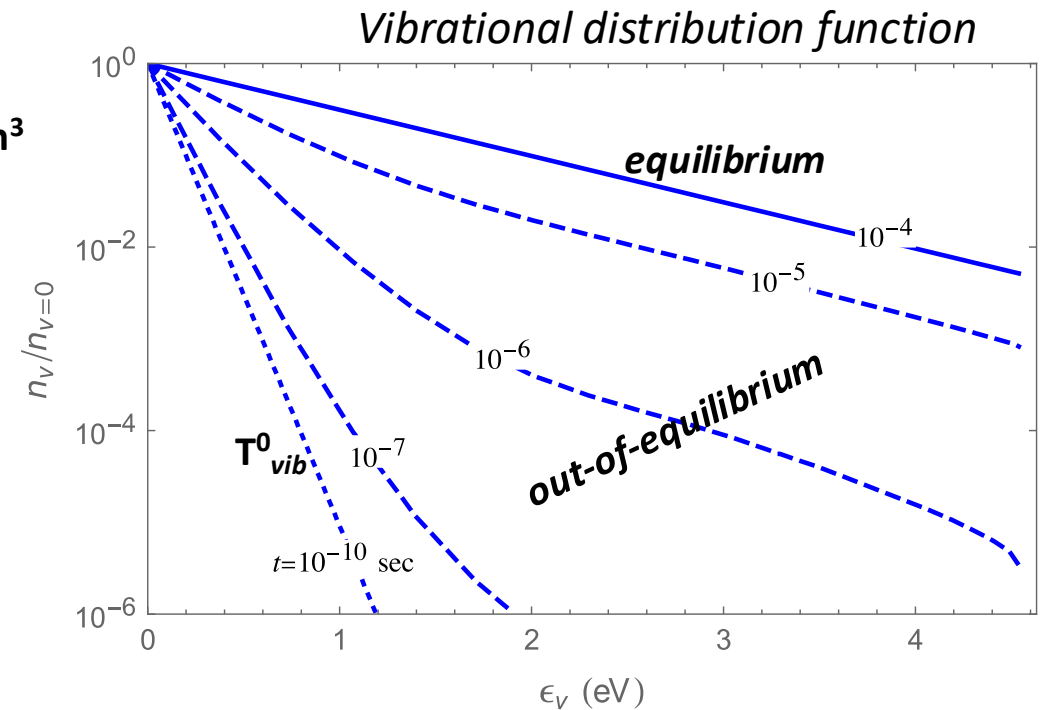
State-to-State kinetics for electron-D₂ collisions

Master equation approach

$$\frac{dn_v}{dt} = n_e \sum_{w=0}^{20} [k_{w,v} n_w - k_{v,w} n_v] , \quad v = 0, \dots, 20 ,$$



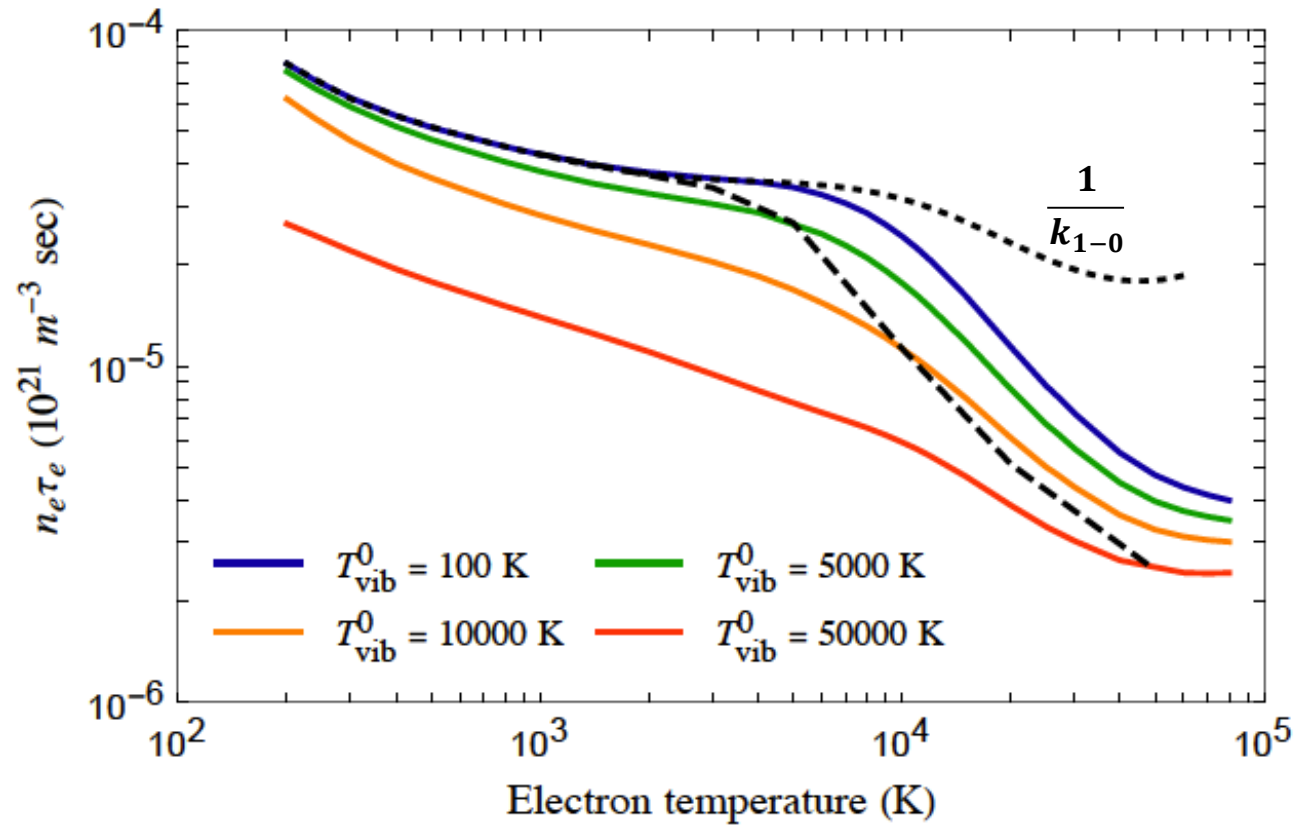
$n_{\text{tot}} = 10^{22} \text{ part/m}^3$
 95% of D_2
 5% of e
 $T_{\text{gas}} = 10000 \text{ K}$
 $T_{\text{vib}}^0 = 1000 \text{ K}$



Electron-vibration energy exchange

Vibrational Relaxation time of D₂

$$\frac{dE_{vib}}{dt} = \frac{E_{vib}^* - E_{vib}}{\tau_e},$$



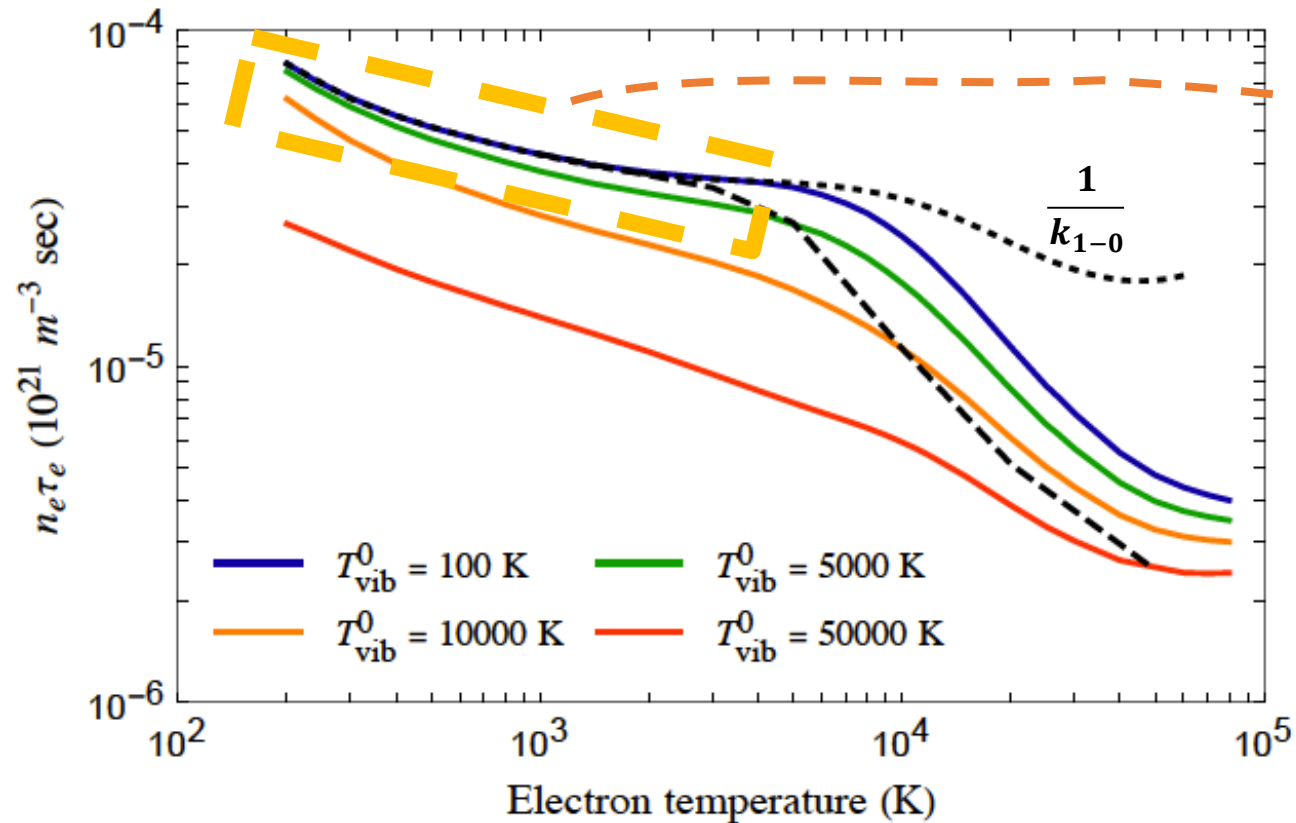
$n_{\text{tot}} = 10^{22} \text{ part/m}^3$

95% of D₂ 5% of e

Electron-vibration energy exchange

Vibrational Relaxation time of D₂

$$\frac{dE_{vib}}{dt} = \frac{E_{vib}^* - E_{vib}}{\tau_e},$$



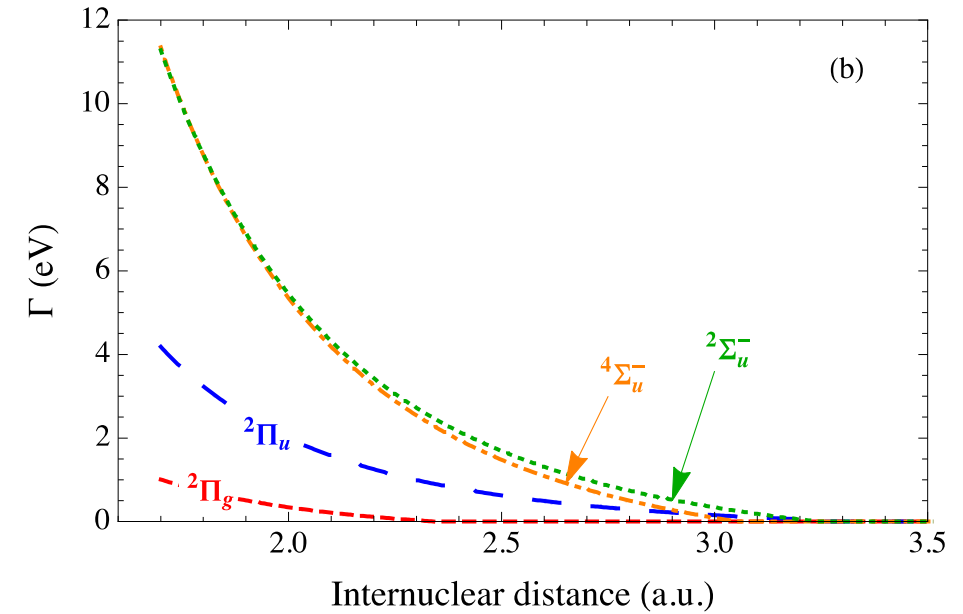
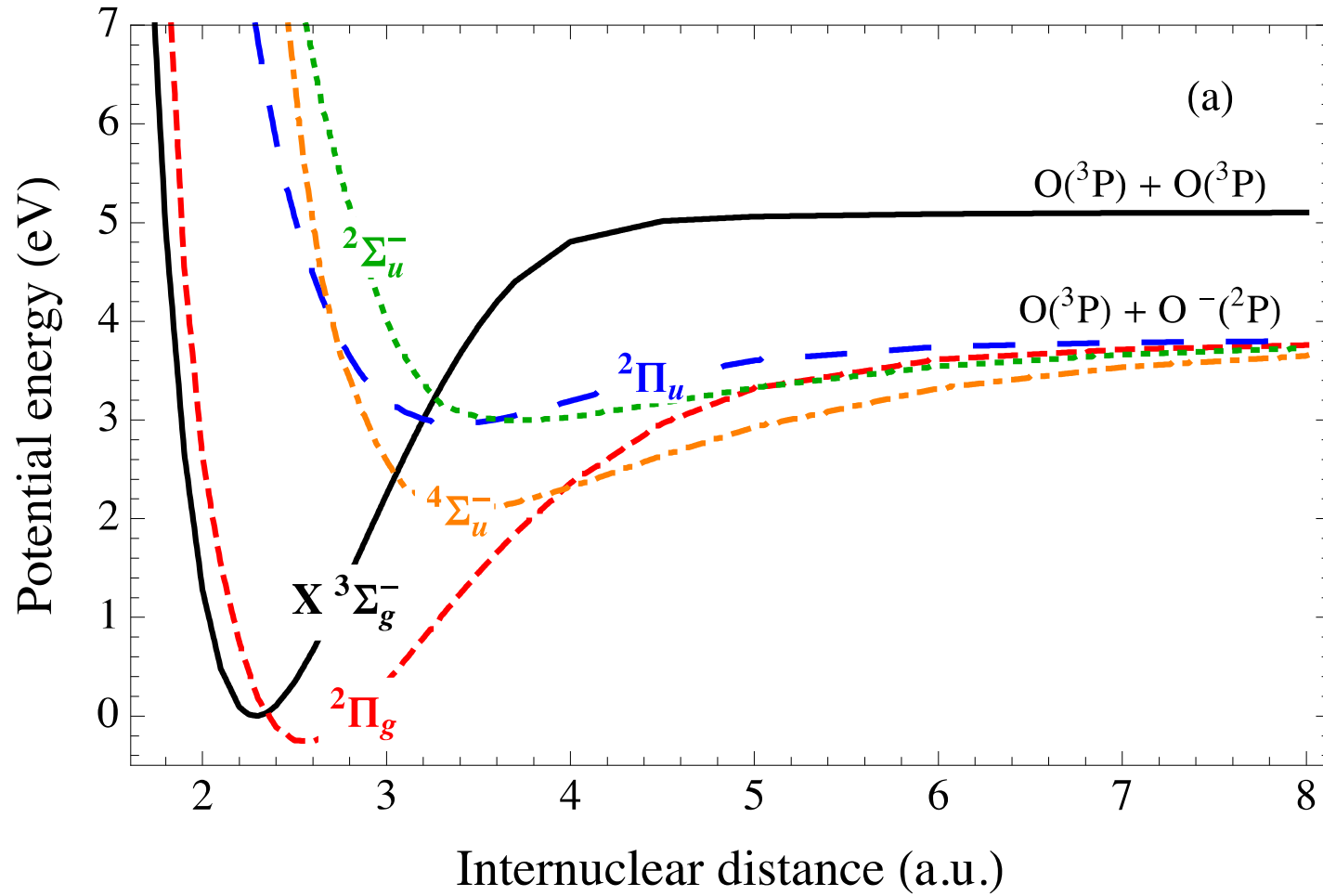
Landau-Teller model

$$\tau_{LT}^{-1} = n_A k_{1,0} (1 - \exp(-\hbar\omega/k_B T)).$$

$$n_{\text{tot}} = 10^{22} \text{ part/m}^3$$

95% of D₂ 5% of e

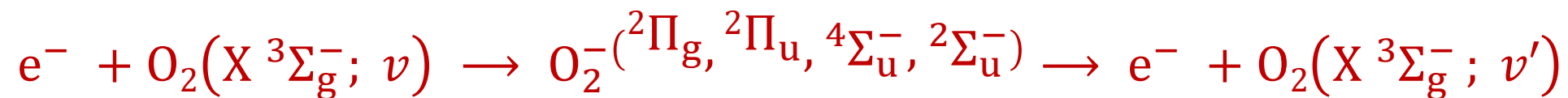
electron-O₂ cross sections



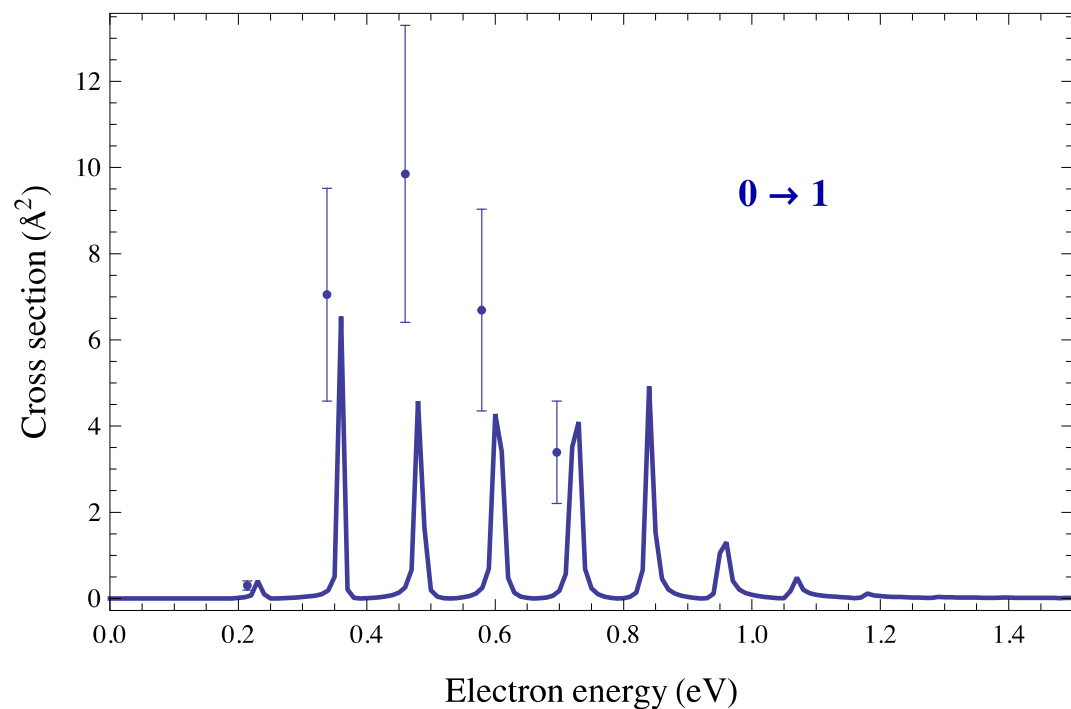
V. Laporta, R. Celiberto and J. Tennyson, *Phys. Rev. A* **91**, 012701 (2015).

V. Laporta, R. Celiberto and J. Tennyson, *Plasma Sources Sci. Technol.* **22**, 025001 (2013)

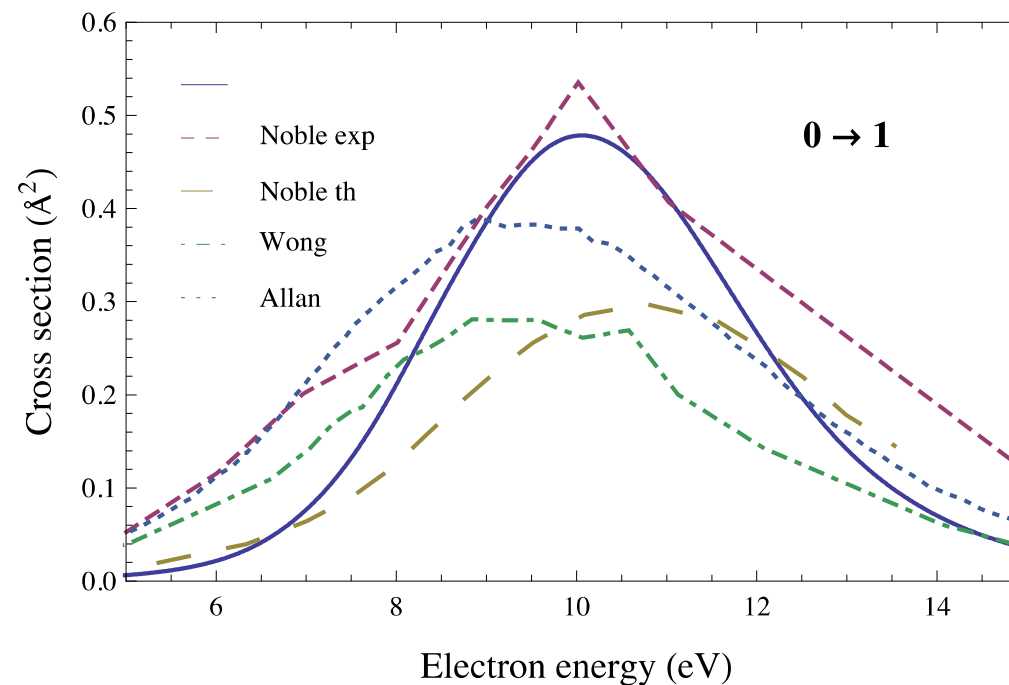
Vibrational-Excitation cross sections



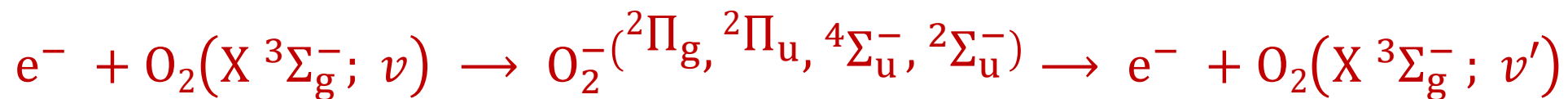
Low energy dominated by $^2\Pi_g$ symmetry
comparison with Allan's results



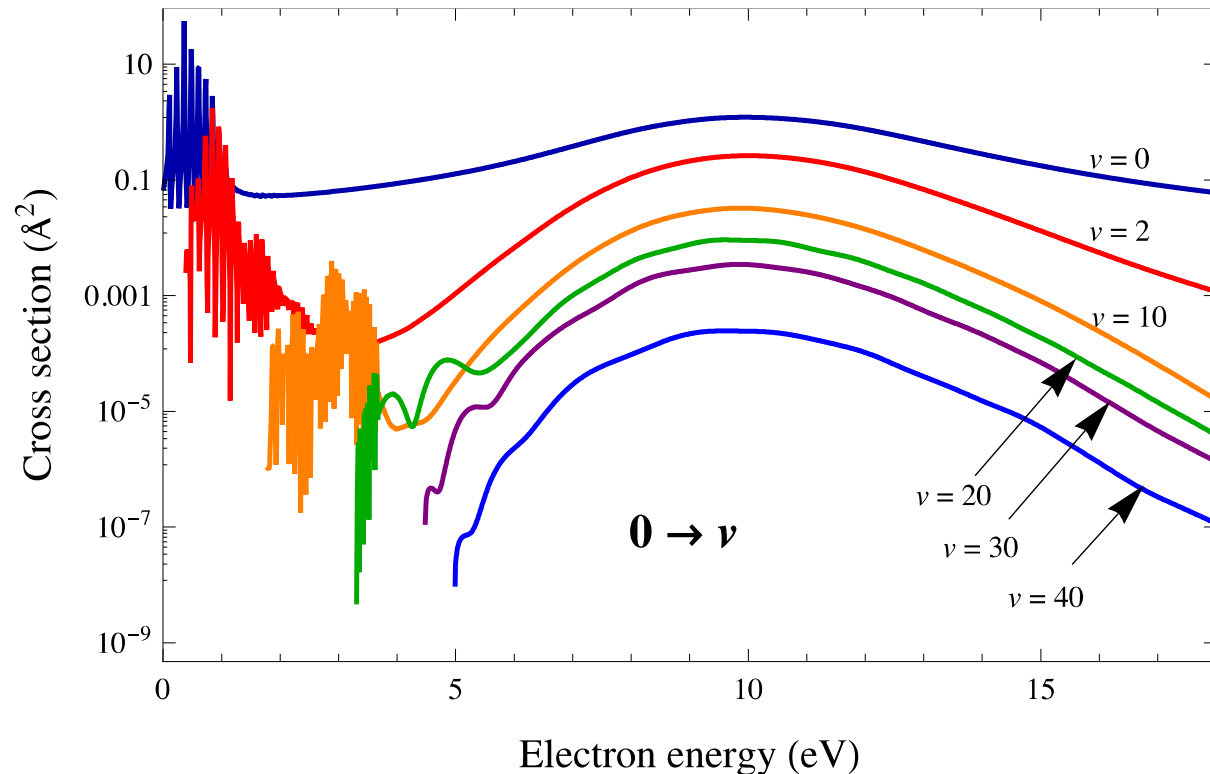
Resonance at 10 eV dominated by $^4\Sigma_u^-$ symmetry



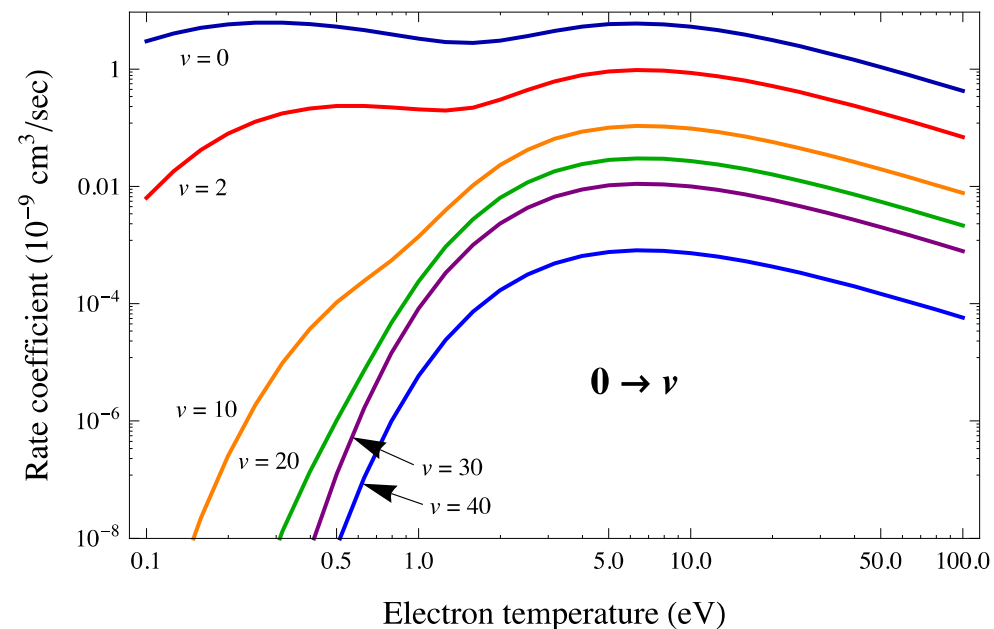
Vibrational-Excitation cross sections



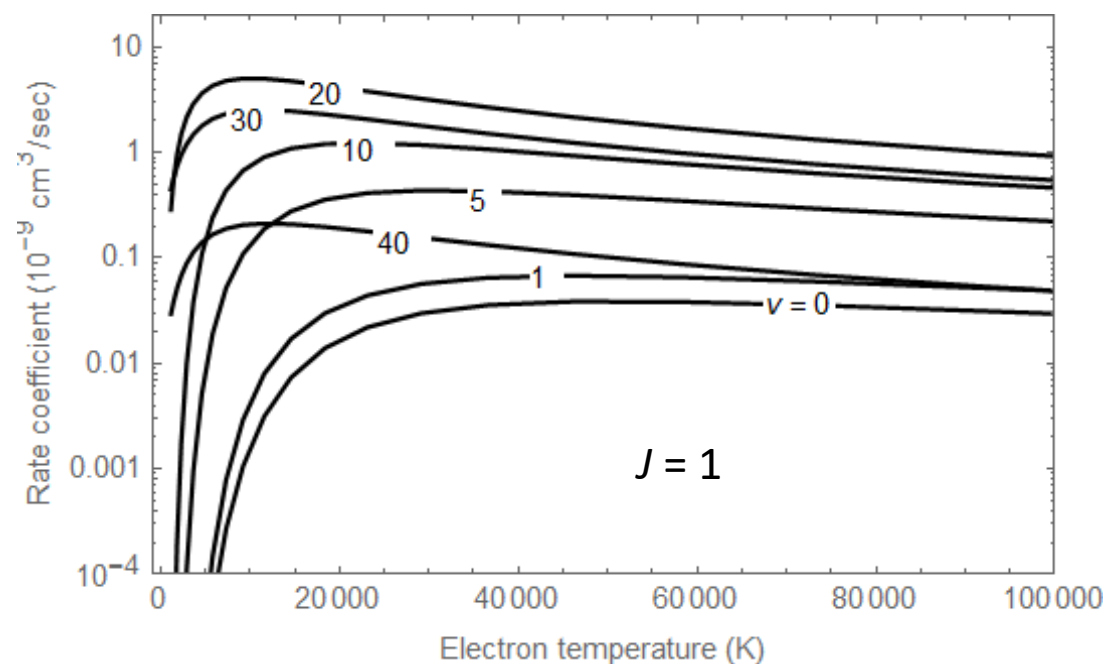
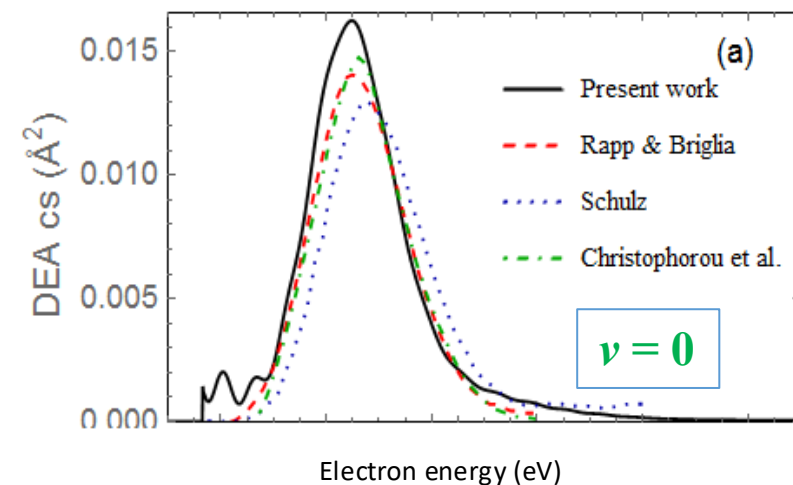
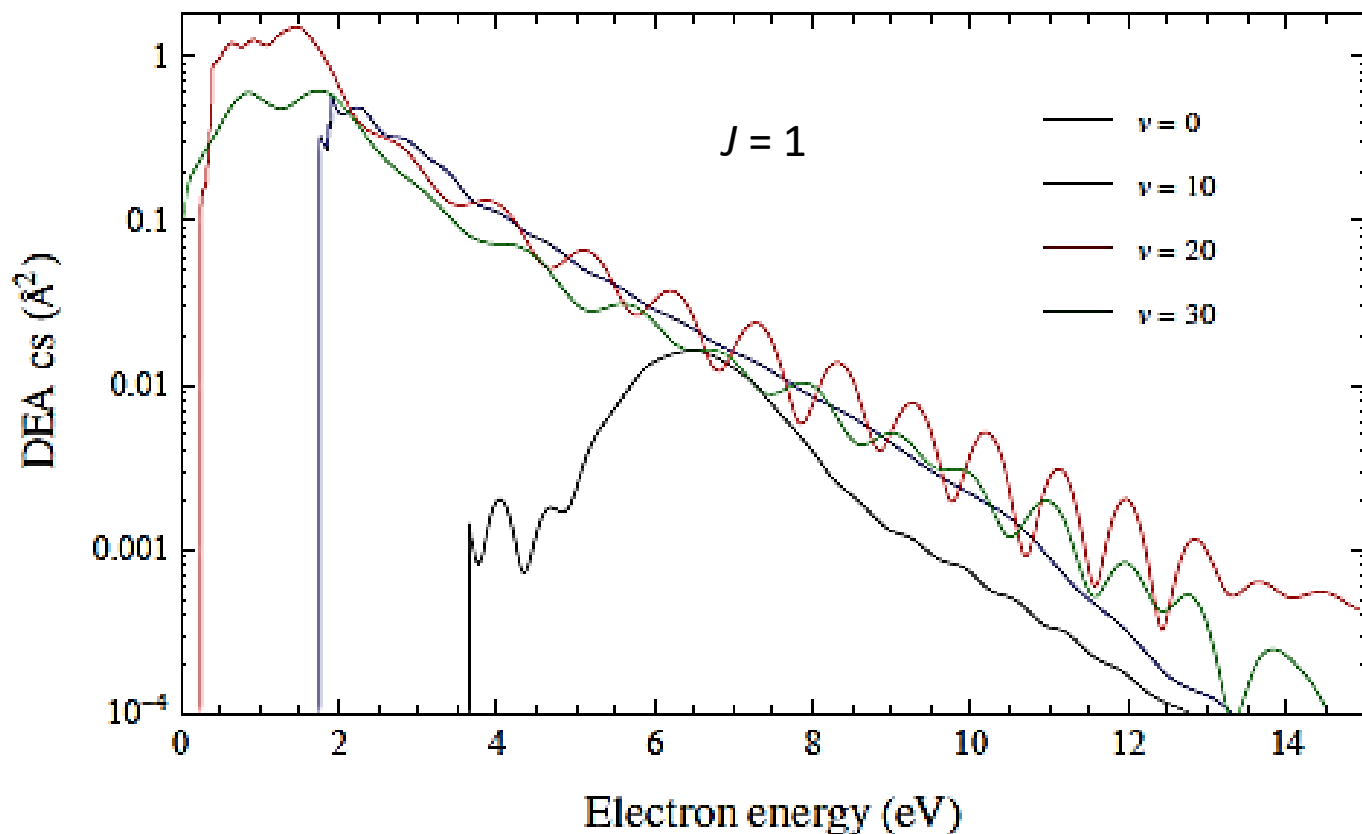
Full set of *Vibrational Excitation* cross sections for $j = 1\dots$



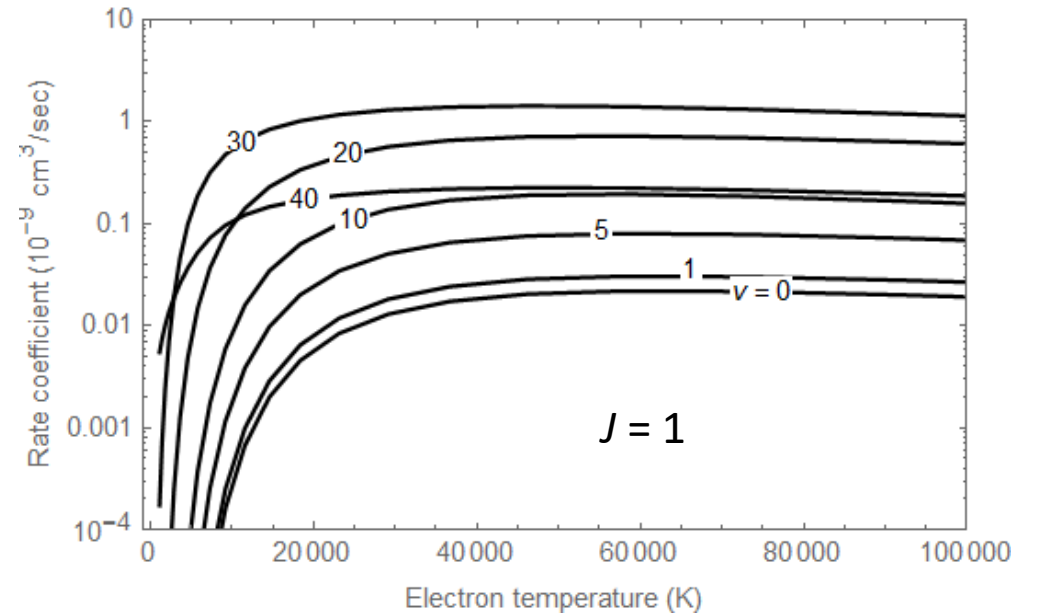
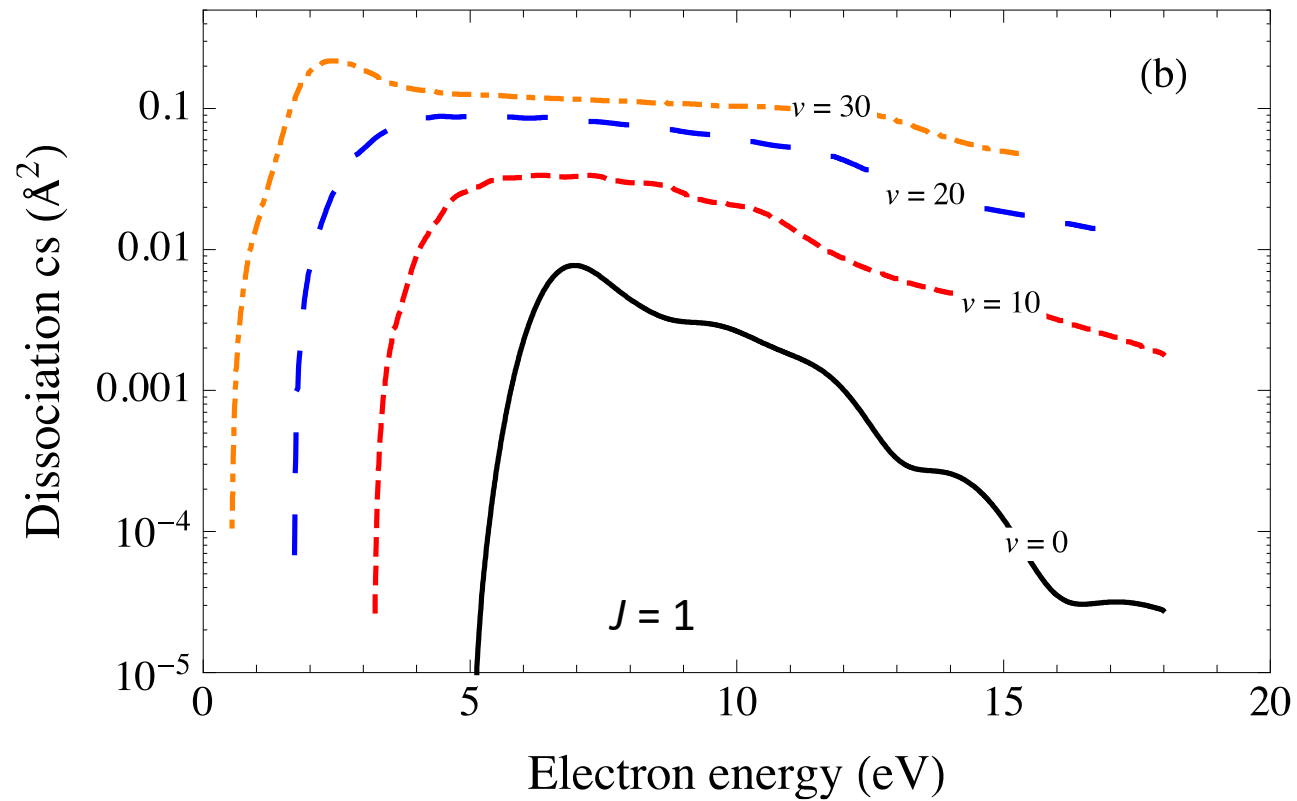
...and the corresponding rate coefficients



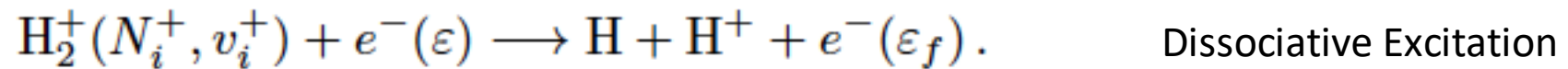
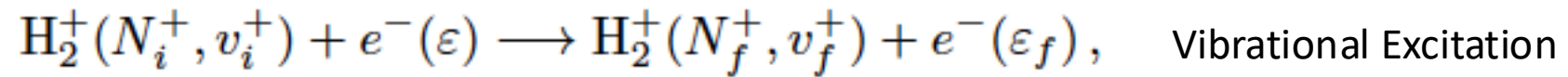
Dissociative-Electron-Attachment



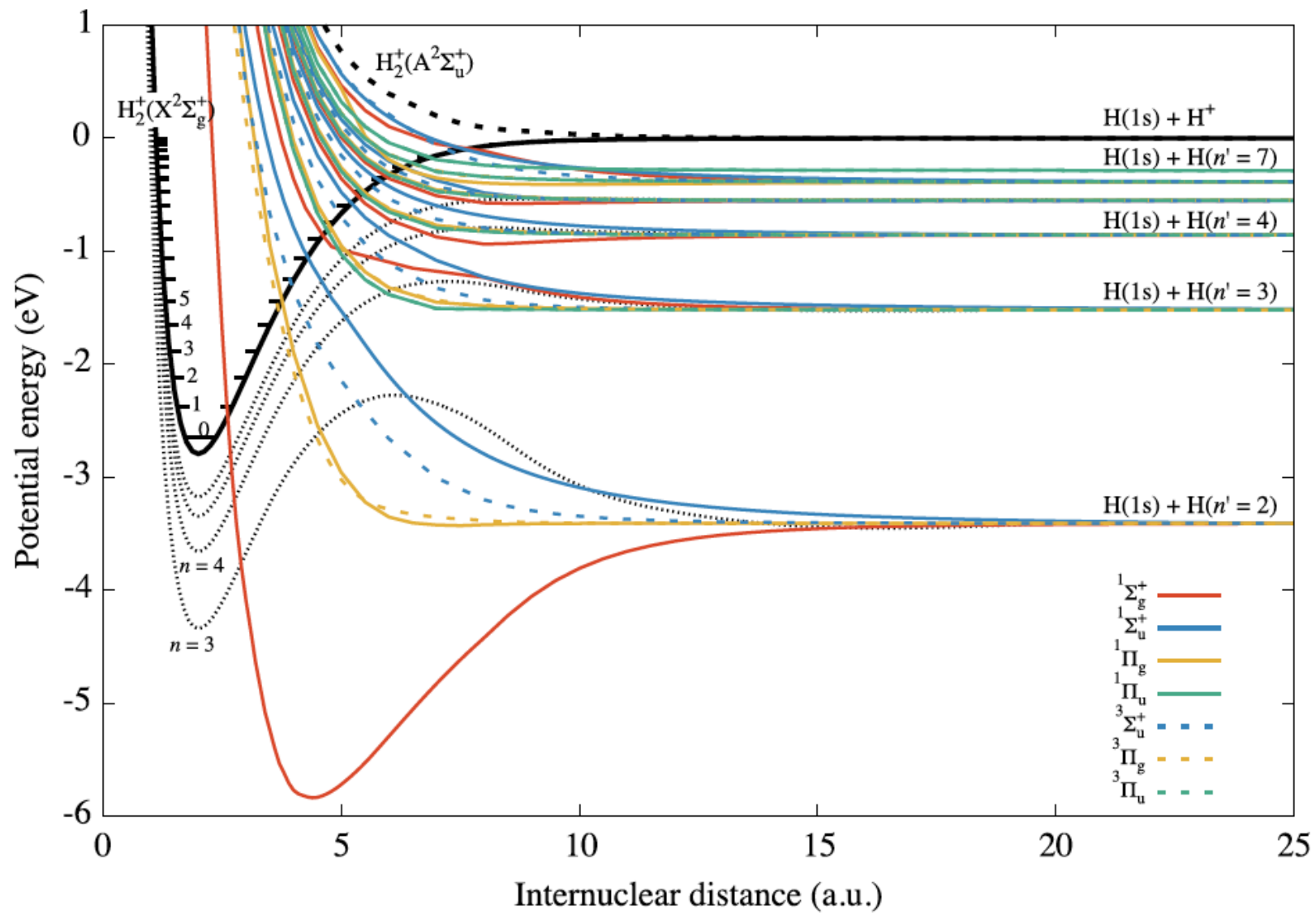
Electron-impact dissociative excitation cross sections



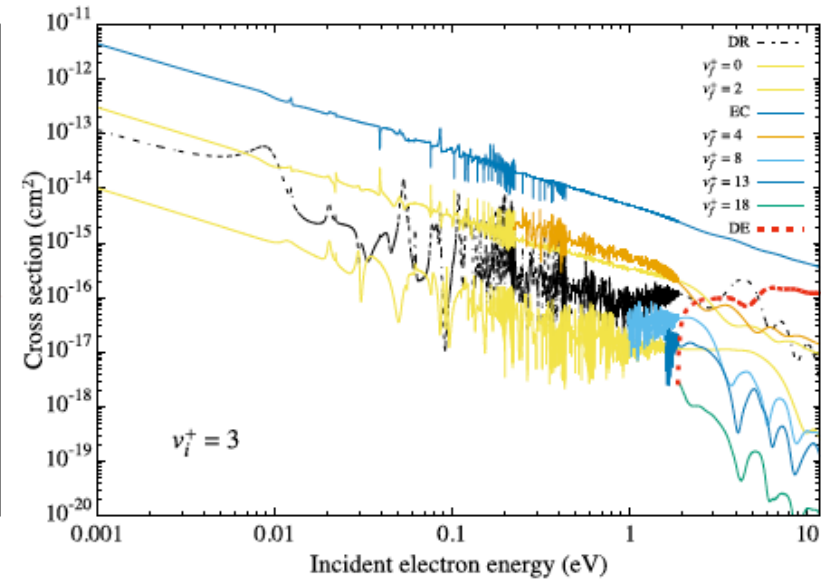
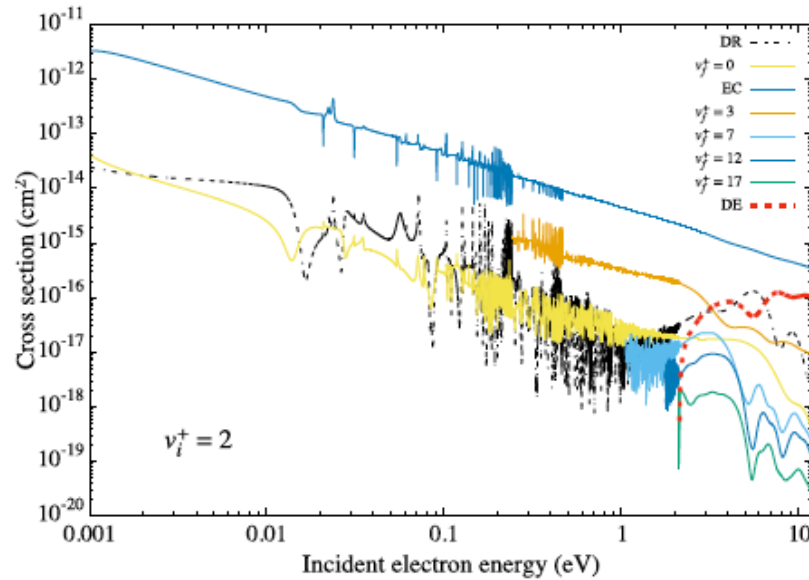
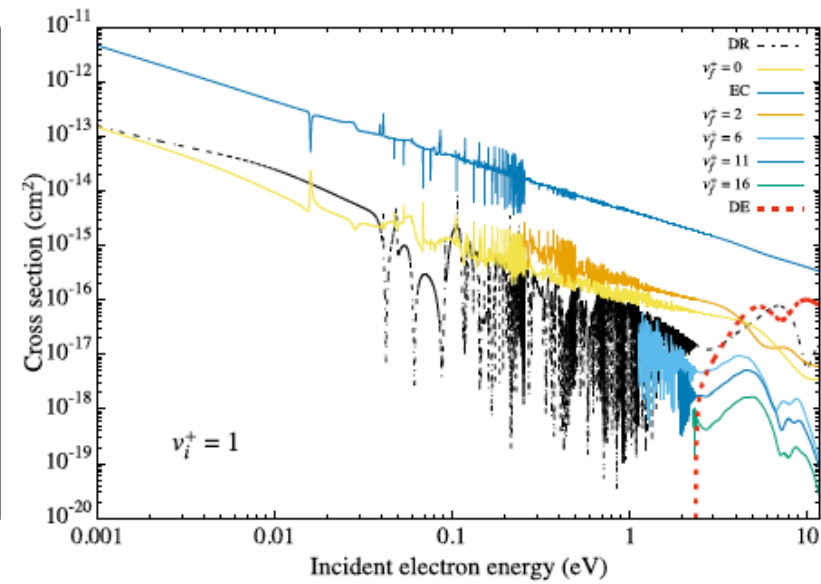
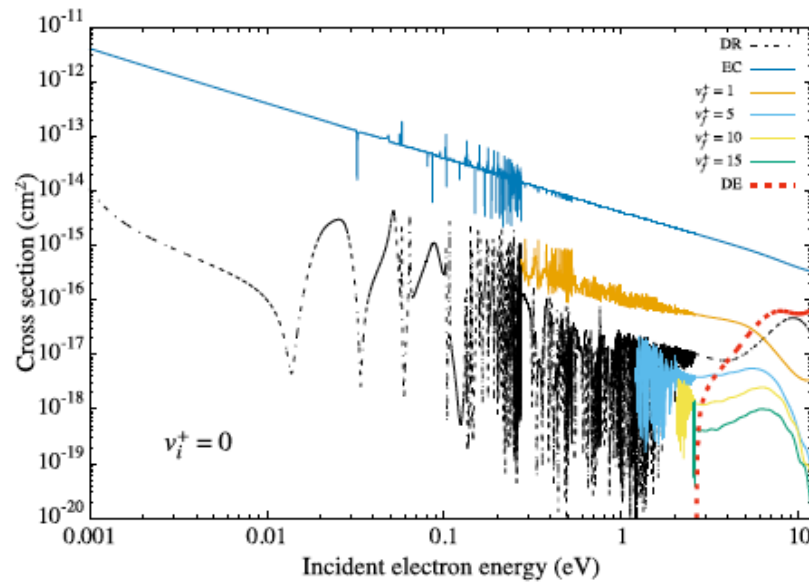
electron- H_2^+ scattering



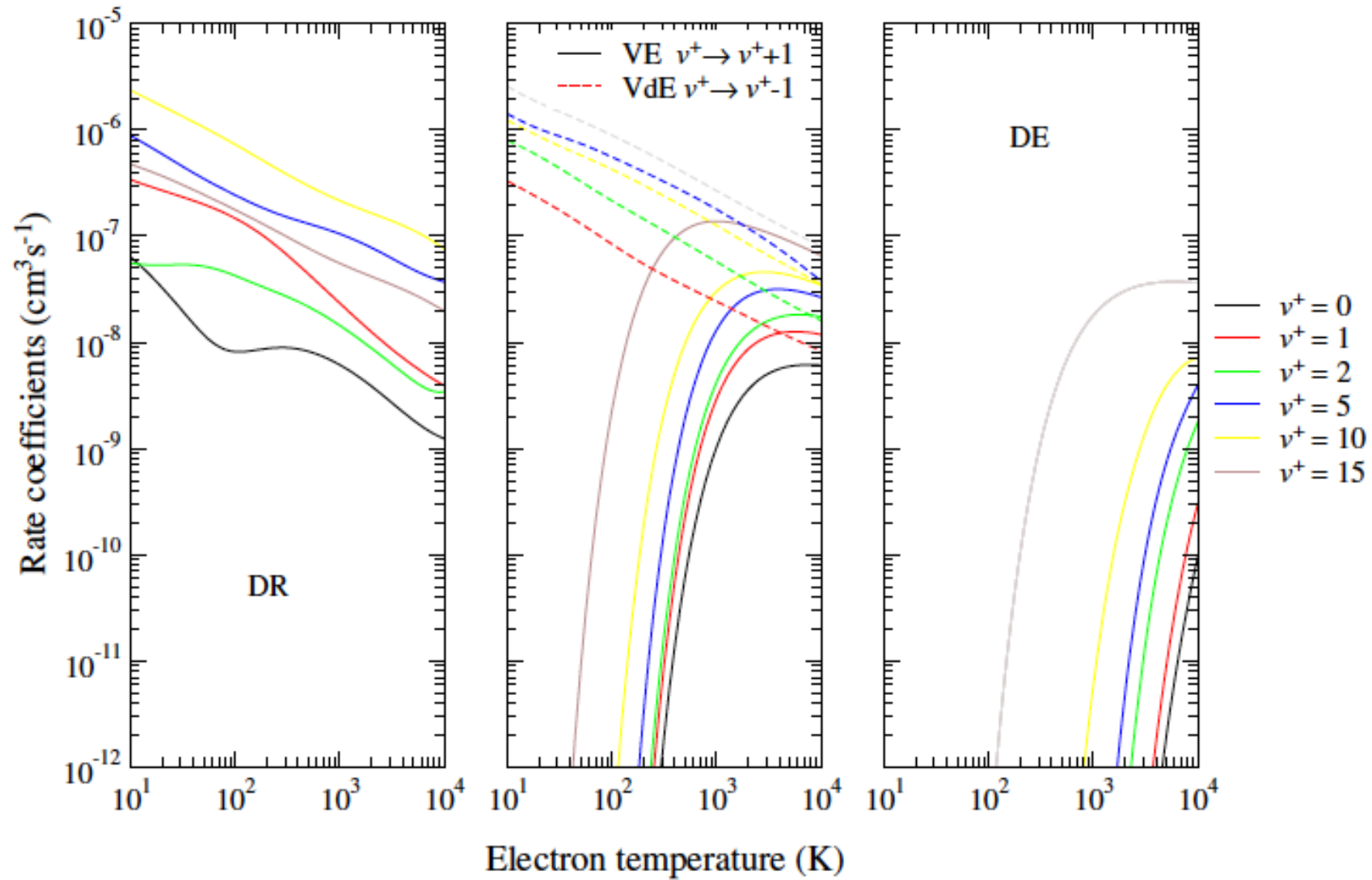
Potentials energy curves for H_2^+ and H_2^*



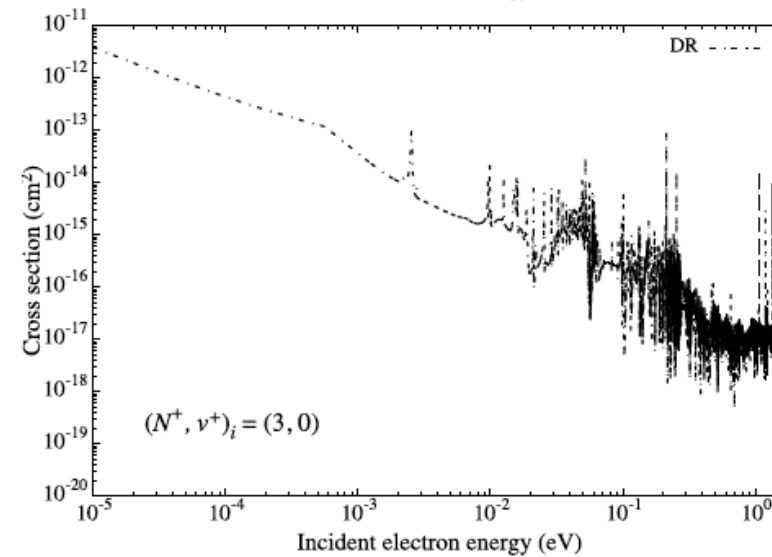
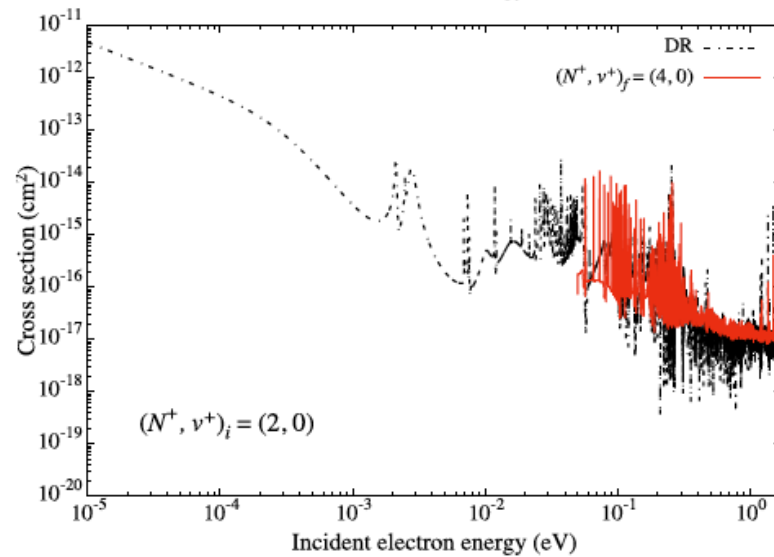
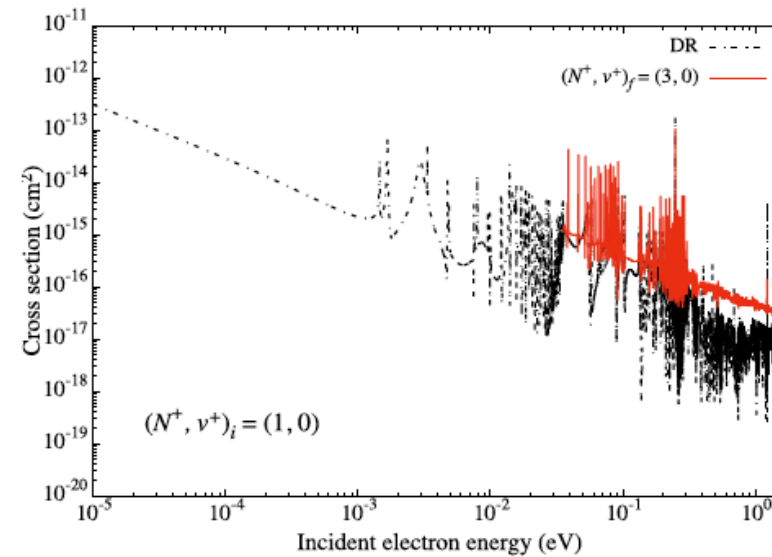
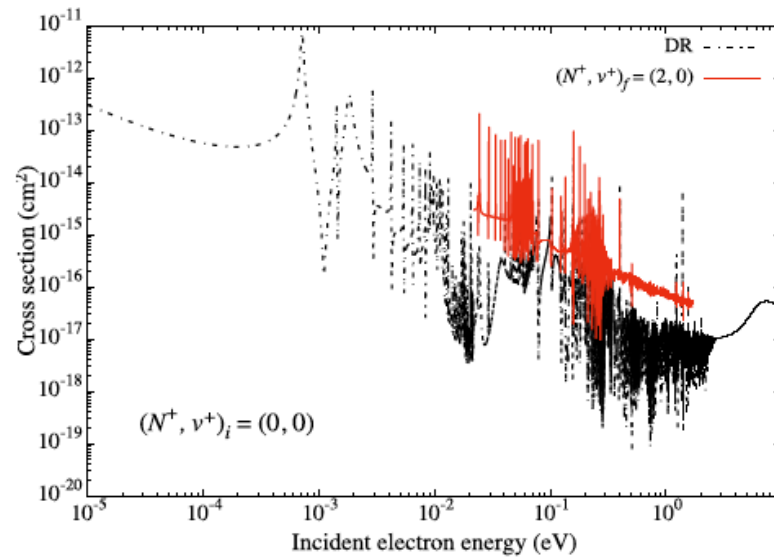
electron- H_2^+ cross sections



electron- H_2^+



Rotationally resolved rate coefficients



Ro-vibrational cross sections for HD^+

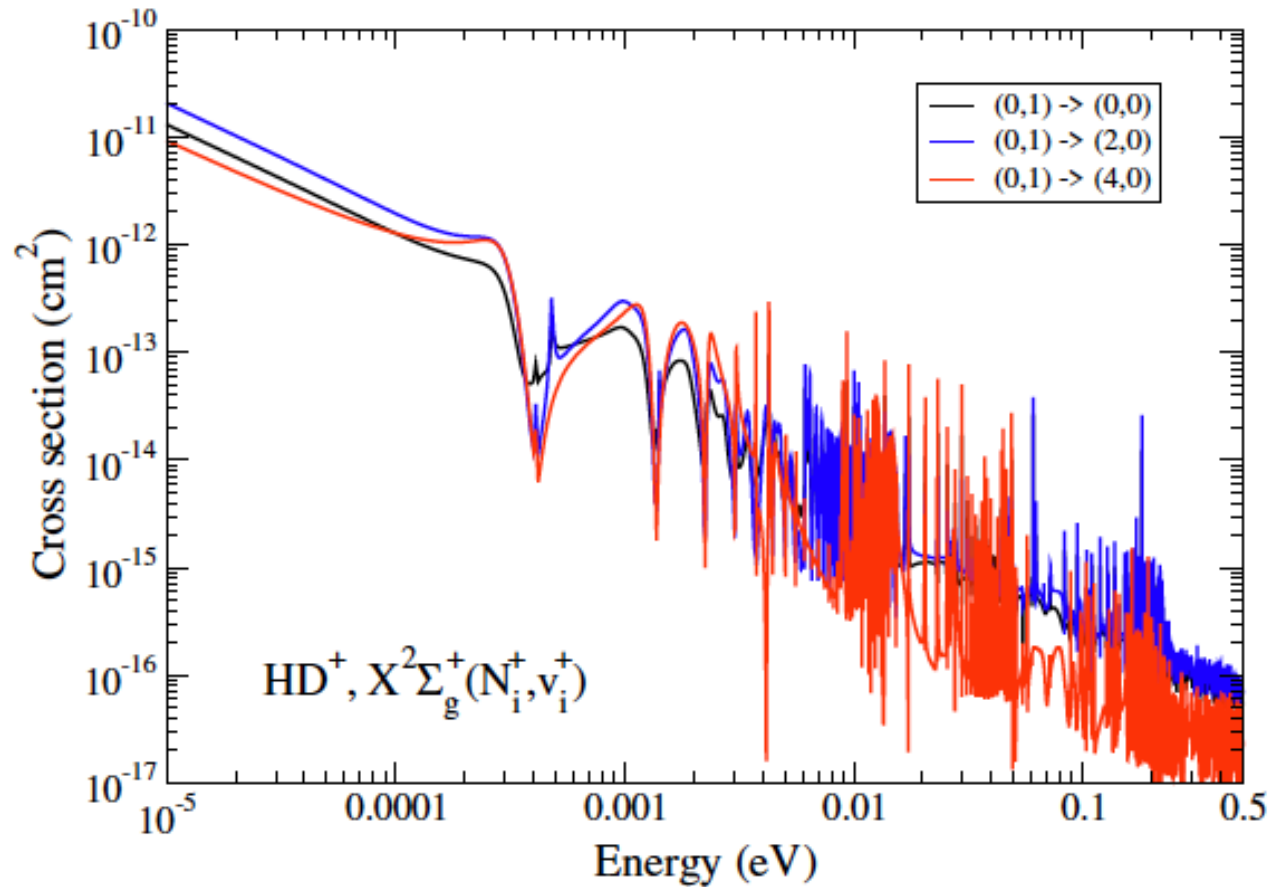
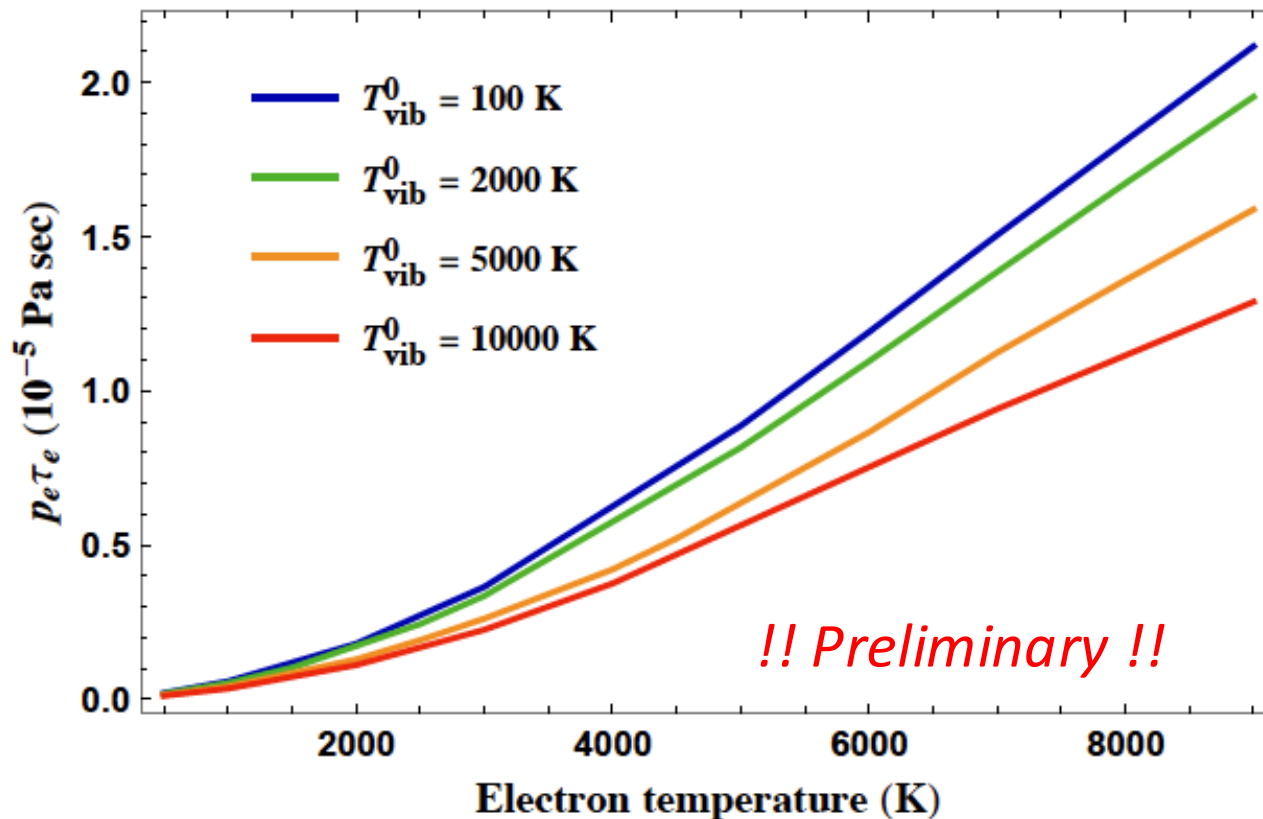


Fig. 3 – De-excitation of the lowest vibrationally-excited level ($N_i^+ = 0, v_i^+ = 1$) of $\text{HD}^+(\text{X}^2\Sigma_g^+)$, dependence on the *final* ro-vibrational state: ($N_i^+ = 0, v_i^+ = 0$) - vibrational de-excitation, black, ($N_i^+ = 2, v_i^+ = 0$) and ($N_i^+ = 4, v_i^+ = 0$) - rotational excitation and vibrational de-excitation, blue and red respectively.

Vibrational Relaxation time of H_2^+

$$\frac{dn_{v+}}{dt} = n_e \sum_{w+=0}^{18} [k_{w+,v+} n_{w+} - k_{v+,w+} n_{v+}] , \quad v^+ = 0, \dots, 18,$$



$$\frac{dE_{vib}}{dt} = \frac{E_{vib}^* - E_{vib}}{\tau_e},$$

$$n_{\text{tot}} = 10^{22} \text{ part/m}^3$$

95% of H_2^+ 5% of e^-

Conclusions

I hope to convince you about the importance to have ab-initio (and state resolved) cross sections and rate constants for elementary processes to describe kinetics of cold plasmas.

LCP and MQDT models are the only serious theoretical frameworks - **completely ab initio** - to describe state-resolved electron-molecule collisions which are able to take into account correctly **nuclear vibrations (and rotations)**.

LCP and MQDT models are the only approaches able to calculate **Dissociative Attachment** and **Dissociative Recombination** processes.

Molecular input data come from ab initio quantum chemistry approaches, *i.e.* **R-Matrix**.

Special issue on journal ATOMS:

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Thank you for your attention

