

# Radiative electron attachment to molecules of astrophysical interest: Direct and indirect mechanisms

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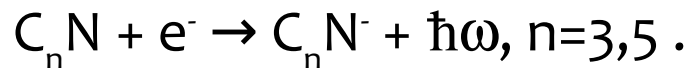
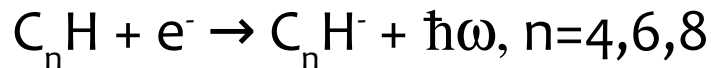


Computing support



# Negative ions in the interstellar medium (ISM)

- Possibility for atomic negative molecular ions to exist in the ISM was suggested by McDowell (1961) and Dalgarno&McCray (1972). The ions are predicted to be formed by radiative attachment.
- Herbst (1981) suggested that large polyatomic molecules may form negative ions by the process of radiative attachment.
- 6 negative molecular ions have been recently found in interstellar clouds:  $C_4H^-$ ,  $C_6H^-$ ,  $C_8H^-$ ,  $CN^-$ ,  $C_3N^-$ ,  $C_5N^-$ .
- The proposed mechanism of formation of  $C_nH^-$  and  $C_nN^-$  in the ISM is radiative electron attachment (REA):

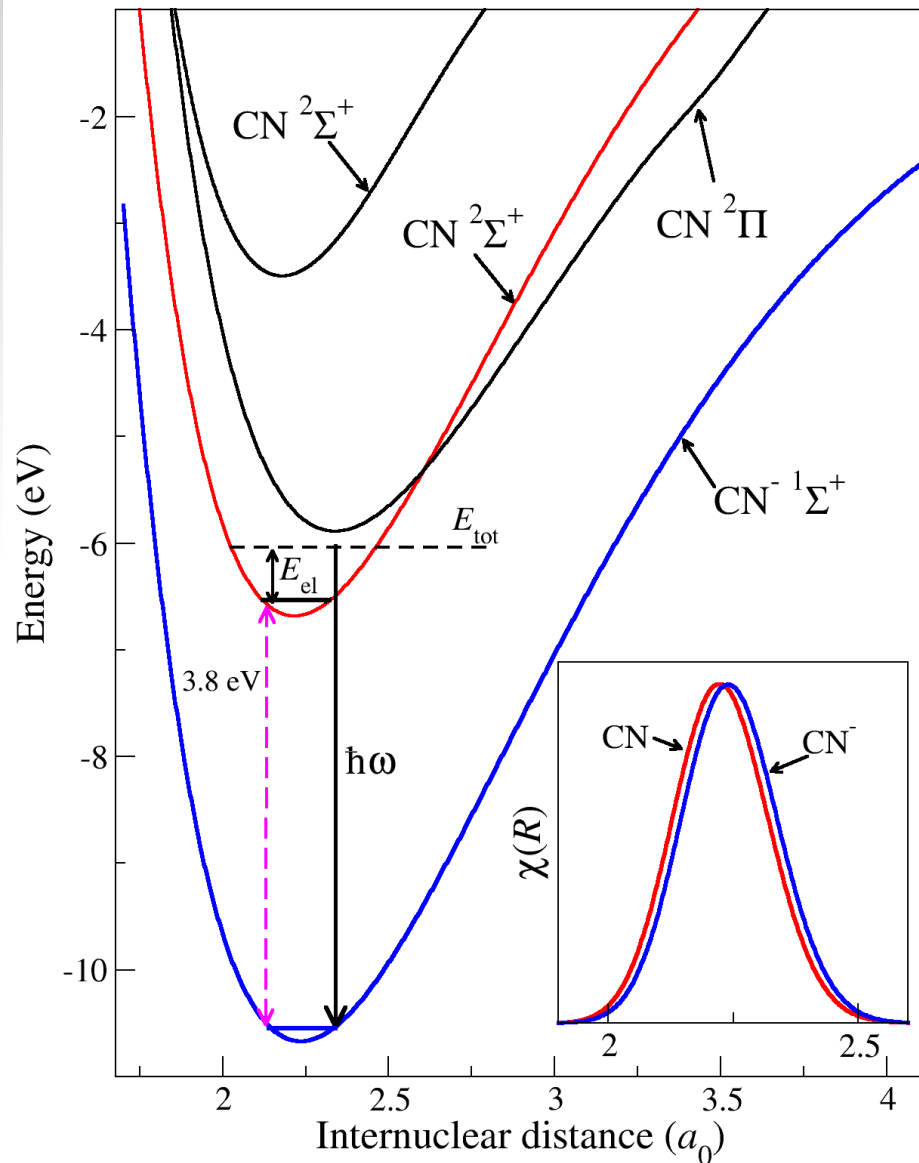


# Theory of radiative electron attachment to $C_nH$ or $C_nN$

- 30 year ago, Eric Herbst has proposed a theoretical approach for the estimation of REA rate coefficients.
- The first step in the approach is the electron capture by the molecule. The cross section for the electron capturing is approximated by the unitary limit formula for the s-wave scattering,  $\sigma_{\text{capt}} = \pi/k^2$  (Herbst & Osamura'08).
- The second step: Once the electron is captured, the system can emit a photon (stabilization) or the electron can detach.
- The stabilization of the  $e^- - C_nH$  (or  $C_nN$ ) complex is represented as an emission of a photon by a set of harmonic oscillators the molecule (in the normal mode approximation of molecular vibration).
- The approach gives REA rate coefficients ( $2 \times 10^{-9} \sim 6 \times 10^{-8} \text{ cm}^3/\text{s}$ ) that suggests that all anions (except  $CN^-$ ) observed in the ISM are indeed formed by REA.
- In this talk, I would like to argue that the  $2 \times 10^{-9} \sim 6 \times 10^{-8} \text{ cm}^3/\text{s}$  rate coefficients, used by the community, are probably too high.

# Radiative electron attachment to CN

- Electronic bound states of CN and CN<sup>-</sup>, and the affinity of CN have been determined using Molpro.
- Continuum states and transition dipole moments have been obtained using the complex-Kohn variational method together with the MESA software suit.



# Theory of radiative electron attachment to molecules

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

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

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

- The final state is

$$\Psi_{v_f \Lambda_f}^{J_f M_f} = \sqrt{\frac{2J_f + 1}{8\pi^2}} [D_{M_f \Lambda_f}^{J_f}(\Omega)]^* \chi_{v_f}^{J_f}(R) \Psi_f(\mathbf{r}_N)$$

- Cross-section for the radiative attachment is then obtained by dividing the Einstein coefficient with the density of electron current in the incident wave,  $\hbar k_a / m_e$  in this case.

# Initial state $|i\rangle$

➤ The scattering state of the  $e^-$ -AB system behaves at large distances  $r$  between  $e^-$  and AB as

$$\Psi_{vjm_j}^\Gamma \rightarrow e^{i\vec{k}_{vj}\cdot\vec{r}}\phi_{vjm_j}^\Gamma + \sum_{v'j'm_j'\Gamma'} \frac{e^{ik_{v'j'}r}}{r} A_{vjm_j\Gamma\rightarrow v'j'm_j'\Gamma'} \times (\vec{k}_{vj}, \vec{r})\phi_{v'j'm_j'}^{\Gamma'}$$

where  $\phi_{vjm_j}^\Gamma$  represent wave functions of the target molecule, AB

$$\phi_{vjm_j}^\Gamma = \sqrt{\frac{2j+1}{8\pi^2}} [D_{m_j\mu}^j(\Omega)]^* \chi_v^j(R) \omega_\Gamma(\mathbf{r}_{N-1}),$$

$A_{\bar{a}''\bar{a}}^\Gamma$  is the scattering amplitude in the laboratory frame.

➤ In the basis of partial waves it is expanded as

$$\Psi_{vjm_j}^\Gamma \rightarrow \frac{2\pi i}{r\sqrt{k_{vj}}} \sum_{l=0}^{\infty} \sum_{m_l=-l}^l Y_{lm_l}(\hat{k}_{vj}) i^l \sum_{l'm_l'} \sum_{v'j'm_j'\Gamma'} \frac{1}{\sqrt{k_{v'j'}}} \phi_{v'j'm_j'} Y_{l'm_l'}(\hat{r})$$

$$\times \left[ \delta_{v'v} \delta_{l'l} \delta_{m_l'm_l} \delta_{j'j} \delta_{m_j'm_j} \delta_{\Gamma\Gamma'} e^{-i(k_{v'j'}r - \frac{l'\pi}{2})} - S_{v'j'm_j'l'm_l';vjm_jlm_l}^{\Gamma'\Gamma} e^{i(k_{v'j'}r - \frac{l'\pi}{2})} \right]$$

# Electronic states

➤ The electronic wave function representing the electron-neutral scattering, with the neutral target in a state  $|\Gamma\rangle$ , is calculated using complex Kohn method. It has the following form

sum over  $N$ -electron configuration-state functions  $\Theta_j$  representing penetration and correlation terms

sum over energetically open neutral states described by  $(N - 1)$ -electron wave functions  $\chi_r$

$$\Psi_{\Gamma l \lambda} = \sum_j b_j^{\Gamma} \Theta_j + \hat{A} \sum_{\Gamma' j'} \chi_{\Gamma'} c_{j'}^{\Gamma' \Gamma} \phi_{j'}(r) + \hat{A} \sum_{\Gamma' l' \lambda'} \omega_{\Gamma'} Y_{l' \lambda'}(\hat{r})$$

$$\times \frac{i}{2r} \left[ h_{l'}^-(k_{\Gamma'} r) \delta_{l' l} \delta_{\lambda' \lambda} \delta_{\Gamma' \Gamma} - S_{l' \lambda'; l \lambda}^{\Gamma' \Gamma} h_{l'}^+(k_{\Gamma'} r) \right]$$

Sum over incoming and outgoing waves  
(Spherical Hankel functions)

$$h_{l'}^+(k_{\Gamma'} r) \rightarrow \frac{1}{\sqrt{k_{\Gamma'}}} \exp \left( i \left[ k_{\Gamma'} r - \frac{l' \pi}{2} \right] \right)$$

# REA cross-section

$$\sigma_{f;i} = \frac{A_{f;i}}{j} = \frac{4 \omega^3}{3 j \hbar c^3} |\langle f | \vec{d} | i \rangle|^2;$$

$$\sigma_{fi} = \frac{16}{3} \frac{g_f}{g_i} \frac{\pi \omega^3 m_e}{k_{vj}^2 \hbar^2 c^3} \sum_{Jl} \left| \sum_{\lambda\pi} C_{J\Lambda 1\pi}^{J_f \Lambda_f} C_{l\lambda j\mu}^{J\Lambda} d_{\pi, \Gamma l \lambda}^{(v \rightarrow v_f)} \right|^2$$

Sum over partial waves and their projections on the molecular axis

If the sum over all possible final angular momenta  $J_f$  is evaluated, we obtain

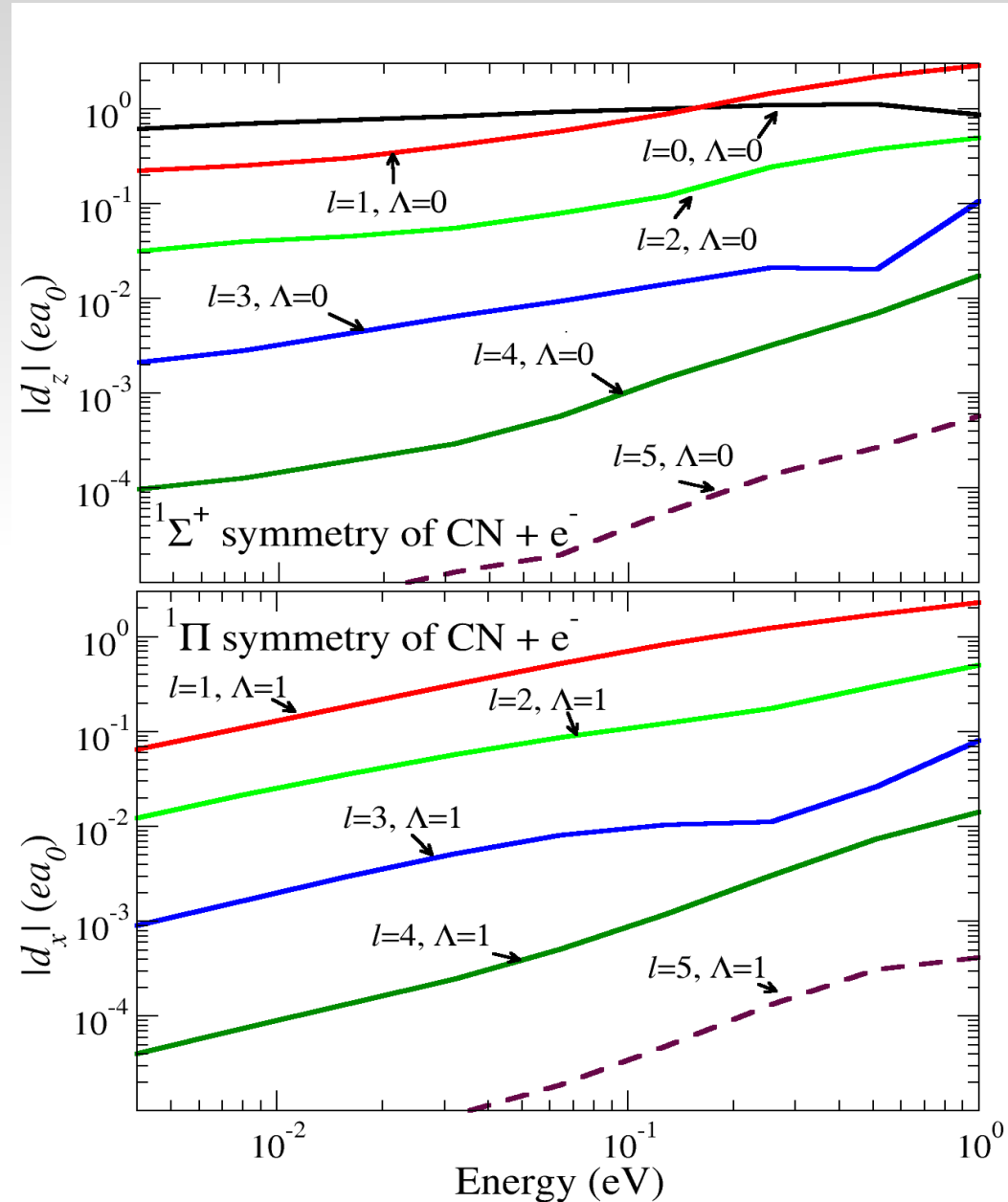
$$\sigma_i = \frac{4}{3} \frac{\pi \omega^3 m_e}{k^2 \hbar^2 c^3} \sum_{l\pi} |d_{\pi, \Gamma l - \pi}^{(v \rightarrow v_f)}|^2$$



# Dipole moments as a function of energy

➤ Figure shows the transition dipole moments calculated for the equilibrium CN<sup>-</sup> distance,  $R=2.25 a_0$  between the electronic bound state  $|f\rangle$  of CN<sup>-</sup> and different initial continuum CN+e<sup>-</sup> states  $|E_i\rangle$ .

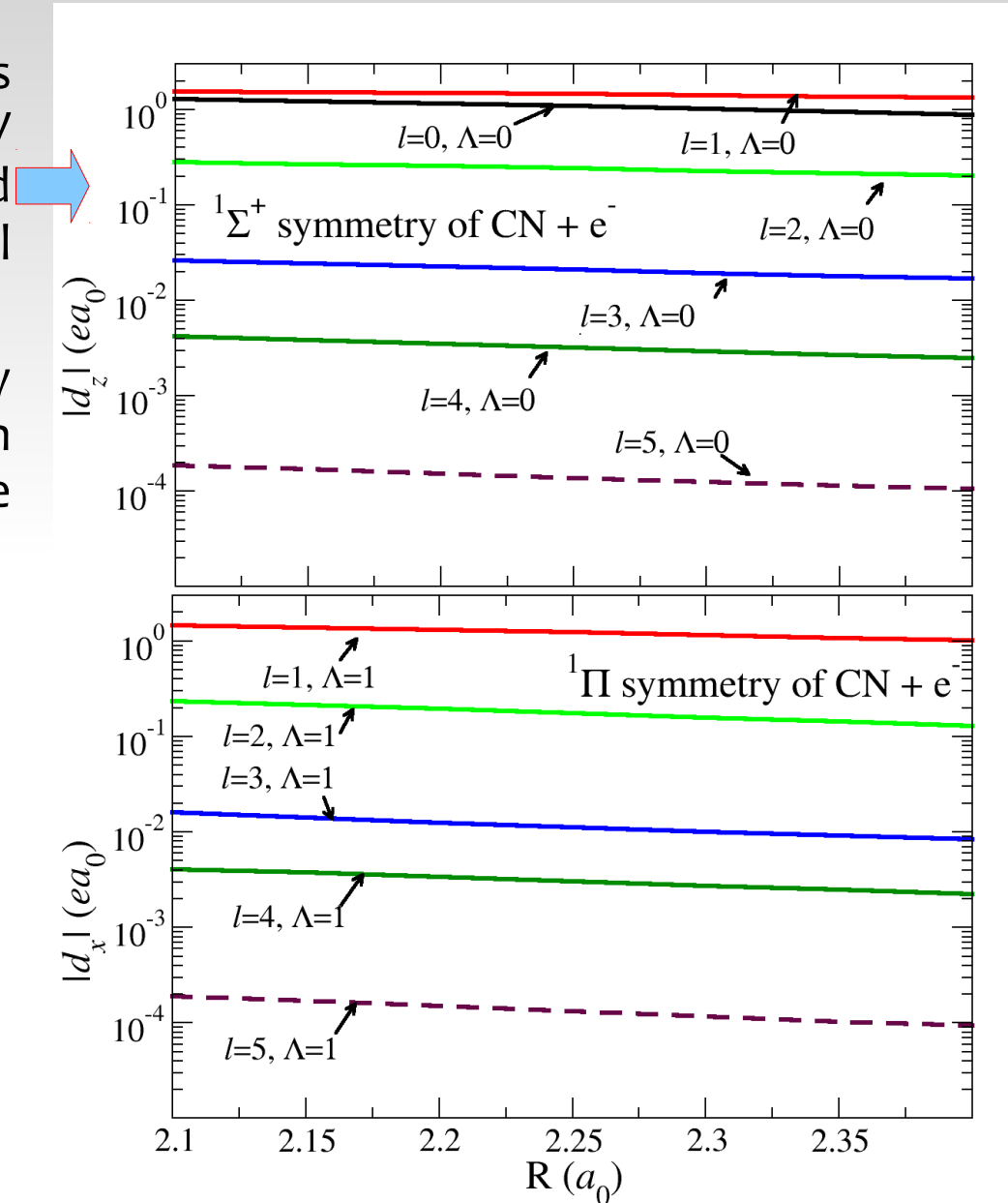
➤ The initial states  $|E_i\rangle$  differ by the symmetry of the wave function and by partial wave  $l$  in the incident channel.



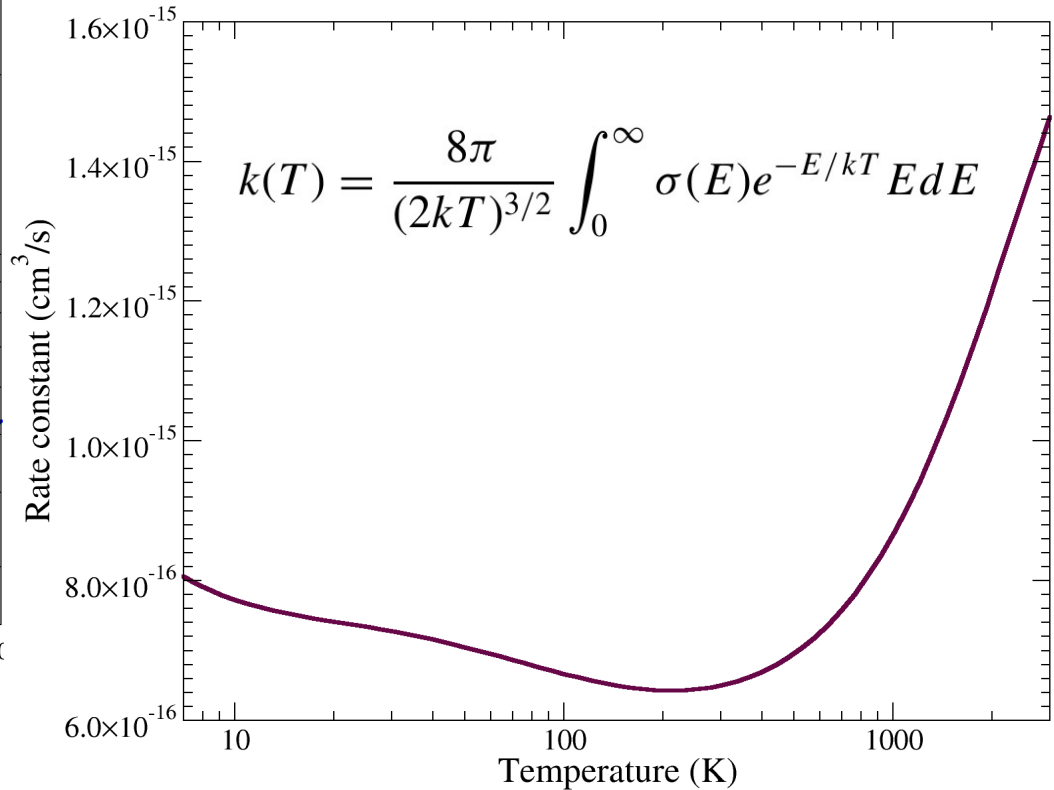
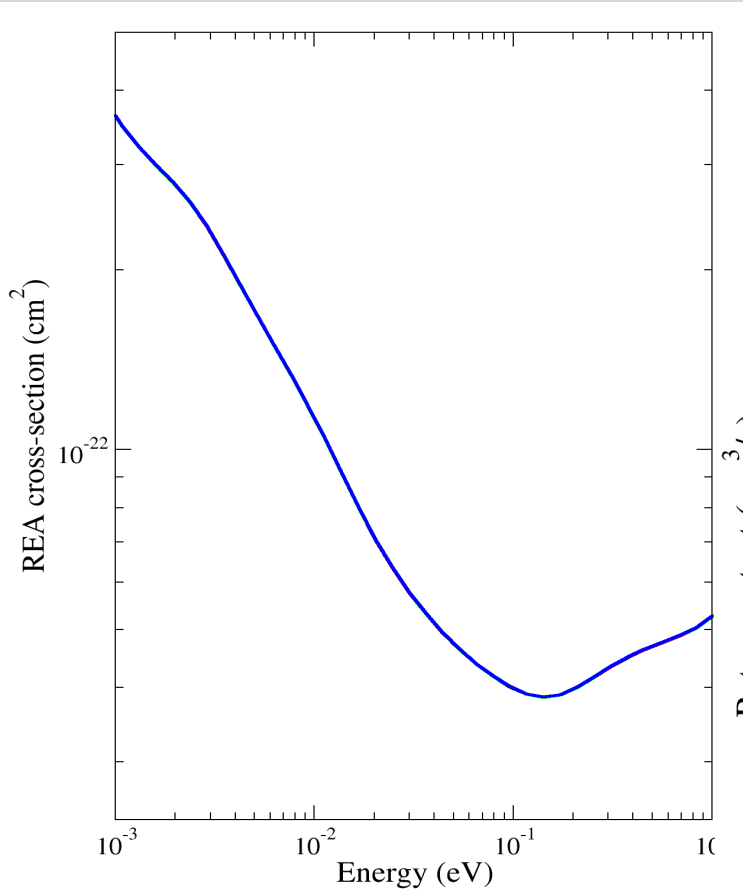
# Dipole moments vs internuclear distance

➤ Transition dipole moments calculated for energy  $E=0.25$  eV between the electronic bound state  $|f\rangle$  of  $\text{CN}^-$  and different initial continuum  $\text{CN}+e^-$  states  $|E_i\rangle$ .

➤ The dipole moments are nearly geometry independent. One can simply compute them for the equilibrium geometry of  $\text{CN}/\text{CN}^-$ .

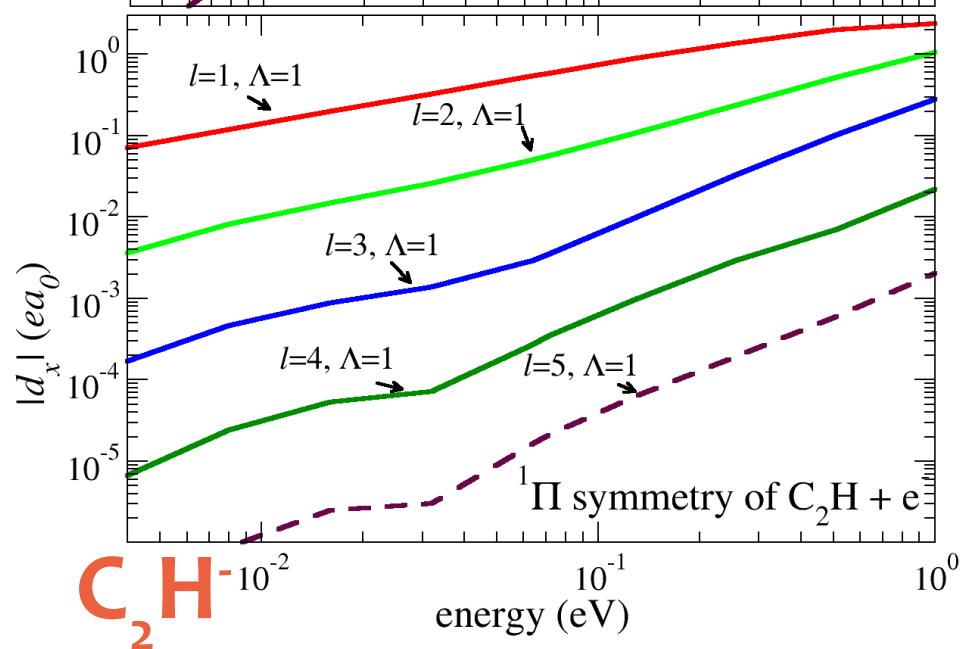
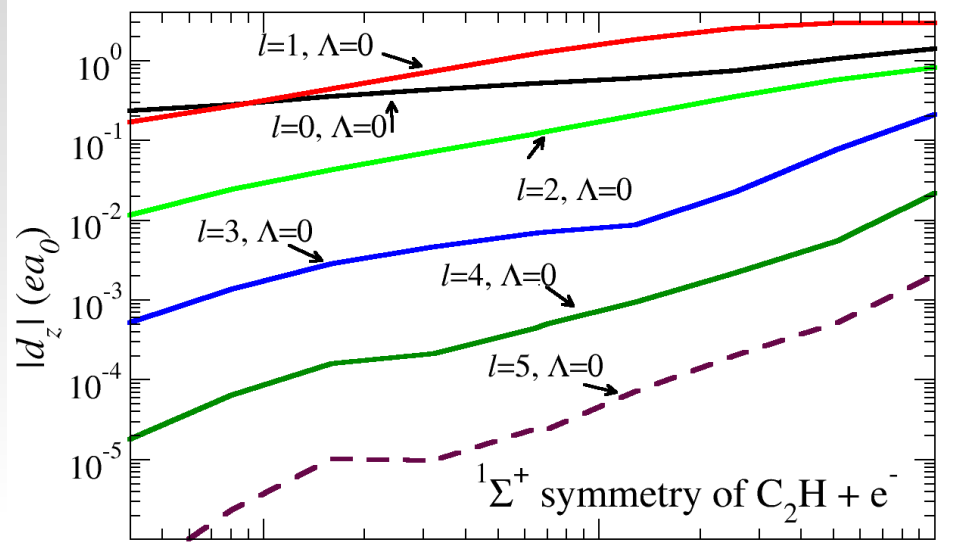


# REA cross section and rate coefficient

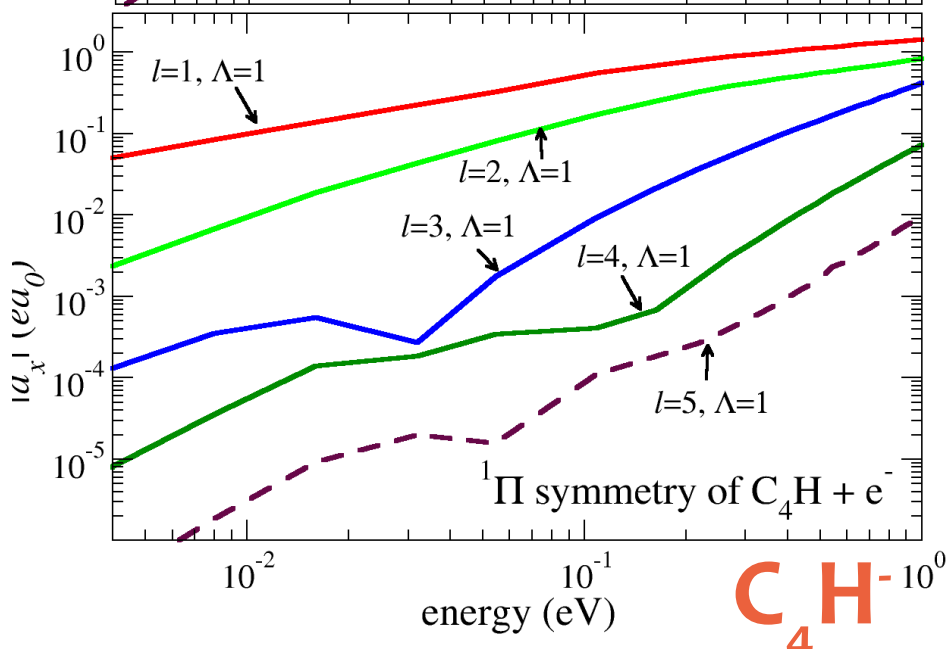
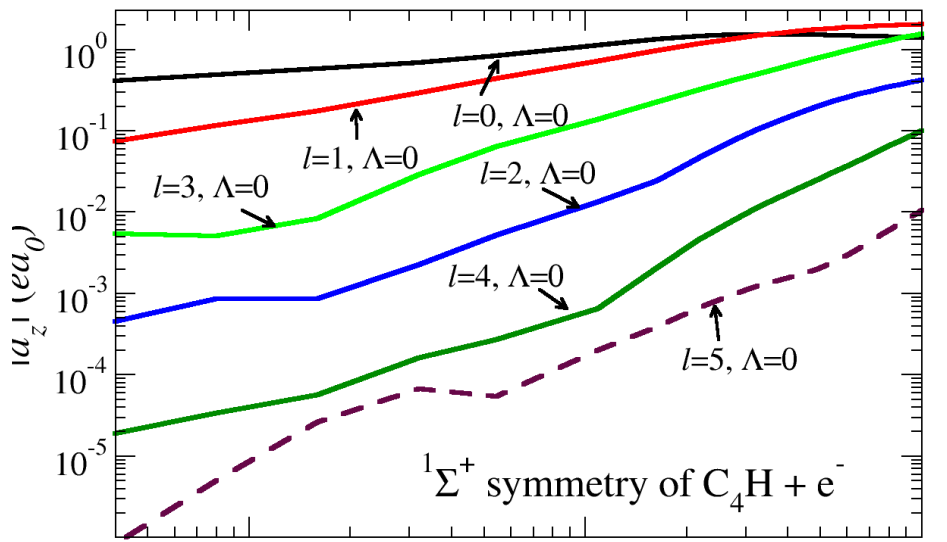


➤ Herbst's theory predicts the rate coefficient of the order of 10<sup>-16</sup>-10<sup>-15</sup> cm<sup>3</sup>/s.

# Results for $C_2H^-$ and $C_4H^-$ : dipole moments



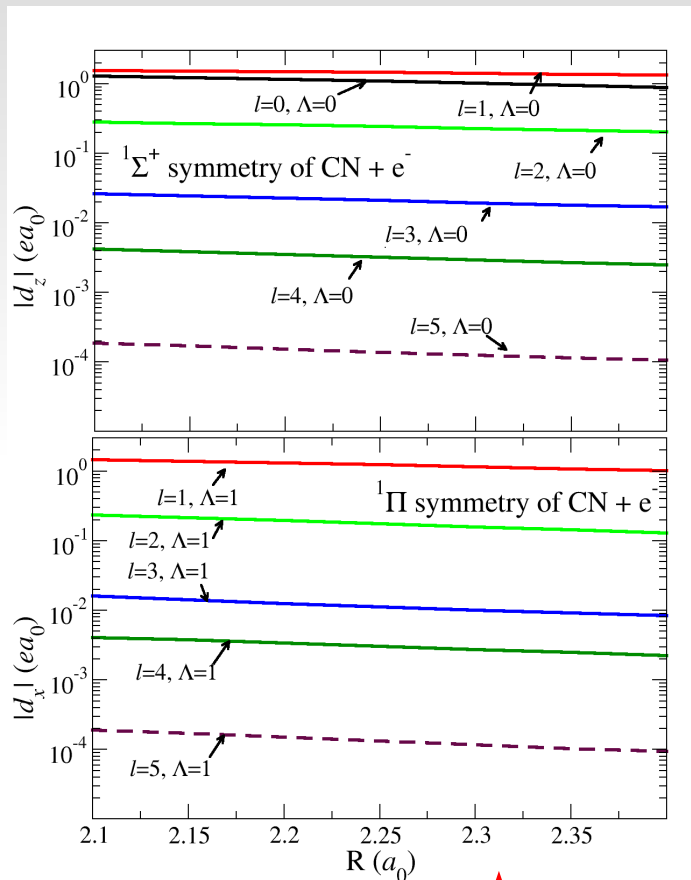
$C_2H^-$



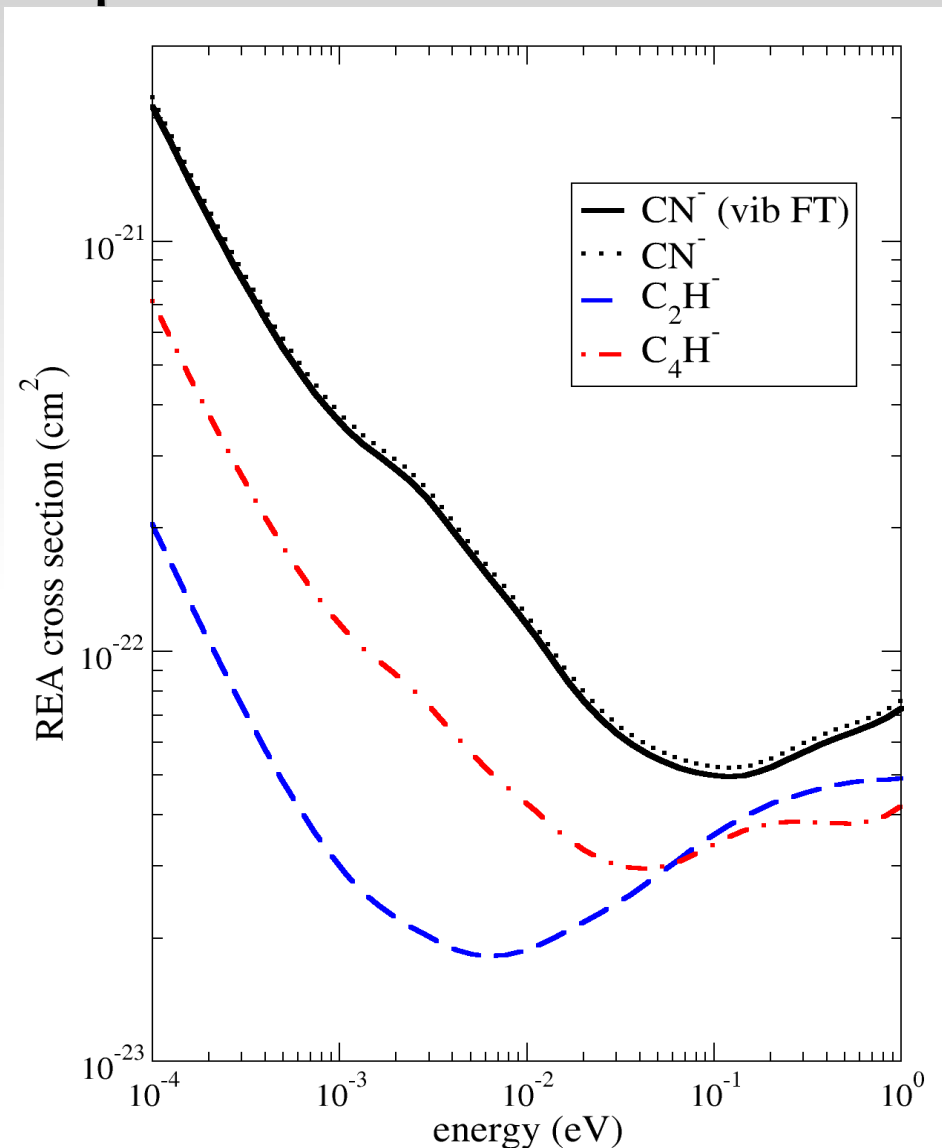
$C_4H^-$

# Results for $C_2H^-$ and $C_4H^-$ : cross sections

## CN<sup>-</sup>

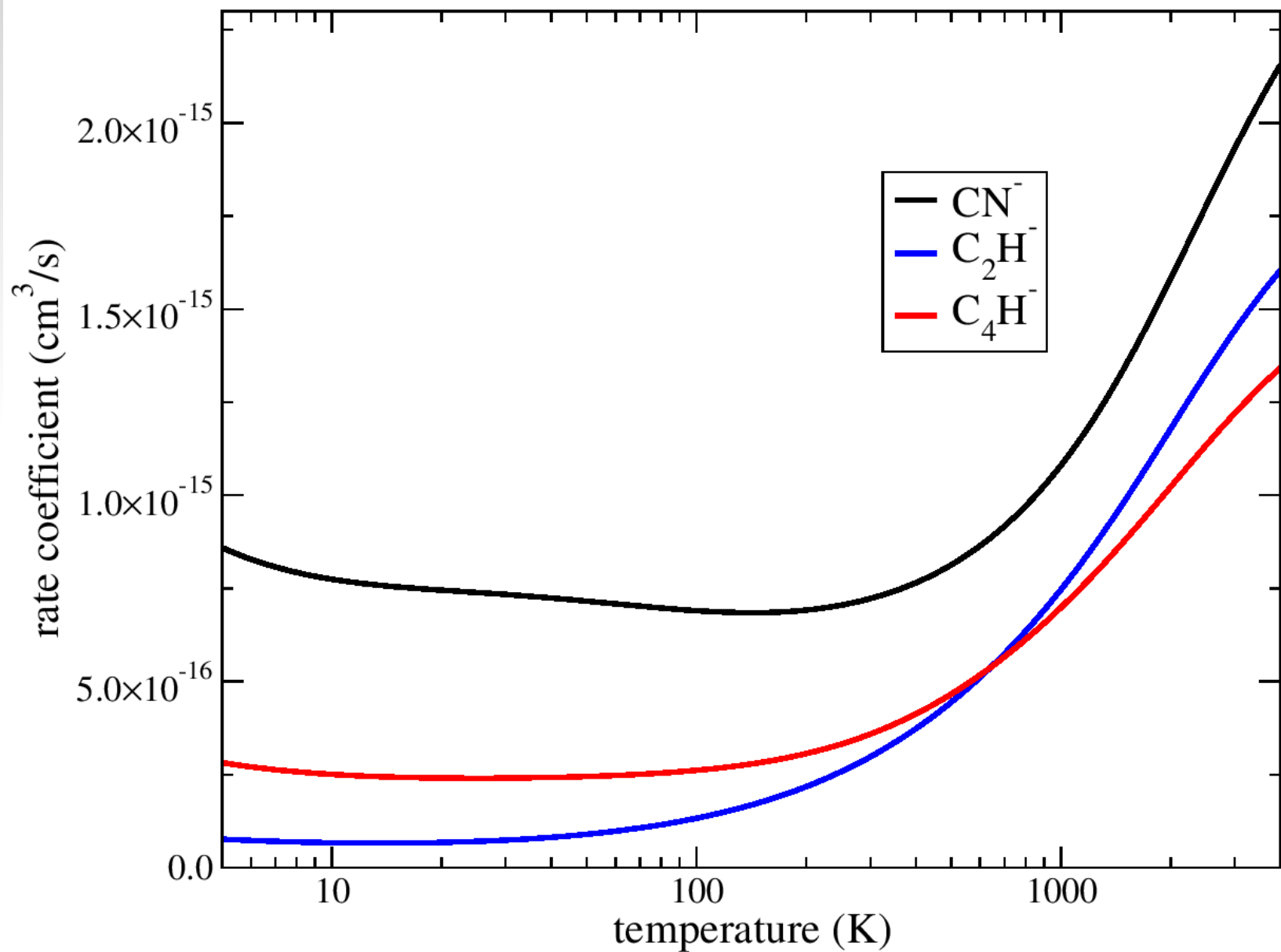


Dipole moments depend weakly on geometry (at least, for  $CN/CN^-$ ). Therefore, the vibrational integral could be approximated by the value of the dipole moments at the equilibrium geometry.



For  $C_2H^-$  and  $C_4H^-$ , vibrational integrals are approximated by values of the dipole moments at the equilibrium geometry.

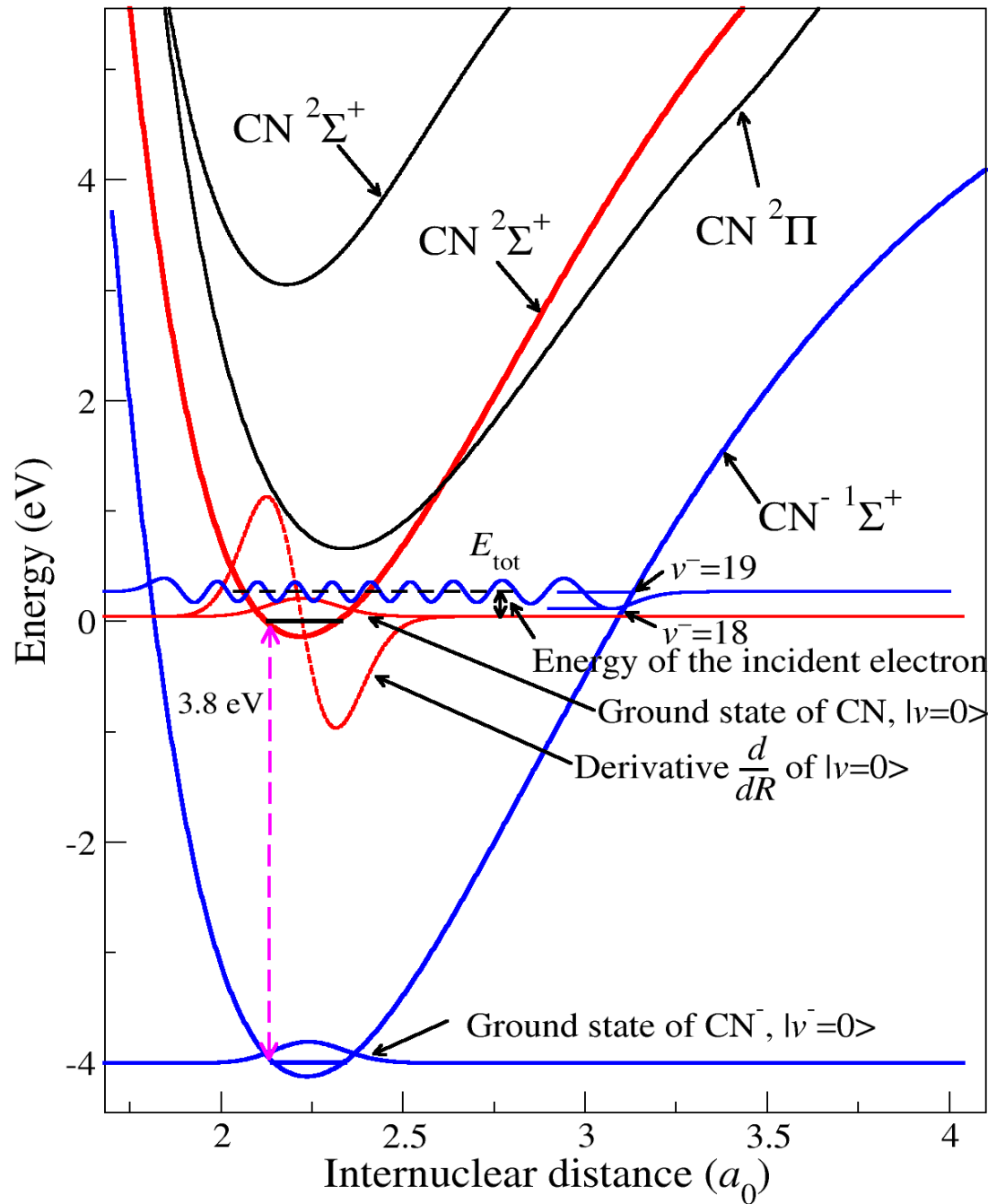
# Thermal rate constants



# About two-step process of REA

- The first step in the phase space approach by Herbst & Osamura (2008) is a capture of the electron into a vibrationally excited level of the ion.
- The capture occurs due to non-adiabatic vibronic coupling between the initial electron continuum state of  $\text{CN} + e^-$  and the bound electronic state of  $\text{CN}^-$ .
- In the study by Herbst & Osamura (2008), the cross section for the electron capturing is approximated by the unitary limit formula for the  $s$ -wave scattering,  $\sigma_{\text{capt}} = \pi/k^2$ .
- We can estimate numerically the cross section for the electron capture by the non-adiabatic coupling in CN.

# About two-step process of REA





# Non-adiabatic coupling

$$\Lambda_{f,\Gamma l \lambda} = \frac{\hbar^2}{\mu_{CN}} \left\langle \Psi_f \left| \frac{\partial}{\partial R} \right| \Psi_{\Gamma l \lambda} \right\rangle_r \frac{\partial}{\partial R} + \frac{\hbar^2}{2\mu_{CN}} \left\langle \Psi_f \left| \frac{\partial^2}{\partial R^2} \right| \Psi_{\Gamma l \lambda} \right\rangle_r$$

$$\left\langle \chi_{v-}^{j-} \left| \Lambda_{f,\Gamma l \lambda} \right| \chi_v^j \right\rangle_R \approx \frac{\hbar^2}{\mu_{CN}} \left\langle \chi_{v-}^{j-} \left| \left\langle \Psi_f \left| \frac{\partial}{\partial R} \right| \Psi_{\Gamma l \lambda} \right\rangle_r \frac{\partial}{\partial R} \right| \chi_v^j \right\rangle_R$$

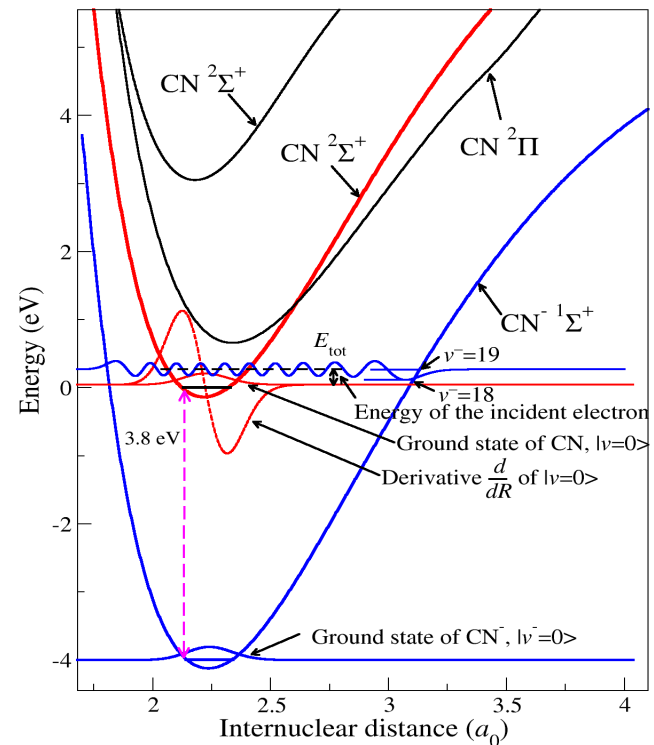
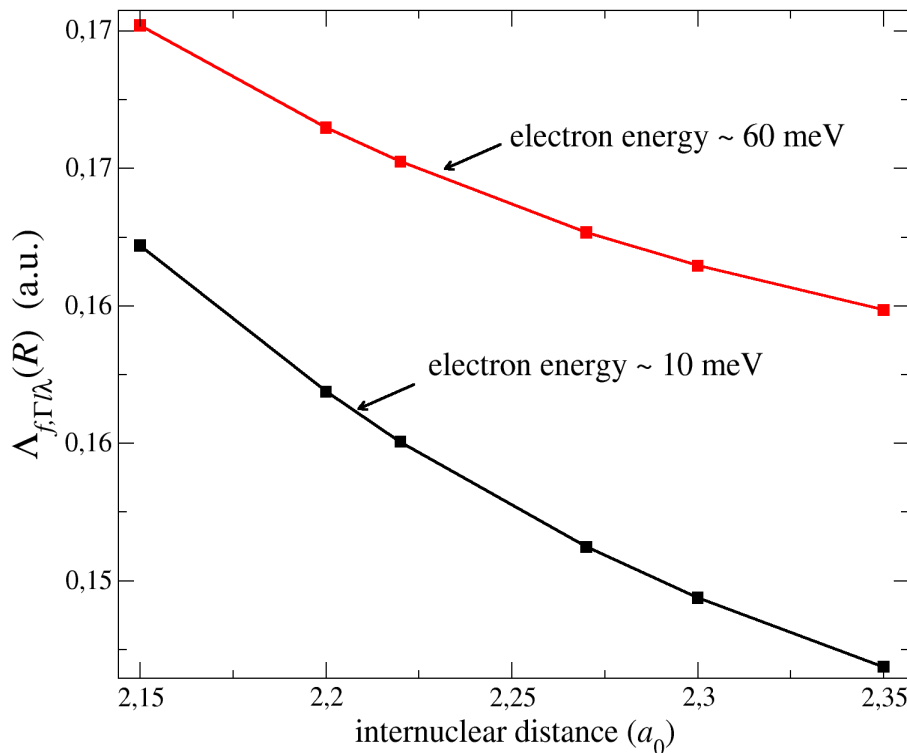
Electronic continuum state of CN+e<sup>-</sup>

Electronic bound state of CN<sup>-</sup> (X<sup>1</sup>Σ<sup>+</sup>)

# Non-adiabatic coupling

$$\left\langle \chi_{v-}^{j-} \left| \Lambda_{f, \Gamma l \lambda} \right| \chi_v^j \right\rangle_R \approx \frac{\hbar^2}{\mu_{CN}} \left\langle \chi_{v-}^{j-} \left| \left\langle \Psi_f \left| \frac{\partial}{\partial R} \right| \Psi_{\Gamma l \lambda} \right\rangle_r \frac{\partial}{\partial R} \right| \chi_v^j \right\rangle_R$$

The non-adiabatic coupling between the final electronic bound state of CN<sup>-</sup> and two “box” electronic states of <sup>1</sup>Σ<sup>+</sup> symmetry with energies above the energy of electronic detachment was calculated using the code for the complex Kohn method. Then, the coupling was renormalized to represent the initial state to be energy-normalized.



# Cross section for non-adiabatic electron capture

The probability (per unit time) of a transition from the initial rovibronic state  $|i\rangle$  of the  $e^- + \text{CN}$  into a final state of  $\text{CN}^-$  being in a vibrationally excited state  $v^- \sim 19$  is given by the Fermi Golden rule

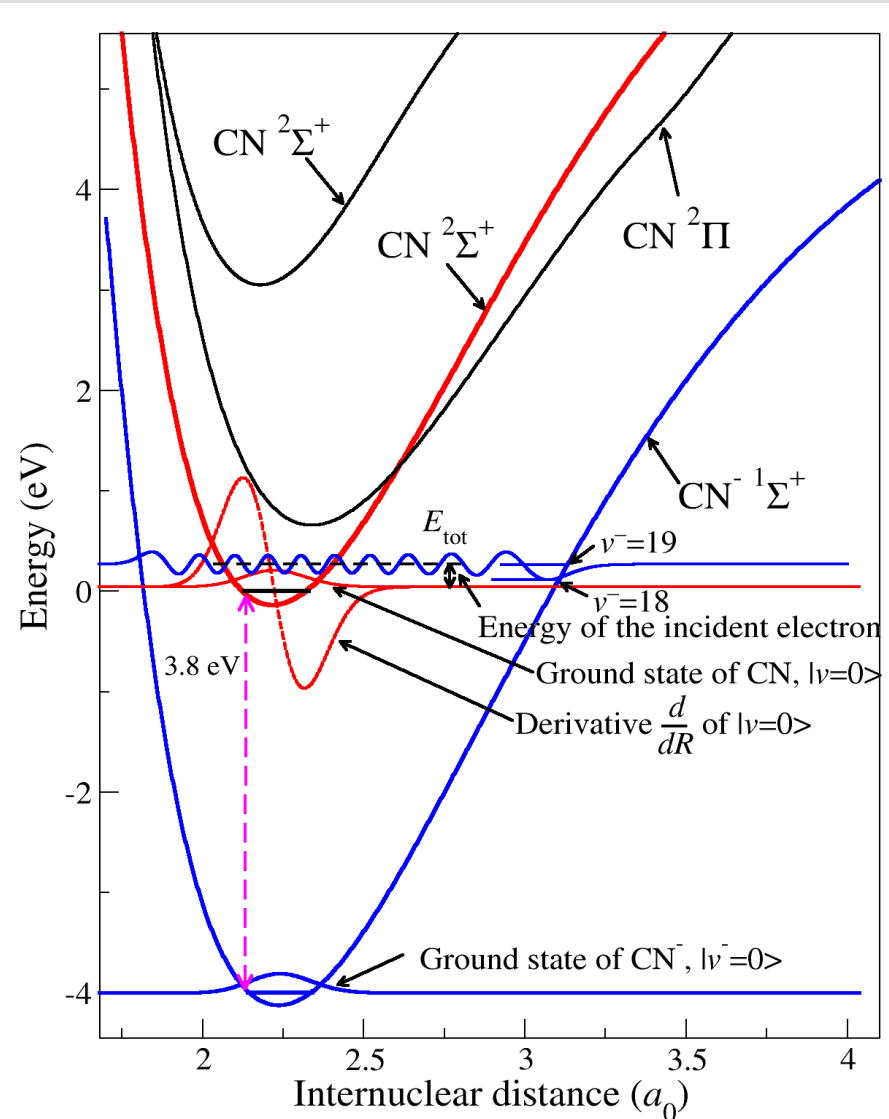
$$P = \frac{2\pi}{\hbar} \left| \langle f | \hat{\Lambda} | i \rangle \right|^2 \rho(E_c)$$

Where  $\rho(E_c)$  is the density of final vibrational states

$$\rho(E_c) \sim \frac{1}{\Delta E_v}$$

and  $\Delta E_v$  is the energy of vibrational splitting for the  $\text{CN}^-$  potential near energy  $E_{\text{tot}}$ ,  $\Delta E_v = 2 \times 10^{-4}$  hartree.

The cross section is then obtained by dividing the probability with the current density in the incident flux of electrons.



# Cross section for non-adiabatic electron capture

$$\sigma = \frac{P}{j_{cd}} \approx \frac{\pi}{E_{el}} \frac{1}{\Delta E_{rv}} \left| \int dR \chi_{v_f}(R) \left[ \int d^3r_1, \dots, d^3r_N \Psi_f^*(r, R) \frac{\hbar^2}{\mu_{CN}} \frac{\partial}{\partial R} \Psi_{\Gamma\Lambda}(r, R) \right] \frac{\partial}{\partial R} \chi_v(R) \right|^2$$

$$\int dR \chi_0^0(R) \left[ \int d^3r_1, \dots, d^3r_N \Psi_f^*(r, R) \frac{\partial}{\partial R} \Psi_{\Gamma\Lambda}(r, R) \right] \frac{\partial}{\partial R} \chi_0^0(R) = -1.9 \times 10^{-5} \text{ a.u.}$$

Then the cross section to capture an electron into a vibrational level is on the order of

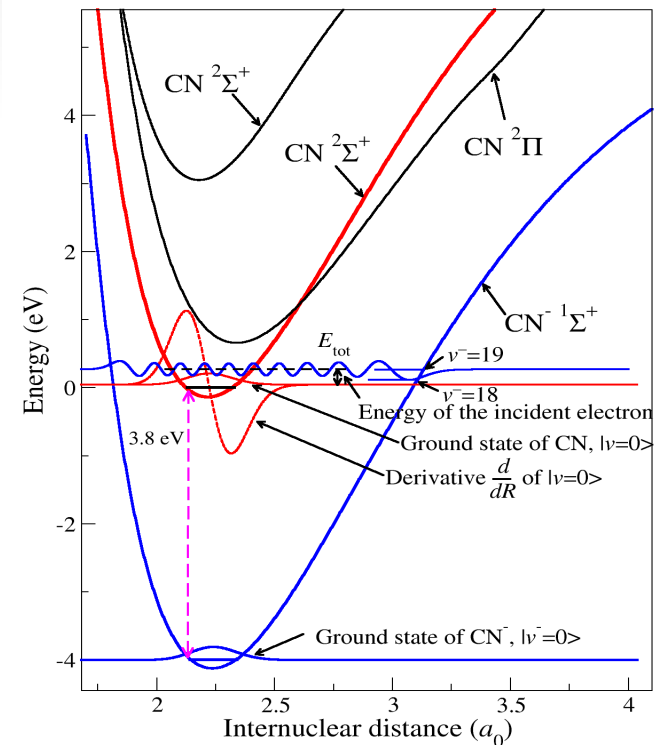
$$\sigma_c \approx \frac{6 \times 10^{-16}}{E_{el}} a_0^2$$

Where  $E_{el}$  is in hartree. The cross section for the electron attachment is reduced with respect to the  $\sigma_c$  because the formed  $\text{CN}^-$  resonance can decay by autodetachment.

$$\sigma_{IREA} = \frac{\Gamma_{sp}}{\Gamma_{tot}} \sigma_c \leq \sigma_c$$

Therefore, the cross section due to non-adiabatic coupling is small (as expected).

The role of near-threshold resonances has not yet studied

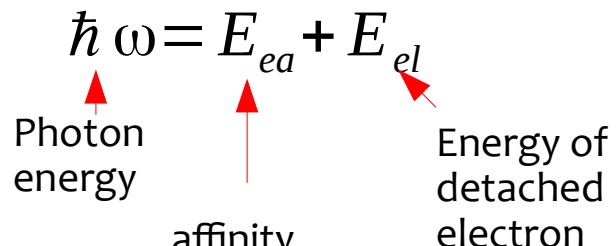


# Comparison with photodetachment experiments

There is no experimental data on the radiative attachment to the CN, C<sub>2</sub>H, and C<sub>4</sub>H molecules. However, the calculated transition dipole moments can be used to determine photodetachment cross sections, for which experimental data have been recently obtained.

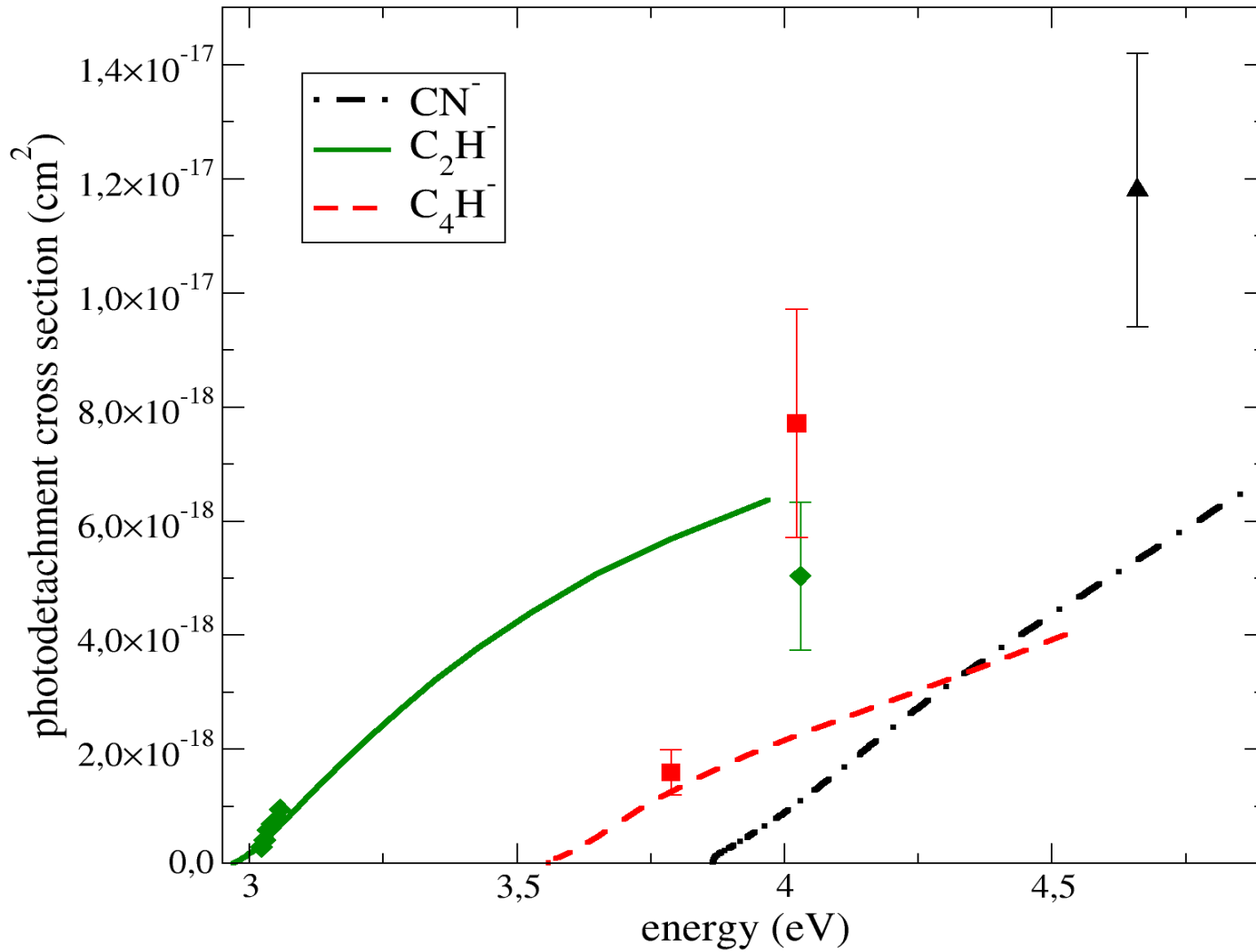
With the chosen normalization of electronic continuum wave functions, the photodetachment cross section is

$$\sigma_{PD} = \frac{8 m_e \pi \omega}{3 \hbar^2 c} \sum_{l\pi} \left| d_{\pi, \Gamma l - \pi}^{(v \rightarrow v_f)} \right|^2 \quad \text{with} \quad \hbar \omega = E_{ea} + E_{el}$$

  
Photon energy                      affinity                      Energy of detached electron

# Comparison with photodetachment experiments

$$\sigma_{PD} = \frac{8 m_e \pi \omega}{3 \hbar^2 c} \sum \left| d_{\pi, \Gamma l - \pi}^{(v \rightarrow v_f)} \right|^2$$



# Conclusion

➤ Widely-accepted rates of anion formation in ISM by radiative attachment should probably be revisited.



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BIMOLECULAR REACTIONS 48

TERMOLECULAR REACTIONS 1

SURFACE REACTIONS 0

48 result(s)

Type	Reaction	$\alpha$	$\beta$	$\gamma$	$T(K)$	Formula	Evaluation
ER	$C_4H + e^- \rightarrow C_4H^- + \text{Photon}$	1.10E-8	-5.00E-1	0.00E+0	10-280	Kooij	
ER	$C_6H + e^- \rightarrow C_6H^- + \text{Photon}$	6.00E-8	-5.00E-1	0.00E+0	10-280	Kooij	
ER	$C_8H + e^- \rightarrow C_8H^- + \text{Photon}$	6.00E-8	-5.00E-1	0.00E+0	10-280	Kooij	
ER	$C_3N + e^- \rightarrow C_3N^- + \text{Photon}$	2.00E-10	-5.00E-1	0.00E+0	10-280	Kooij	

# Conclusions

- We have calculated the cross-section for the radiative electron attachment to CN, C<sub>2</sub>H<sup>-</sup>, C<sub>4</sub>H<sup>-</sup> and C<sub>3</sub>N<sup>-</sup>. The theoretic approach is “fully” quantum-mechanical (at least, for CN<sup>-</sup>).
- For CN<sup>-</sup>, it confirms the previous assessment by E. Herbst that CN<sup>-</sup> is unlikely to be formed by REA in the ISM. However, for C<sub>4</sub>H<sup>-</sup> our approach gives much smaller rate coefficient (comparable to CN<sup>-</sup>) than the phase space theory.
- Weakly-bound (dipolar) electronic states in such molecules as C<sub>6</sub>H<sup>-</sup>, C<sub>5</sub>N<sup>-</sup> can possibly enhance the REA process. Our preliminary results (made for C<sub>3</sub>N<sup>-</sup>) show that rotational resonances in the presence of dipolar electronic states does increase the REA rates but not by orders of magnitude.
- CN<sup>-</sup> and some other anions could possibly formed in the ISM by a different mechanism(s). For example, HCN+H<sup>-</sup> → CN<sup>-</sup>+H<sub>2</sub> ( $k \sim 10^{-9}$  cm<sup>3</sup>/s) **OR** H<sub>2</sub>CN+e<sup>-</sup> → CN<sup>-</sup> + H<sub>2</sub> and HCN+H<sup>-</sup>.