Electron-molecule scattering using Quantemol in applications for astrophysics

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Rotational and vibrational excitations of molecular ions by an electron

Cross sections for rotational and vibrational excitation of molecules by an electron impact are needed to model planetary atmospheres and the interstellar gases as well as to interpret observations.

Summary of the approach

- Cross sections for rotational and vibrational excitation are obtained from the scattering matrix, $S_{r'v';\,rv}(E)$.
- The scattering matrix depends strongly on energy if vibrational (or rotational) resonances are present.
- The energy-dependent $S_{r'v';rv}(E)$ is obtained from the scattering matrix $s_{r'v';rv}$ calculated assuming that all vibrational channels are open. $s_{r'v';rv}$ depends weakly on energy.
- The smooth matrix $s_{r'v';rv}$ is obtained by frame transformation integrating $s(R)$ over internuclear distances.
- The matrix $s(R)$ is obtained for fixed geometry R using Quantemol.

Frame transformation

* The scattering matrix for e^--AB(v,j) collisions is obtained from the fixed-geometry K-matrix by the recoupling frame-transformation.

$$\langle v'j'|\hat{S}|vj\rangle = \sum_{b'b} \langle v'j'|b'\rangle \langle b'|\hat{S}|b\rangle \langle b|vj\rangle$$

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

$$\langle \Lambda|j\rangle = \sqrt{\frac{2j+1}{2J+1}}\, C(l,j,J;\Lambda-\Lambda^+,\Lambda^+)$$

$$\hat{S}(R) = \frac{1+i\hat{K}(R)}{1-i\hat{K}(R)}$$

Ch. Jungen and O. Atabek, JCP'77

Cross section $vj \rightarrow v'j'$

If rotational structure is accounted for, the cross section is

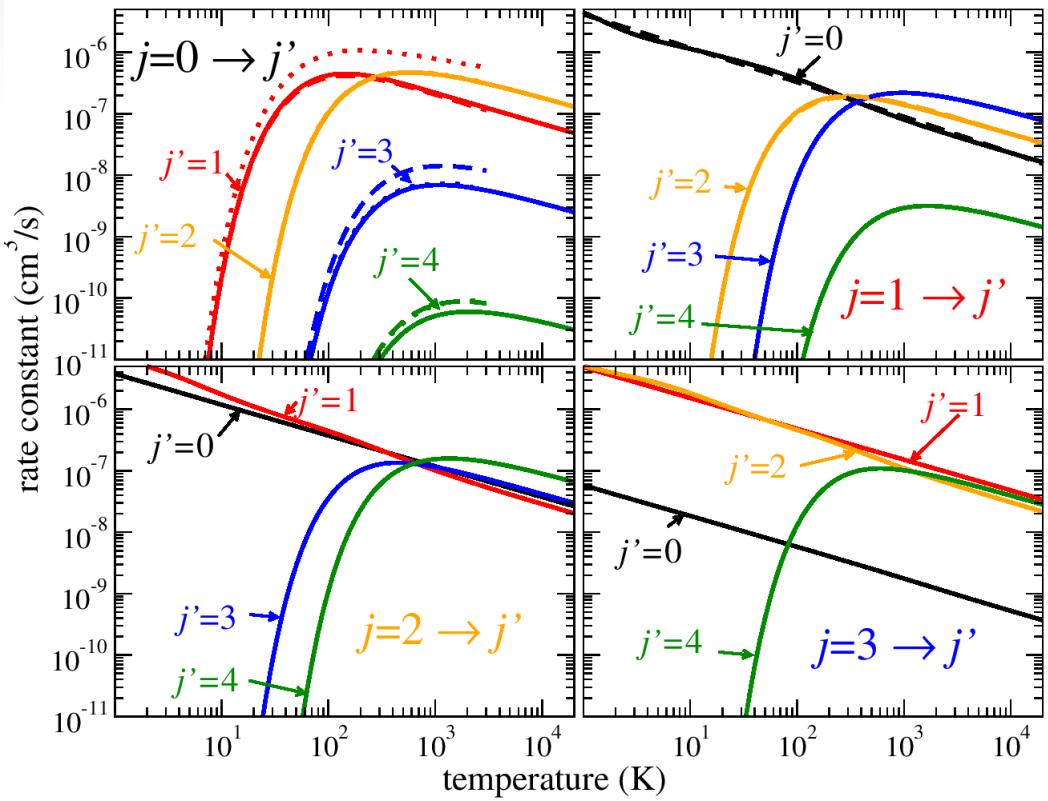
$$\sigma_{v'j' \leftarrow vj} = \frac{\pi}{2E_{el}} \frac{2J+1}{2j+1} \times \sum_{J,l'l\Lambda} \left| S_{v'j'l'\Lambda, v^+ jl\Lambda} - \delta_{v'j'l', vjl} \right|^2$$

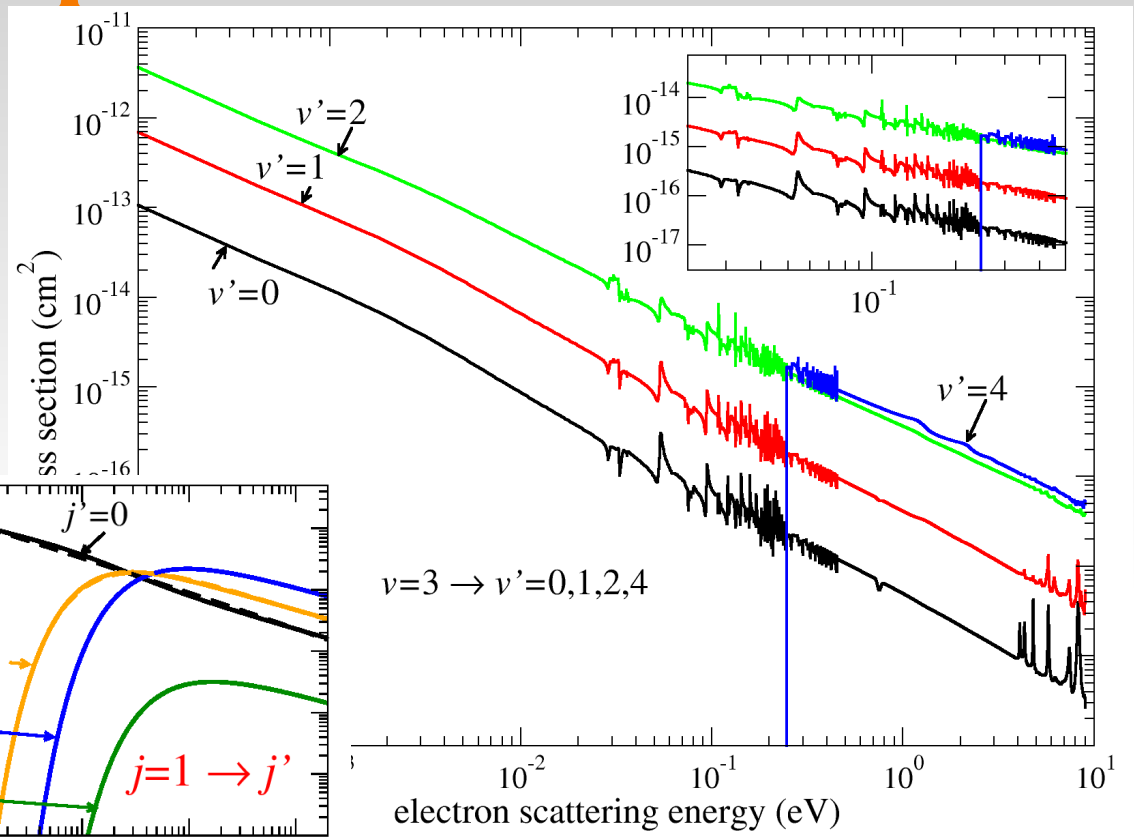
If rotational structure is neglected (averaging over initial rotational states and summed over final states), the cross section can be approximated as

$$\sigma_{v^+ \leftarrow v^+} = \frac{\pi}{2E_{el}} \sum_{l'l\Lambda} \left| S_{v^+ l'\Lambda, v^+ l\Lambda} - \delta_{v^+ l', v^+ l} \right|^2$$

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

Rate coefficients for $j \rightarrow j'$





Cross sections for $v \rightarrow v'$

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.

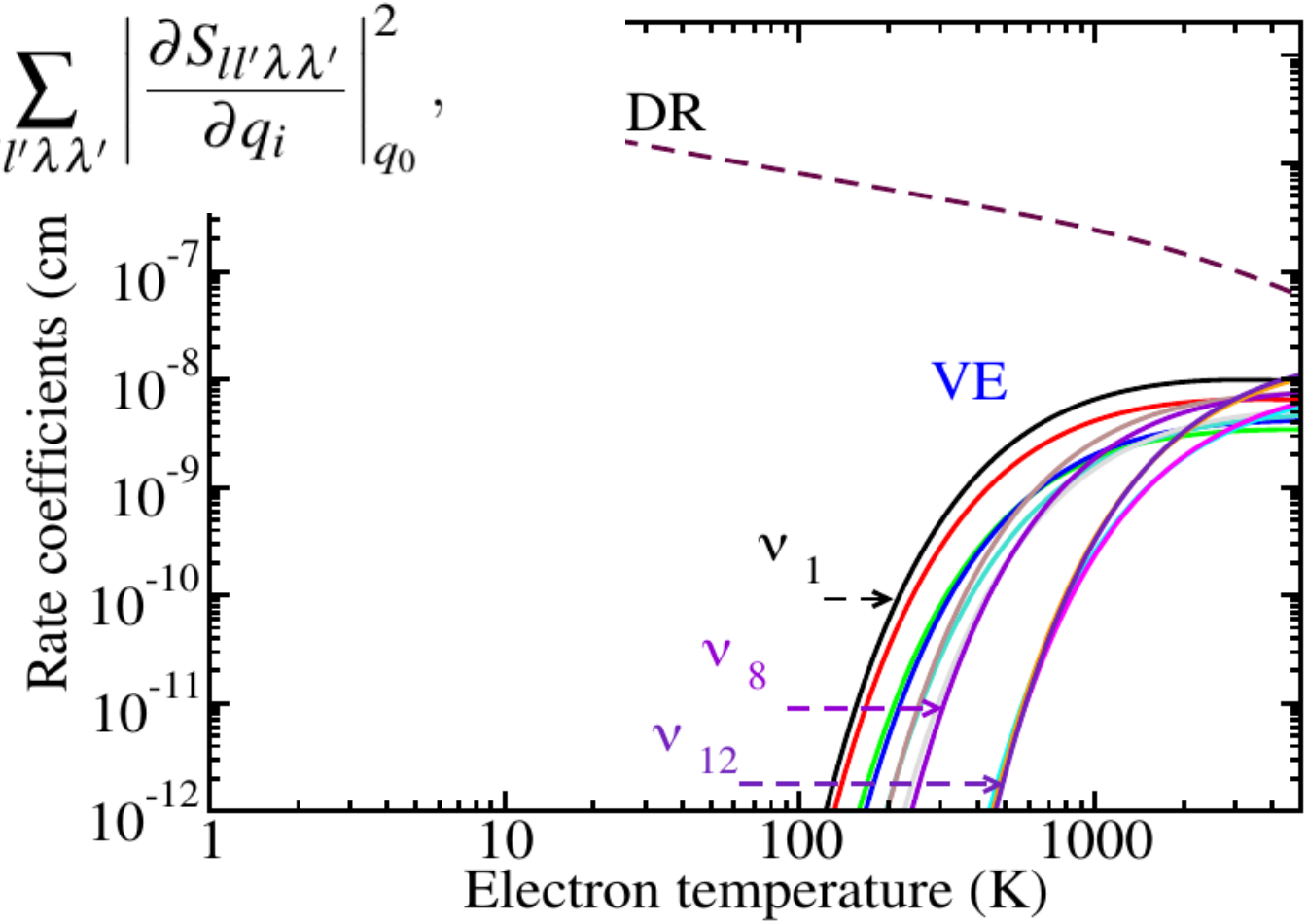
*The geometry-dependent S-matrix $s(\boldsymbol{R})$ should be calculated for many geometries.

* 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.

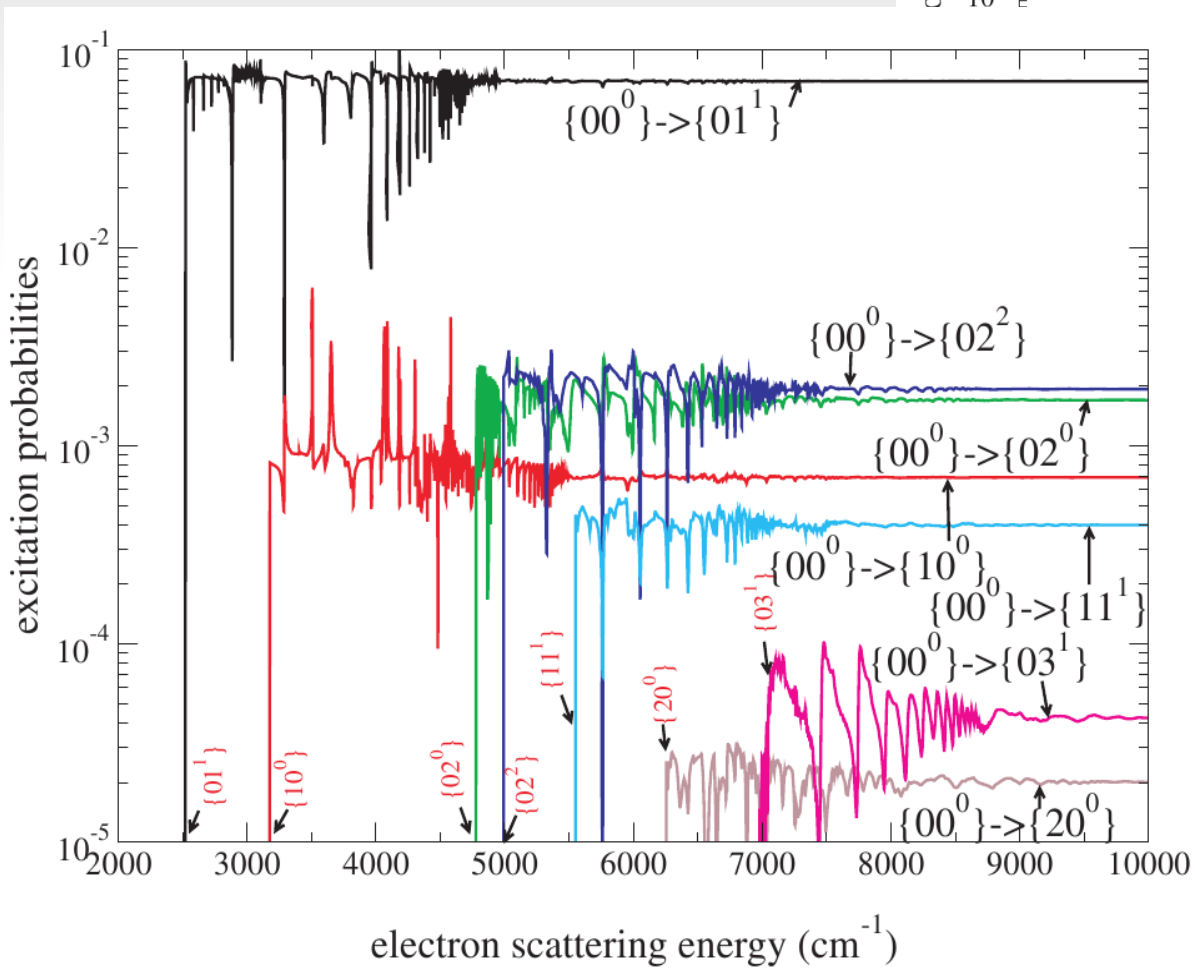
Example: Vibrational excitation of $CH_2NH_2^+$

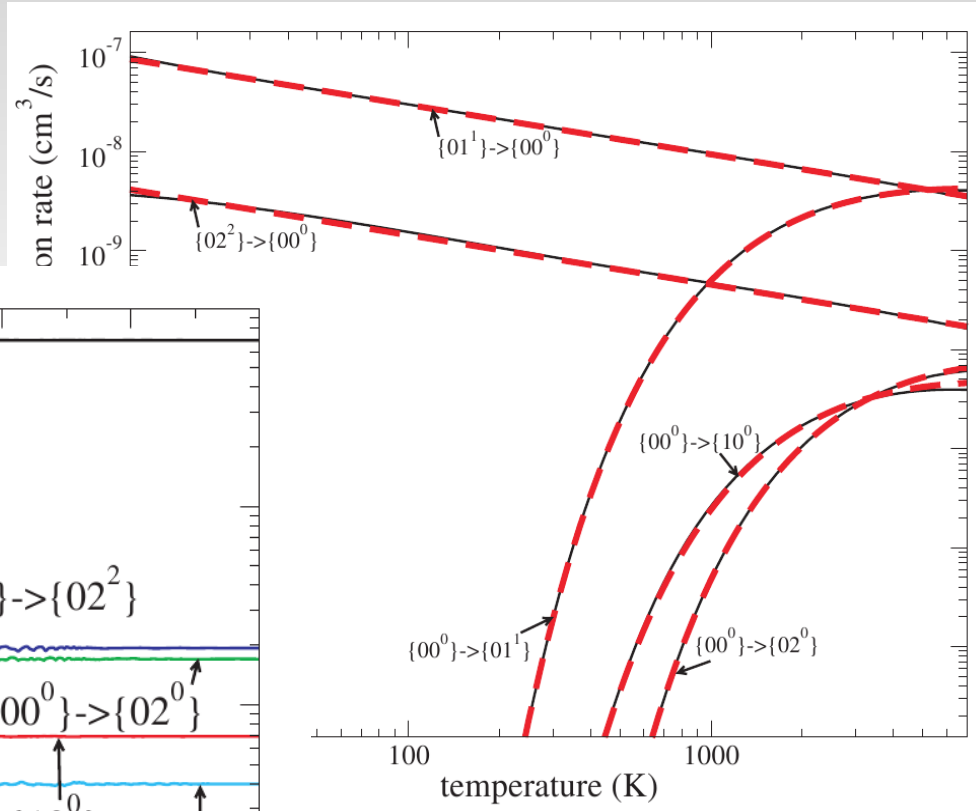
$$\sigma_{v_i'+1\leftarrow v_i'}(\varepsilon) = \frac{\pi\hbar^2}{2m_e\varepsilon}(v_i'+1)\theta(\varepsilon-\hbar\omega_i)\,P_i$$

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

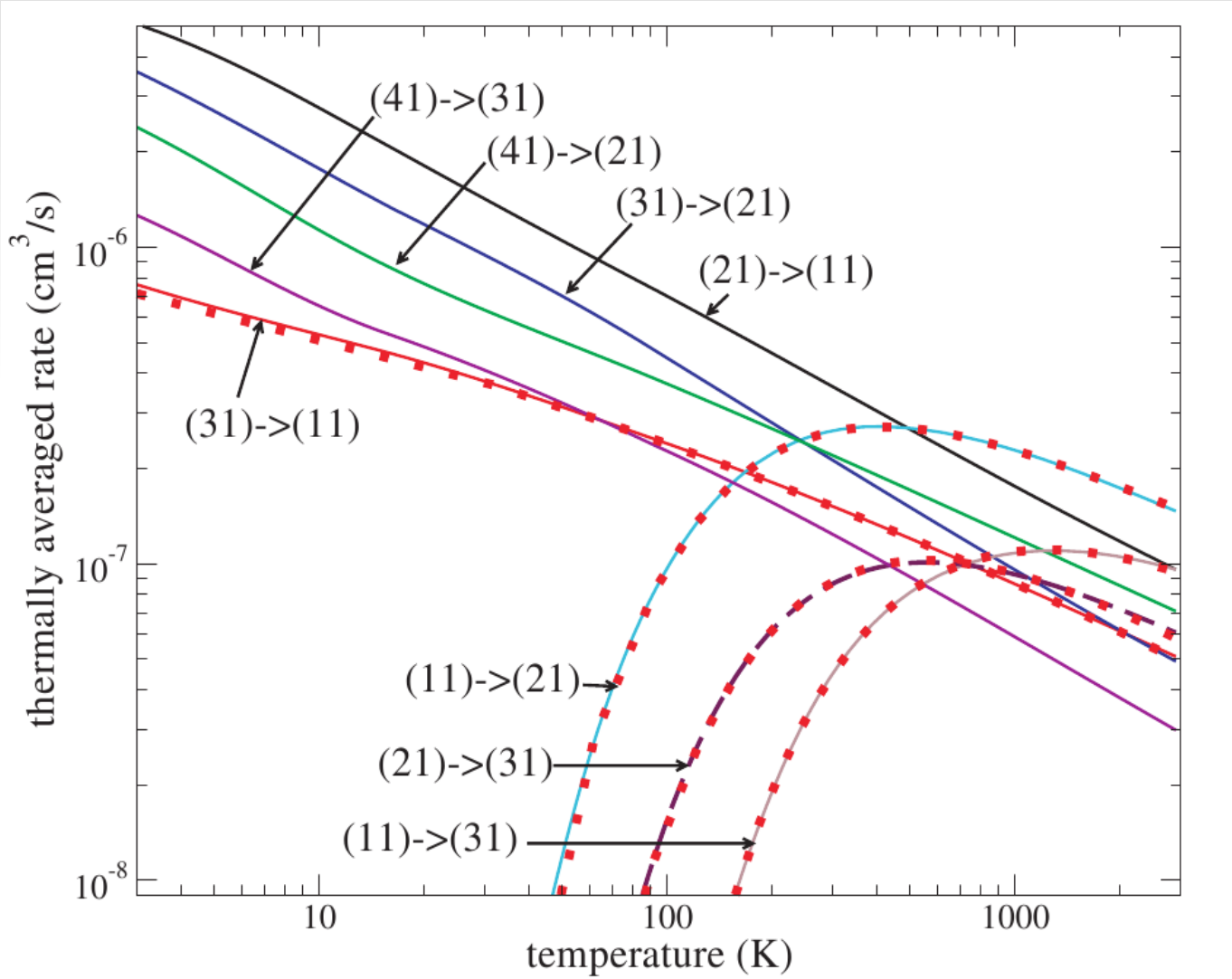


Vibrational excitation of H_3^+





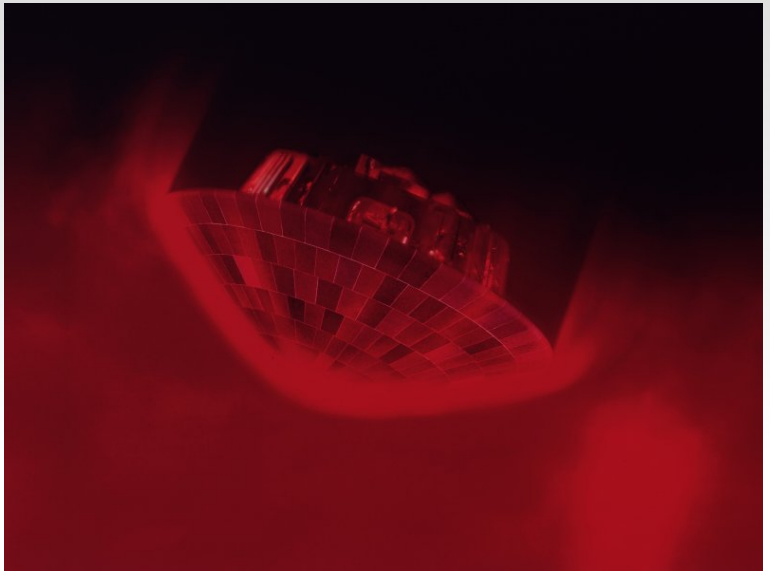
Rotational excitation of H_3^+ ground vibrational level



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

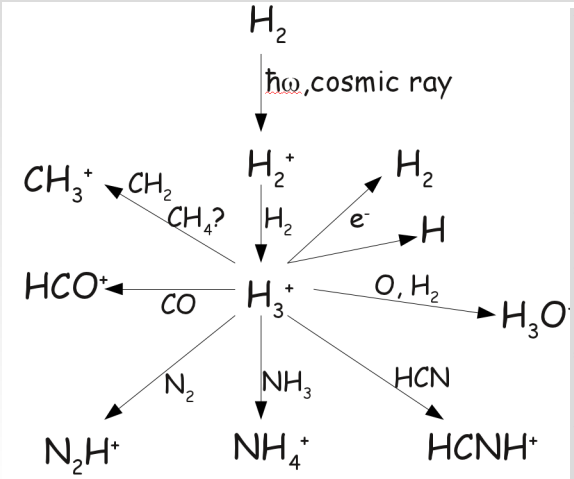
Examples:

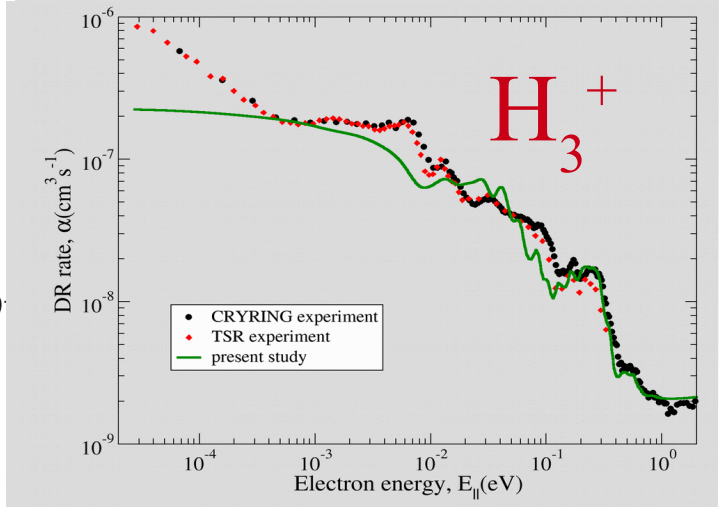
$O_2^+ + e^- \rightarrow O + O^* \rightarrow O + O + \hbar\omega$ (Earth aurora

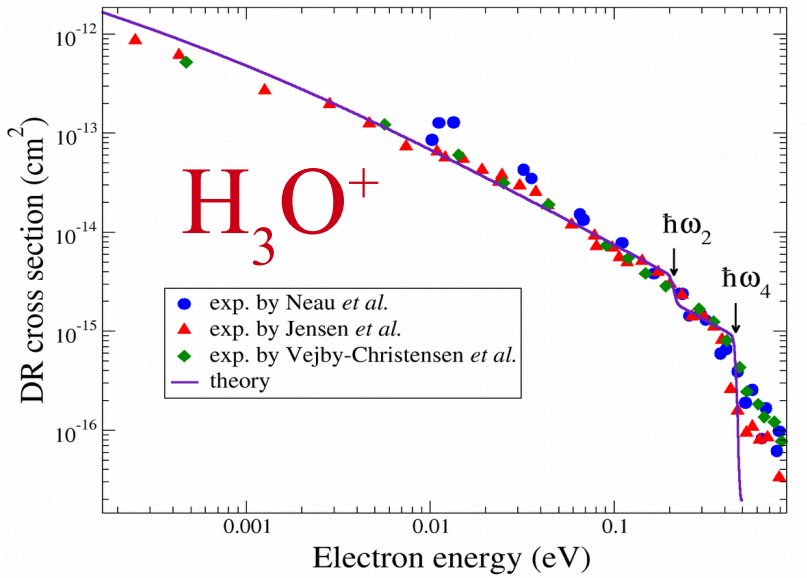
$CH^+ + e^- \rightarrow C + H$, $SH^+ + e^- \rightarrow S + H$ (Mercury exosphere)

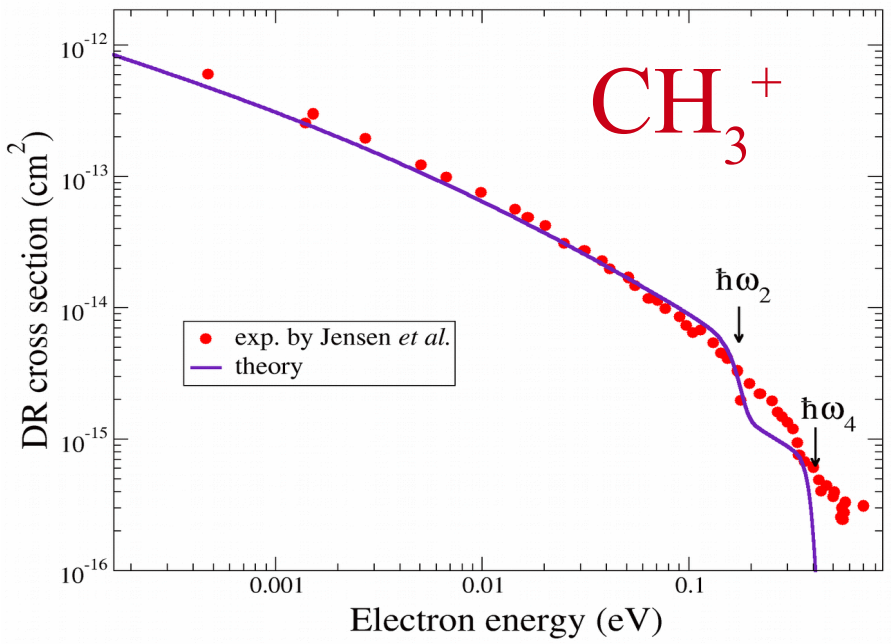
$H_3^+ + e^- \rightarrow H_2 + H$ or $H + H + H$ (Jupiter, Saturn)

DR in Titan's atmosphere







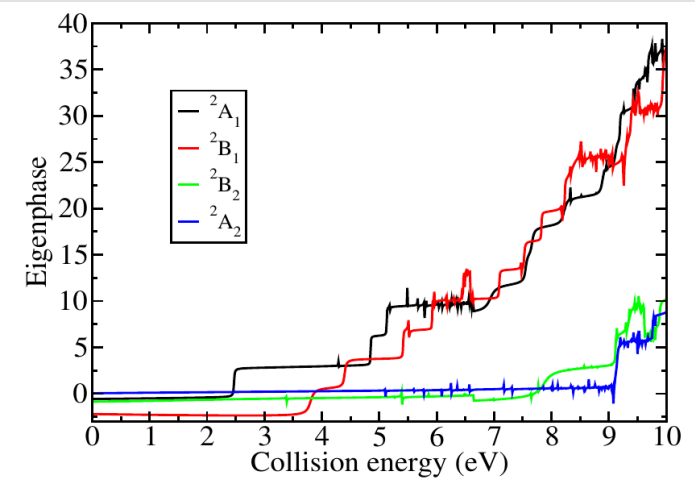


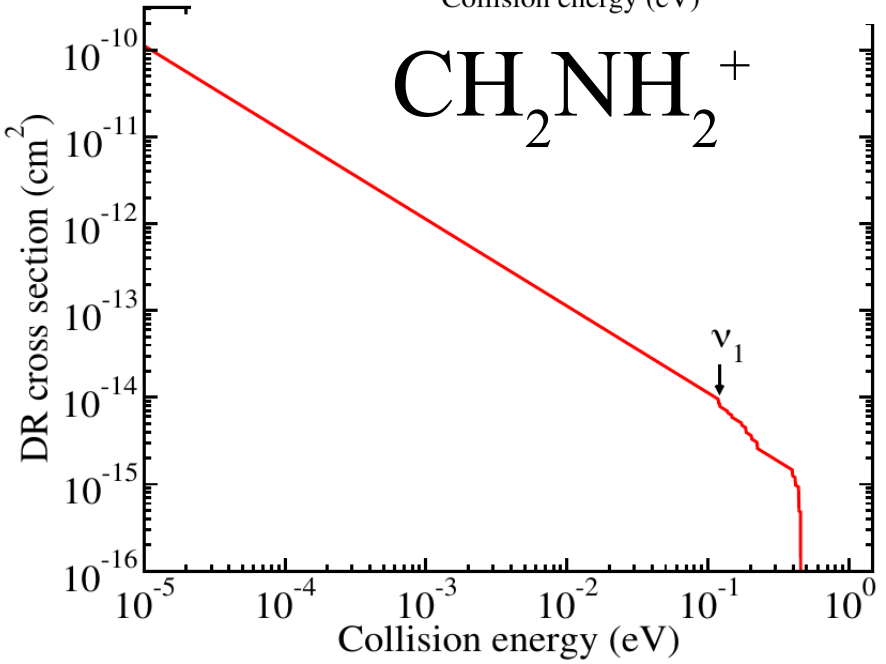
Simple theoretical method for polyatomic ions

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

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

$$\hat{S}(\vec{q}) = \frac{1+i\hat{K}(\vec{q})}{1-i\hat{K}(\vec{q})}$$





Negative molecular ions in the interstellar medium

Negative ions in the interstellar medium (ISM)

- 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):

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

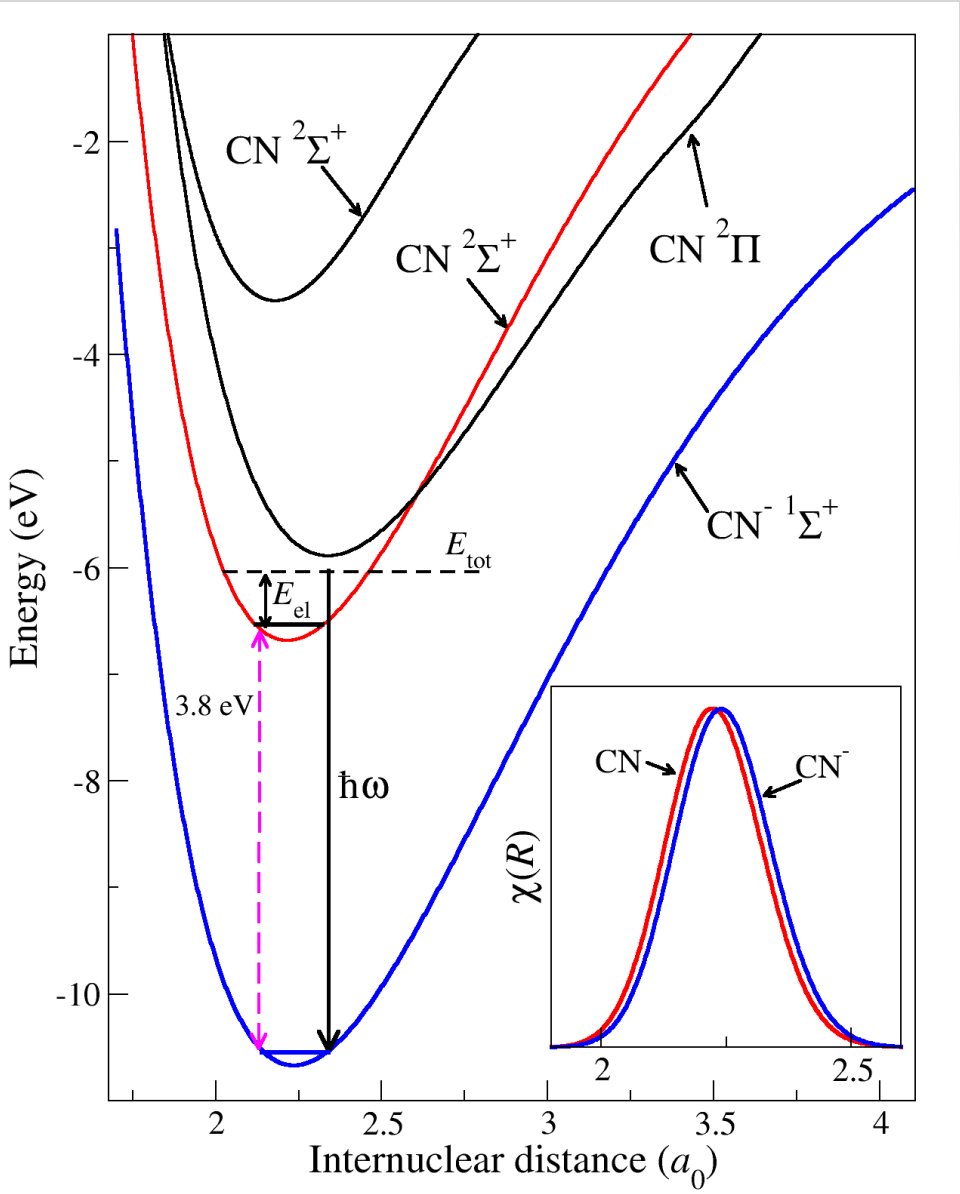
Anion formation by the radiative attachment

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.

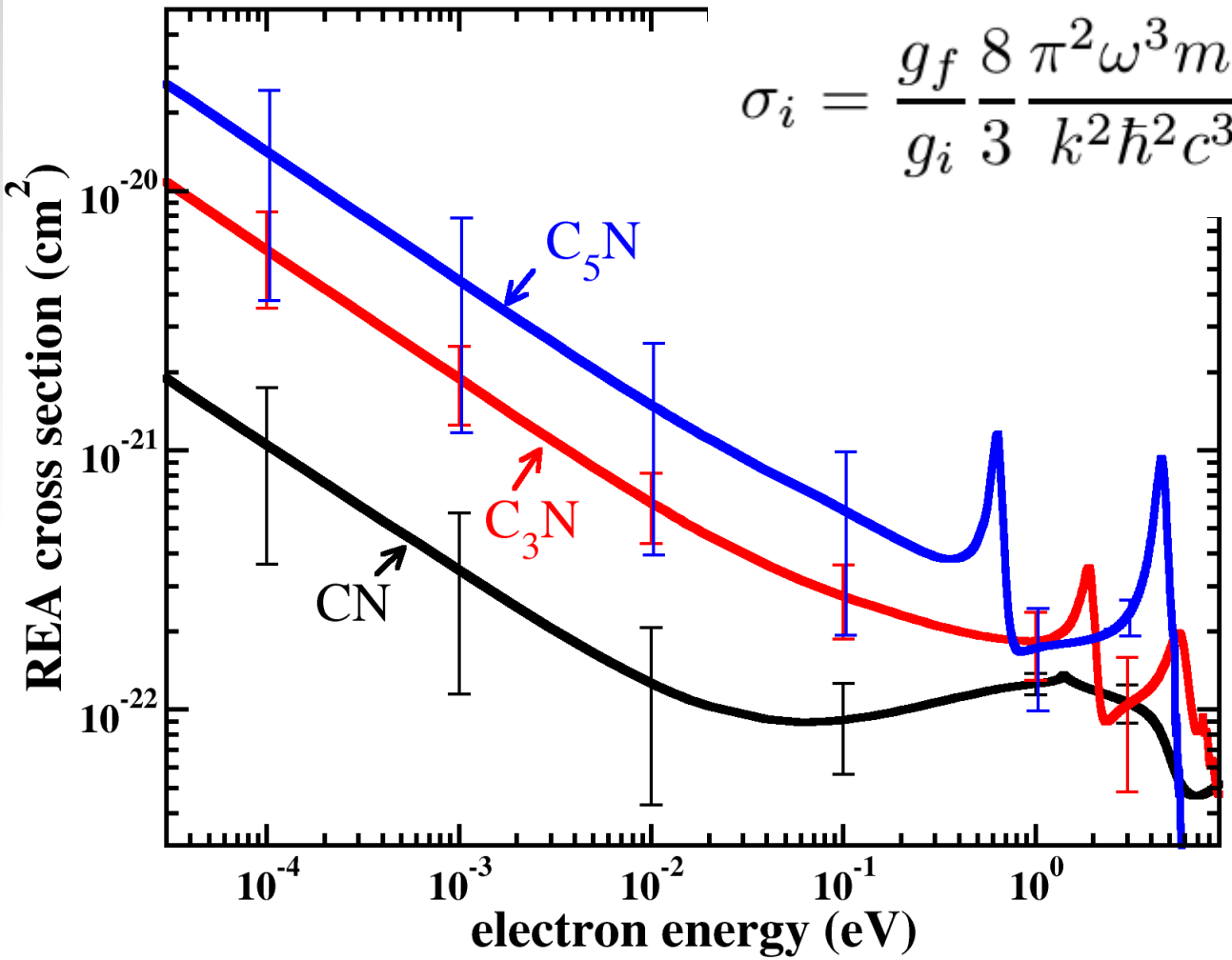
$$\sigma_i = \frac{g_f}{g_i}\frac{8}{3}\frac{\pi^2\omega^3 m_e}{k^2\hbar^2 c^3}\sum_{l\pi}\left|d^{(v_i\rightarrow v_n)}_{\pi,\Gamma l-\pi}\right|^2$$

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

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

REA cross sections

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



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

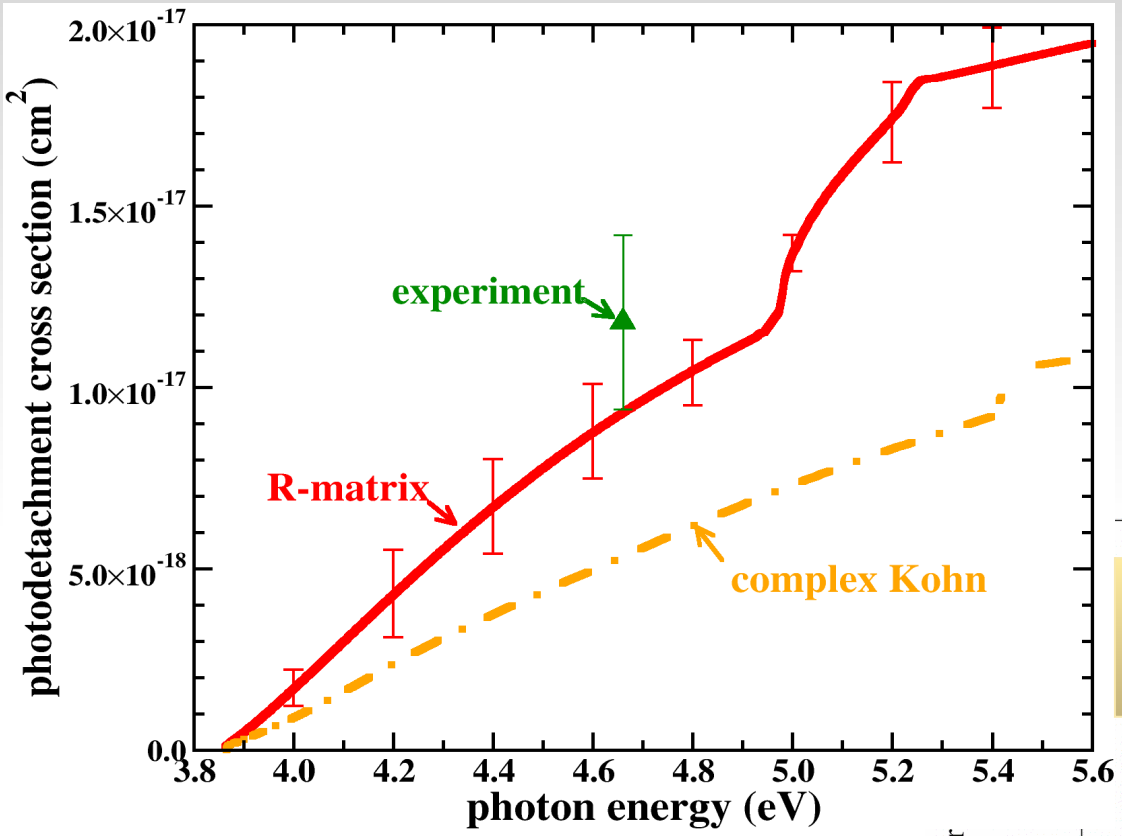
Photodetachment

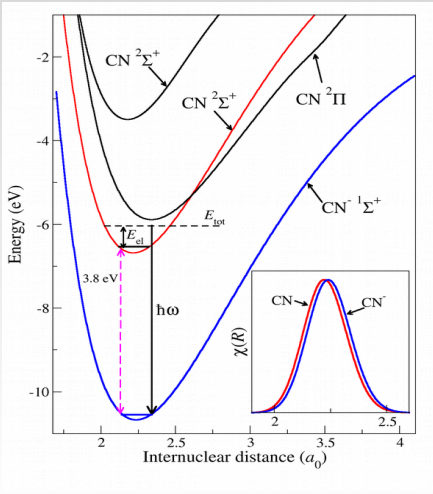
There is no experimental data on radiative attachment to the C_nH and C_nN molecules. But the calculated transition dipole moments can be used to compute photodetachment cross sections, which could be compared with experimental data obtained by R. Wester's group.

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

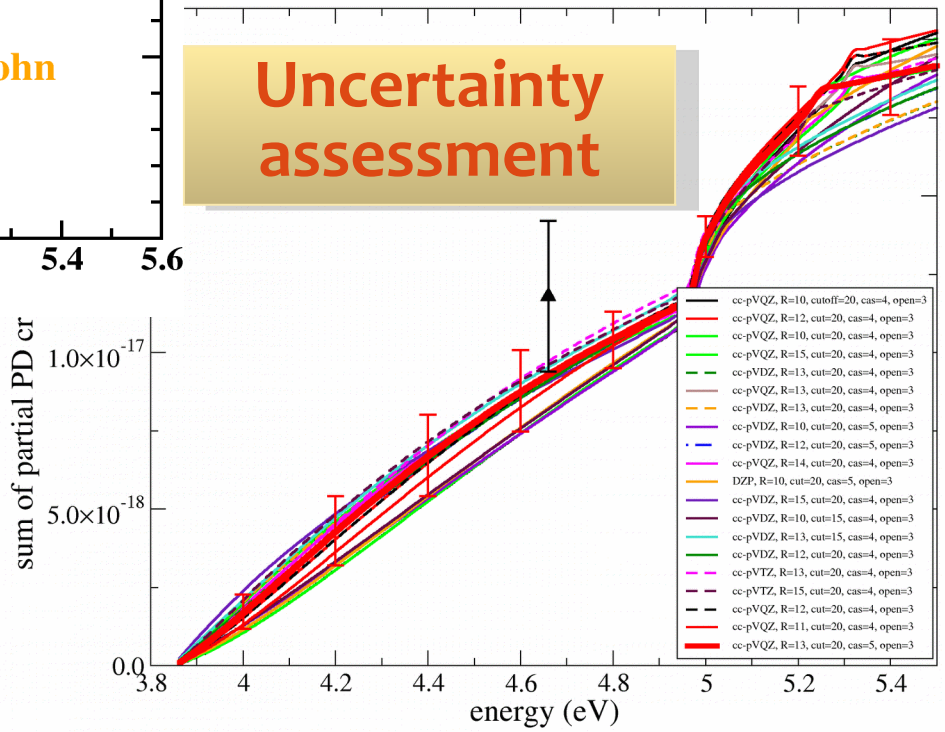
$$\sigma_{PD} = \frac{4m_e\pi^2\omega}{3\hbar^2 c}\sum_{l\pi}\left|d^{(v_i\to v_n)}_{\pi,\Gamma l-\pi}\right|^2$$

CN^- photodetachment cross section



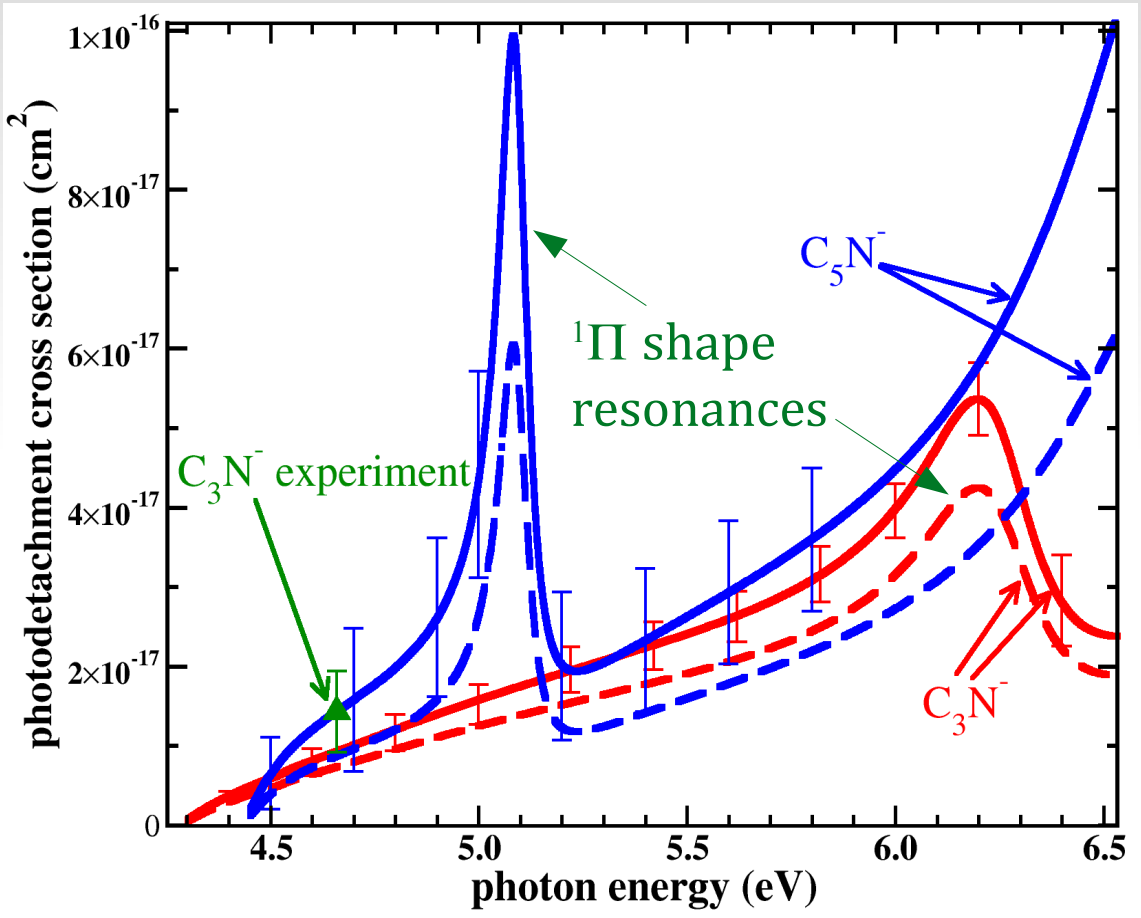


Uncertainty assessment



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

PD cross sections for C_3N^- and C_5N^-

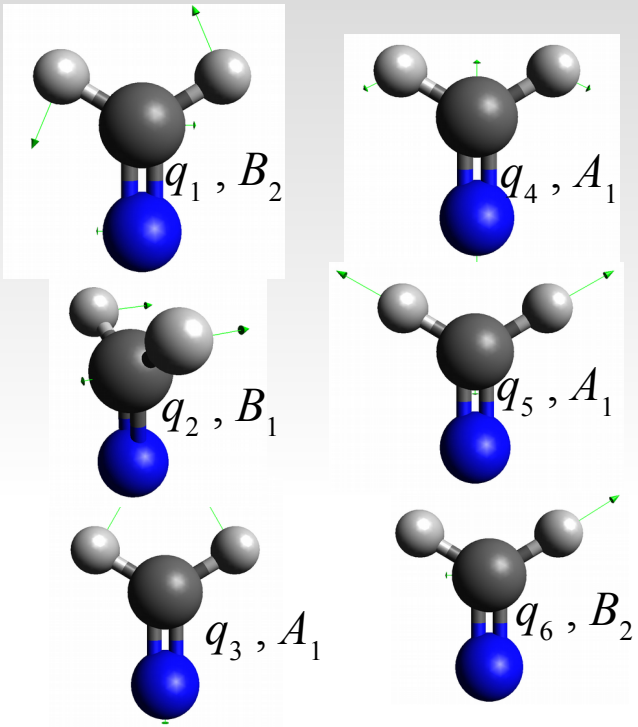


C_3N^- exp: Kumar *et al.* ApJ (2013)

Dissociative electron attachment

$H_2CN + e^- \rightarrow H_2 + CN^-$

- DEA to closed shell molecules is usually energetically impossible at low temperatures.
- For open-shell molecules, DEA could be allowed at zero (small) collision energies.
- The methylene amidogen radical (H_2CN) was was detected in interstellar clouds in 1994. The DEA is possible at low collision energies.



$H_2CN + e^- \rightarrow H_2 + CN^-$

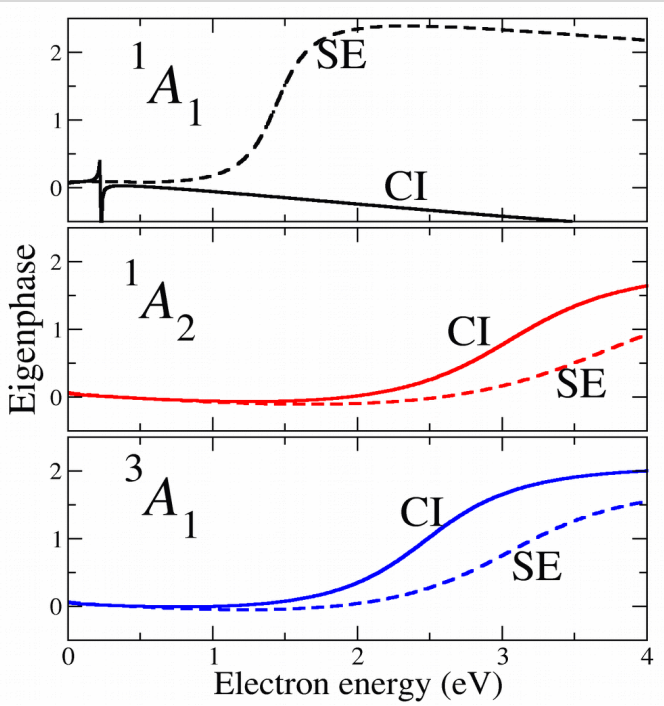
Three shape resonances at low energies.

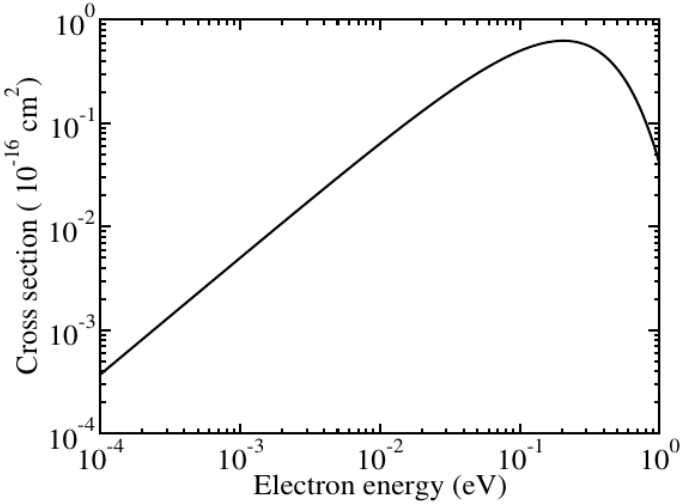
The lowest one $^1A_1$ is open at zero collision energy and leads to H_2+CN^- dissociation.

Normal-mode approximation near the equilibrium of H_2CN to decribe the vibrational state $\zeta(s)$ of the target and the steepst descent dissociative coordinate s of H_2CN^- to describe initial motion along towards dissociation.

We have adapted O'Malley's theory for DEA for polyatomic ions

$$\sigma = \frac{2\pi^2}{k^2} g \frac{\Gamma_c(s_E)}{U_d'(s_E)} \left|\zeta(s_E)\right|^2$$





Conclusions

The UK R-matrix and Quantemol offer the most efficient tool to study processes in electron-molecule collisions in applications in astrophysics.

The UK-matrix produces scattering data (reactance matrix, transition dipole moments, etc.) for fixed molecular geometries.

A low energies, <10 eV, rotational and vibrational motion should be accounted for. The methods to account for the motion depend on the process of interest and scattering energy.

There are a few theoretical methods that are general enough to be applied to a wide range of systems.

Those includes methods for dissociative recombination and rovibrational excitation of closed-shell molecular ions.

Could some of these methods be included as a part of Quantemol additional options?

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