Recent advances in theoretical studies of electron-impact excitation and dissociation of molecules

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Some theory

as a recognition of

the contribution by

Orsay theorists of old school:

Osman Atabek, Mireille Aymar,

Christian Jungen, Jean-Marie Lecomte,

Eliane Luc, Annick Suzor-Weiner,...

Quantum defect method for e-ion collisions

- At present, theory can provide reliable cross sections for dissociative recombination and rovibrational excitation for a large number of molecular ions.
- But not all ions can be treated using the standard MQDT approach.
- In plasma, many ions have open shell and highly-reactive. But theory has difficulties to describe collisions of such ions with electrons.
- The goal of this study is to develop a general method able to deal with such ions.

Summary of the approach

- Cross sections for DR as well as for rotational, vibrational, electronic excitations are obtained from the scattering matrix $S_{e'r'v';\,erv}(E)$.
- The scattering matrix depends strongly on energy if (electronic or/and rovibrational) resonances are present.
- Energy-dependent $S_{e'r'v';erv}(E)$ is obtained from the scattering matrix $s_{e'r'v';erv}$ calculated assuming that all rovibrational channels are open. $s_{e'r'v';erv}$ depends weakly on energy.
- The smooth matrix $s_{e'r'v';erv}$ is obtained by the frame transformation integrating $s_{e'e}(R)$ over internuclear distances.
- The matrix $s_{e'e}(R)$ is obtained for a number of fixed geometries R using electron scattering codes.

Frame transformation

- The electron scattering takes place only when the electron is close to the target.
- If the Hamiltonian is diagonal, the scattering matrix is also diagonal.
- For small e^--AB distances, the Hamiltonian and S are diagonal with respect to R and Λ (the projection of the electronic angular momentum on molecular axis).
- The electron moves quickly from the long-range region to the short-range one: The amplitudes for electron scattering from long distances to short are obtained by projecting long-range wave functions on short range.
- For large e^--AB distances, the Hamiltonian is diagonal with respect to v and $j \rightarrow S$ is diagonal with respect to v and j.

Cross section $evj \rightarrow e'v'j'$

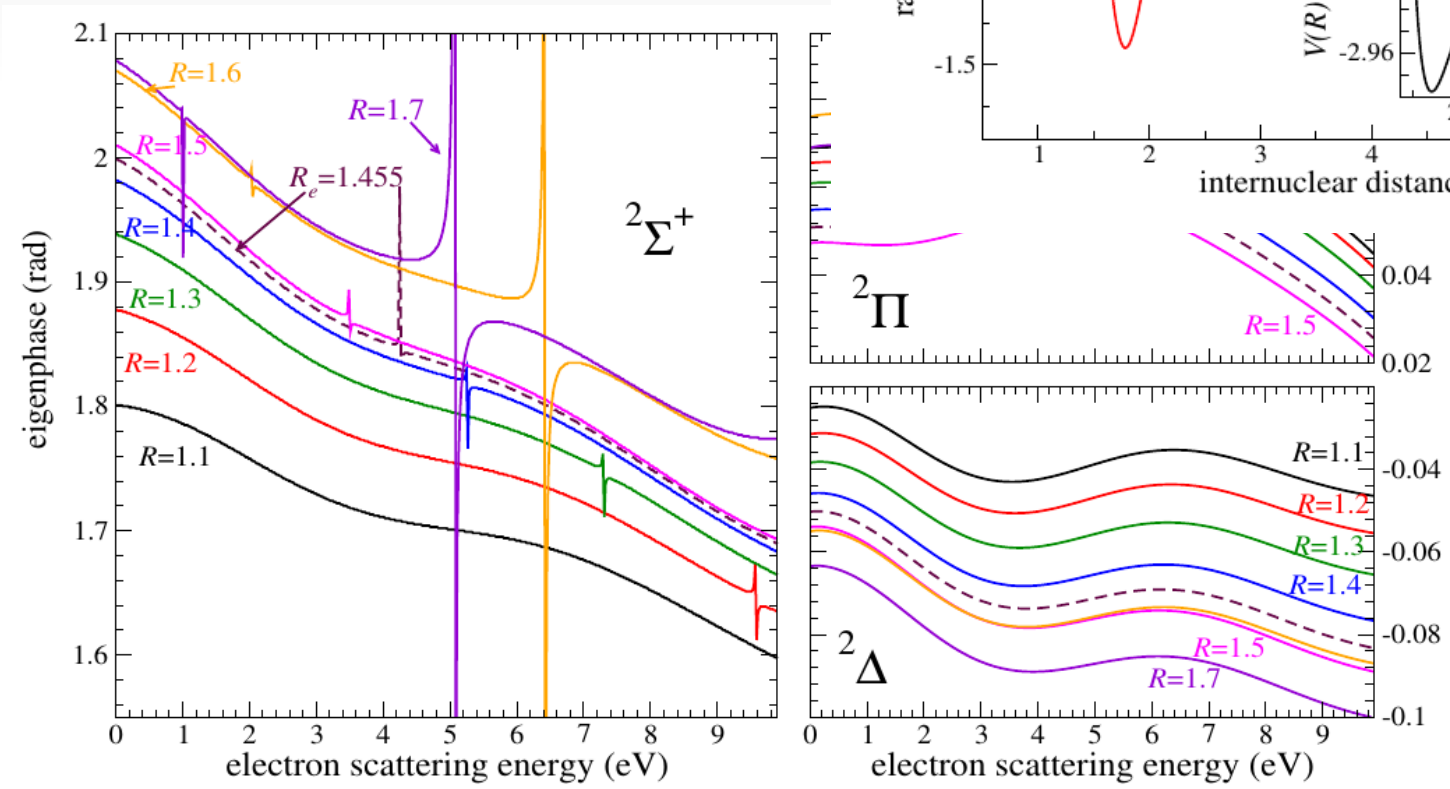
If rotational structure is accounted for, the cross section is

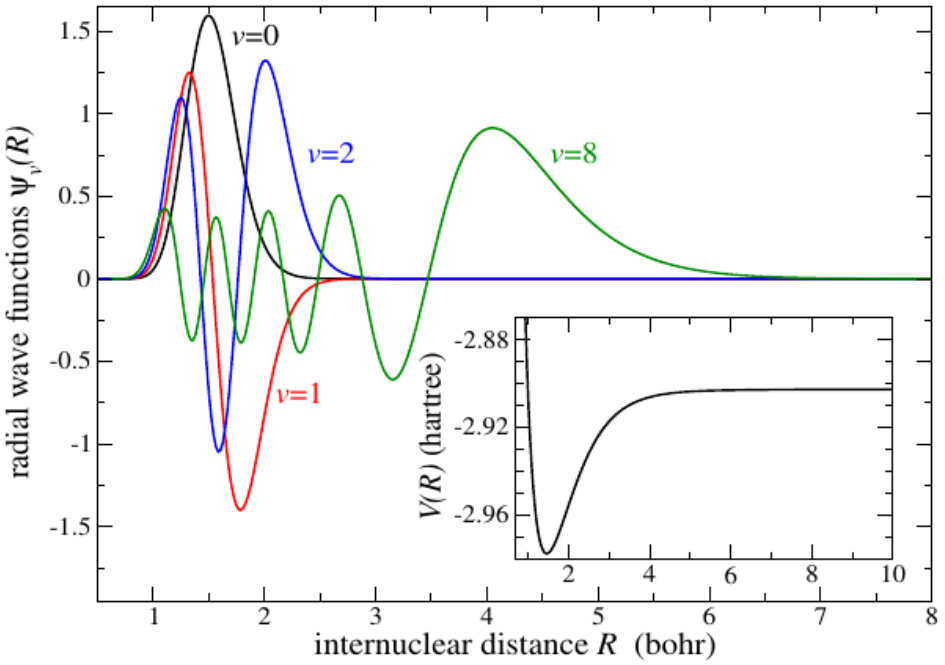
$$\sigma_{e'v'j'\mu'\leftarrow evj\mu}=\frac{\pi}{k^2}\sum_{J,l'l\Lambda}\frac{2j'+1}{2J+1}\left|S^{(J\Lambda)}_{e'v'j'\mu'l'evj\mu l}\right|^2$$

If the rotational structure is neglected (averaging over initial rotational states and taking a sum over final states), the cross section can be simplified as

$$\sigma_{e'v'\leftarrow ev}=\frac{\pi}{k^2}\sum_{l'l\Lambda}\left|S_{e'v'l'\Lambda,evl\Lambda}\right|^2$$

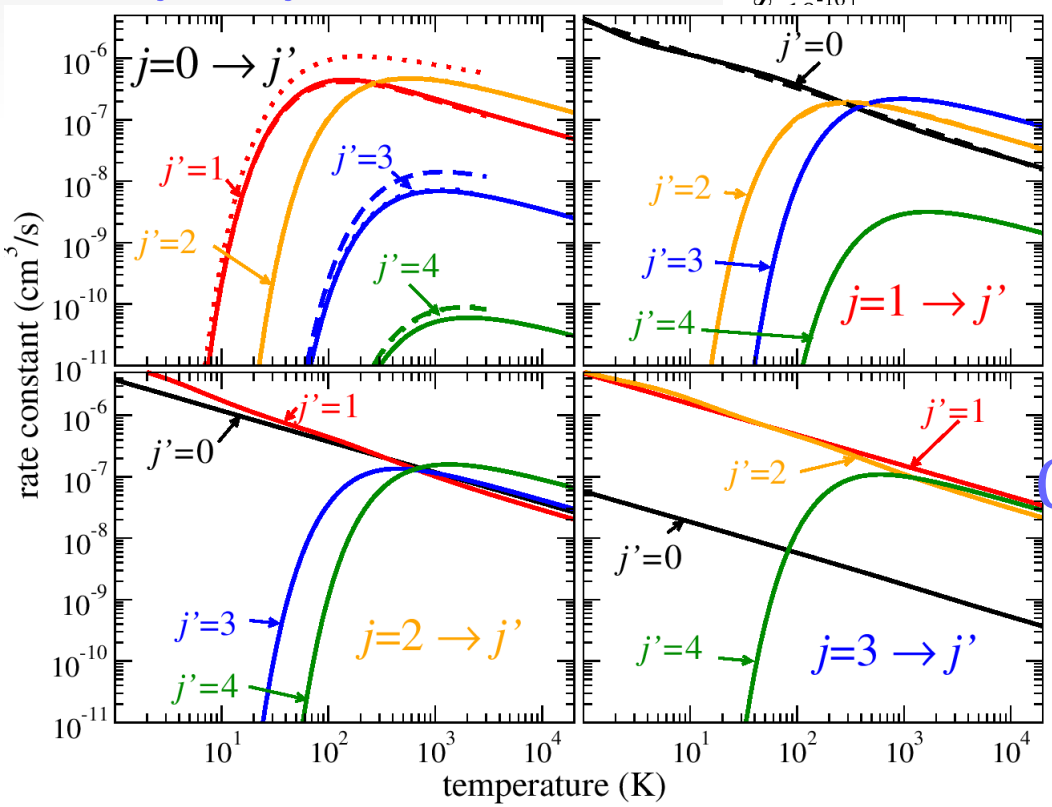
Example: e^-+^{4}HeH$^+$

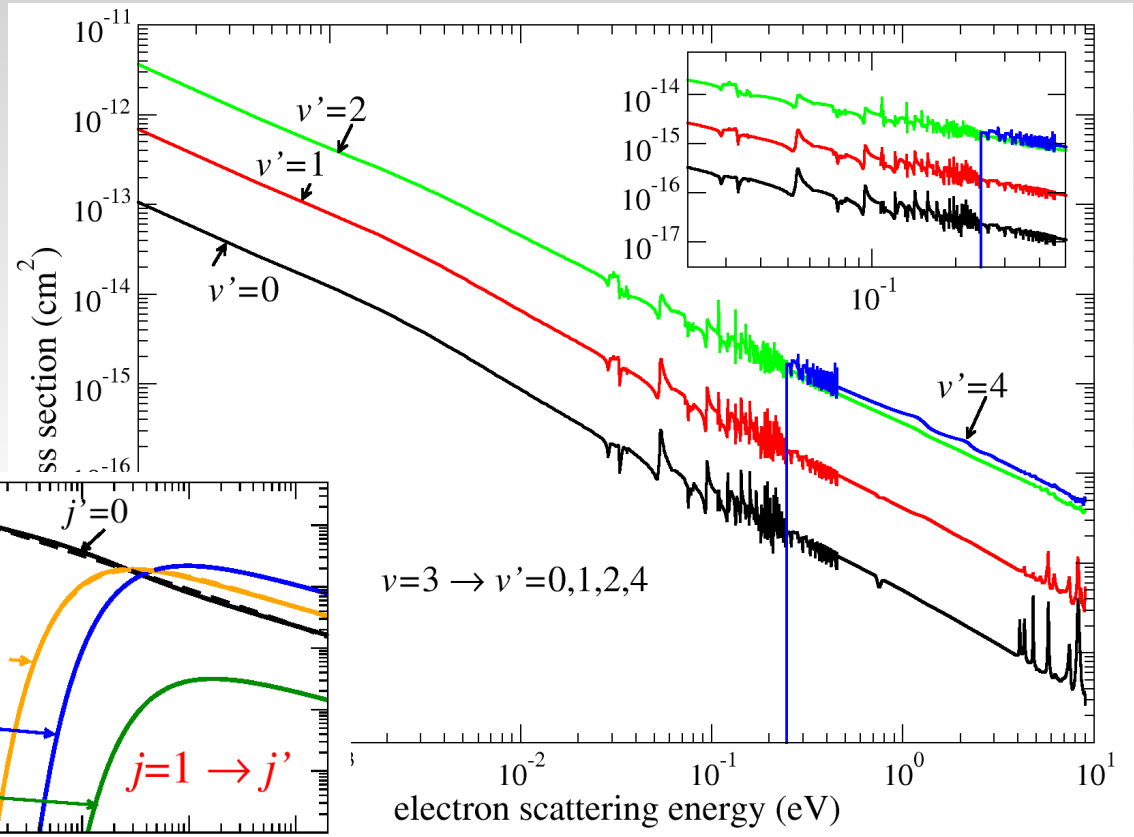




Example: e^-+^{4}HeH$^+$

Rate coefficients for $j \rightarrow j'$

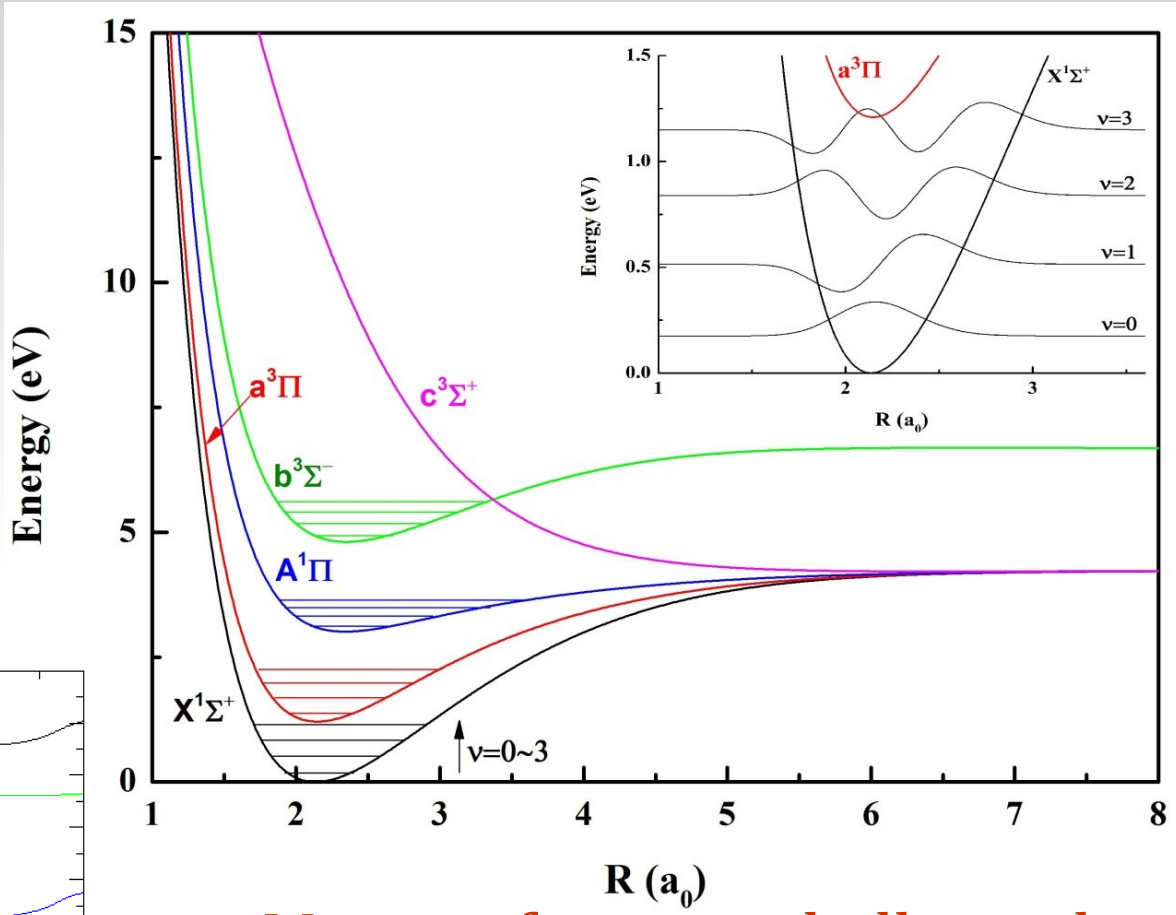


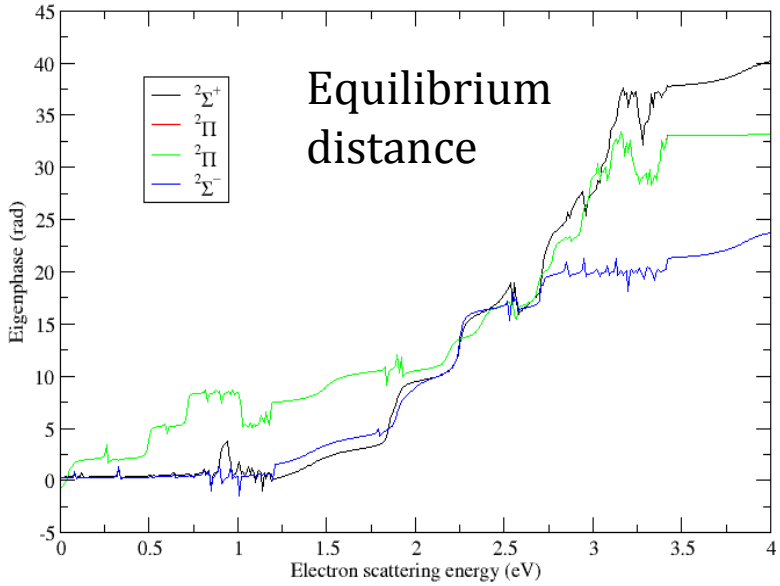


Cross sections for $v \rightarrow v'$

CH^+ electronic structure

*Ions with low-energy excited electronic states are difficult to describe using the standard QDT approach





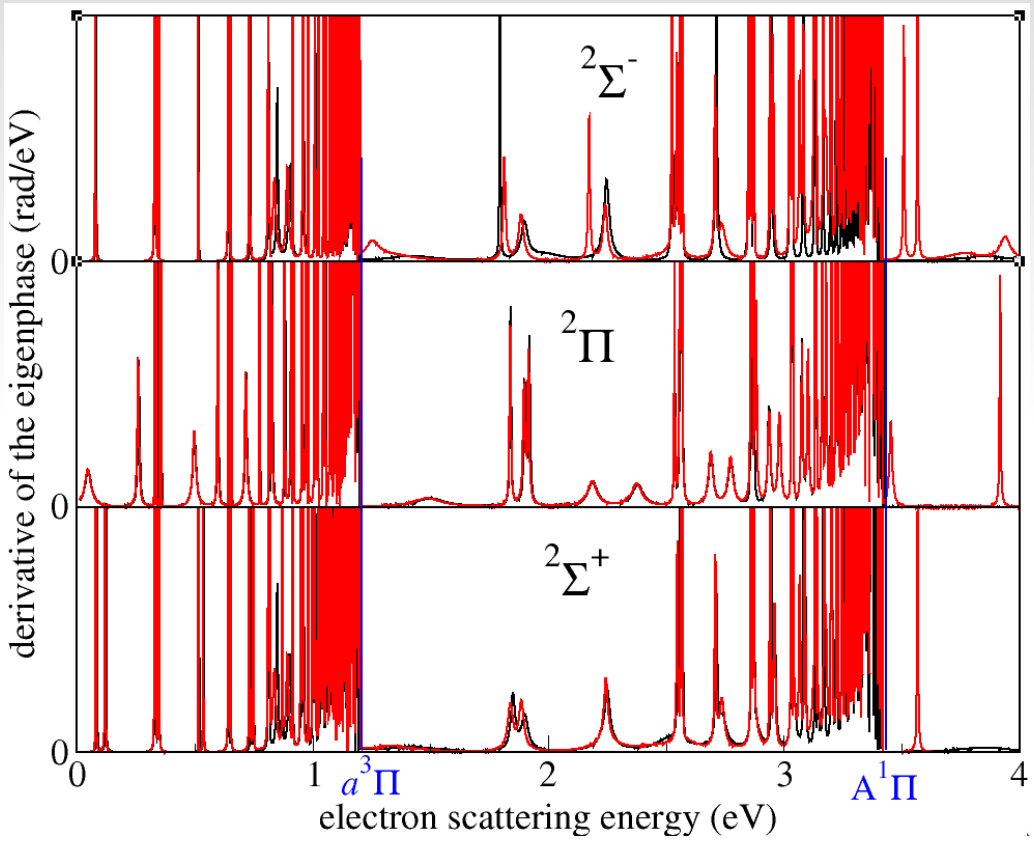
*Most of open-shell and some closed-shell ions are of this type

Electronic resonances due to excited electronic states

*The idea is to represent electronic and rovibrational resonances in a uniform way.

*For a given geometry, the low-energy scattering matrix (and all relevant cross sections) vary a lot due to low-energy excited electronic states.

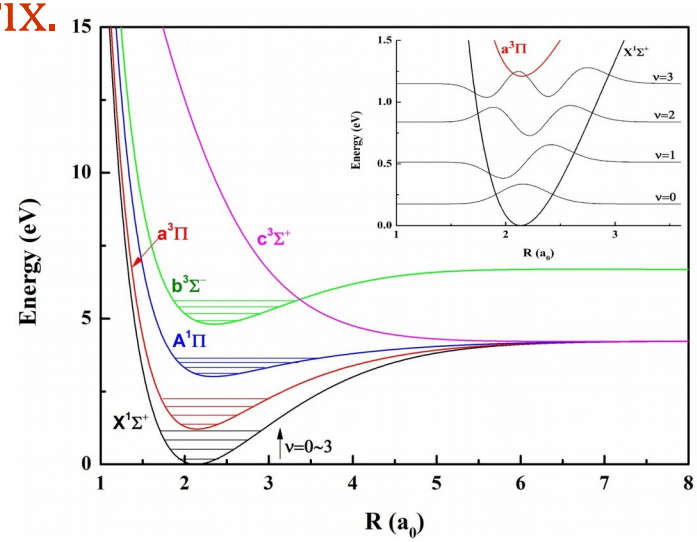
*This energy-dependence could be described by a smooth scattering matrix where a few low-energy excited electronic states are open.

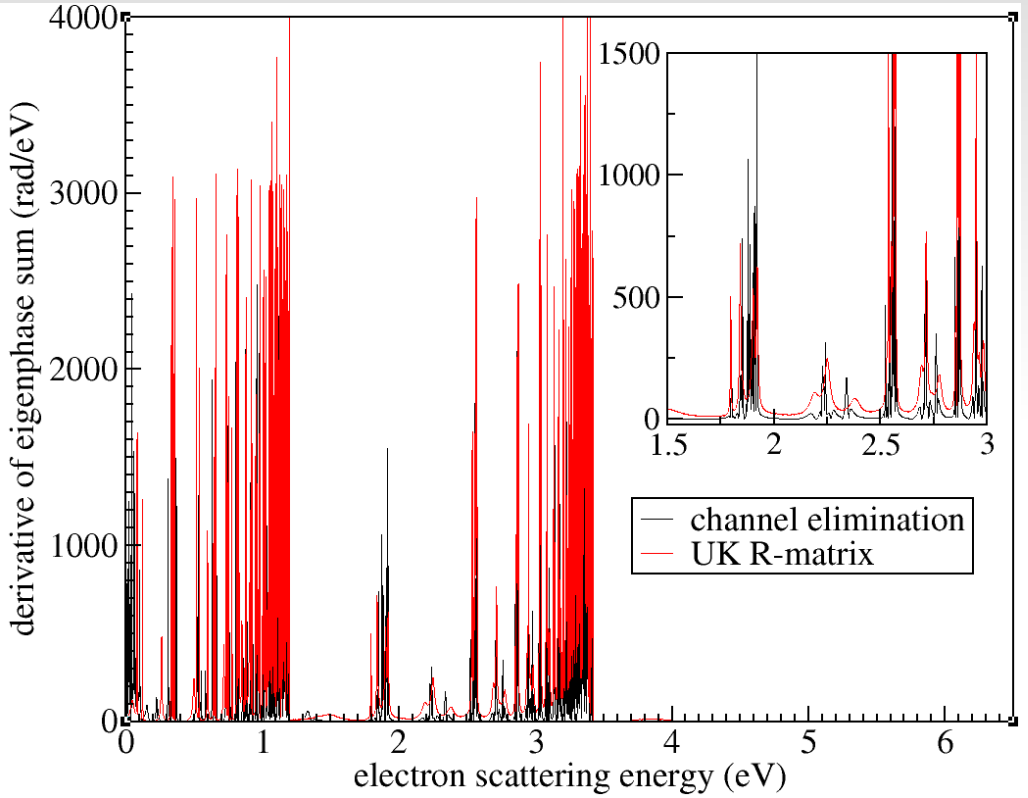


UK R-matrix calculations: Black curves are obtained taking into account only three lowest electronic states of CH^+. Red curves are obtained with 14 states.

QDT description of excited electronic states

- The electronic resonances could, in principle, be represented by the QD channel elimination technique.
- For a given geometry, the electronic 1x1 energy-dependent scattering matrix is replaced with a 3x3 energy independent matrix.

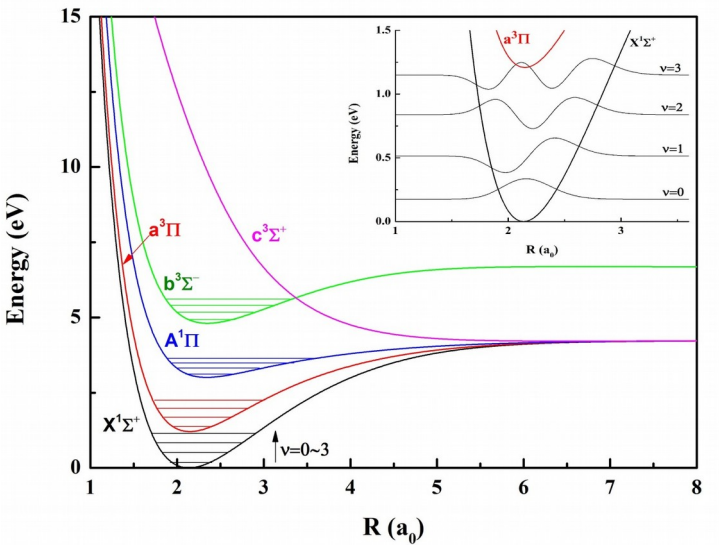


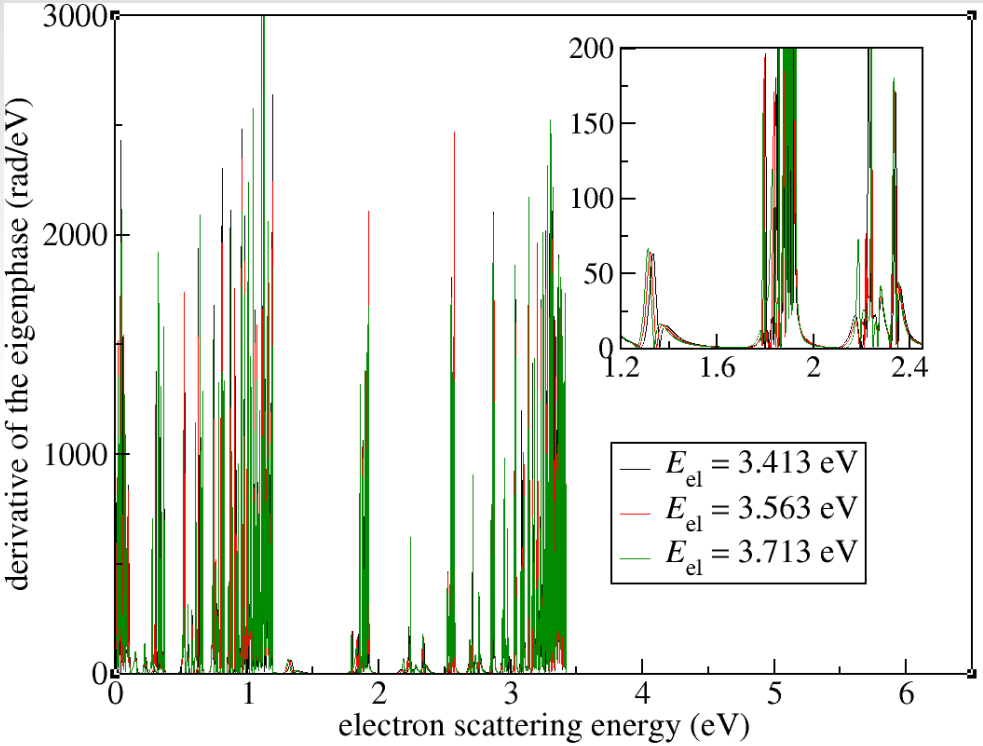


Comparison between the R-matrix and QDT calculations

Week energy-dependence of the scattering matrix

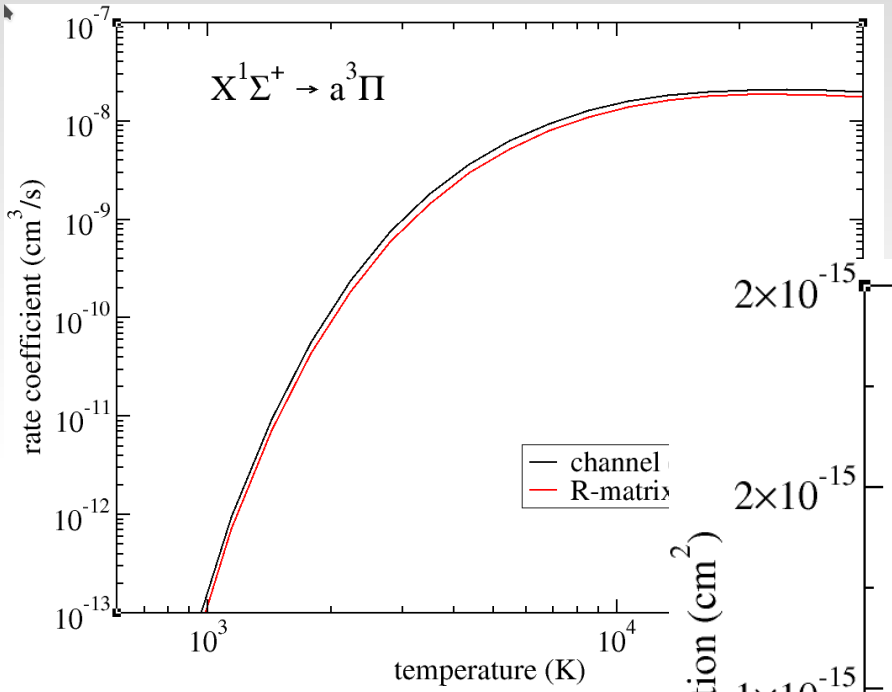
- The matrix is obtained in electron scattering calculations performed at energies above the $A^1\Pi$ state.
- There is an uncertainty in the choice of the energy at which the 3x3 matrix is evaluated



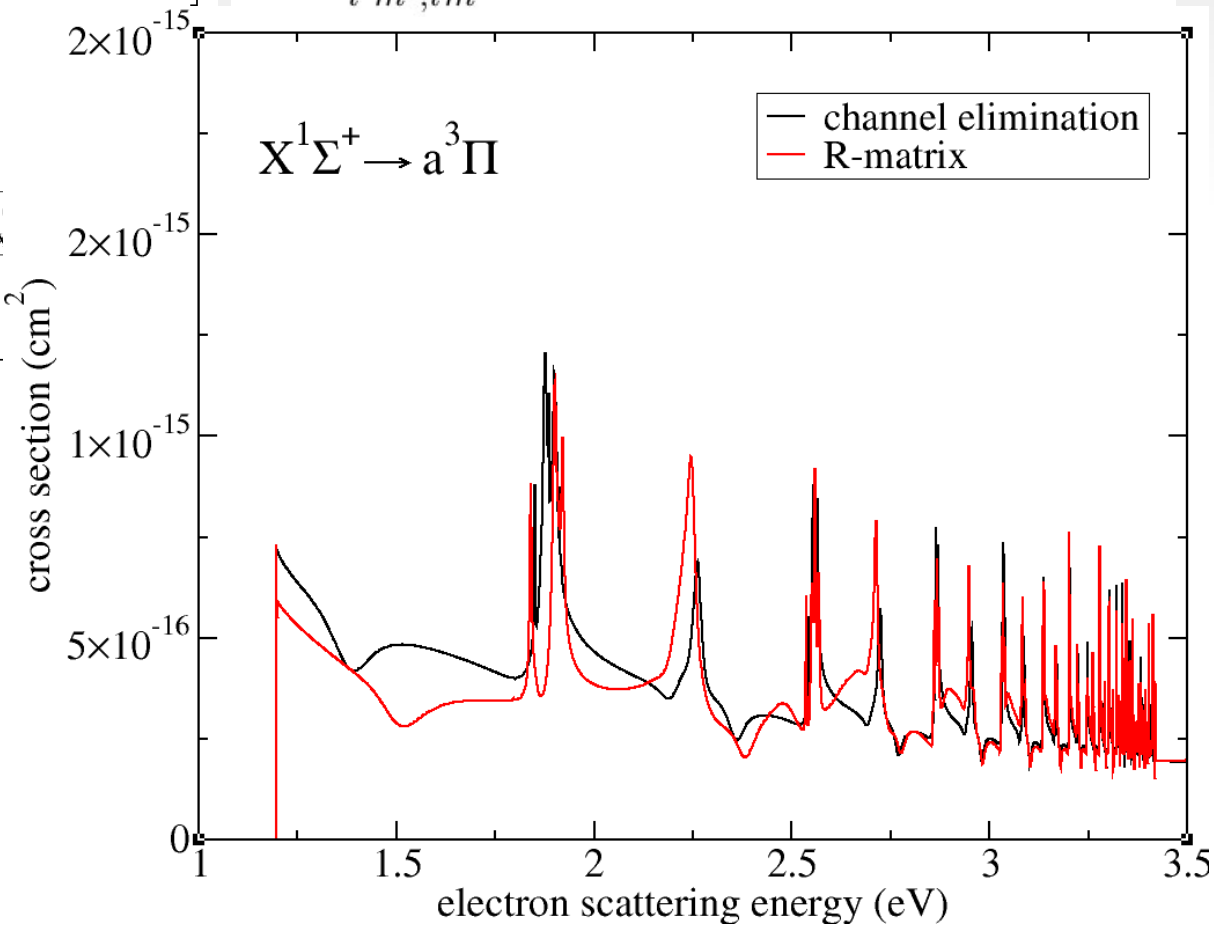


QDT calculations performed for the S-matrix calculated at three different energies above the $A^1\Pi$ state.

Comparison of cross sections and rate coefficients



$$\sigma_{i',i}\left(E_{\mathrm{el}}, R_{\mathrm{e}}\right) = \frac{\pi\hbar^2}{2m_e E_{\mathrm{el}}} \times \sum_{l'm',lm} \left| S^{phys}_{l'm'i',lmi}\left(E_{\mathrm{el}}, R_{\mathrm{e}}\right) - \delta_{l'm'i',lmi} \right|^2$$



Vibronic excitation

*From the energy-independent 3x3 scattering matrix (from electron scattering codes) the S-matrix for vibronic excitation is constructed as

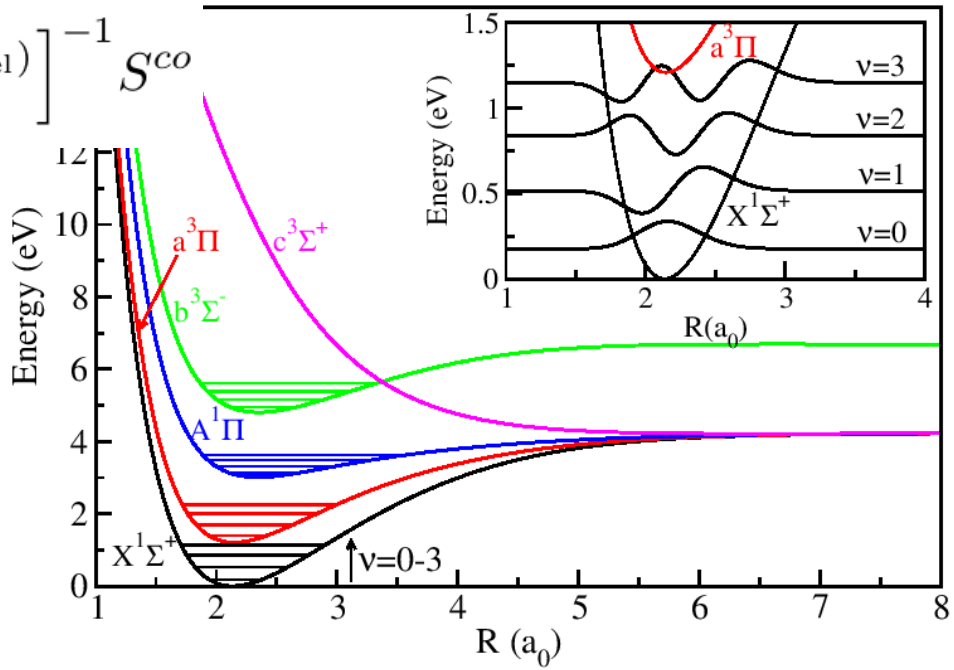
$$S_{l'm'v'i',lmvi}\left(E_{\mathrm{el}}\right) = \left\langle \varphi_{v'i'}\left(R\right) \left| S_{l'm'i',lmi}\left(E_{\mathrm{el}},R\right) \right| \varphi_{vi}\left(R\right) \right\rangle$$

*The vibronic channel-elimination procedure treats vibrational and electronic resonances in a uniform way.

$$S^{phys}\left(E_{\mathrm{el}}\right) = S^{oo} - S^{oc}\left[S_{cc} - e^{-2i\beta(E_{\mathrm{el}})}\right]^{-1} S^{co}$$

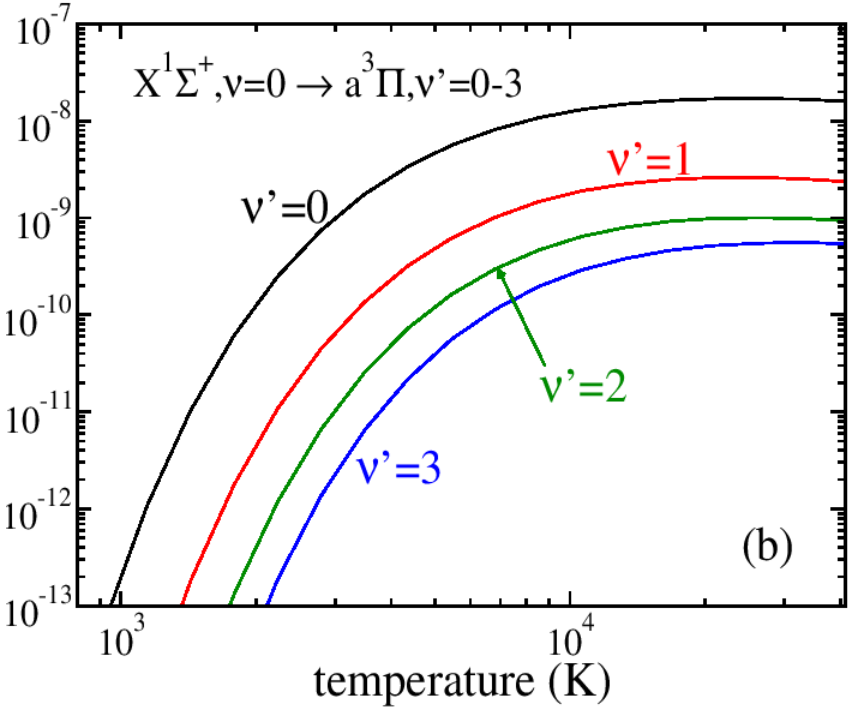
$$S\left(E_{\mathrm{el}}\right) = \begin{pmatrix} S^{oo} & S^{oc} \\ S^{co} & S^{cc} \end{pmatrix}$$

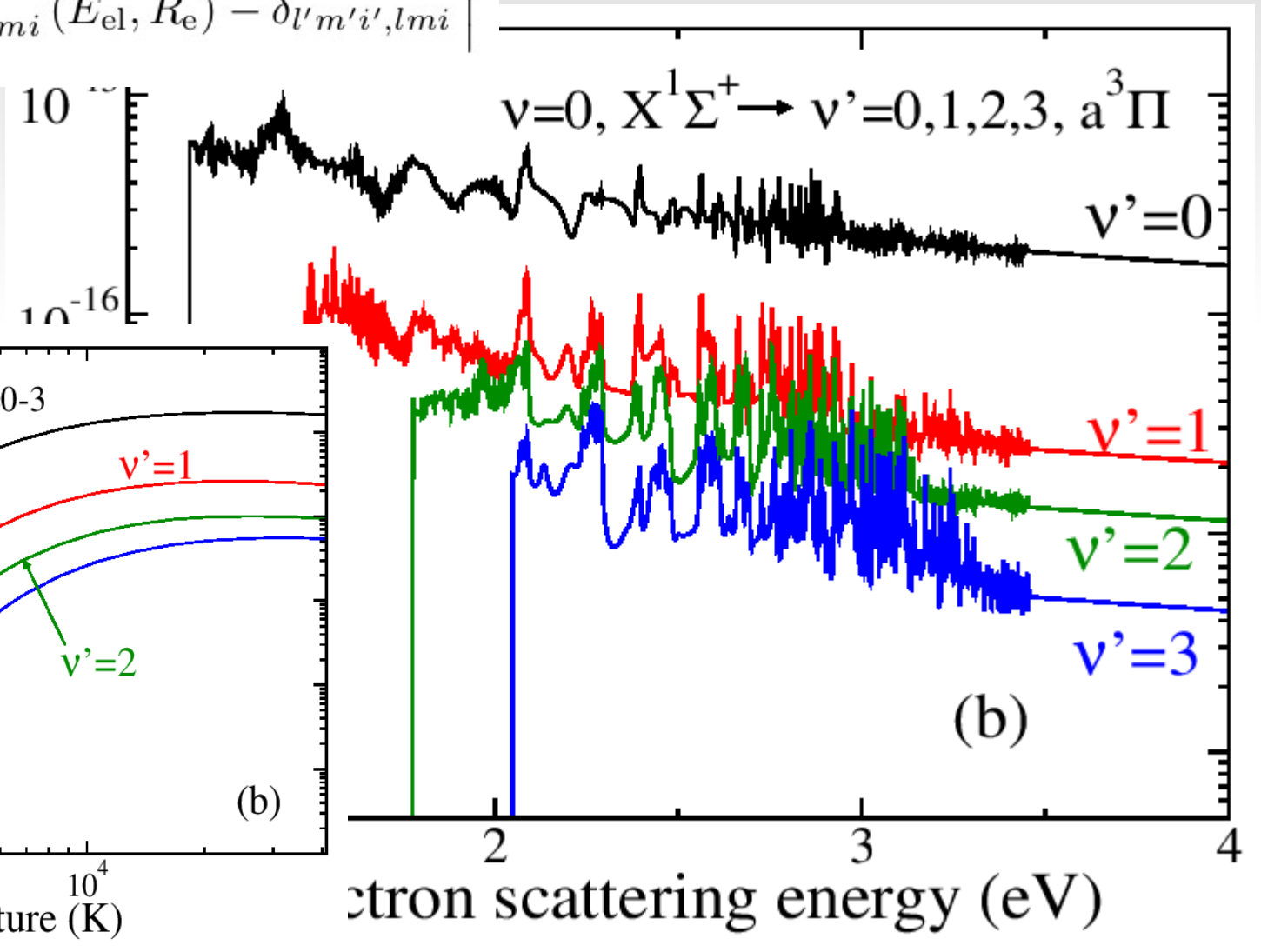
$$\beta\left(E_{\mathrm{el}}\right) = \frac{\pi}{\sqrt{2\left(E_{vi} - E_{\mathrm{el}}\right)}}\delta_{v'i',vi}$$



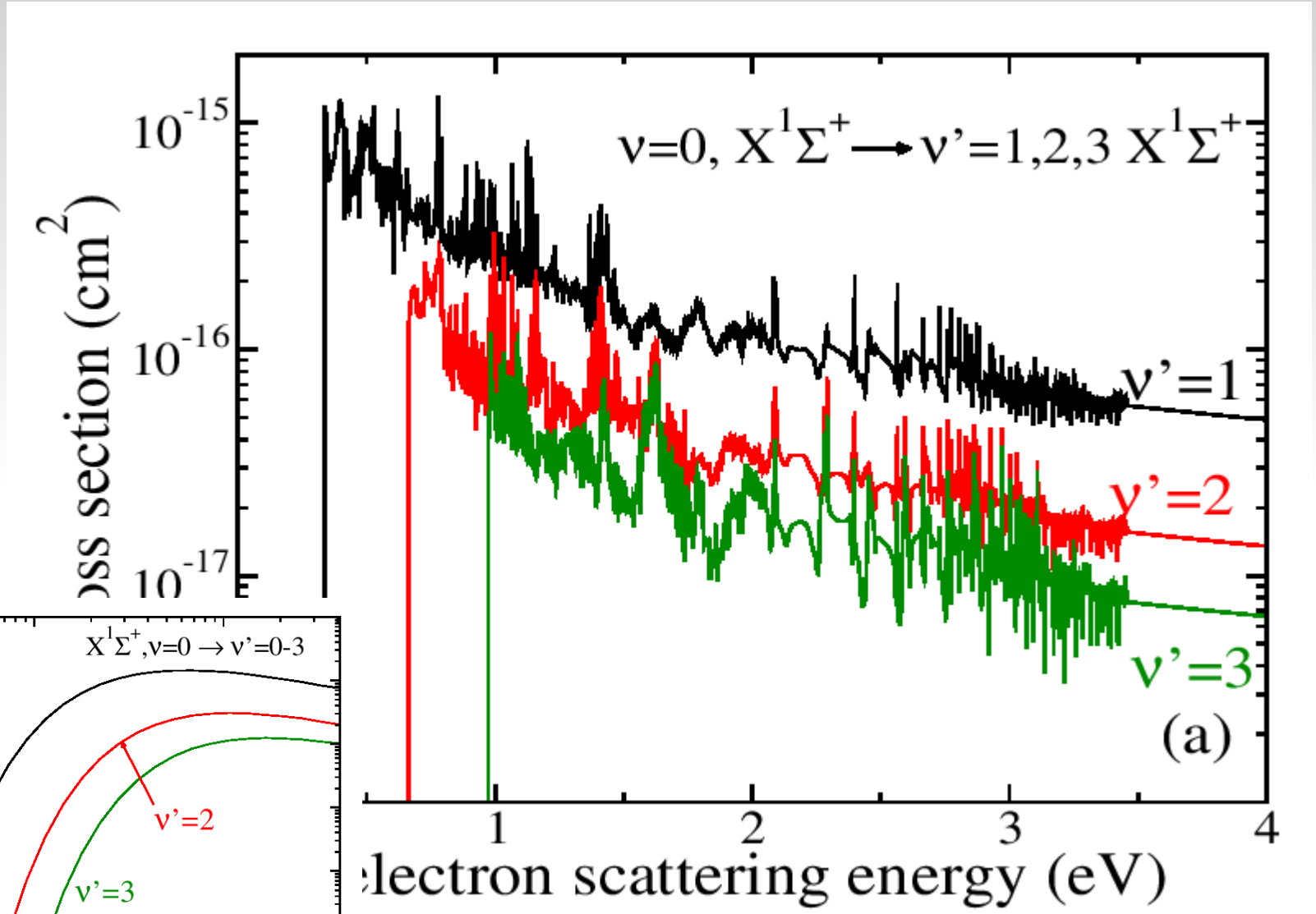
Cross sections for vibronic excitation

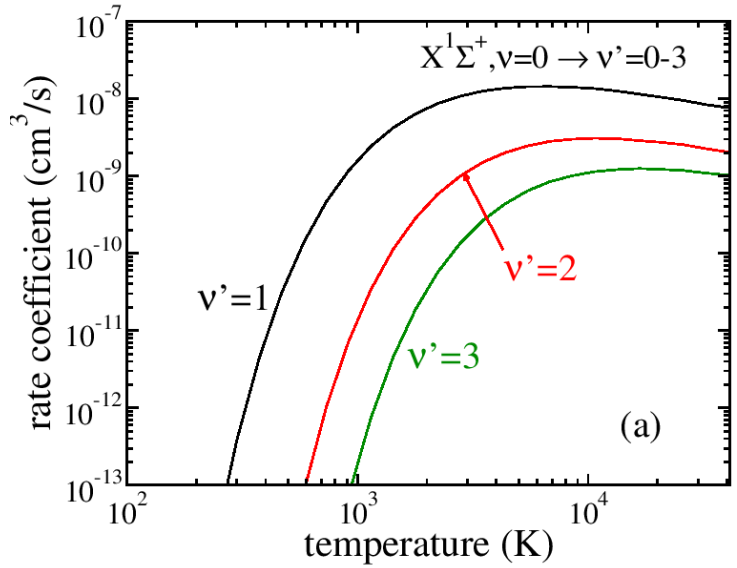
$$\sigma_{i',i}\left(E_{\mathrm{el}}, R_{\mathrm{e}}\right) = \frac{\pi\hbar^2}{2m_e E_{\mathrm{el}}} \times \sum_{l'm',lm} \left| S^{phys}_{l'm'i',lmi}\left(E_{\mathrm{el}}, R_{\mathrm{e}}\right) - \delta_{l'm'i',lmi} \right|^2$$



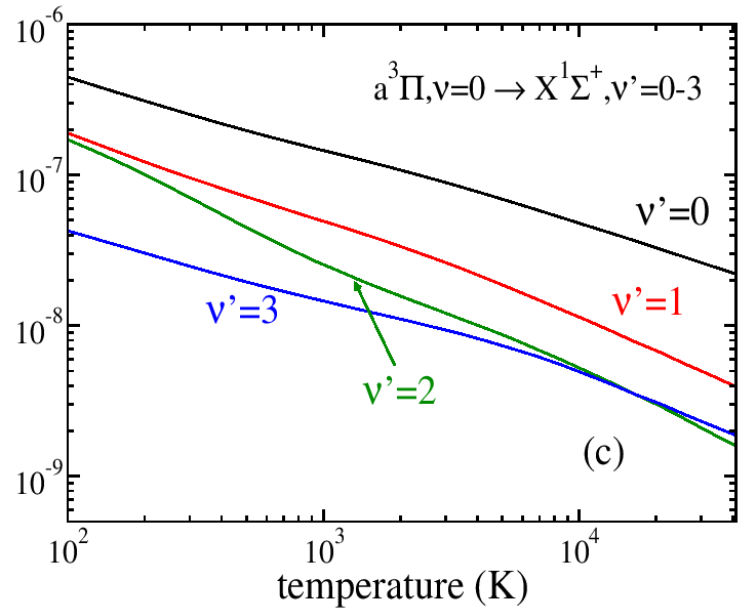


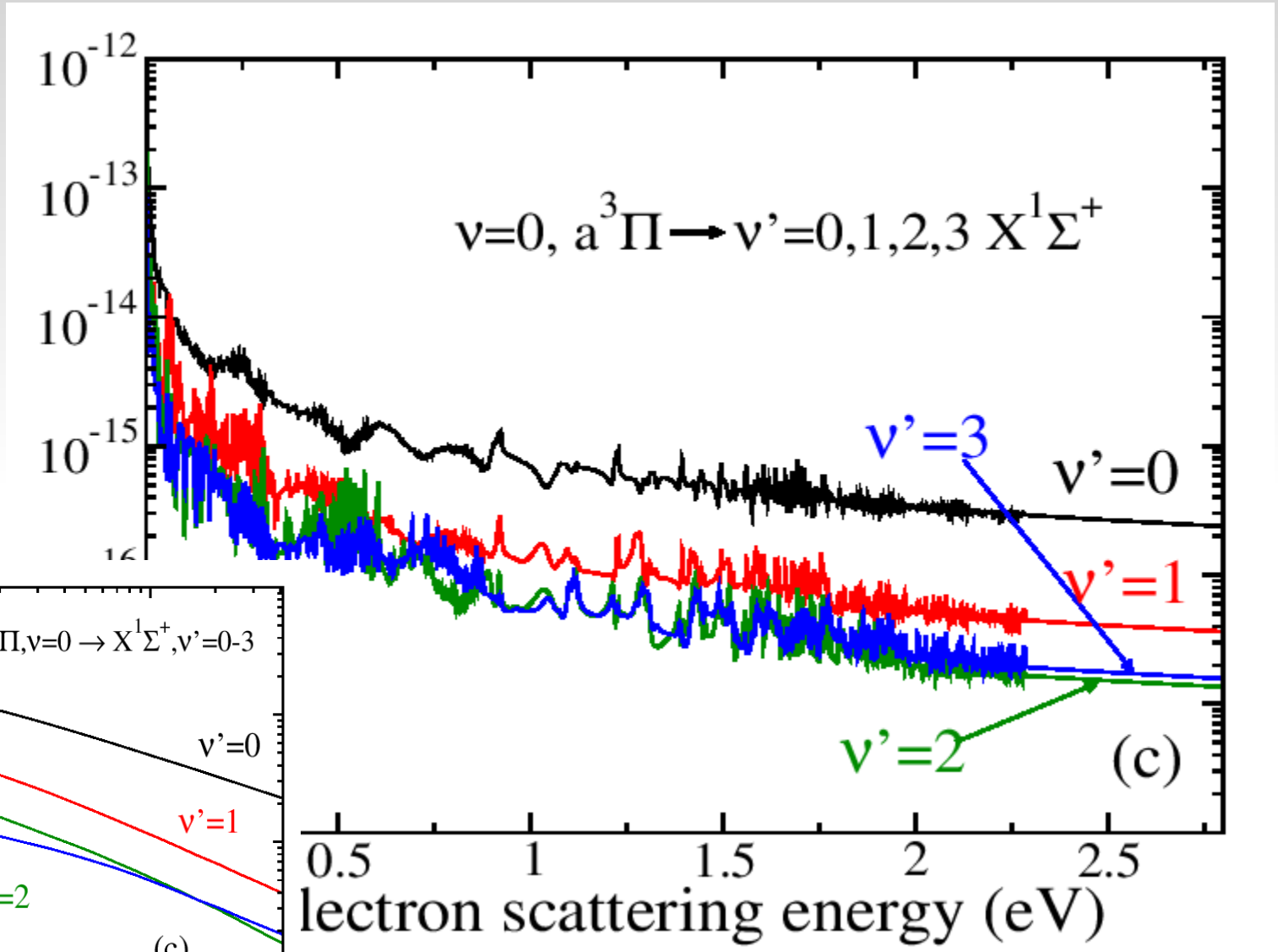
Cross sections for vibronic excitation





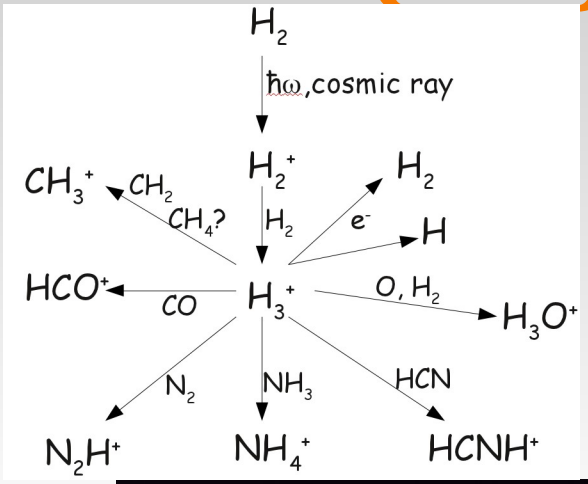
Cross sections for vibronic excitation





Dissociative recombination

Dissociative recombination (DR)



In the ISM

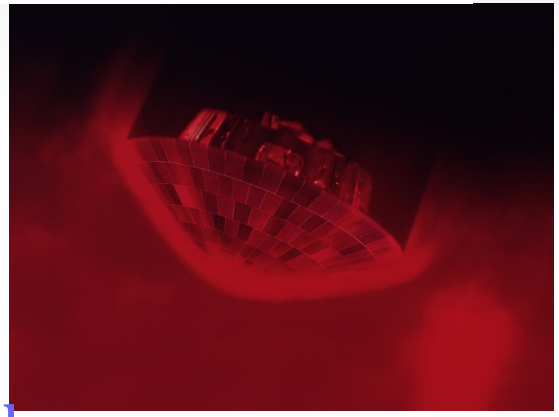
Examples: CH^+, SH^+, H_3^+, $CH_2NH_2^+$, H_3O^+, etc.

Spacecraft re-entry:

Plasma is created by collisional ionization:

N_2^+, O_2^+, NO^+, N^+,O^+, CO_2^+,CO^+,C_2^+, etc.

Destroyed by dissociative and radiative recombination



In planetary atmospheres

Examples:

$O_2^+ + e^- \rightarrow O + O^* \rightarrow O + O + \hbar\omega$ (Earth aurora)

$CH^+ + e^- \rightarrow C + H$, $SH^+ + e^- \rightarrow S + H$ (Mercury exosphere)

$H_3^+ + e^- \rightarrow H_2 + H$ or $H + H + H$ (Jupiter, Saturn)

Polyatomic targets

$$\langle b|v\ j\rangle = \Psi_v(R)\langle \Lambda|j\rangle ; \langle b'|\hat{S}|b\rangle = S^{\Lambda}_{l',l}(R)\delta(R',R)$$

*For non-linear molecules, the rotational frame transformation is modified.

*For the vibrational frame transformation, vibrational functions are needed.

*The vibrational wave functions could in principle be calculated in full dimensionality, which is only possible (with a reasonable effort) for triatomic molecules.

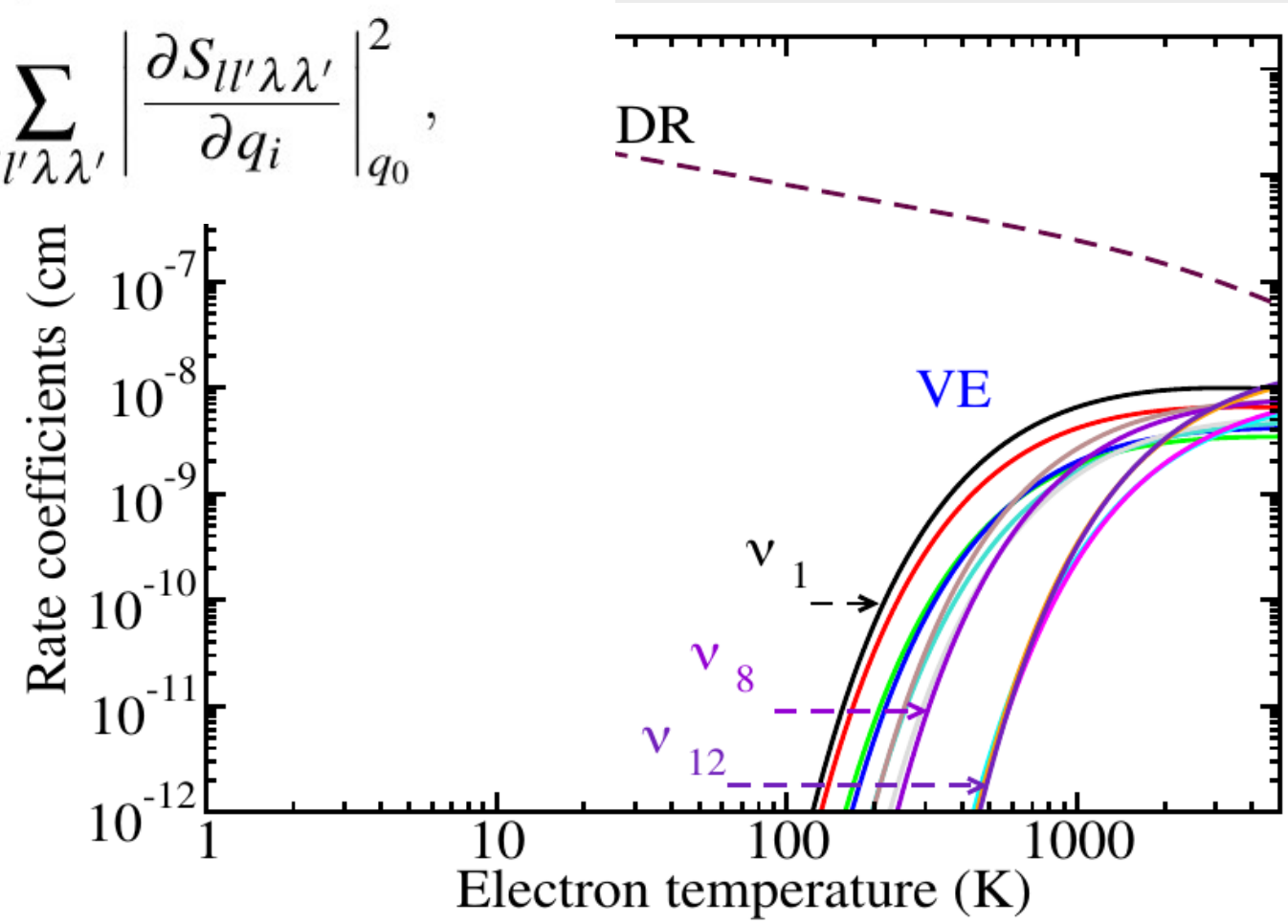
*The geometry-dependent S-matrix $s(\boldsymbol{R})$ should be calculated for many geometries.

* A simpler approach is to use normal modes. The normal modes approach can be used for larger molecules. Less geometries in the electron-scattering calculations are needed.

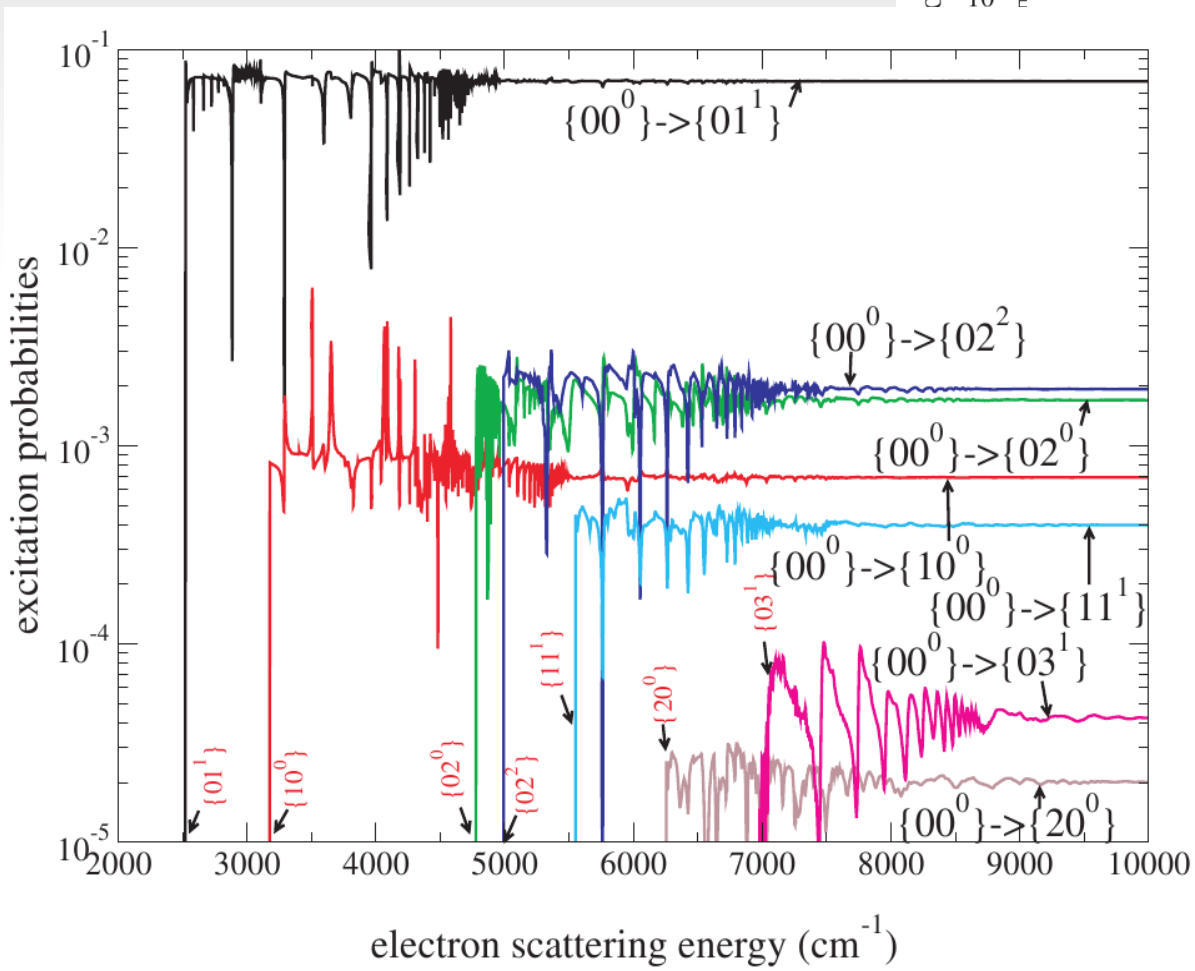
Example: Vibrational excitation of $CH_2NH_2^+$

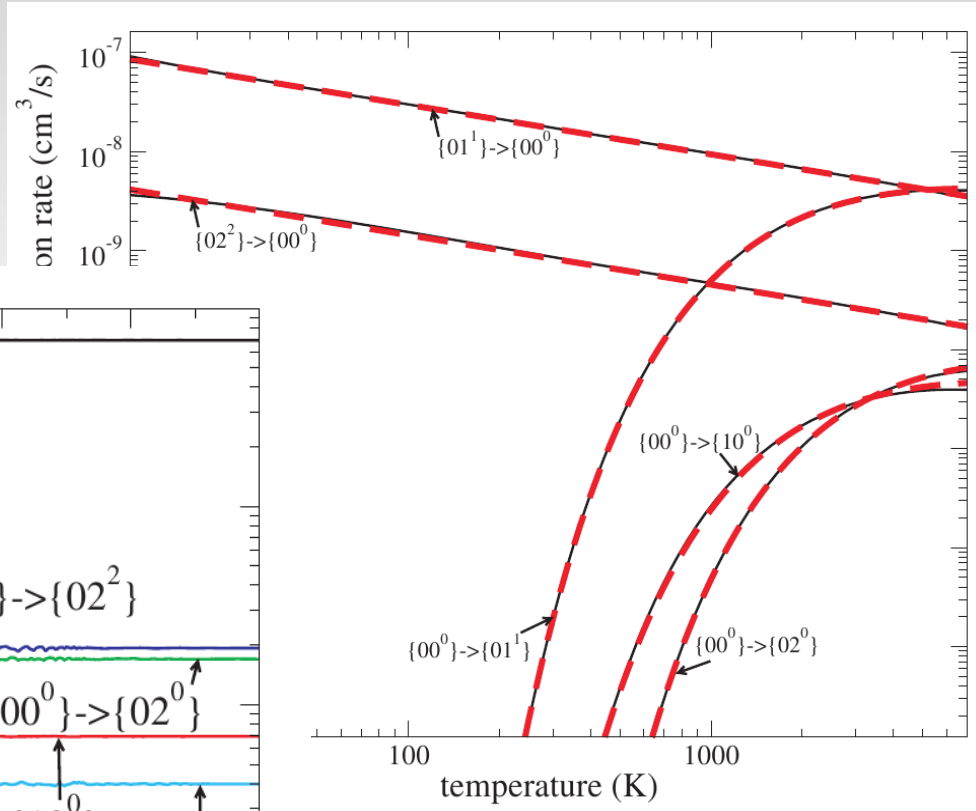
$$\sigma_{v_i'+1\leftarrow v_i'}(\varepsilon) = \frac{\pi\hbar^2}{2m_e\varepsilon}(v_i'+1)\theta(\varepsilon-\hbar\omega_i)\,P_i$$

$$P_i = \frac{1}{2}\sum_{ll'\lambda\lambda'}\left|\frac{\partial S_{ll'\lambda\lambda'}}{\partial q_i}\right|^2_{q_0},$$

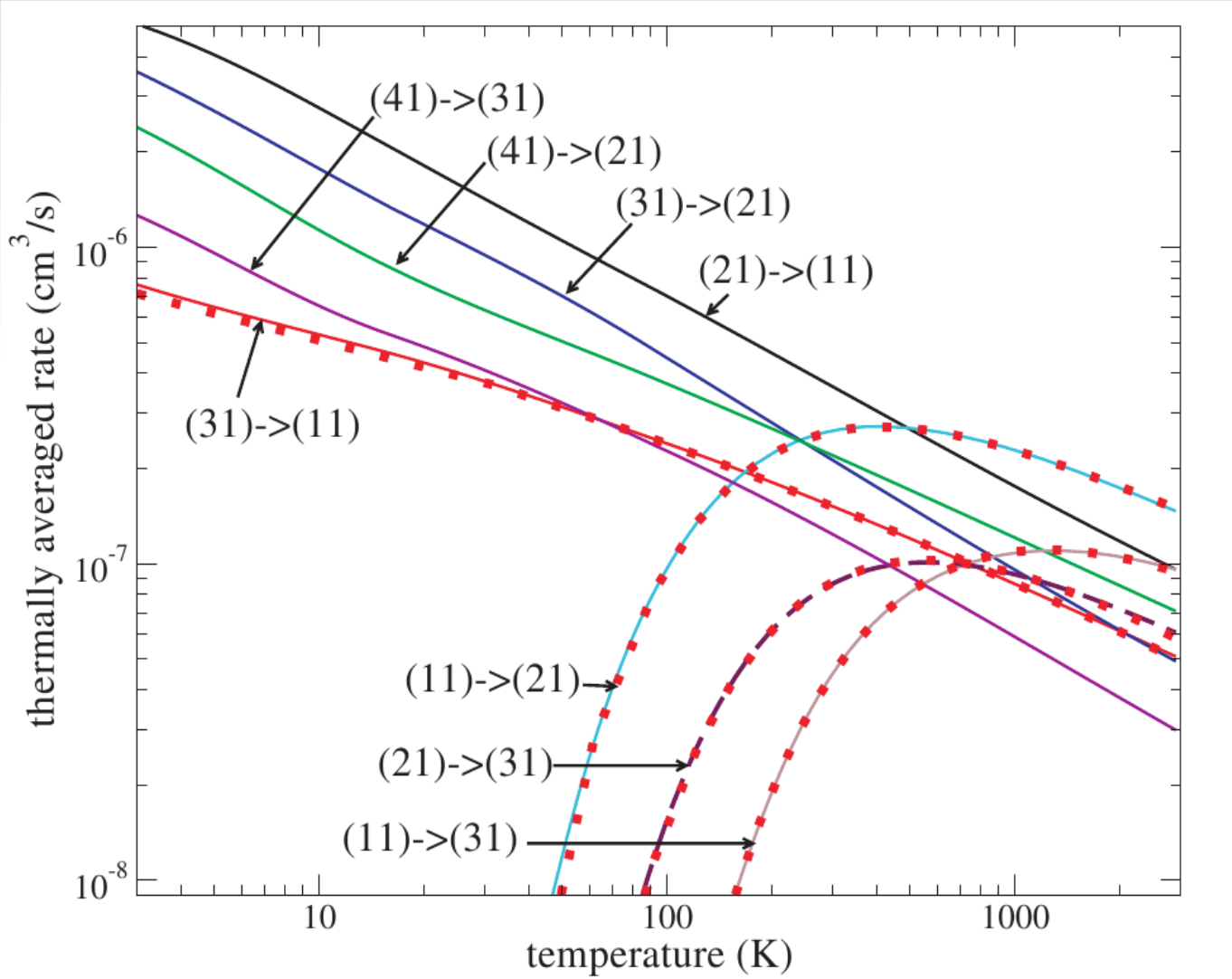


Vibrational excitation of H_3^+





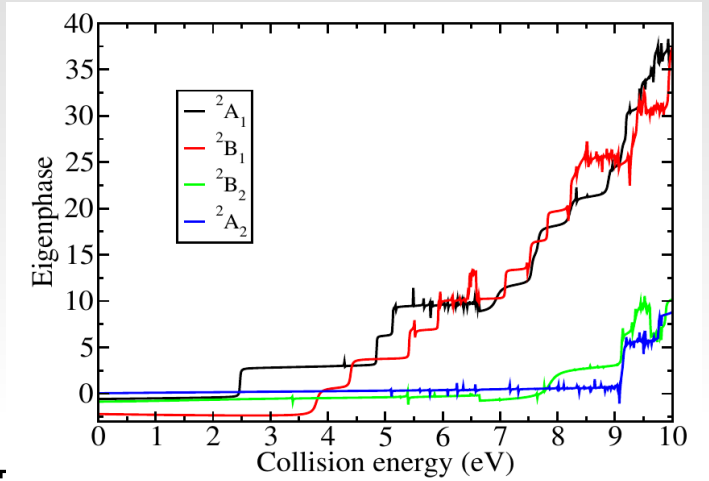
Rotational excitation of H_3^+ ground vibrational level

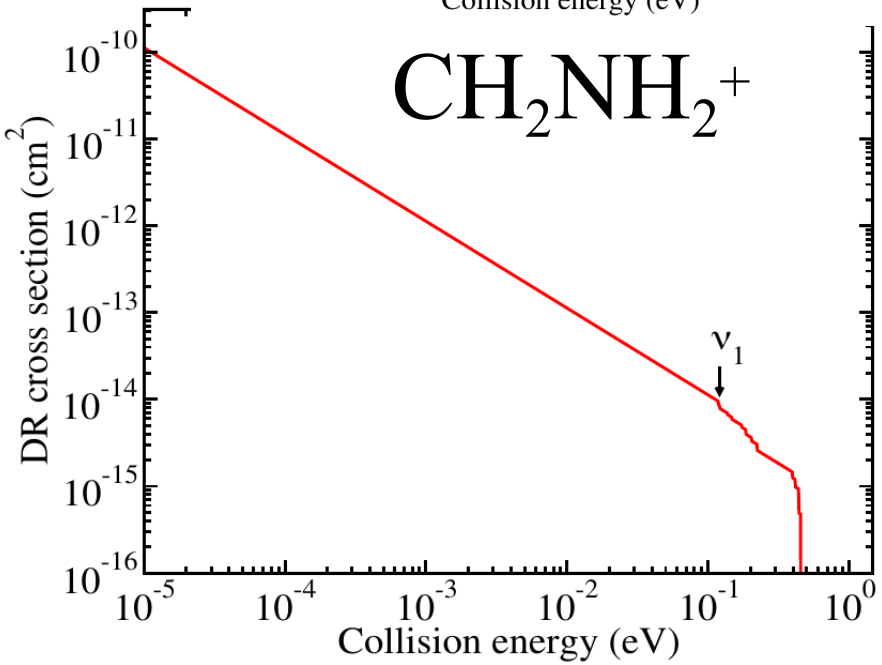


Simple theoretical method for polyatomic ions

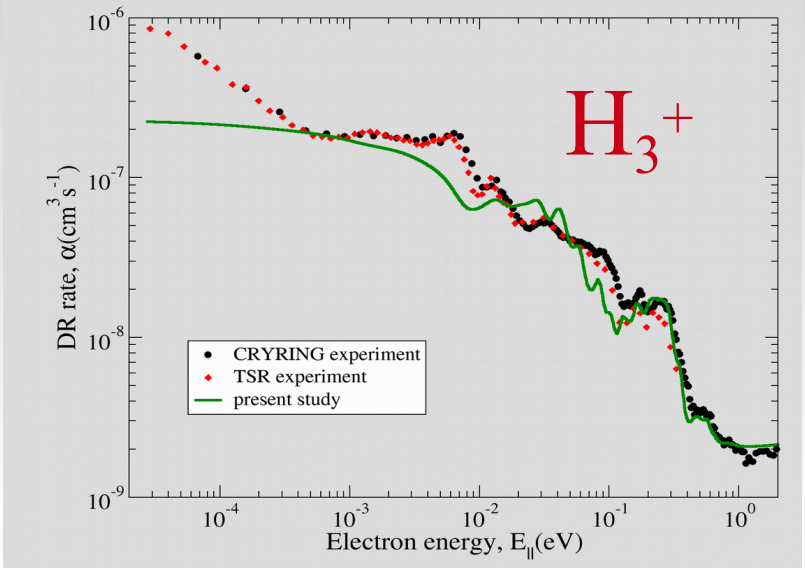
$$\langle \sigma^{DR}_{\{v'\}}(\varepsilon) \rangle = \frac{\pi\hbar^2}{2m_e\varepsilon} \sum_i^{12} (v'_i + 1)\theta(\hbar\omega_i - \varepsilon) P_i$$

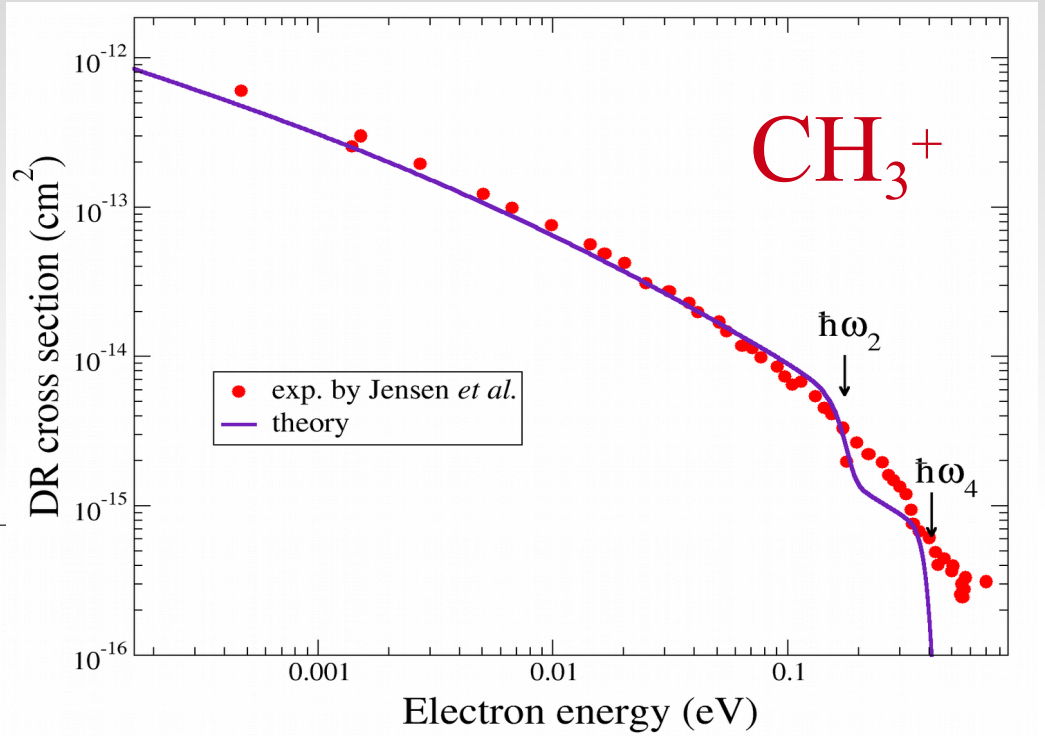
$$P_i = \frac{1}{2} \sum_{ll'\lambda\lambda'} \left| \frac{\partial S_{ll'\lambda\lambda'}}{\partial q_i} \right|^2_{q_0}$$

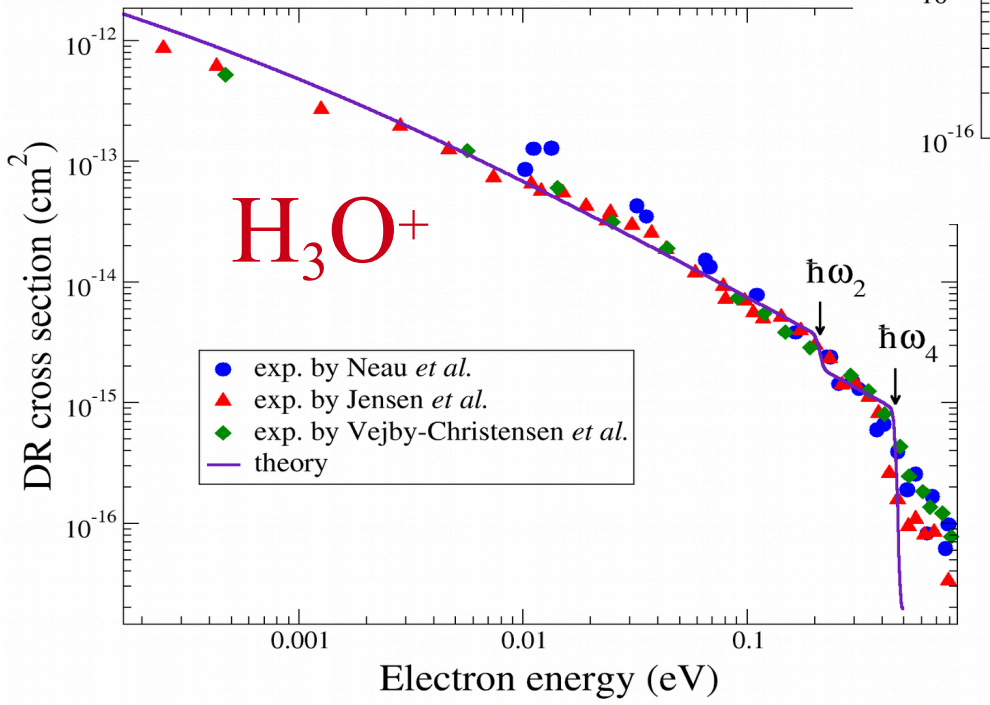


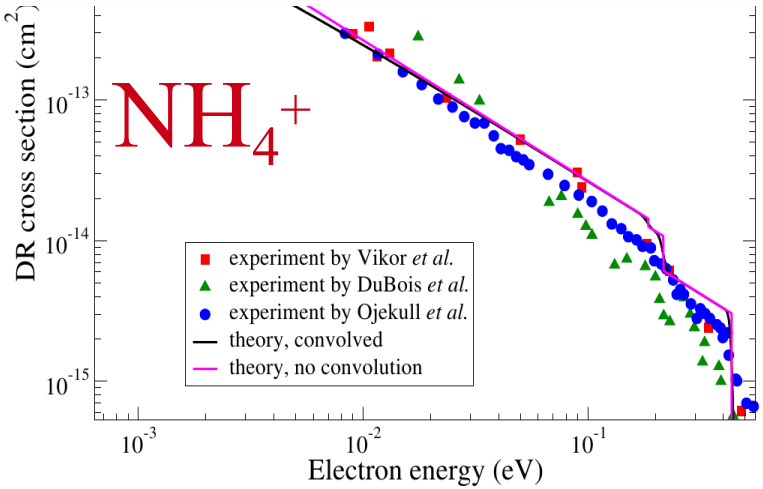


Some other examples









Negative molecular ions

formation by the radiative attachment

Negative ions in the interstellar medium

- 6 negative molecular ions have been recently found in interstellar clouds: C_4H^-, C_6H^-, C_8H^- , CN^-, C_3N^-, C_5N^- .
- In 1980's it was suggested that large polyatomic molecules may form negative ions by the process of radiative attachment.
- The proposed mechanism of formation of C_nH^- and C_nN^- in the ISM is radiative electron attachment (REA):

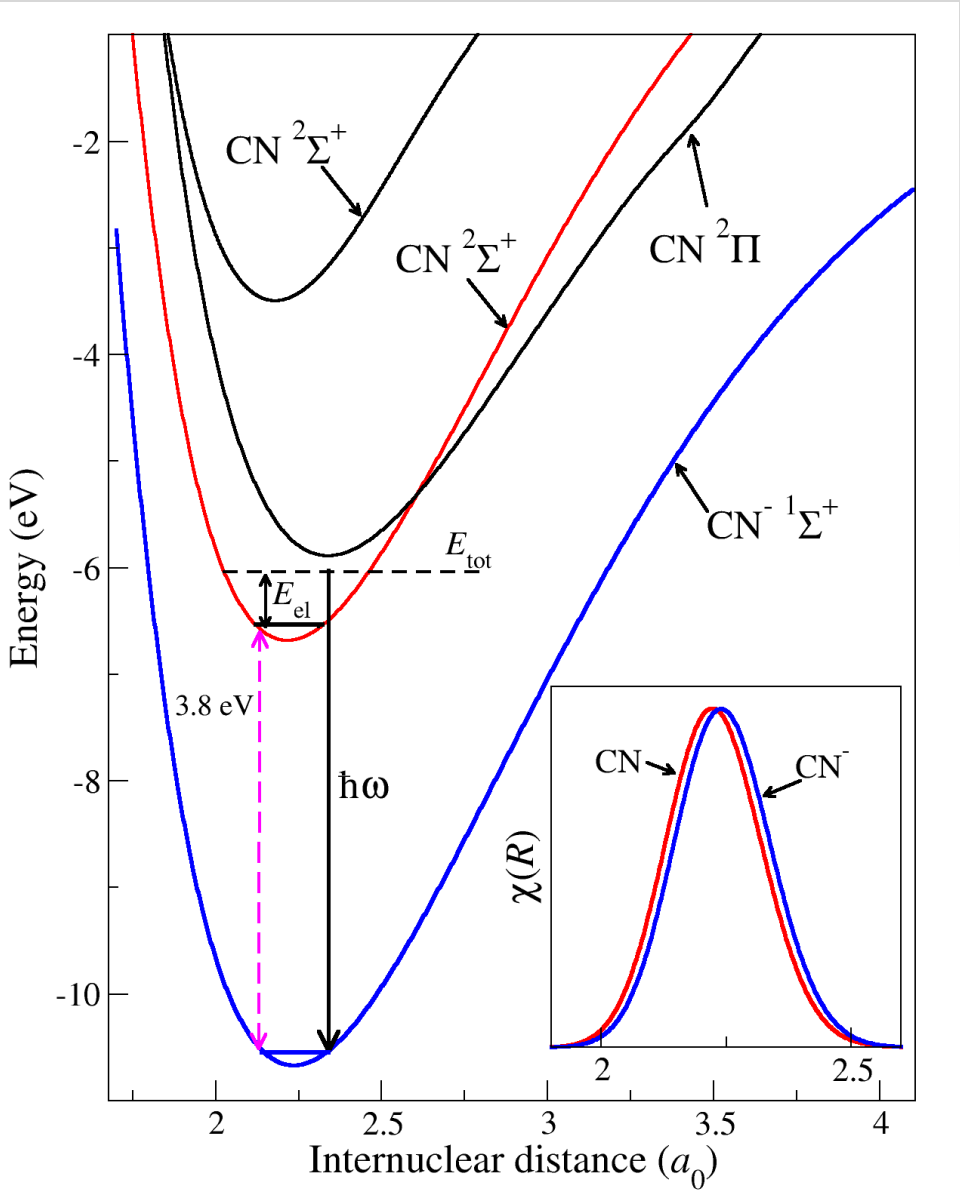
$$C_nH + e^- \rightarrow C_nH^- + \hbar\omega, \quad C_nN + e^- \rightarrow C_nN^- + \hbar\omega$$

Quantum approach for REA

We have developed a quantum approach to study REA.

It is based on the first principles. Electron-scattering calculations are performed using the complex Kohn and UK R-matrix methods.

We apply the approach to seven molecules, C_nH^-, (n=2,4,6,8) and C_nN^- (n=1,3,5).



Few elements of the approach

The Einstein coefficient for spontaneous emission of a photon from an electronic continuum state with incident-electron energy E into a bound state $|f\rangle$:

$$P_{f\leftarrow i} = \frac{4}{3}\frac{\omega^3}{\hbar c^3}|\langle f|\vec{d}|i\rangle|^2$$

with $\hbar\omega = E_i + A$, A is the electron affinity.

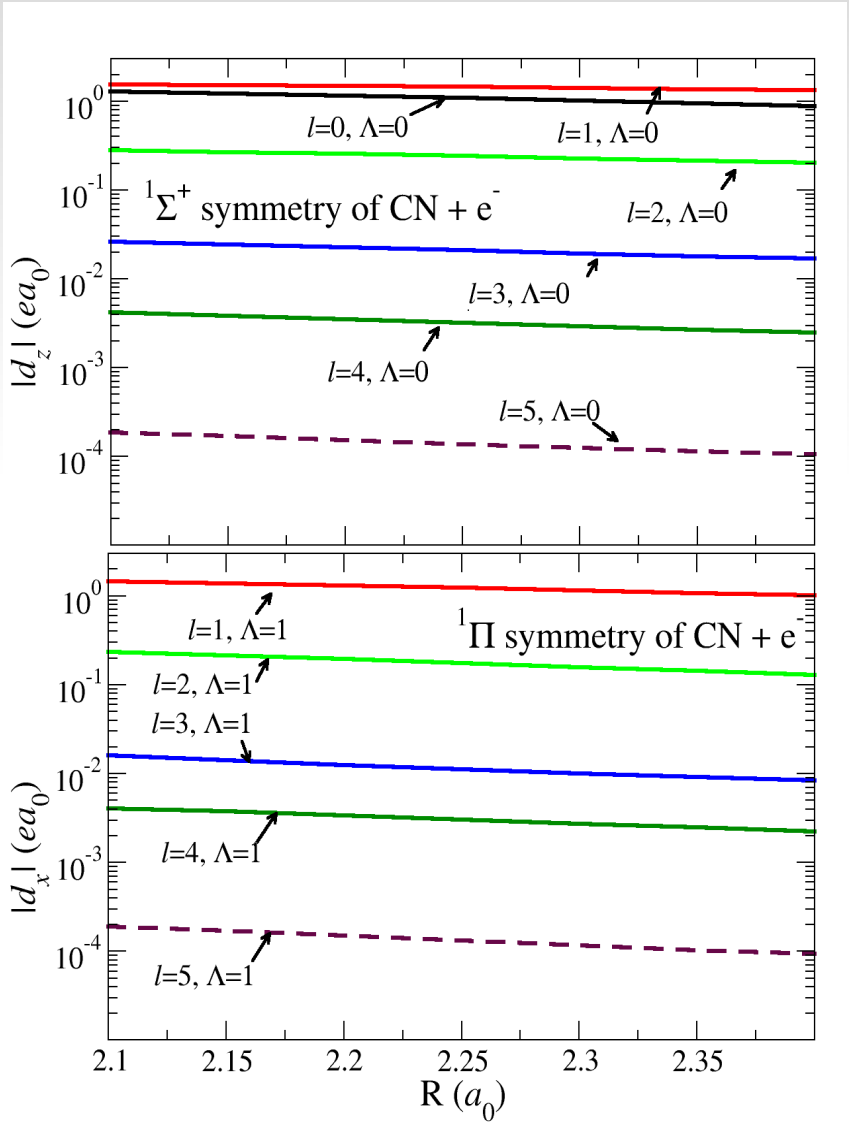
Cross-section for the radiative attachment is then obtained by dividing the Einstein coefficient with the density of electron current in the incident wave. In our case, the current density is velocity.

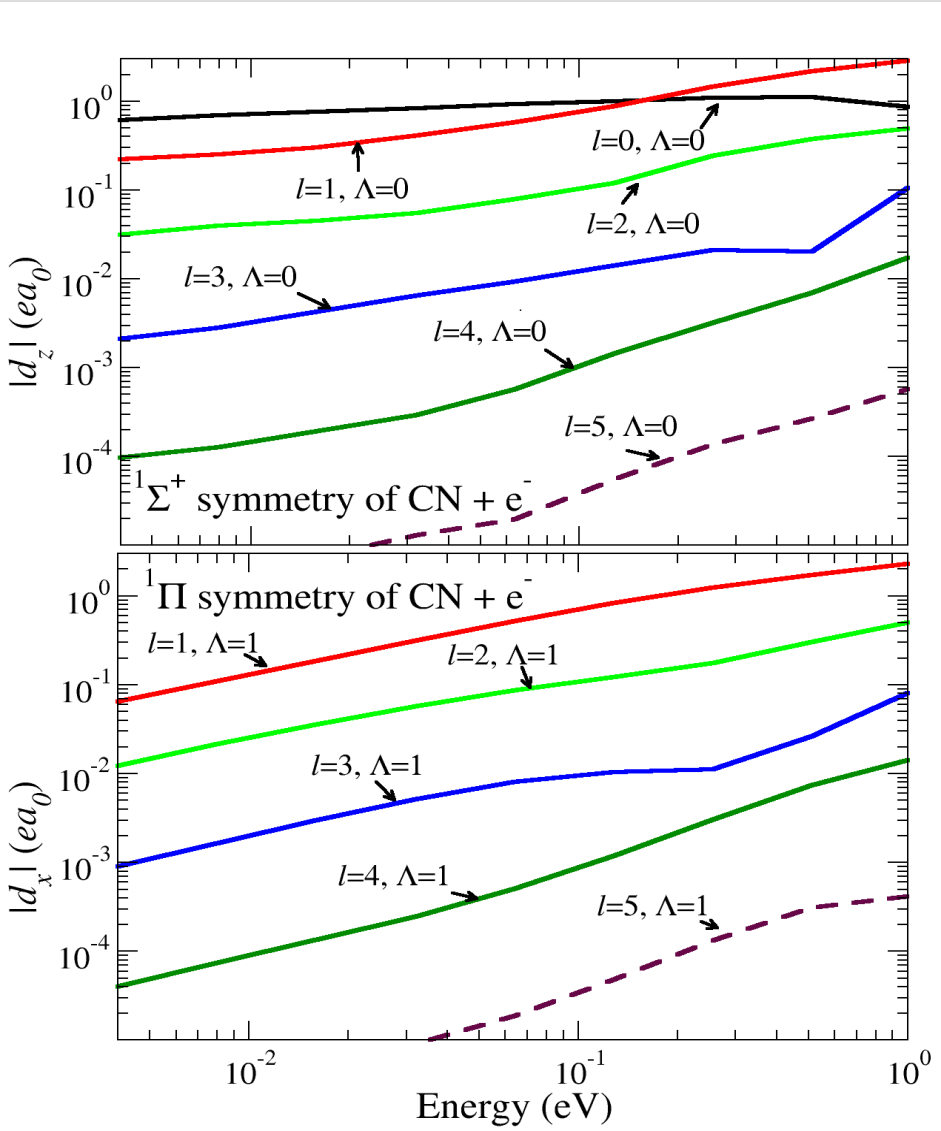
$$\sigma_i = \frac{g_f}{g_i}\frac{8}{3}\frac{\pi^2\omega^3 m_e}{k^2\hbar^2c^3}\sum_{l\pi}\left|d^{(v_i\to v_n)}_{\pi,\Gamma l-\pi}\right|^2$$

$$d_{\pi,\Gamma l\lambda} \equiv \langle\Psi_f|d_\pi|\Psi_{\Gamma l\lambda}\rangle = -\sum_{k=1}^{N}\int \Psi^*_f(r_1,\ldots,r_N)er_{k\pi}\Psi_{\Gamma l\lambda}(r_1,\ldots,r_N)\,d^3r_1,\ldots,d^3r_N$$

$$d^{(v\to v_f)}_{\pi,\Gamma l\lambda} = \int \chi^{J_f}_{v_f}(R)\langle\Psi_f|d_\pi|\Psi_{\Gamma l\lambda}\rangle_r\,\chi^j_v(R)dR$$

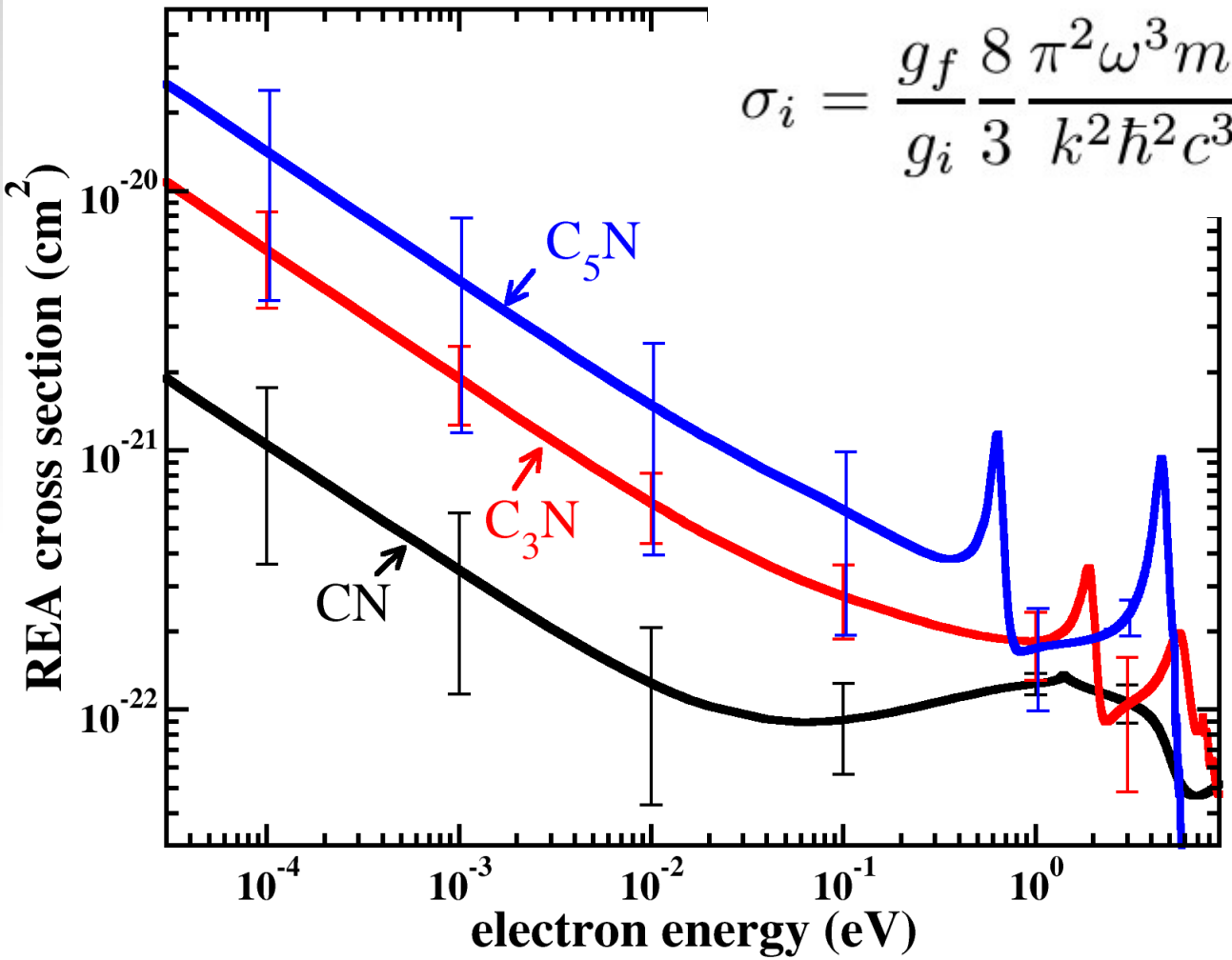
Transition dipole moments as a function of energy and geometry





REA cross sections

$$\sigma_i = \frac{g_f}{g_i}\frac{8}{3}\frac{\pi^2\omega^3 m_e}{k^2\hbar^2c^3}\sum_{l\pi}\left|d^{(v_i\to v_n)}_{\pi,\Gamma l-\pi}\right|^2$$



Obtained REA cross sections and rate coefficients are too small to explain the observed anion abundance in the ISM (If one assumes that the anions are formed by REA).

Photodetachment

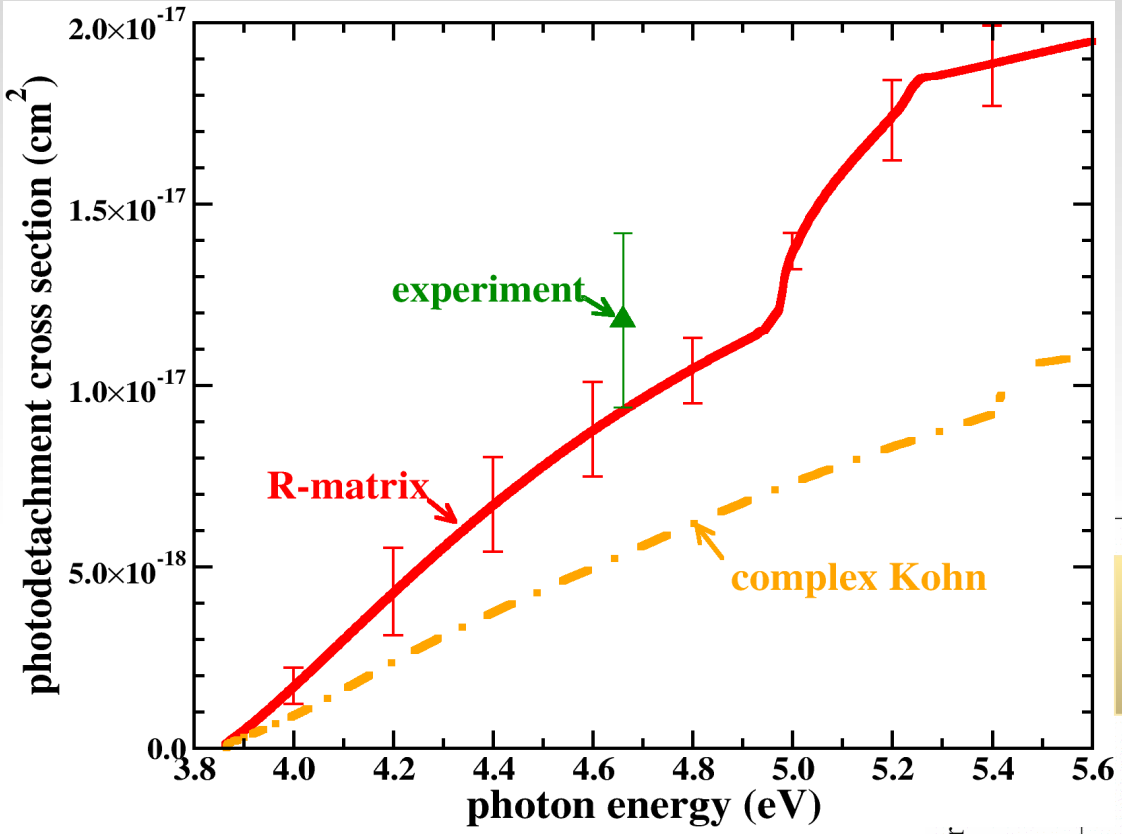
Photodetachment

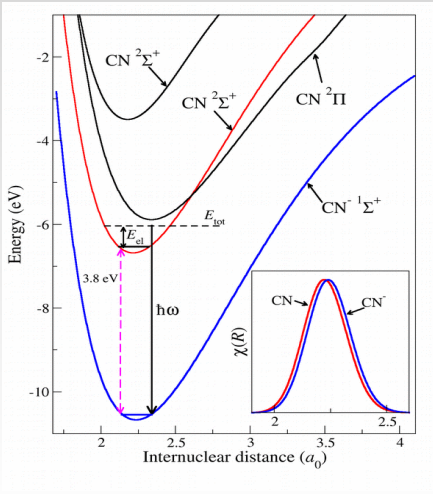
There is no experimental data on radiative attachment to the C_nH and C_nN molecules. But the calculated transition dipole moments can be used to compute photodetachment cross sections, which could be compared with experimental data obtained by R. Wester's group.

With the chosen normalization (the UK R-matrix code) of electronic continuum wave functions, the photodetachment cross section is

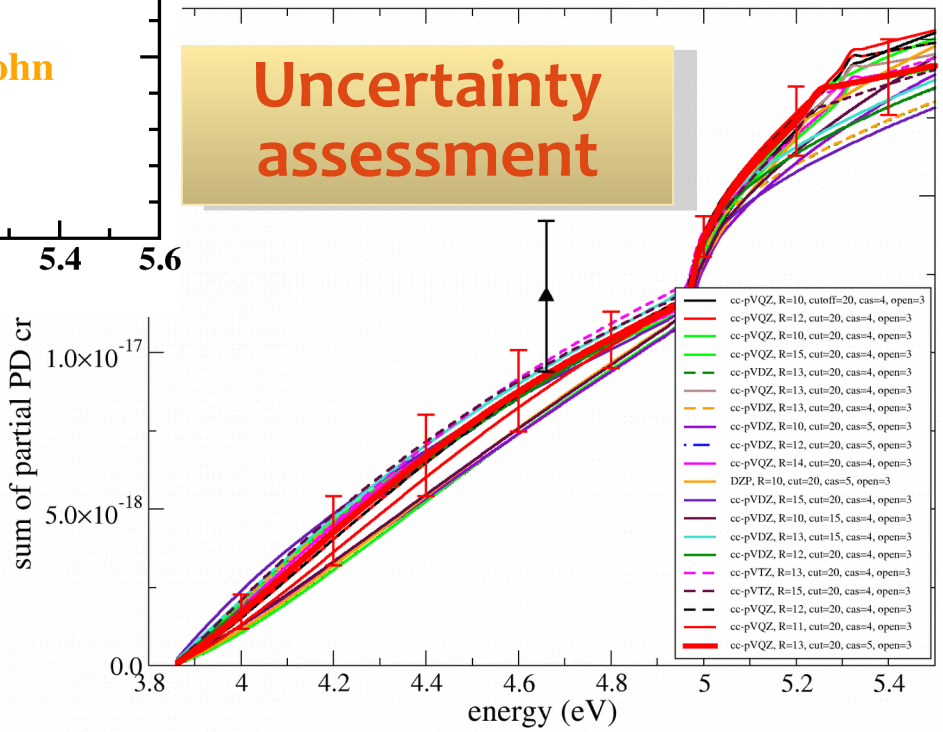
$$\sigma_{PD} = \frac{4m_e\pi^2\omega}{3\hbar^2 c} \sum_{l\pi} \left| d^{(v_i \to v_n)}_{\pi,\Gamma l-\pi} \right|^2$$

CN- photodetachment cross section



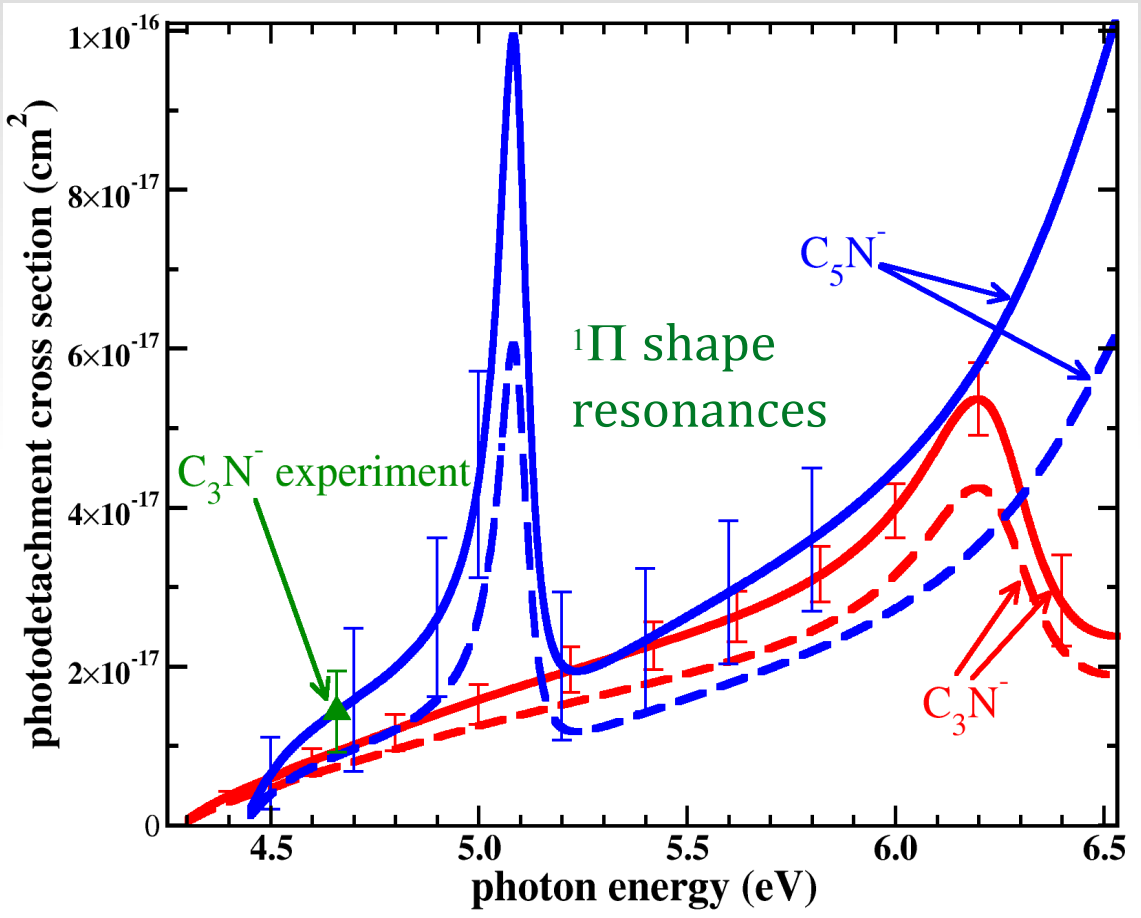


Uncertainty assessment



CN- exp: Kumar *et al.* ApJ (2013)

PD cross sections for C_3N^- and C_5N^-



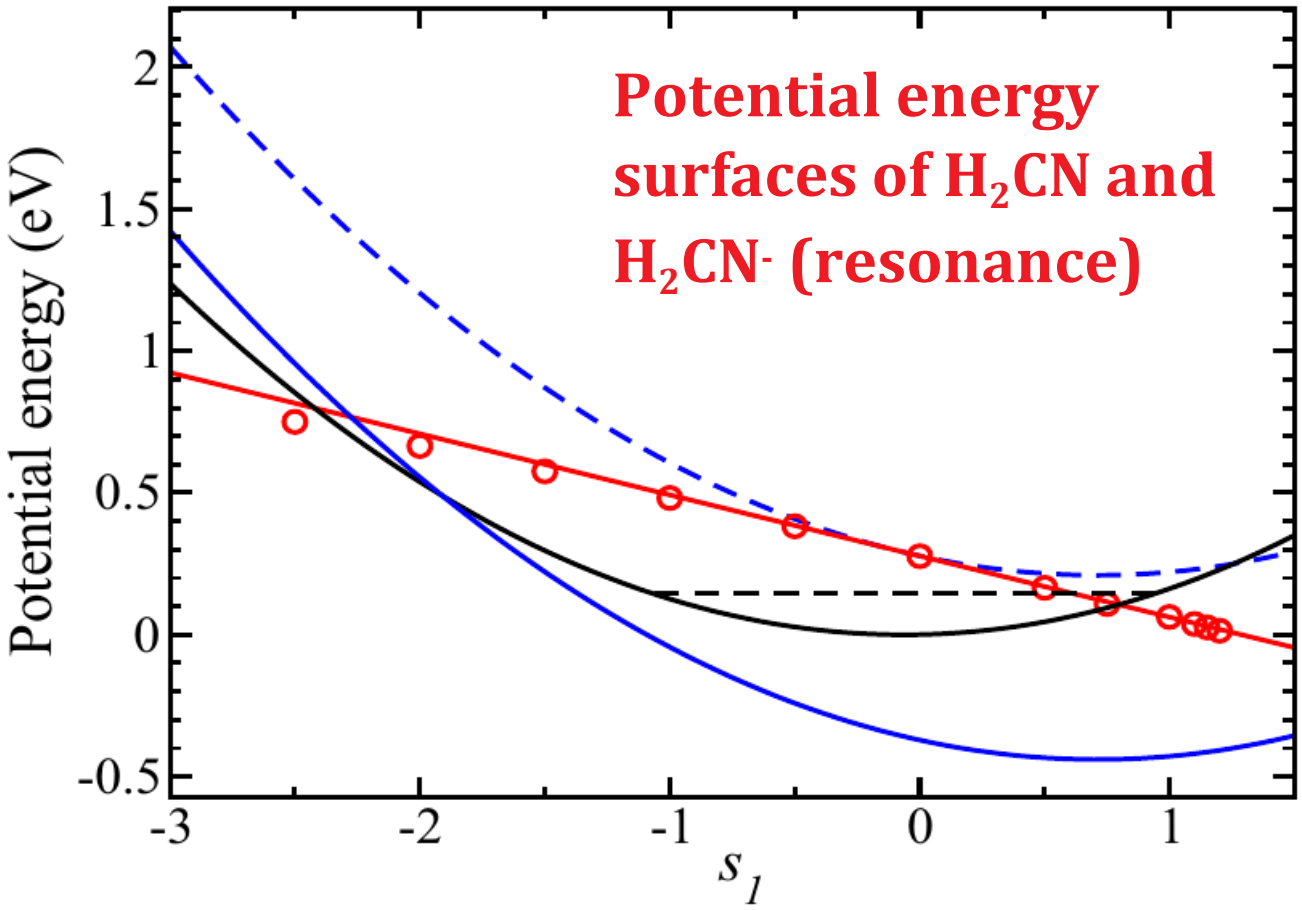
C_3N^- exp: Kumar *et al.* ApJ (2013)

What else can produce negative molecular ions in the ISM?

Dissociative electron attachment? For example: $H_2CN + e^- \rightarrow H_2 + CN^-$

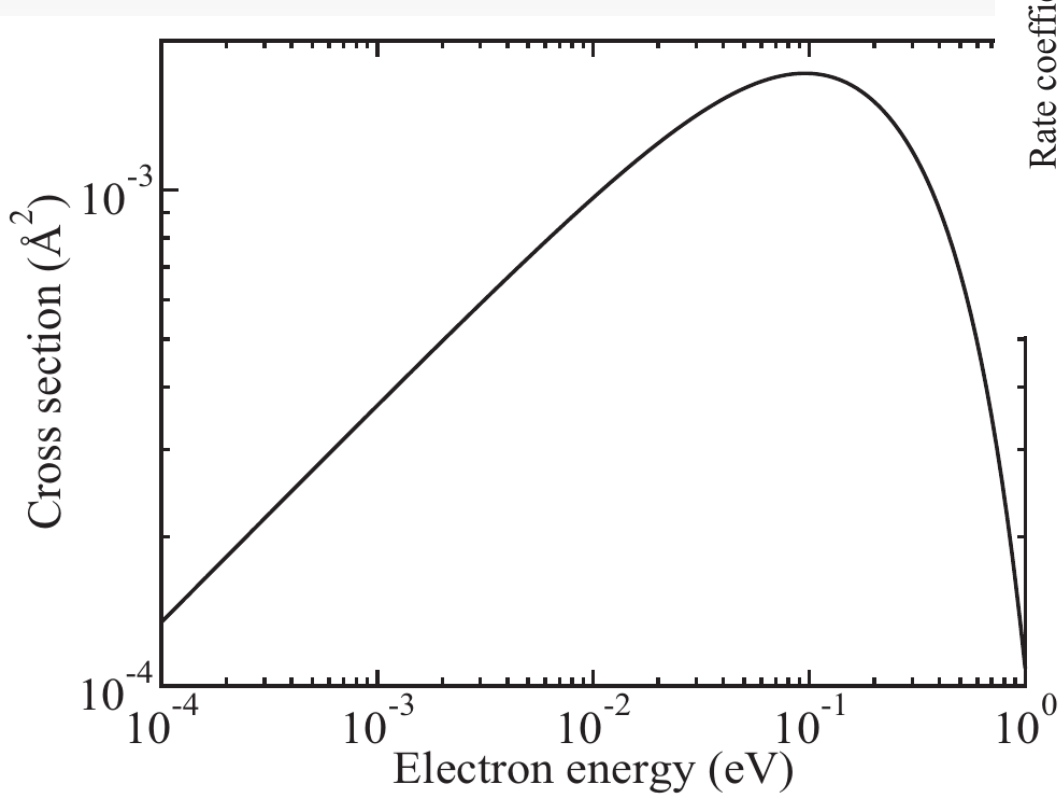
Simplified model to treat the electron attachment of complex molecules: Application to H_2CN and the quest for the CN^- formation mechanism

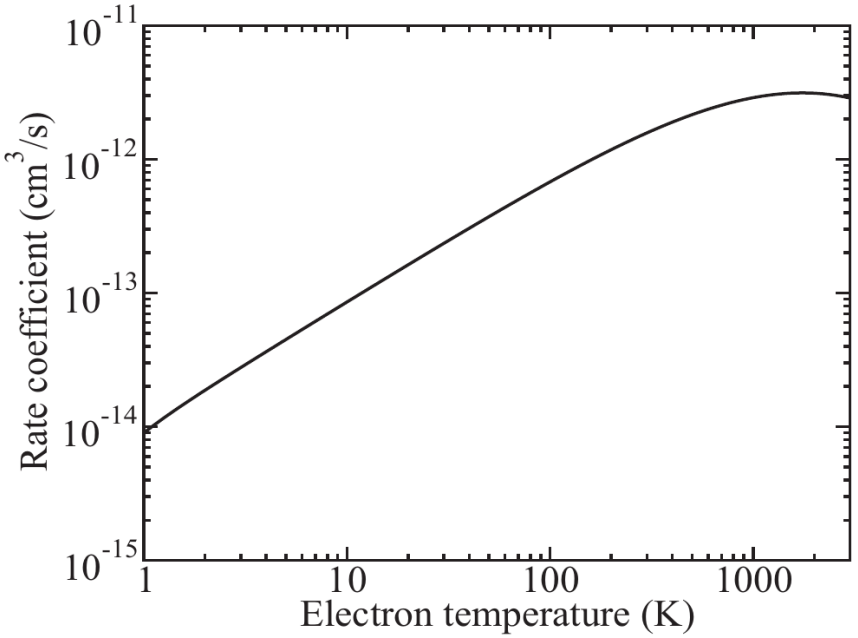
C. H. Yuen,[1] N. Douguet,[1] S. Fonseca dos Santos,[2] A. E. Orel,[3] and V. Kokoouline[1]



Cross section and rate coefficient are small

$$\sigma_{\mathrm{cap}}(\varepsilon) = g\frac{2\pi^2}{k^2}\frac{\Gamma(s_\varepsilon)}{|U_d'(s_E)|}|\zeta_1(s_E)|^2$$





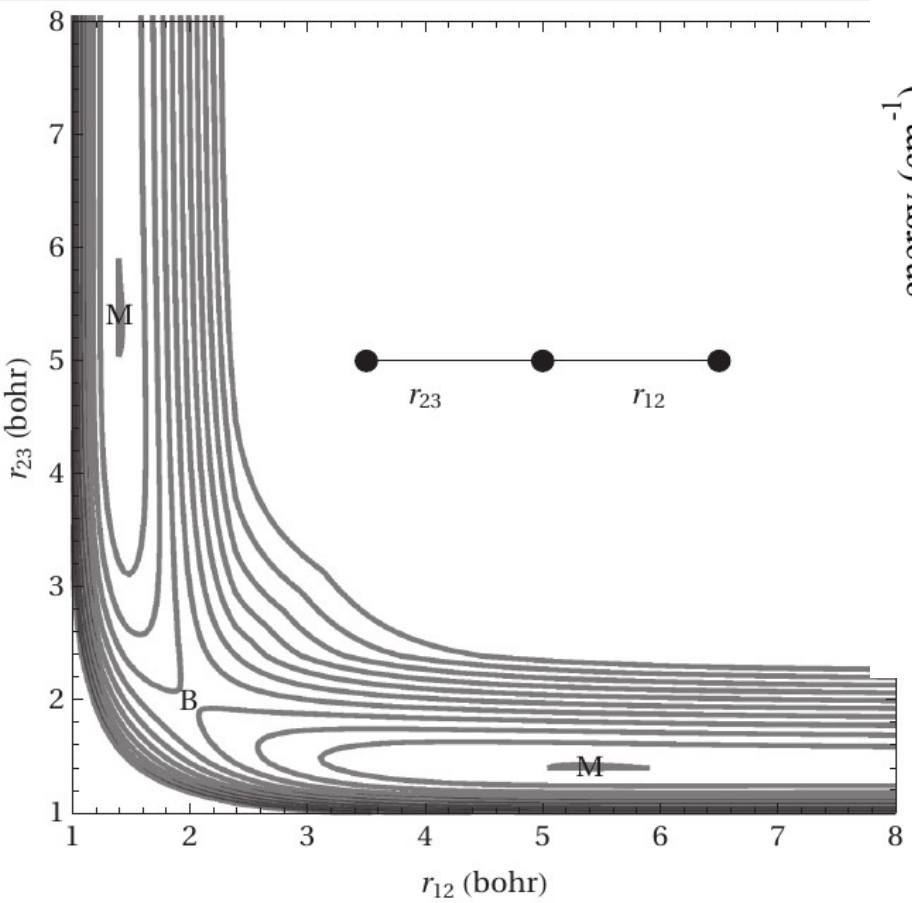
Any other ideas how negative molecular ions are formed in the ISM?

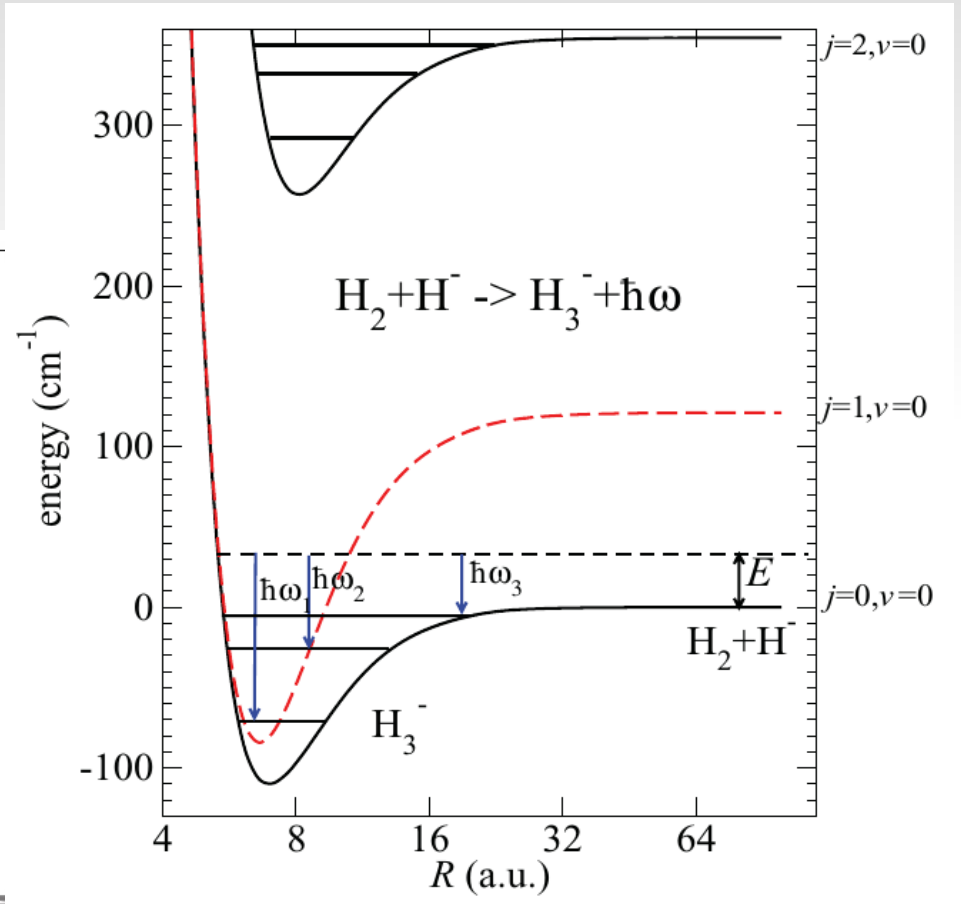
Tunneling in slow atom-molecule collisions

H_2+H^- and H_2+D^- collisions

Formation of H_3^- by radiative association

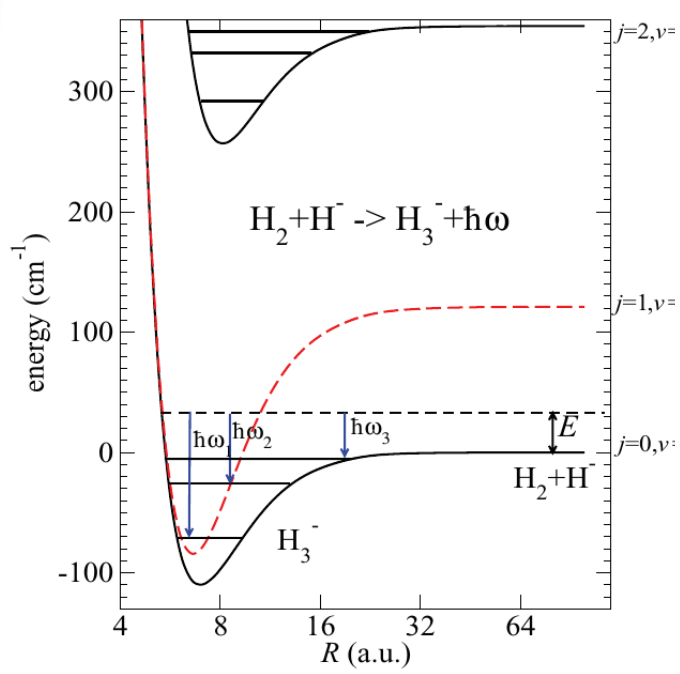
Ayouz *et al.* 2011

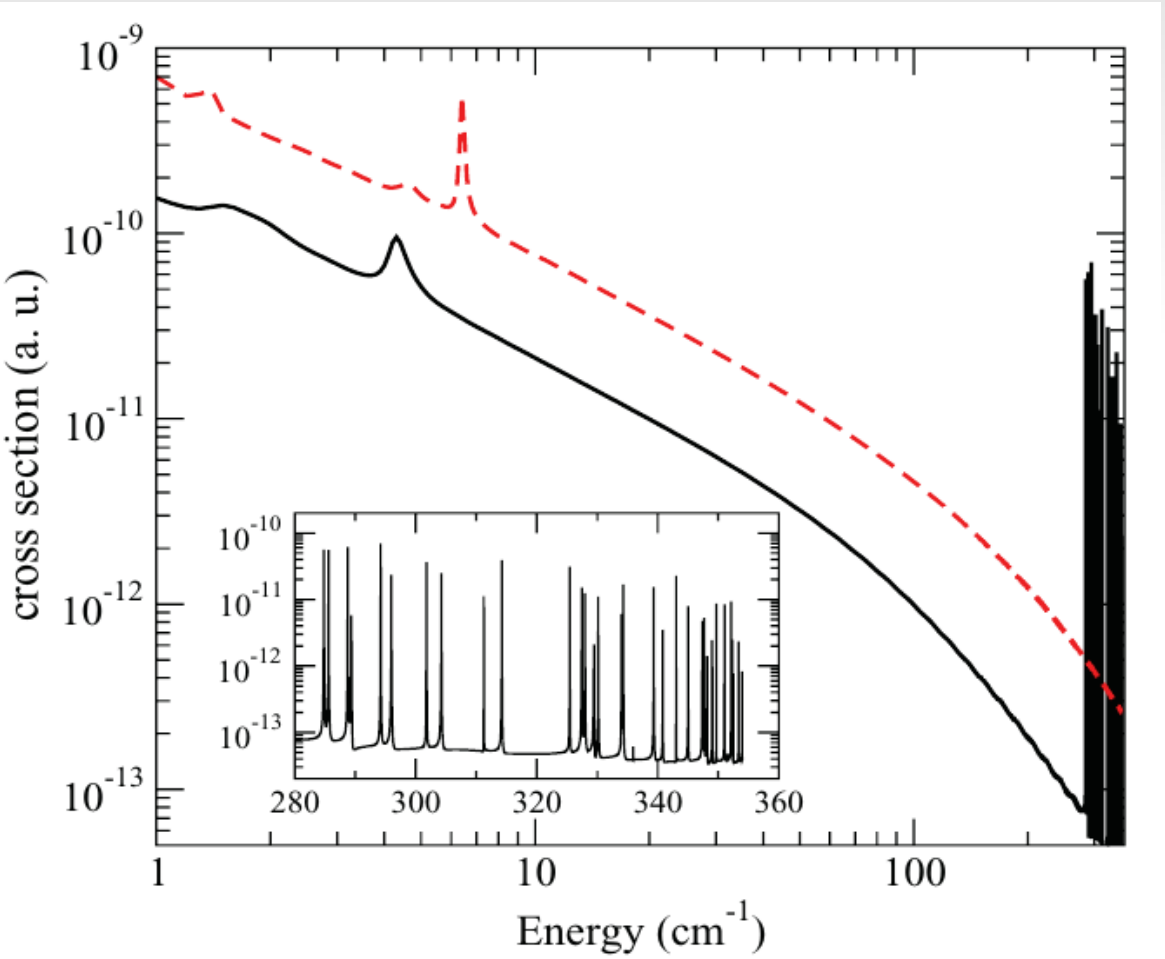




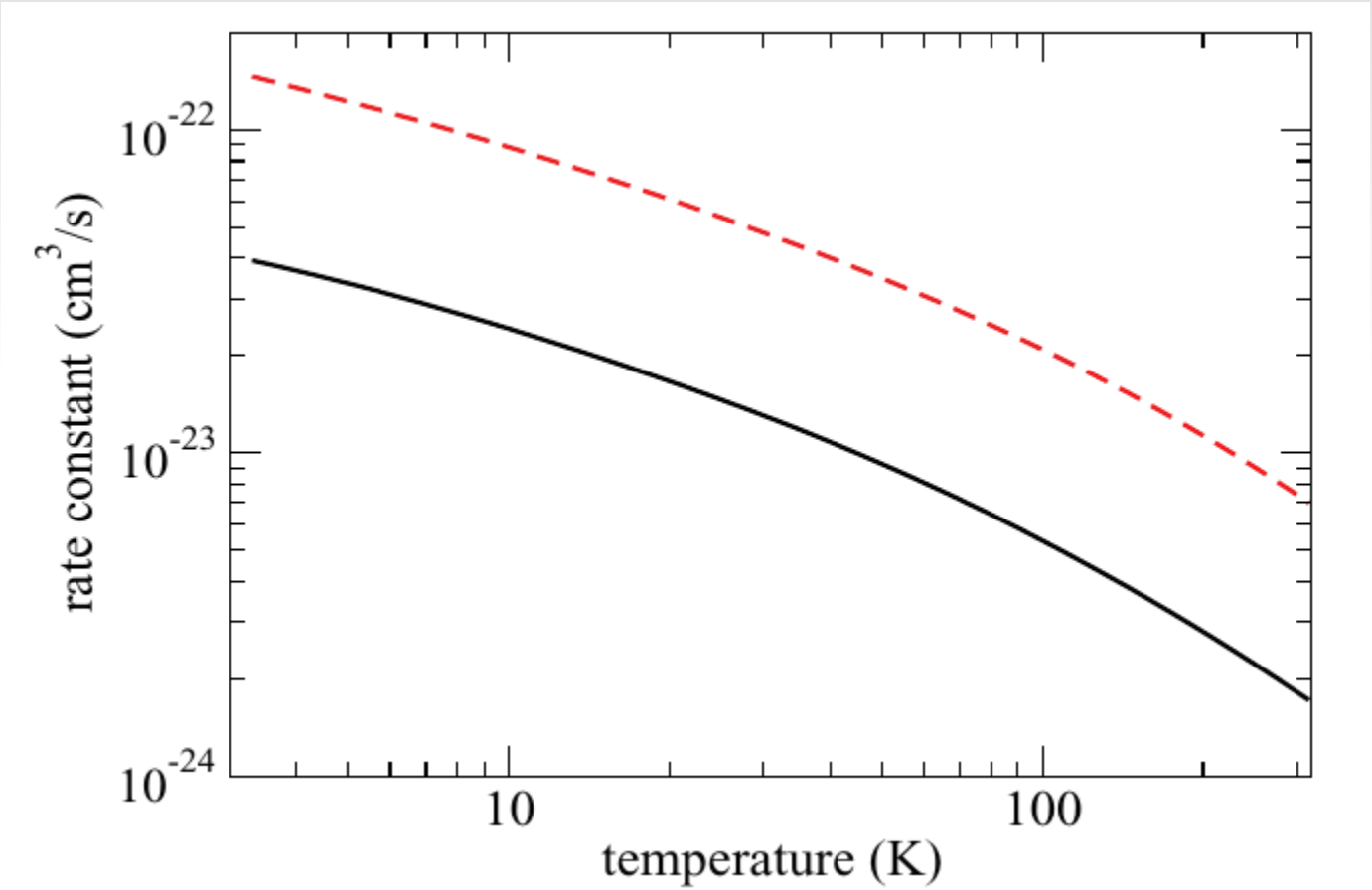
Radiative association cross section is very small

Ayouz *et al.* 2011



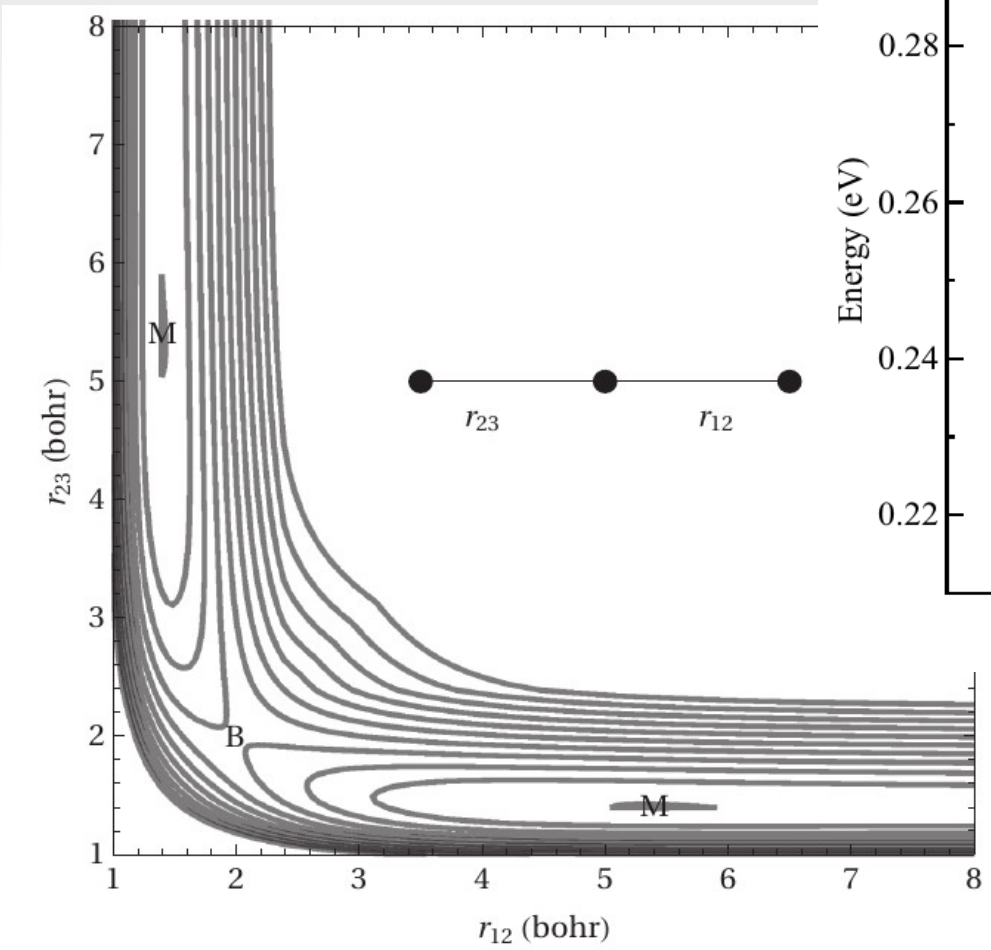


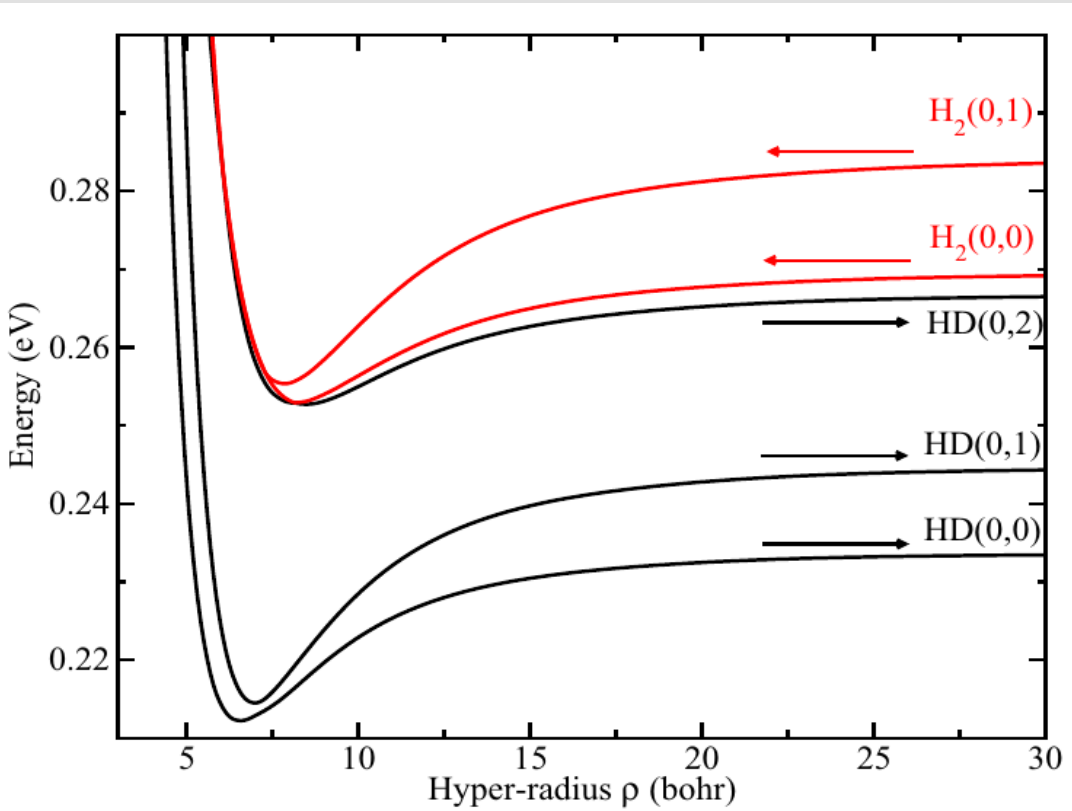
Rate coefficient is too small to produce detectable amount of H3- in the ISM



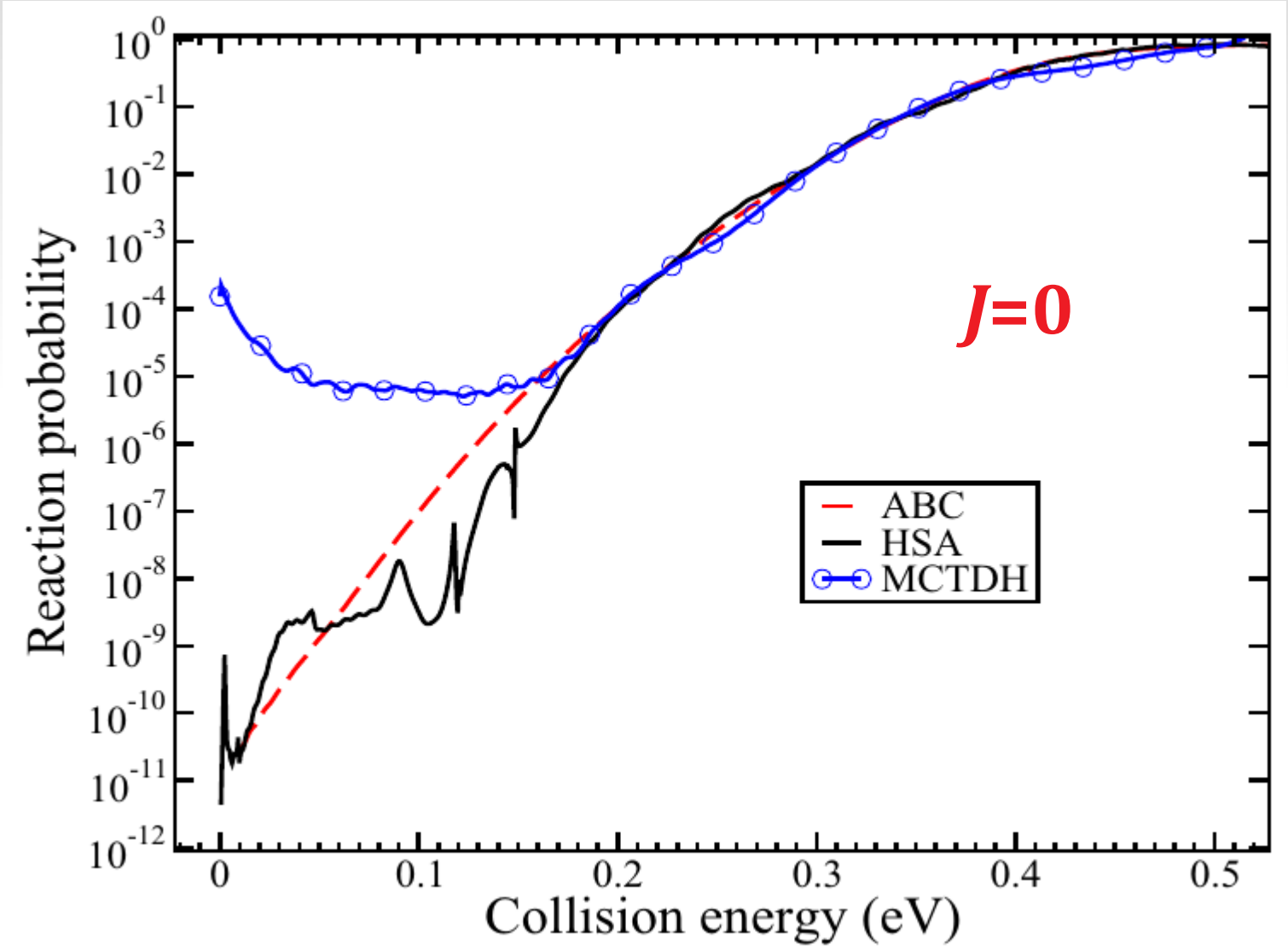
$H_2+D^- \rightarrow HD+H^-$

The reaction was studied by the Innsbruck group

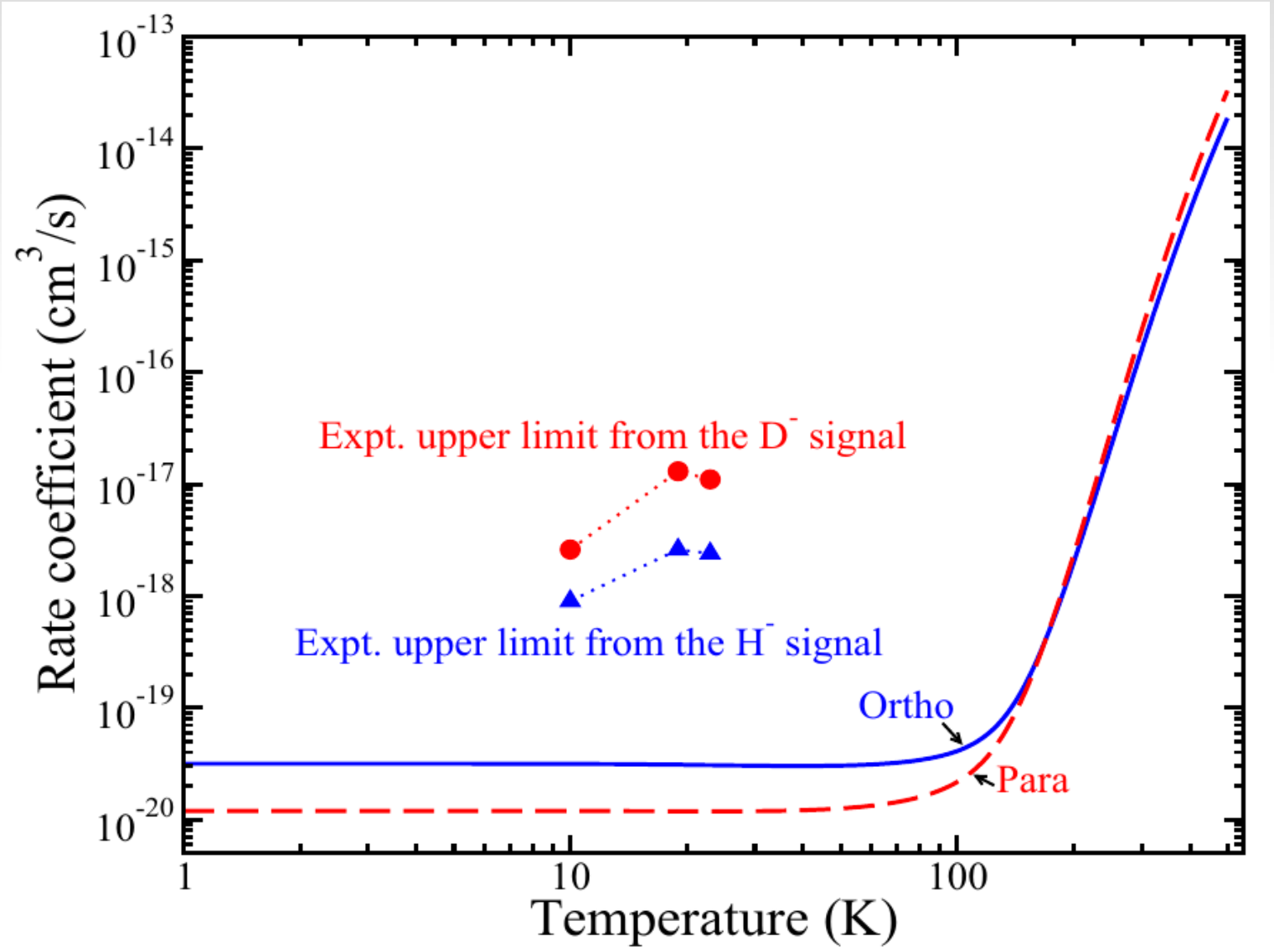




Technically difficult problem due to a small tunneling probability



The rate coefficient for the reaction is small



Conclusions: e^--*Mol*$^+$ collisions

- Polyatomic ions: Theory can now give quite reliable rate coefficients for dissociative recombination and vibronic excitation of closed-shel molecular ions.
- Now the approach could be applied to the ions with low-energy excited states. Such ions were known to be difficult to treat theoretically using previous theoretical methods.
- We applied the method for vibronic excitation of CH^+. We expect that the method should work also for dissociative recombination of such ions and photoionization of molecules with complex electronic structure.
- Diatomic ions: Curik and Greene have just demonstrated that for DR HeH^+ the theory wth energy-dependent quantum defects is able to describe accurately positions of individual resonances in the experimental spectrum. Normally, the present approach has that energy dependence (of the scattering matrix) included.

Conclusions: Anion formation

- Cross sections for the radiative association and radiative attachments are too small to form the H_3^- and C_nH^-/C_nN^- ions in the ISM. Fully quantum approach was applied and later confirmed by independent calculations by the Bordeaux group (Stoeklin *et al.*).
- On the other hand, the same theory agrees with the experimental results of photodetachment of CN^-, C_3N^-, C_5N^-.
- Other mechanisms for anion formation in the ISM?
- We studied H2 + D- → HD + H- reaction.

Acknowledgments

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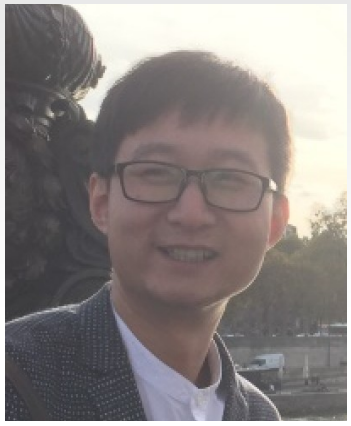

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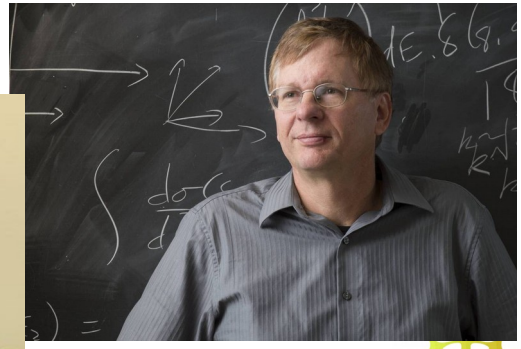

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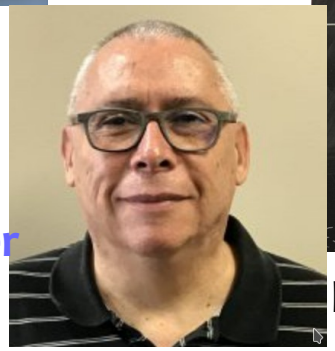

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