

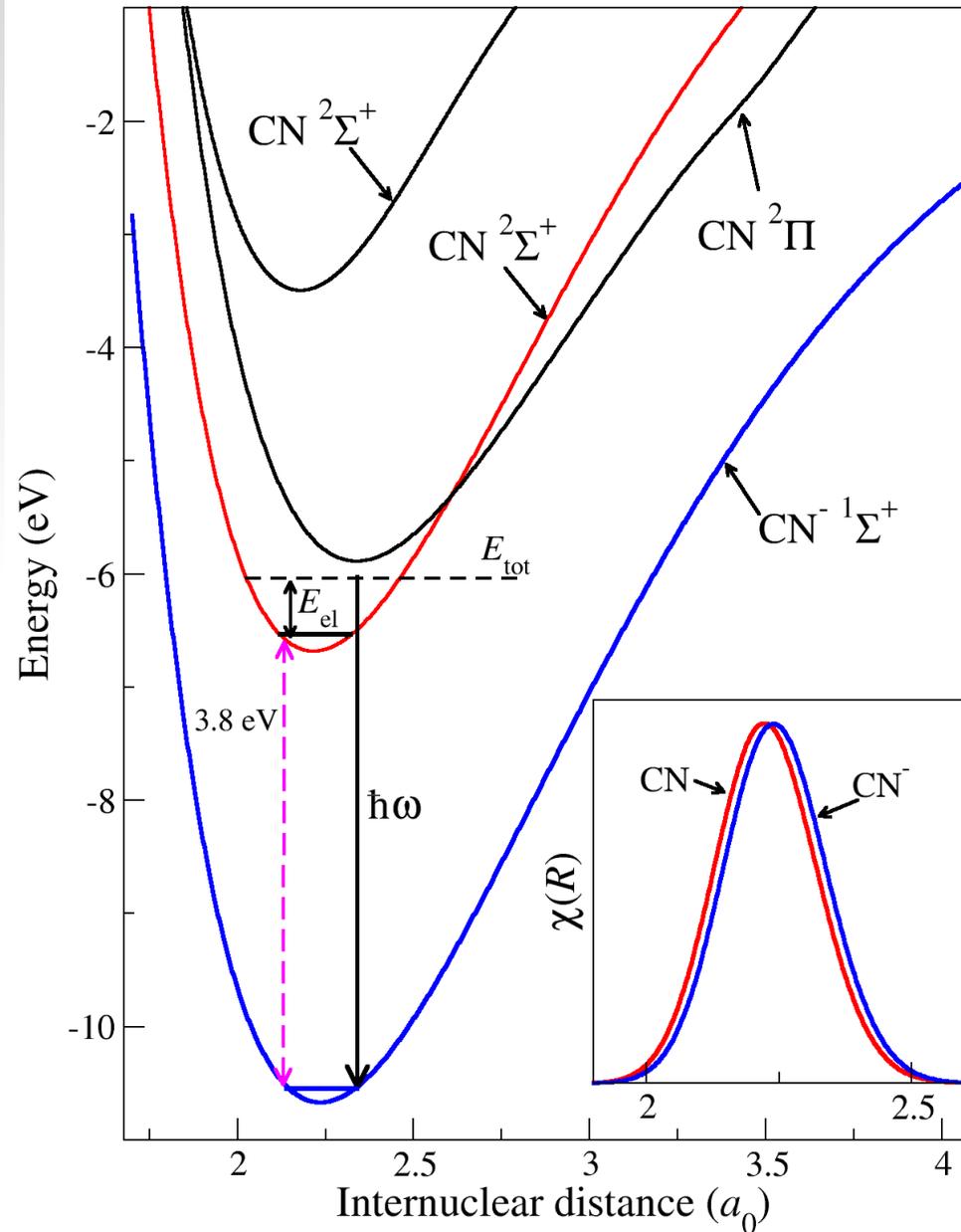
**Collisions between  
electrons and molecules,  
photon-assisted  
collisions**

**Photodetachment of an  
electron from a negative  
molecular ion,  
radiative electron attachment**

# Motivation: negative ions in the interstellar medium (ISM)

- \*In 1981 E. Herbst 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):
- \*  $C_nH + e^- \rightarrow C_nH^- + \hbar\omega$ ,  $C_nN + e^- \rightarrow C_nN^- + \hbar\omega$

# Quantum-mechanical picture



# Radiative electron attachment

- \*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.

- \*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.

# Initial state $|i\rangle$

- \* The scattering state of the e<sup>-</sup>-M system behaves at large distances  $r$  between e<sup>-</sup> and M as

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

$\phi_{v'j'm_j'}^{\Gamma'}$  is a wave function of the target molecule

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

$A_{aa'}$  is the scattering amplitude in the laboratory frame.

# Laboratory and molecular reference frames

\* The form (LF)

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

is not adapted for theoretical calculations.

In theoretical calculations of electron-molecule scattering, one uses the molecular reference frame (MF) and partial waves.

One needs to represent the wave function above in the molecular frame.

One starts from the formula of decomposition of the plane-wave into spherical harmonics

$$e^{i\vec{k}_{vj} \cdot \vec{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m_l=-l}^l i^l j_l(k_{vj}r) Y_{lm_l}(\hat{k}_{vj}) Y_{lm_l}(\hat{r}),$$

When  $k_{vj}r$  is large

$$j_l(x) \rightarrow \frac{1}{x} \sin\left(x - \frac{l\pi}{2}\right) = \frac{i}{2x} \left( e^{-i(kx - l\pi/2)} - e^{i(kx - l\pi/2)} \right)$$

# Transformation between LF and MF

\*The function

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

is rewritten in terms of partial waves  
(spherical harmonics) as

$$e^{i\vec{k}_{vj} \cdot \vec{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m_l=-l}^l i^l j_l(k_{vj}r) Y_{lm_l}(\hat{k}_{vj}) Y_{lm_l}(\hat{r}),$$

$$j_l(x) \rightarrow \frac{1}{x} \sin\left(x - \frac{l\pi}{2}\right) = \frac{i}{2x} (e^{-i(kx-l\pi/2)} - e^{i(kx-l\pi/2)})$$

$$\begin{aligned} \Psi_{vjm_j}^\Gamma &\rightarrow \frac{2\pi i}{r\sqrt{k_{vj}}} \sum_{l=0}^{\infty} \sum_{m_l=-l}^l Y_{lm_l}(\hat{k}_{vj}) i^l \\ &\times \sum_{l'm_l'} \sum_{v'j'm_j'\Gamma'} \frac{1}{\sqrt{k_{v'j'}}} \phi_{v'j'm_j'}^{\Gamma'} Y_{l'm_l'}(\hat{r}) \\ &\times \left[ \delta_{v'v} \delta_{l'l} \delta_{m_l'm_l} \delta_{j'j} \delta_{m_j'm_j} \delta_{\Gamma\Gamma'} e^{-i(k_{v'j'}r - \frac{l'\pi}{2})} \right. \\ &\left. - S_{v'j'm_j'l'm_l';vjm_jlm_l}^{\Gamma'\Gamma} e^{i(k_{v'j'}r - \frac{l'\pi}{2})} \right]. \end{aligned}$$

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

# Transformation between LF and MF

\*The function

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

is rewritten in MF as

$$\begin{aligned} \Psi_{vjm_j}^{\Gamma} \rightarrow & \frac{2\pi i}{r\sqrt{k_{vj}}} \sum_{JM\lambda} \sum_{lm_l} Y_{lm_l}(\hat{k}_{vj}) i^l (-1)^{l+\lambda} \frac{C_{lm_ljm_j}^{JM} C_{l-\lambda J\Lambda}^{j\mu}}{\sqrt{k_{vj}}} \\ & \times \sum_{l'\lambda'\Gamma'} X_{vl'\lambda'\Gamma'}^{JM} [\delta_{l'l} \delta_{\lambda'\lambda} \delta_{\Gamma'\Gamma} e^{-i(k_{vj}r - \frac{l'\pi}{2})} \\ & - S_{l'\lambda';l\lambda}^{\Gamma'\Gamma}(R) e^{i(k_{vj}r - \frac{l'\pi}{2})}] \end{aligned}$$

$$X_{vl\lambda\Gamma}^{JM} = \sqrt{\frac{2J+1}{8\pi^2}} \chi_v^j(R) \omega_{\Gamma}(\mathbf{r}_{N-1}) [D_{M\Lambda}^J(\Omega)]^* Y_{l\lambda}(\theta', \phi').$$

$$S_{v'l'\lambda';vl\lambda}^J = \int \chi_{v'}^j(R') S_{l'\lambda';l\lambda}^{\Gamma'\Gamma}(R') \chi_v^j(R') dR'$$

# The wave function in the form suitable for ab initio calculation

\*The initial function

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

is represented in terms of quantities calculated numerically (*ab initio*)

$$\Psi_{vjm_j}^\Gamma = \frac{1}{\sqrt{k_{vj}}} \sum_{Jl\lambda} \sqrt{4\pi(2l+1)} i^l (-1)^{l+\lambda} C_{l0jm_j}^{JM} C_{l-\lambda J\Lambda}^{j\mu} |JM\Lambda\rangle \times \chi_v^j(R) \Psi_{\Gamma l\lambda}(r, R).$$

$$|JM\Lambda\rangle = \sqrt{\frac{2J+1}{8\pi^2}} [D_{M\Lambda}^J(\Omega)]^*$$

# Transition dipole moments

\*

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

$$\vec{d} = \sum_i e \vec{r}_i$$

$$\begin{aligned} \Psi_{vjm_j}^\Gamma &= \frac{1}{\sqrt{k_{vj}}} \sum_{Jl\lambda} \sqrt{4\pi(2l+1)} i^l (-1)^{l+\lambda} C_{l0jm_j}^{JM} C_{l-\lambda J\Lambda}^{j\mu} |JM\Lambda\rangle \\ &\times \chi_v^j(R) \Psi_{\Gamma l\lambda}(r, R). \end{aligned}$$

$$|\langle f | \vec{d} | i \rangle|^2 = \sum_p |\langle f | d_p | i \rangle|^2$$

$$d_p = \sum_\pi d_\pi [D_{p\pi}^1(\Omega)]^*$$

$$\langle f | d_p | i \rangle$$

$$= \frac{1}{\sqrt{k_{vj}}} \sum_{Jl\lambda} C_{l0jm_j}^{JM} C_{l-\lambda J\Lambda}^{j\mu} \sqrt{4\pi(2l+1)} i^l$$

$$\times \sum_\pi (-1)^{l+\lambda} \int \chi_{v_f}^{J_f}(R) \langle \Psi_f | \langle J_f M_f \Lambda_f | \hat{d}_\pi [D_{p\pi}^1(\Omega)]^*$$

$$\times |JM\Lambda\rangle_\Omega | \Psi_{\Gamma l\lambda} \rangle_r \chi_v^j(R) dR.$$

# REA cross section

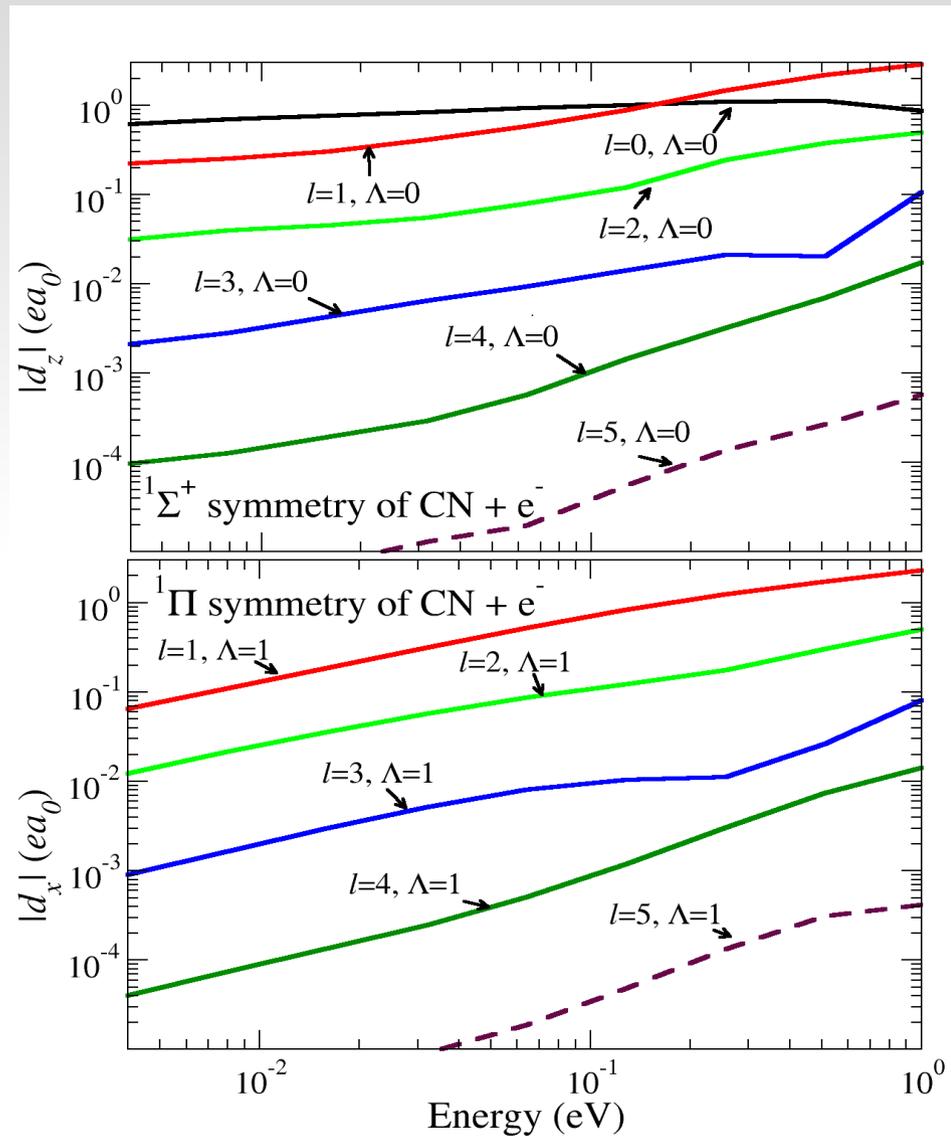
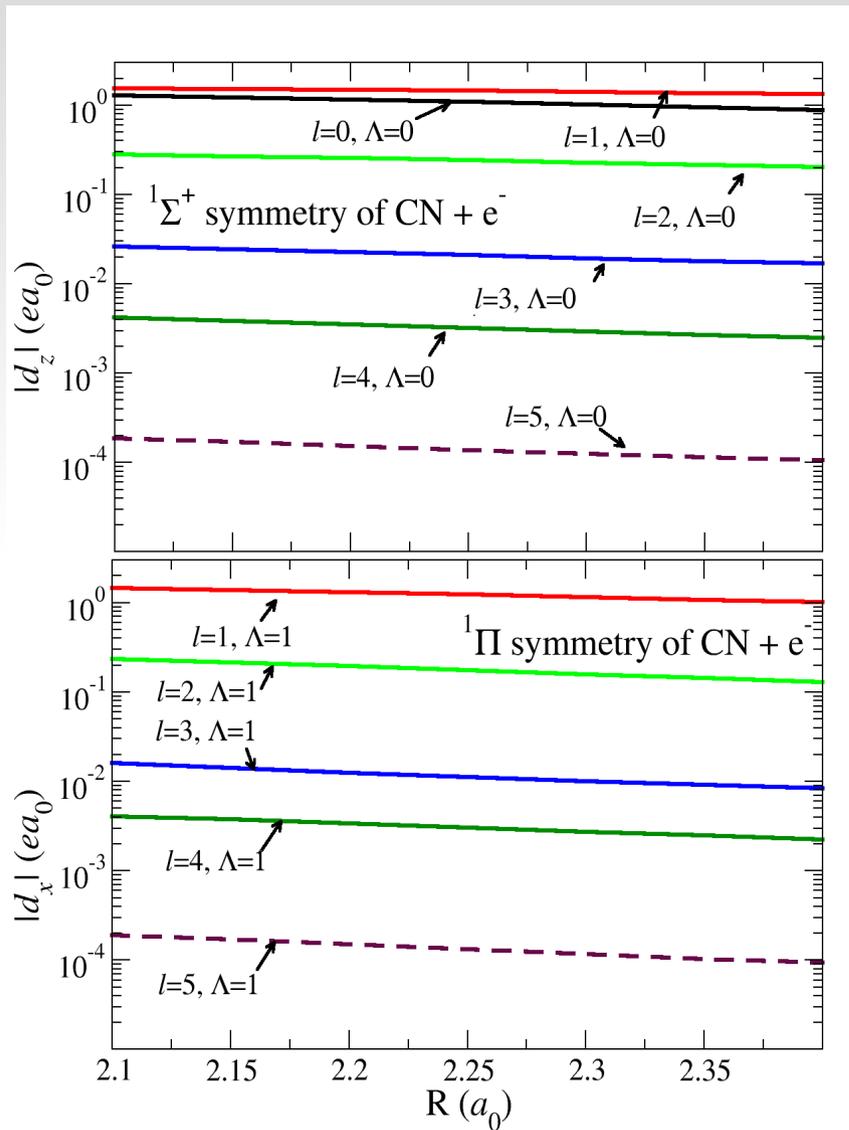
- \*The scattering state  $|i\rangle$  is expanded in the basis of partial waves and transformed into the molecular frame.
- \*In the molecular frame, the scattering wave function is obtained using the complex Kohn method or the UK R-matrix code.
- \*The final expression for the REA cross section in the form suitable for calculations is

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

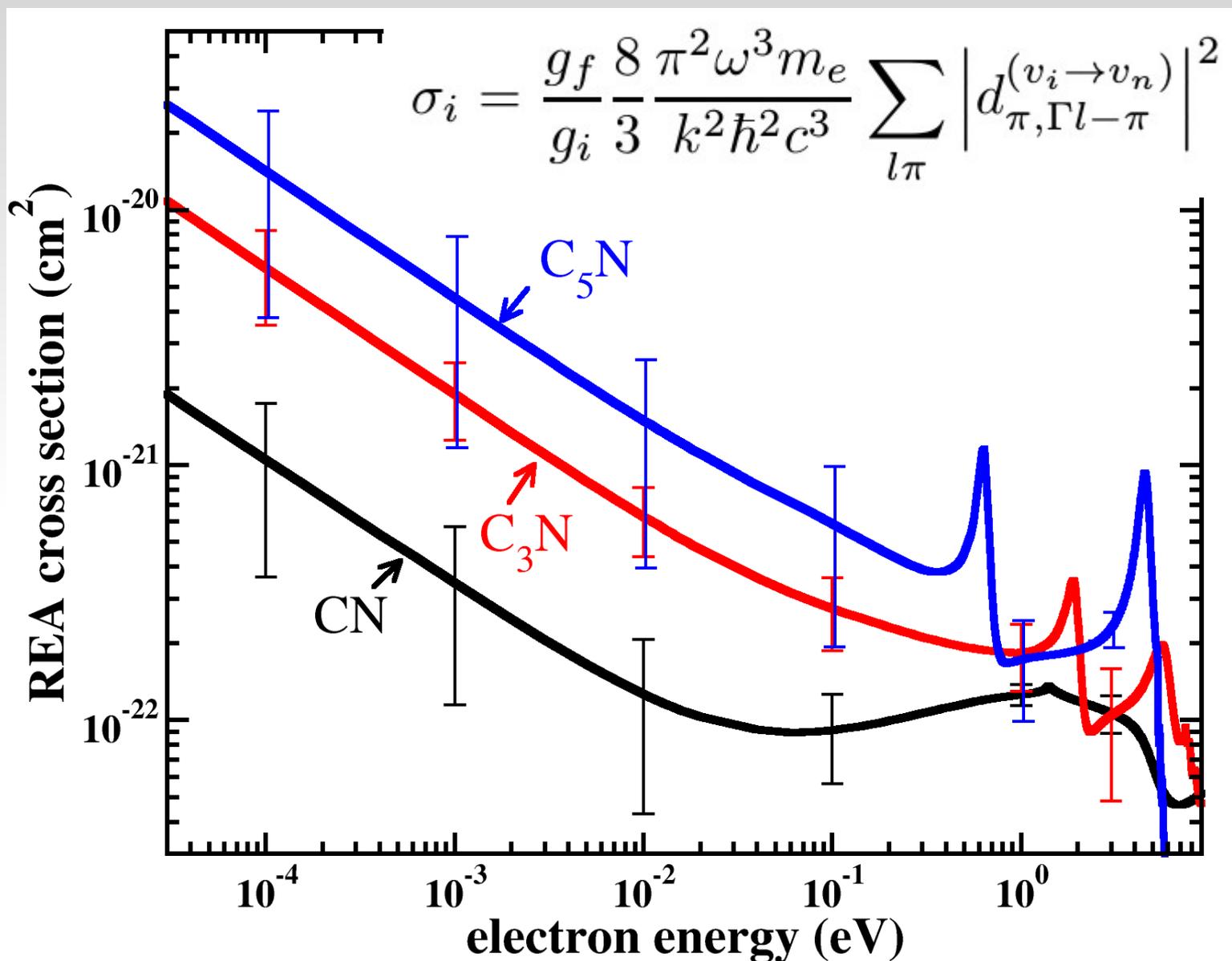
$$d_{\pi, \Gamma l \lambda} \equiv \langle \Psi_f | d_{\pi} | \Psi_{\Gamma l \lambda} \rangle = - \sum_{k=1}^N \int \Psi_f^*(r_1, \dots, r_N) e r_{k\pi} \Psi_{\Gamma l \lambda}(r_1, \dots, r_N) d^3 r_1, \dots, d^3 r_N$$

$$d_{\pi, \Gamma l \lambda}^{(v \rightarrow v_f)} = \int \chi_{v_f}^{J_f}(R) \langle \Psi_f | d_{\pi} | \Psi_{\Gamma l \lambda} \rangle_r \chi_v^j(R) dR$$

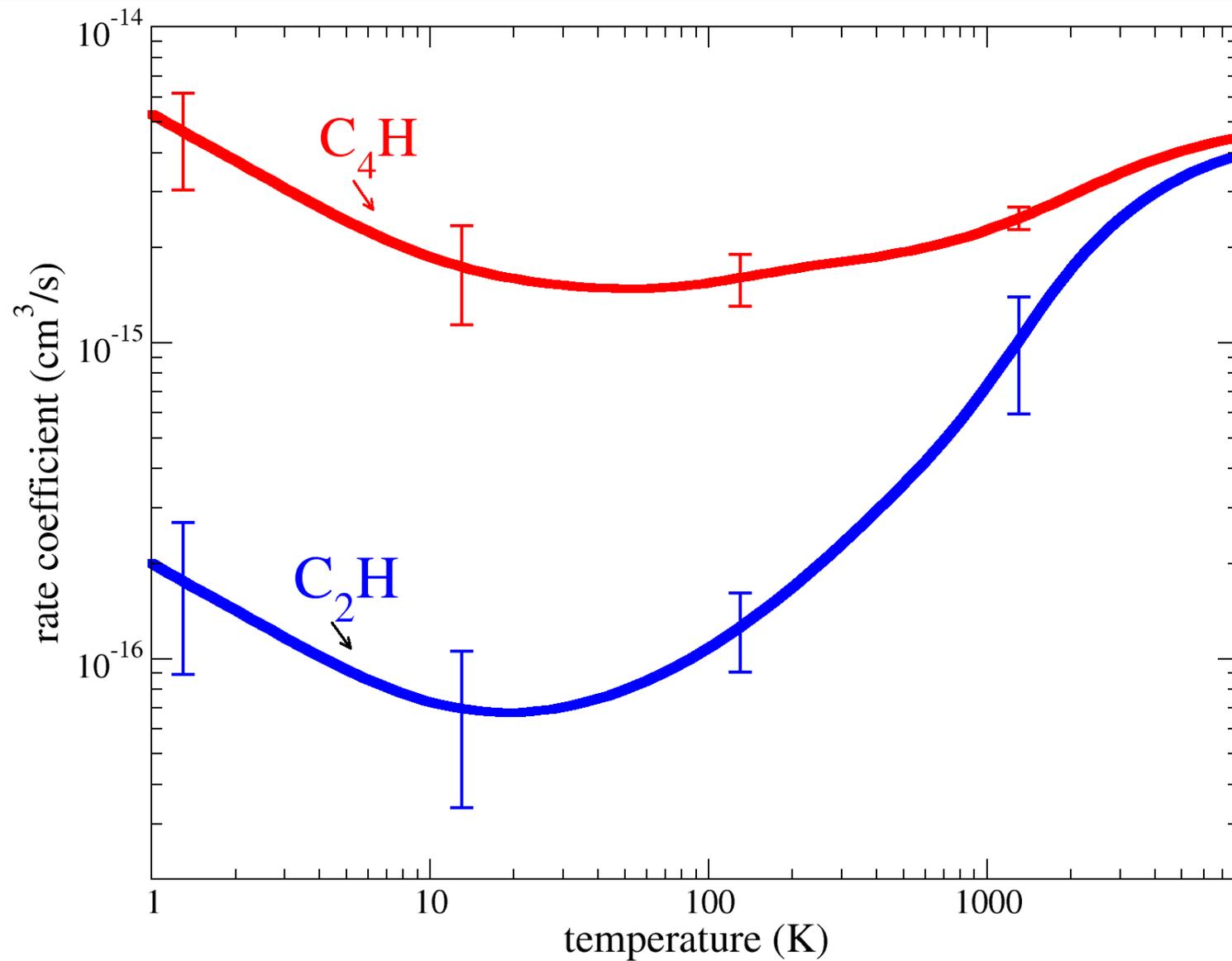
# Transition dipole moments as a function of energy and geometry



# REA cross sections



# REA cross sections



# 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 recently obtained.

\*If the wave function of the detached electron is normalized to energy

$$\int \varphi_d(r) \varphi_{d'}(r) r^2 dr \sin \theta d\theta d\varphi = \delta(E - E')$$

\* the photodetachment cross section is

$$\sigma_{PD} = \frac{4 \pi^2 \omega}{c} \left| \langle f | \vec{p} \cdot \vec{d} | i \rangle \right|^2$$

polarization of  
the laser field

$$\vec{d} = \sum_i e \vec{r}_i$$

# Initial and final states

\*We assume linear polarization along z-axis in LF

$$\vec{p} = (0, 0, 1)$$

\*The photodetachment cross

$$\sigma_{PD} = \frac{4\pi^2\omega}{c} \left| \langle f | \vec{p} \cdot \vec{d} | i \rangle \right|^2 = \frac{4\pi^2\omega}{c} \left| \langle f | d_z | i \rangle \right|^2 \quad d_z = \sum_i e \vec{z}_i$$

with the initial state

$$|i\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D_{M_0}^{J*}(\alpha\beta\gamma) \chi_\sigma \psi_{el}^-$$

and the final state

$$|f\rangle = \sqrt{\frac{2j+1}{8\pi^2}} D_{m_0}^{j*}(\alpha\beta\gamma) \chi_\sigma \psi_{el}$$

product of the electronic function of CN and the wave function of the detached electron

# LF-MF transformation (again)

\*Because the electronic wave function is calculated in MF and the photon is absorbed in LF, we need to bring all factors in the cross section formula to the same frame. I use MF.

$$\sigma_{PD} = \frac{4\pi^2\omega}{c} \left| \langle f | d_{\bar{z}} | i \rangle \right|^2$$

$$d_{\bar{z}} = \sum_{\lambda=-l}^{+l} d_{\lambda} D_{0\lambda}^{l*}$$

$d_{\lambda}$  is the  $\lambda$ -component in the molecular frame

$$\vec{d} = (\underbrace{0, 0, d_{\bar{z}}}_{\text{LFrame}}) = (\underbrace{d_{-1}, d_0, d_{+1}}_{\text{Molecular frame}})$$

Wigner function depending on Euler angles  $\alpha, \beta, \gamma$ .

$$\sigma_{PD}^{M,M} = \frac{4\pi^2\omega}{c} \left| \langle f | \sum_{\lambda} d_{\lambda} D_{0\lambda}^{l*} | i \rangle \right|^2$$

# Some calculations involving quantum angular momentum

\*In the formula

$$\sigma_{PD}^{M,M} = \frac{4\pi^2 \omega}{c} \left| \langle f | \sum_{\lambda} d_{\lambda} D_{0\lambda}^{L*} | i \rangle \right|^2$$

$$\sum_{\lambda} \langle f | d_{\lambda} D_{0\lambda}^{L*} | i \rangle = \sum_{\lambda} \langle D_{m_0}^{j*} | D_{0\lambda}^{L*} | D_{M_0}^{J*} \rangle \sqrt{\frac{(2J+1)(2j+1)}{(8\pi^2)^2}} \\ \times \langle \chi_{\nu} | \chi_{\nu'} \rangle \langle \psi_{el} | d_{\lambda} | \psi_{el} \rangle$$

$$\langle D_{m_0}^{j*} | D_{0\lambda}^{L*} | D_{M_0}^{J*} \rangle = \frac{8\pi^2}{2j+1} C_{JM_0}^{jm} C_{J_0\lambda}^{j_0} \\ \# \\ \text{only if } \lambda=0$$

$$|i\rangle = \sqrt{\frac{2J+1}{8\pi^2}} D_{M_0}^{J*}(\alpha\beta\gamma) \chi_{\nu} \psi_{el}^{-}$$

$$|f\rangle = \sqrt{\frac{2j+1}{8\pi^2}} D_{m_0}^{j*}(\alpha\beta\gamma) \chi_{\nu'} \psi_{el}$$

$$\sigma_{PD}^{M,M} = \frac{4\pi^2 \omega}{c} (2J+1) |\langle \chi_{\nu} | \chi_{\nu'} \rangle|^2 |d_0(E)|^2 \left| C_{JM_0}^{jm} \right|^2 \left| C_{J_0\lambda}^{j_0} \right|^2$$

# Some calculations involving quantum angular momentum

\*The cross section

$$\sigma_{PD}^{m_i, m_f} = \frac{4\pi^2 \omega}{c} (2J+1) |\langle \chi_{\sigma} | \chi_{\sigma'} \rangle|^2 |d_0(E)|^2 |C_{JM10}^{j m_i}|^2 |C_{J010}^{j_0 m_f}|^2$$

\*should be averaged over possible initial states, which cannot be distinguished in the experiment.

\*and summed over all possible final states

$$\sigma_{PD} = \frac{1}{2J+1} \sum_{m_i, m_f} \sigma_{PD}^{m_i, m_f} = \frac{4\pi^2 \omega}{3c} (2j+1) |C_{J010}^{j_0}|^2 |d_0(E)|^2$$

$$\sum_{m, M} |C_{JM10}^{j m}|^2 = \frac{2j+1}{3}$$

# Approximations made in the derivation

$$\sigma_{PD} = \frac{4\pi^2\omega}{3c} (2j+1) \left| C_{j_0 l_0}^{j_0} \right|^2 \left( d_0(E) \right)^2$$

- \*The electronic wave function of the outgoing electron is assumed to be in one channel. Therefore, all resonances are ignored.
- \* $d_0(E)$  is assumed to be calculated at a fixed geometry of the molecule.

# The role of temperature

\*If anions are in a thermal equilibrium at a temperature  $T$ , excited rotational states with  $J > 0$  and energies  $E_J = BJ(J+1)$ , could be populated.

\*The relative population is  $w_{J,T} = N e^{-\frac{E_J}{kT}} (2J+1)$

\*where  $N$  is such that  $\sum_J w_{J,T} = 1$

$$w_{J,T} = \frac{e^{-\frac{E_J}{kT}} (2J+1)}{\sum_J e^{-\frac{E_J}{kT}} (2J+1)}$$

\*Therefore, the number of PD events per unit time is

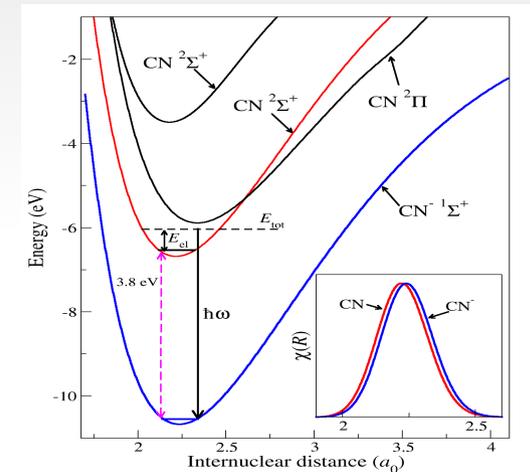
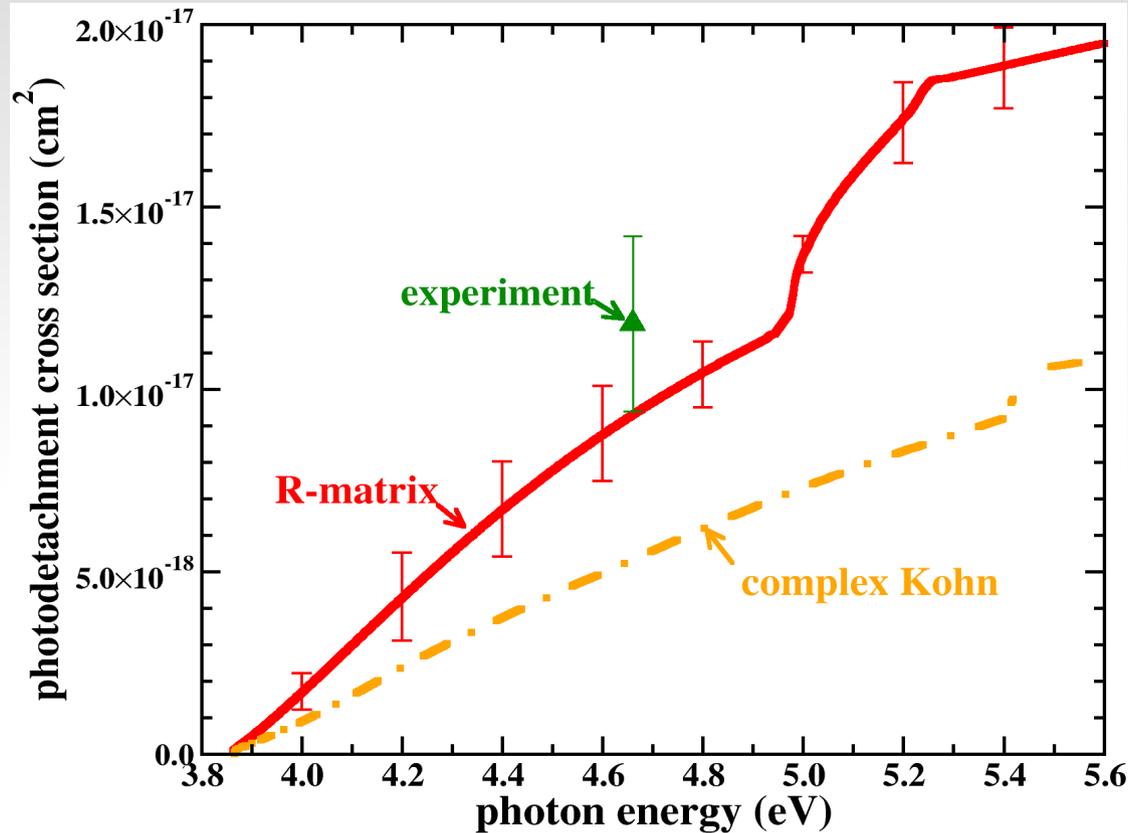
$$n_{PD} \sim \sum_{j,J} w_{J,T} \sigma_{PD}(j \leftarrow J)$$

$$\sigma_{PD} = \frac{4\pi^2 \omega}{3c} (2j+1) |C_{j_0 j_0}^{j_0}|^2 (d_0(E))^2$$

$$d_0(E) = C (E_{kin})^p$$

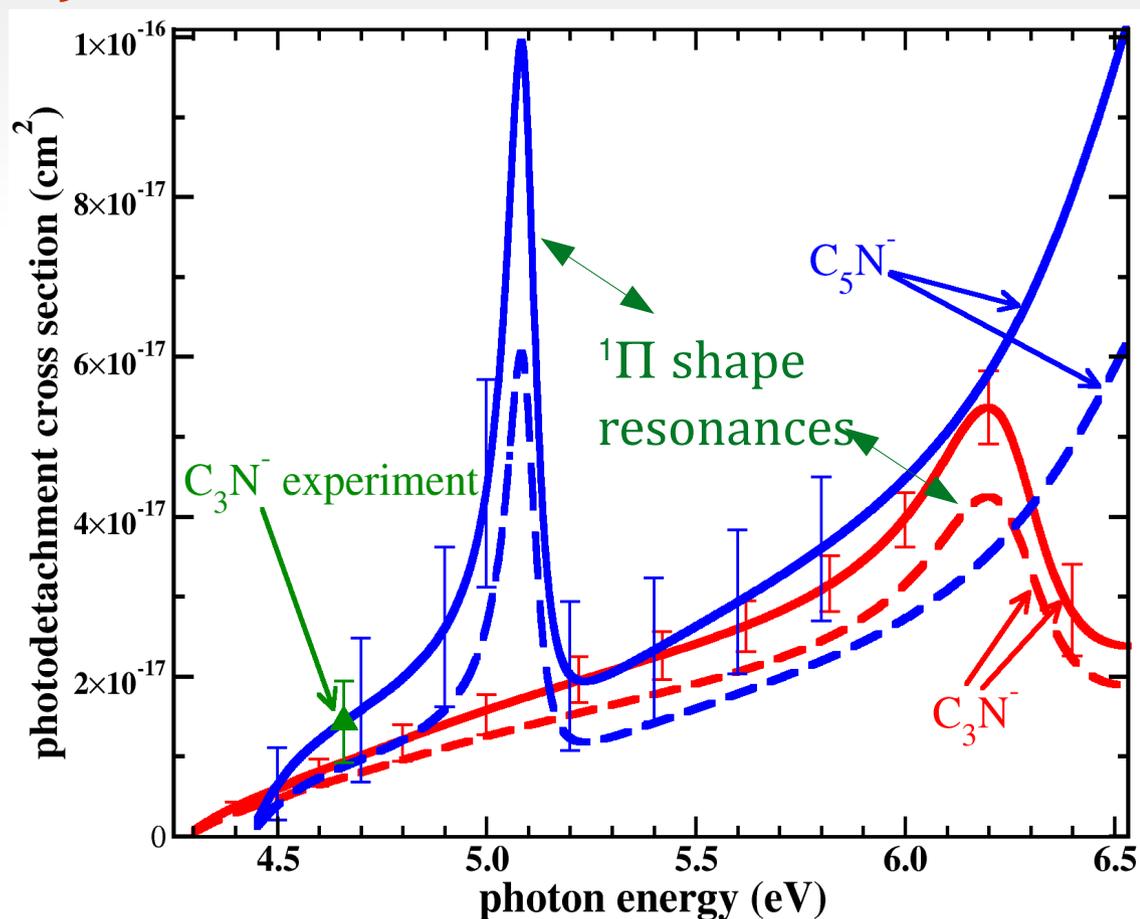
# CN<sup>-</sup> photodetachment cross section

\*Rotational and vibrational structure is neglected

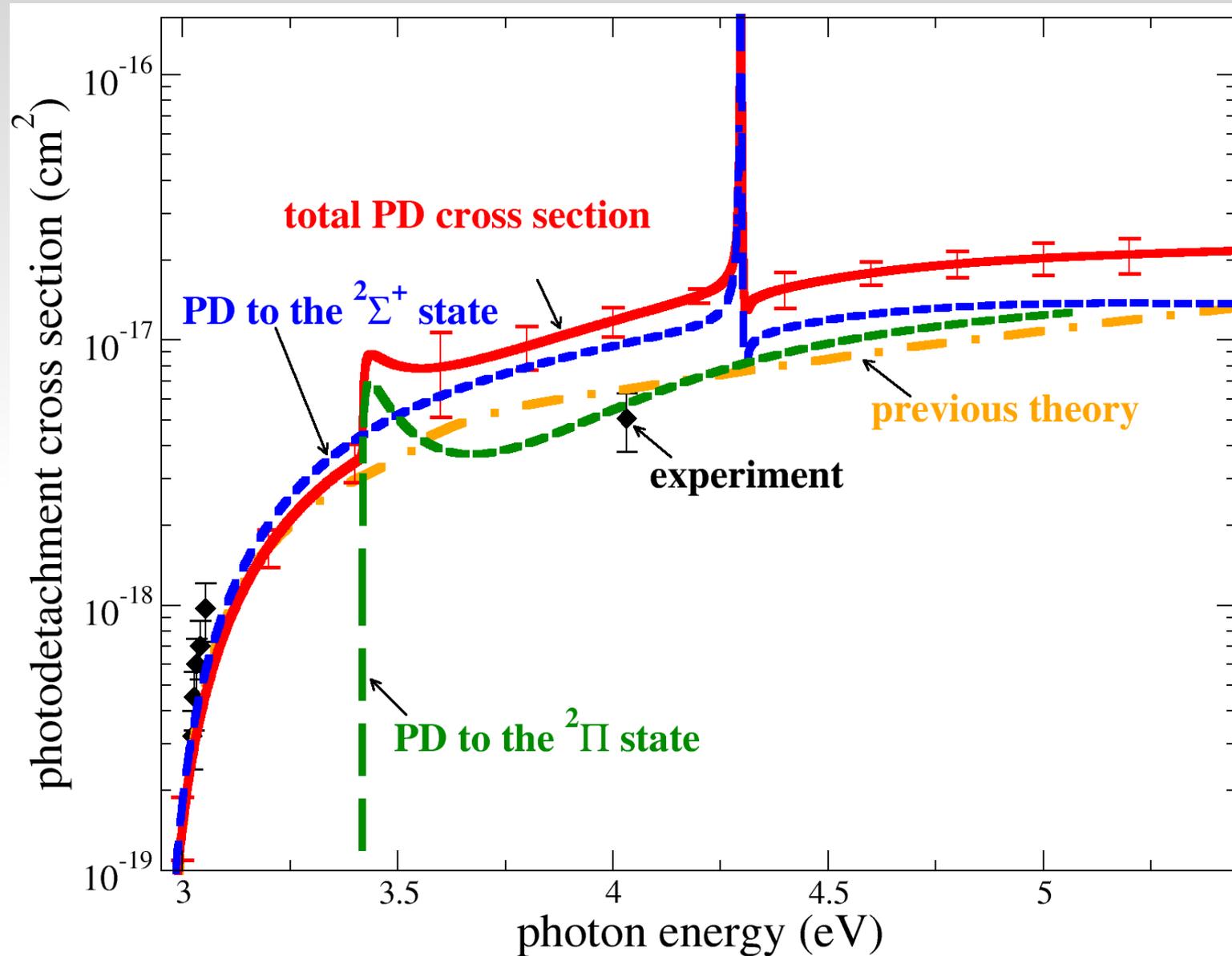


# PD cross sections for $C_3N^-$ and $C_5N^-$

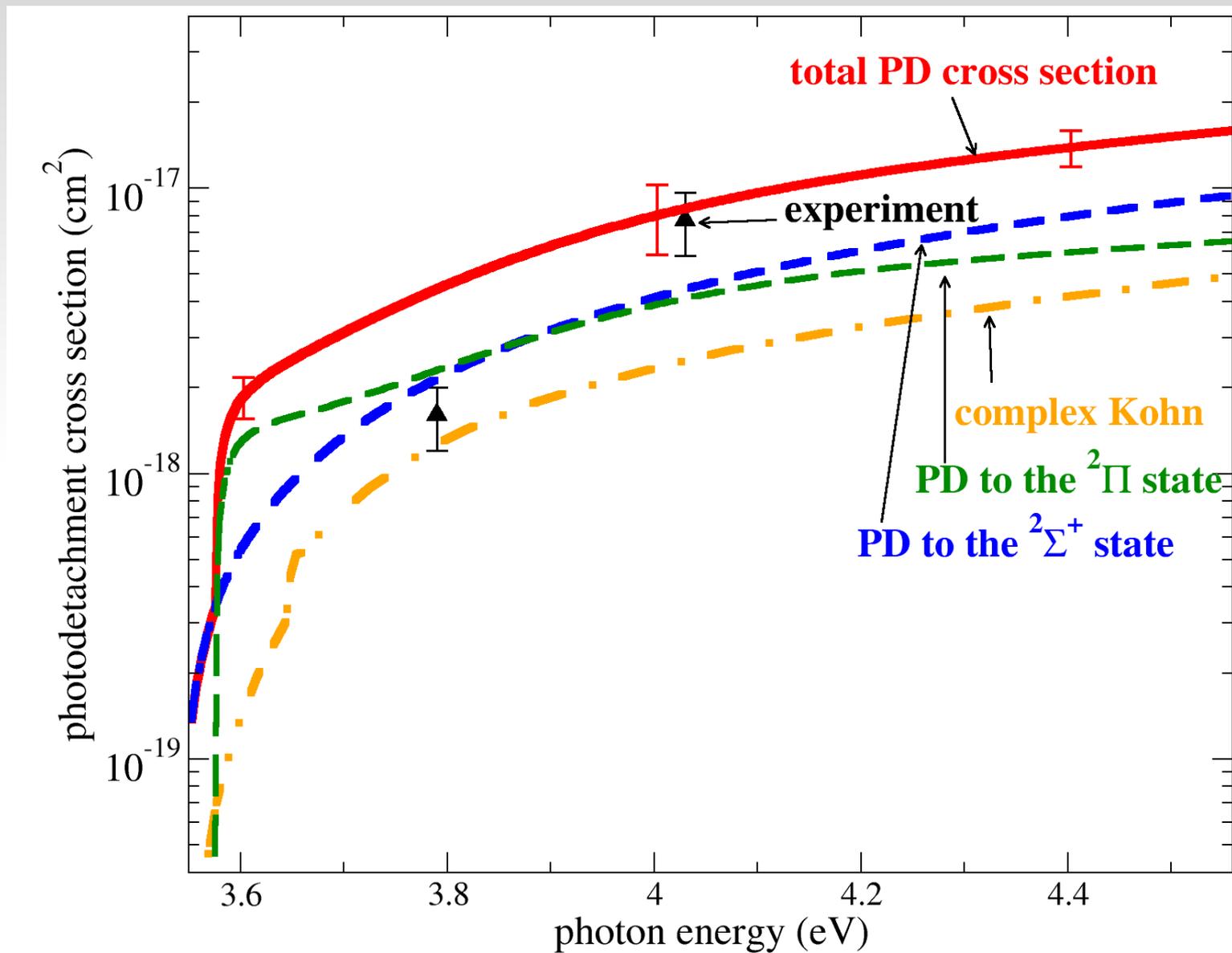
- \*Vibrational modes of the neutral molecules and the corresponding anions are similar, but not the same.
- \*Franck-Condon factor  $\langle v_f | v_i \rangle^2$  is 0.98 for  $CN/CN^-$ , 0.79 for  $C_3N/C_3N^-$ , 0.61 for  $C_5N/C_5N^-$ .



# $C_2H^-$ photodetachment cross section

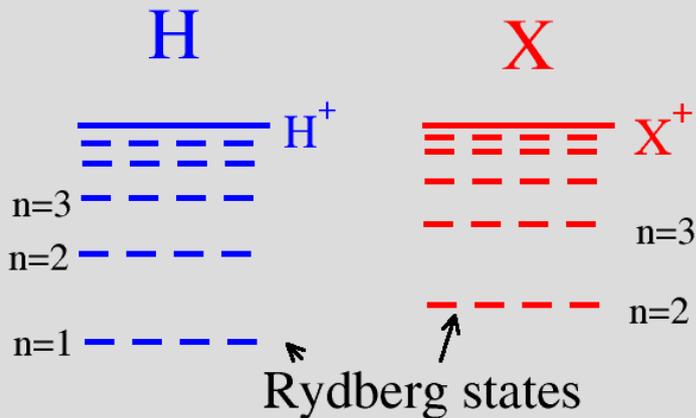
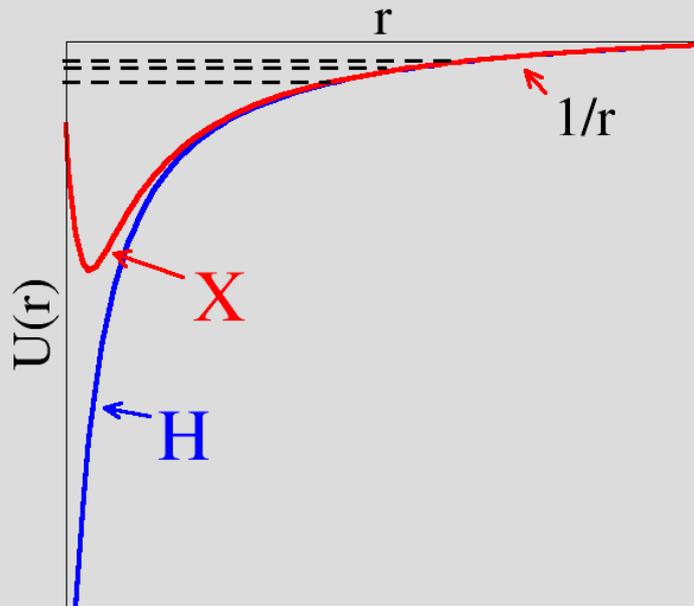


# $C_4H^-$ photodetachment cross section



# **How to deal with e-ion collisions**

# Quantum defect: bound states



Hydrogen atom:

$$E_n = - \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m_e}{2\hbar^2 n^2} = - \frac{1}{2n^2} \text{ (a.u.)}$$

$$\oint p(r) dr = 2\pi\hbar(n + 1/2)$$

$$\frac{1}{2\pi\hbar} \oint dr \sqrt{2m(E_n - 1/r)} = n + 1/2$$

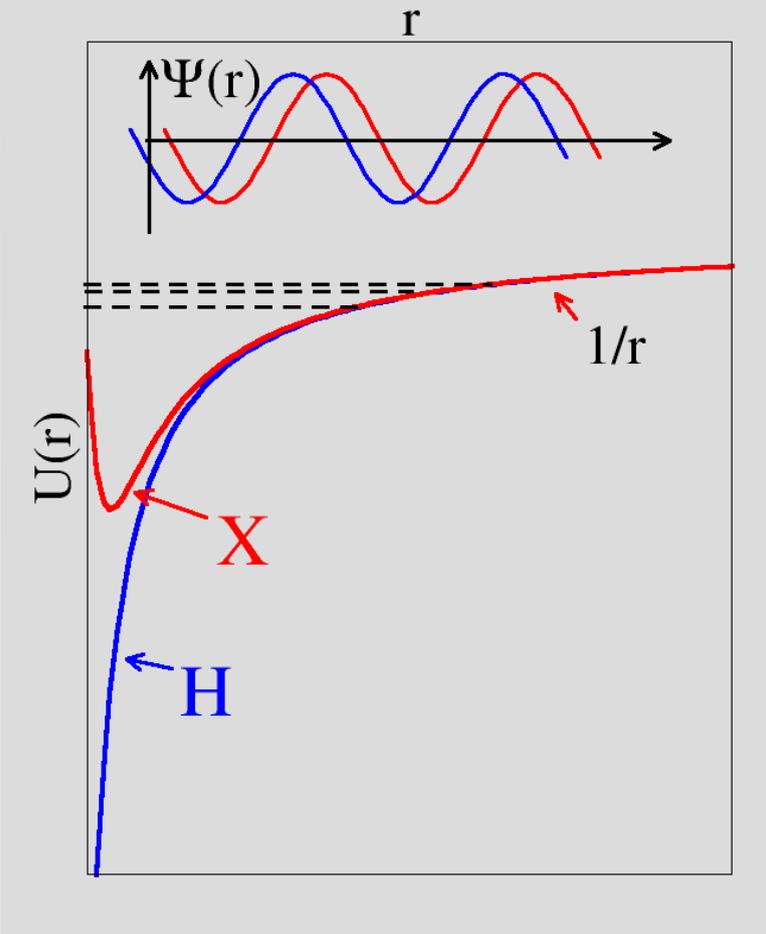
Other atoms:

$$\frac{1}{2\pi\hbar} \oint dr \sqrt{2m(E_n - 1/r) + \mu} = n + 1/2$$

$$E_n = - \frac{1}{2(n - \mu)^2} \text{ (a.u.)}$$

$\mu$  is the quantum defect, it depends on  $l$ .

# QD: continuum states



Hydrogen atom, WKB solution:

$$f^{\pm}(r) = \left( \frac{1}{\pi k(r)} \right)^{1/2} \exp\left( \pm i \int_a^r k(r') dr' \right),$$

$$k(r) = \sqrt{2E + 2/r}$$

Other atoms:

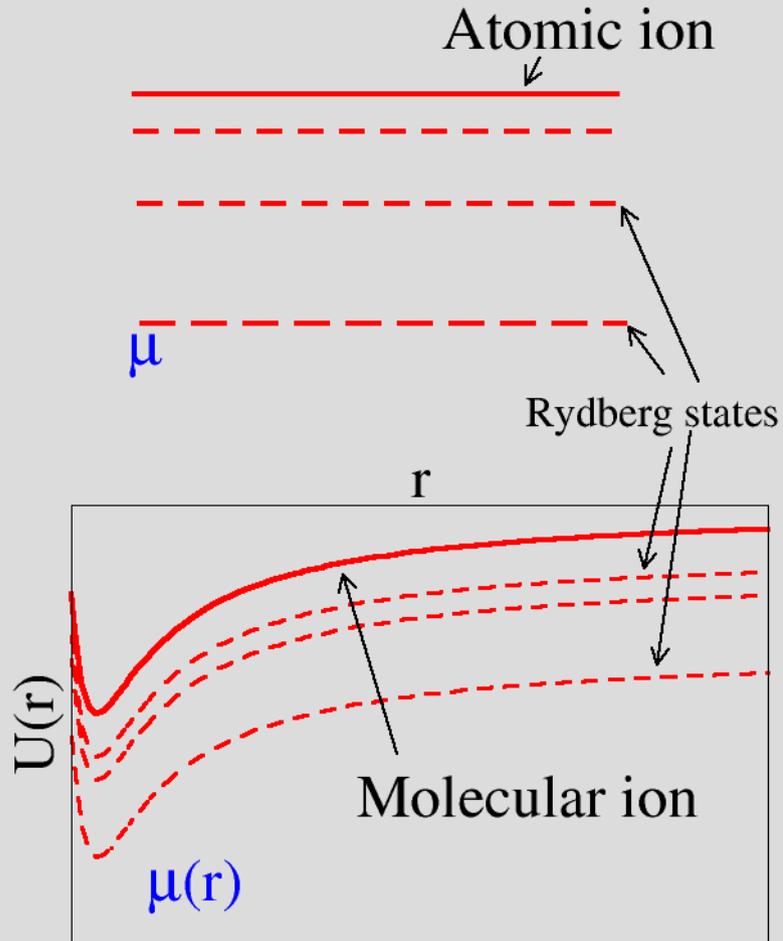
$$\left( \frac{1}{\pi k(r)} \right)^{1/2} \exp\left( \pm i \left[ \int_a^r k(r') dr' + \pi \mu \right] \right)$$

Quantum defect determines the bound and continuum wave functions

$$f_1^{\pm} \rightarrow \frac{1}{\sqrt{\pi k_1}} r^{\pm i l k_1} \exp(\pm i k_1 r \pm i \eta)$$

$$\eta = \frac{1}{k} \ln(2k) + \arg \Gamma\left( l + 1 - \frac{i}{k} \right) - \frac{1}{2} l \pi.$$

# How to obtain quantum defect



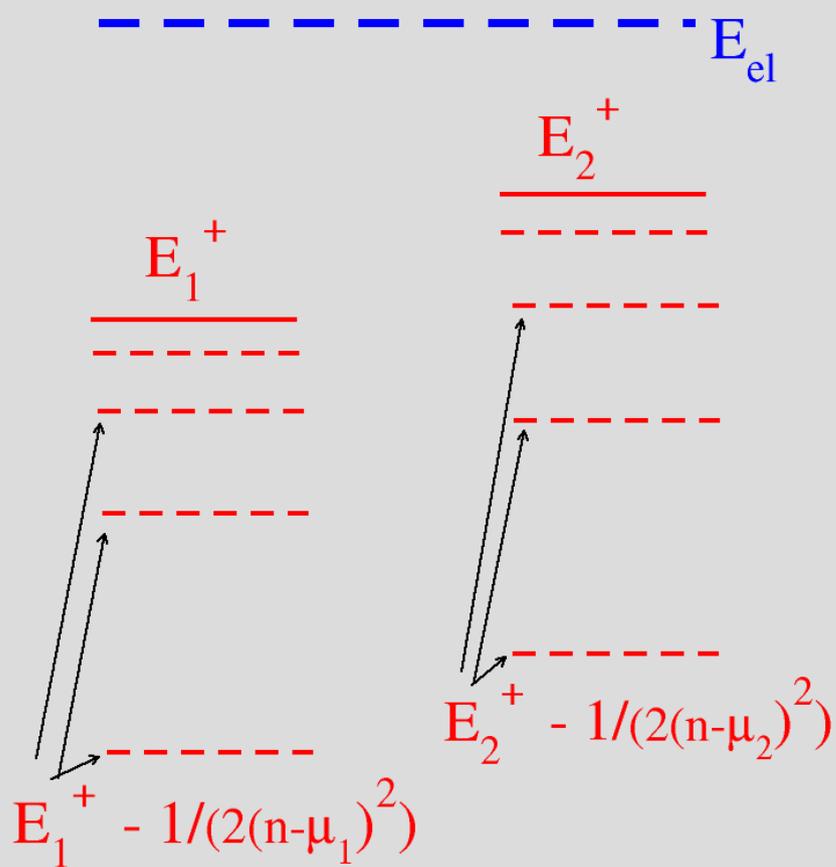
One needs to measure or calculate ion energies  $E^+$  and energies of Rydberg states  $E^n, n=1,2,3..$

$$\mu = n - \frac{1}{\sqrt{2(E^+ - E^n)}}$$

The ion could be a molecular ion (for example  $H_2^+$ ).

For a diatomic molecule  $\mu$  is a function of the internuclear distance  $R$ :  $\mu(R)$

# If the ion could be in two different quantum states?

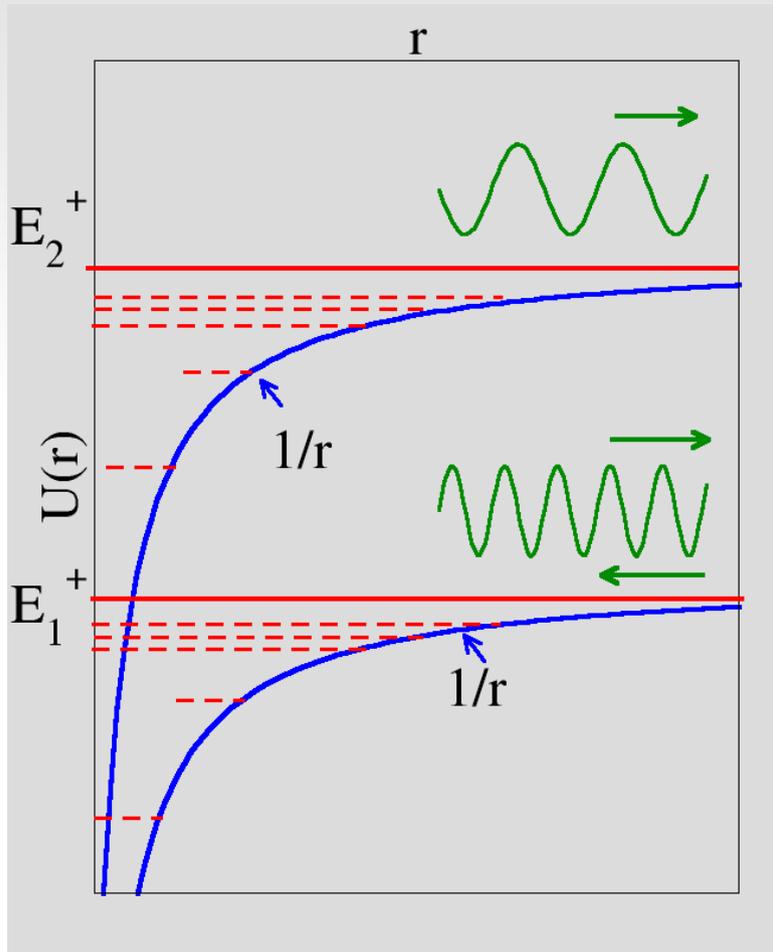


Different quantum states of the ion.

For example, a molecular ion could be in different rotational or/and vibration states

# Two quantum states: continuum wave functions

If the entrance channel is 1



$$M_{11} = f_1^- - f_1^+ S_{11};$$

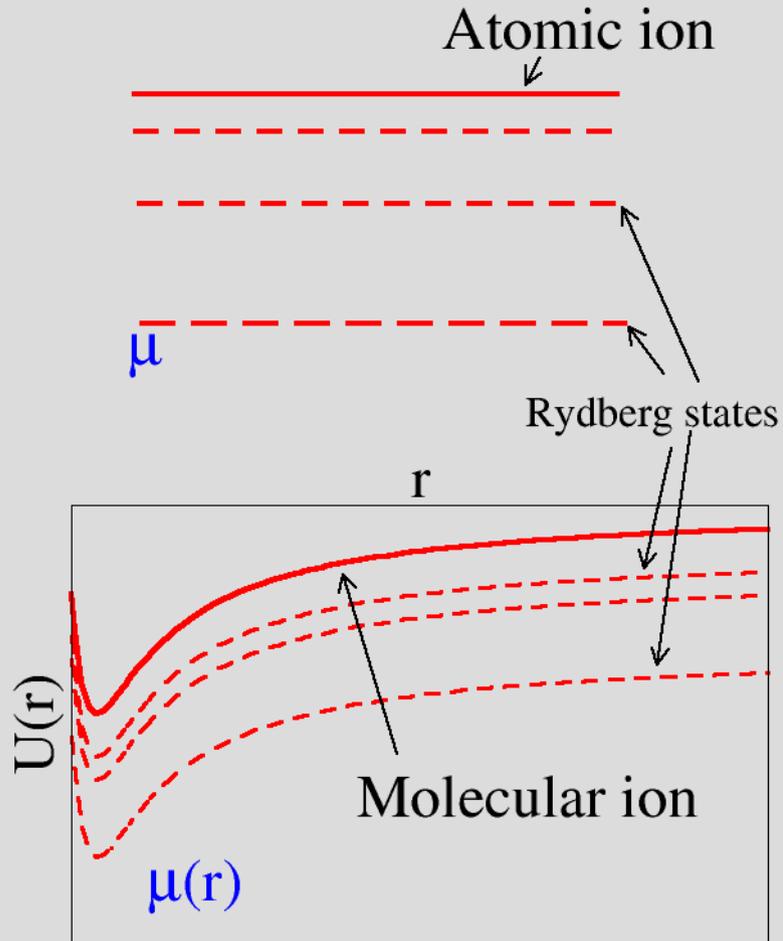
$$M_{21} = -f_2^+ S_{21}$$

More generally:

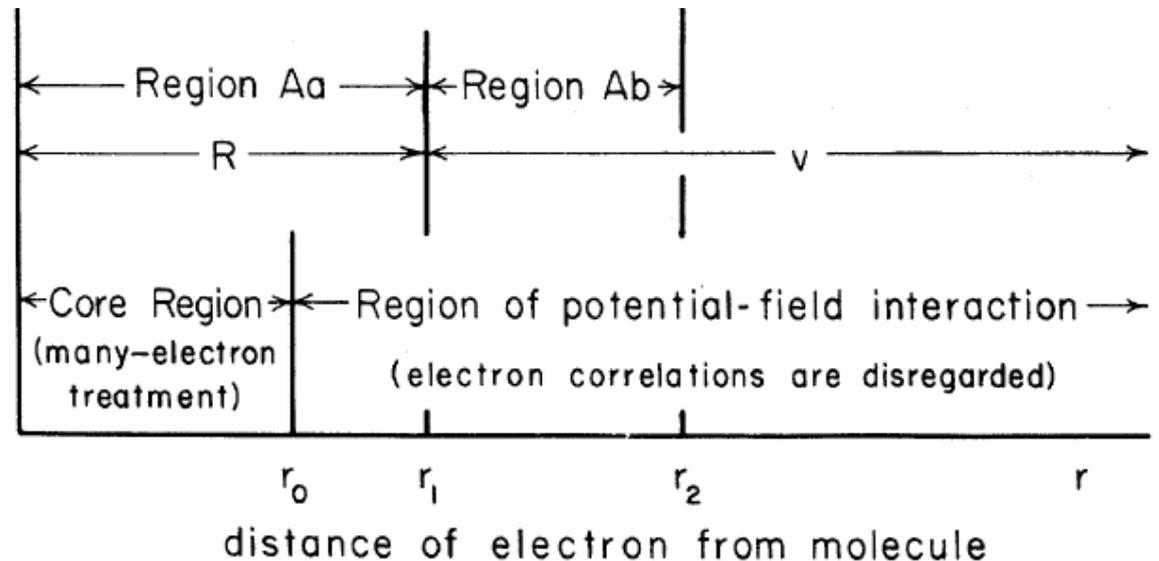
$$M_{jj'} = f_j^- \delta_{jj'} - f_j^+ S_{jj'}$$

$S_{ii'}$  is the probability amplitude, describing the scattering of the electron from channel  $j'$  to the channel  $j$ .

# From $S(R)$ to $S_{v'v}$

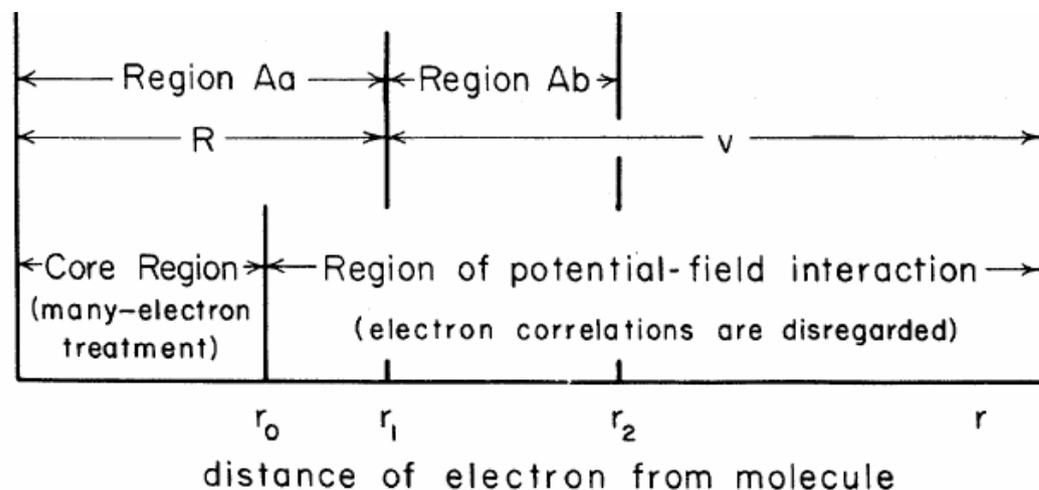


- The above procedure allows us to find  $\mu(R)$  and construct  $S(R)$ .
- But the molecular target is characterized by a vibrational quantum number  $v$ , not  $R$ .
- $S_{v'v}$  is needed rather than  $S(R)$



# Vibrational frame transformation

- The state of the target is unchanged while electron moves from infinity to  $r_1$ .
- The change in the target state takes place only at  $r < r_0$  and is described by  $S(R)$ .
- Therefore, the total S-matrix for motion from infinity (and back to infinity) is
- $$S_{v'v} = \sum_{R',R} \langle \chi_{v'} | R' \rangle \langle R' | S(R) | R \rangle \langle R | \chi_v \rangle = \sum_R \langle \chi_{v'} | R \rangle \langle R | S(R) | R \rangle \langle R | \chi_v \rangle$$



$$S_{v'v} = \int \chi_{v'}^*(R) S(R) \chi_v(R) dR$$

# Some channels open, others are closed

$S$  must be modified, since only one channel is open.

$$M_{jj'} = f_j^- \delta_{jj'} - f_j^+ S_{jj'}$$

$$f_1^\pm \rightarrow \frac{1}{\sqrt{\pi k_1}} r^{\pm i/k_1} \exp(\pm i k_1 r \pm i \eta)$$

$$f^\pm \rightarrow \frac{1}{\sqrt{2\pi\kappa_2}} e^{\pm i\pi/\kappa_2} \left( D^{-1} r^{-1/\kappa_2} e^{\kappa_2 r} \mp i D r^{1/\kappa_2} e^{-\kappa_2 r} \right)$$

If  $S$  is partitioned as

$$S = \begin{pmatrix} S_{oo} & S_{oc} \\ S_{co} & S_{cc} \end{pmatrix}$$

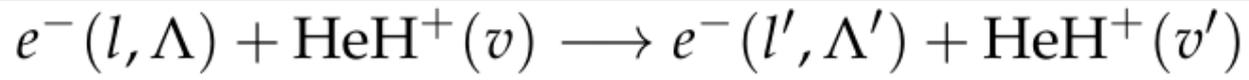
Then, the new  $S$ -matrix

$$S^{phys} = S_{oo} - S_{oc} \left( S_{cc} - e^{-2\pi i/\kappa} \right)^{-1} S_{co}$$

This matrix is able to describe a very complicated spectra with hundreds of overlapping of Rydberg resonances

# Example: vibrational excitation of HeH<sup>+</sup> by an electron impact

We need to construct the scattering matrix for the process



$$S_{\Lambda'v'l', \Lambda vl} = \langle \psi_{v'}(R) | S_{\Lambda'l', \Lambda l}(R) | \psi_v(R) \rangle$$

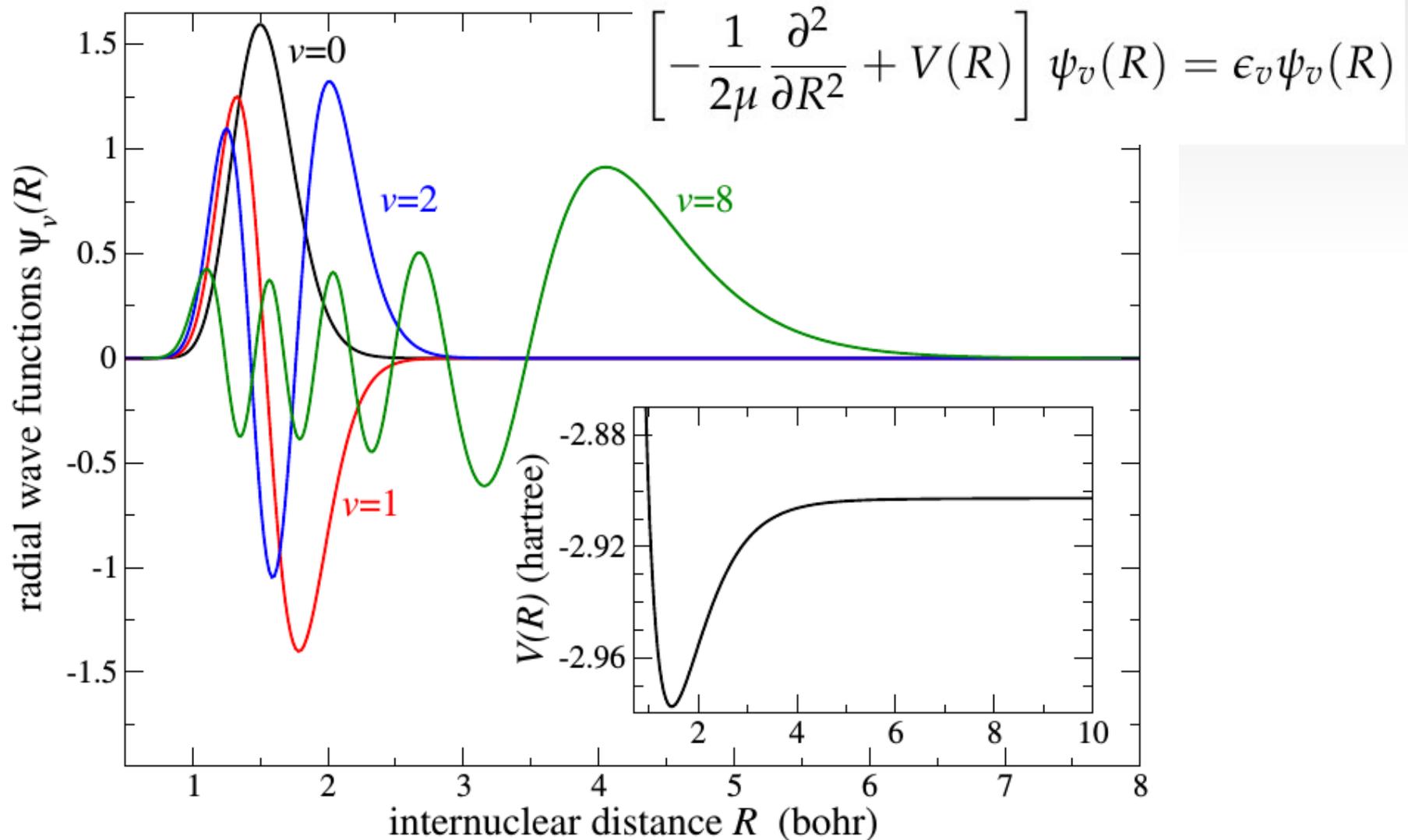
$$S^{phys}(E) = S^{oo} - S^{oc} \left[ S^{cc} - e^{-2i\beta(E)} \right]^{-1} S^{co}$$

$$S = \begin{pmatrix} S^{oo} & S^{oc} \\ S^{co} & S^{cc} \end{pmatrix} \quad \beta_{i'i}(E) = \frac{\pi}{\sqrt{2(E_i - E)}} \delta_{i'i}$$

$$\sigma_{v'v}(E_{el}) = \frac{\pi \hbar^2}{2m_e E_{el}} \sum_{\Lambda'l'\Lambda} \left| S_{\Lambda'l'v', \Lambda lv}^{phys} - \delta_{\Lambda lv, \Lambda'l'v'} \right|^2$$

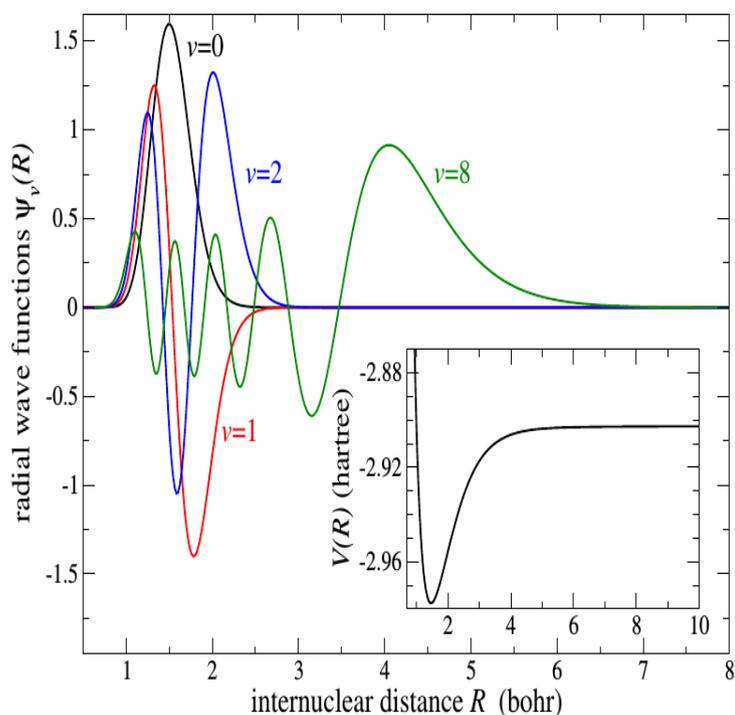
# Vibrational wave functions

Vibrational wave functions of the target ion  $\text{HeH}^+$ .



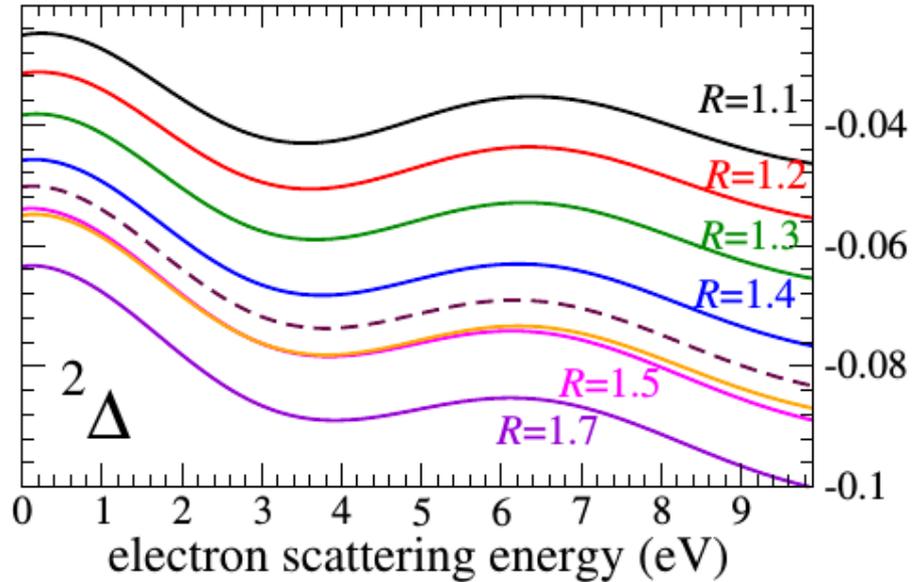
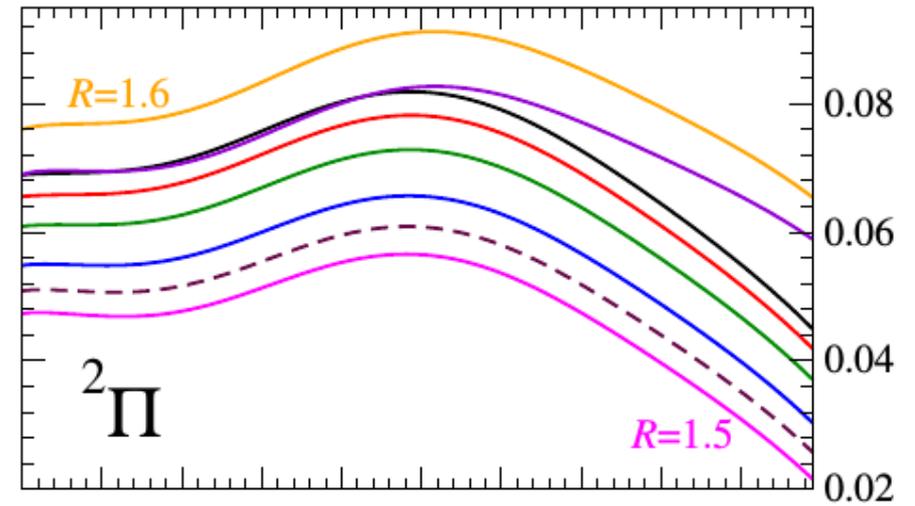
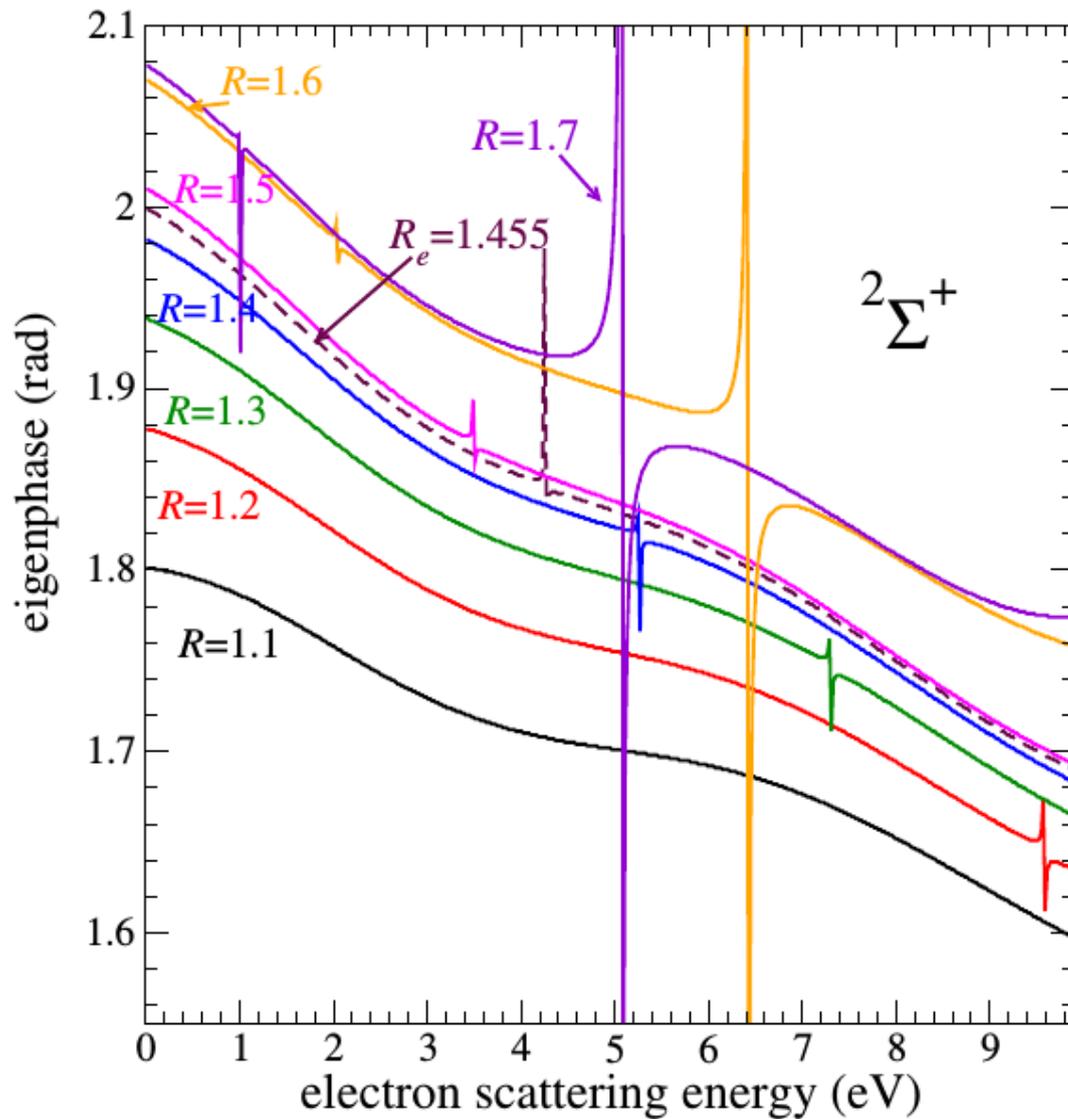
# Accuracy

The vibrational frequencies  $\Delta_\nu = E_{\nu+1} - E_\nu$  for transitions  $\nu \rightarrow \nu+1$  and rotational constants  $B_\nu$  obtained in the present study and compared with previous calculations. All values are in  $\text{cm}^{-1}$ .



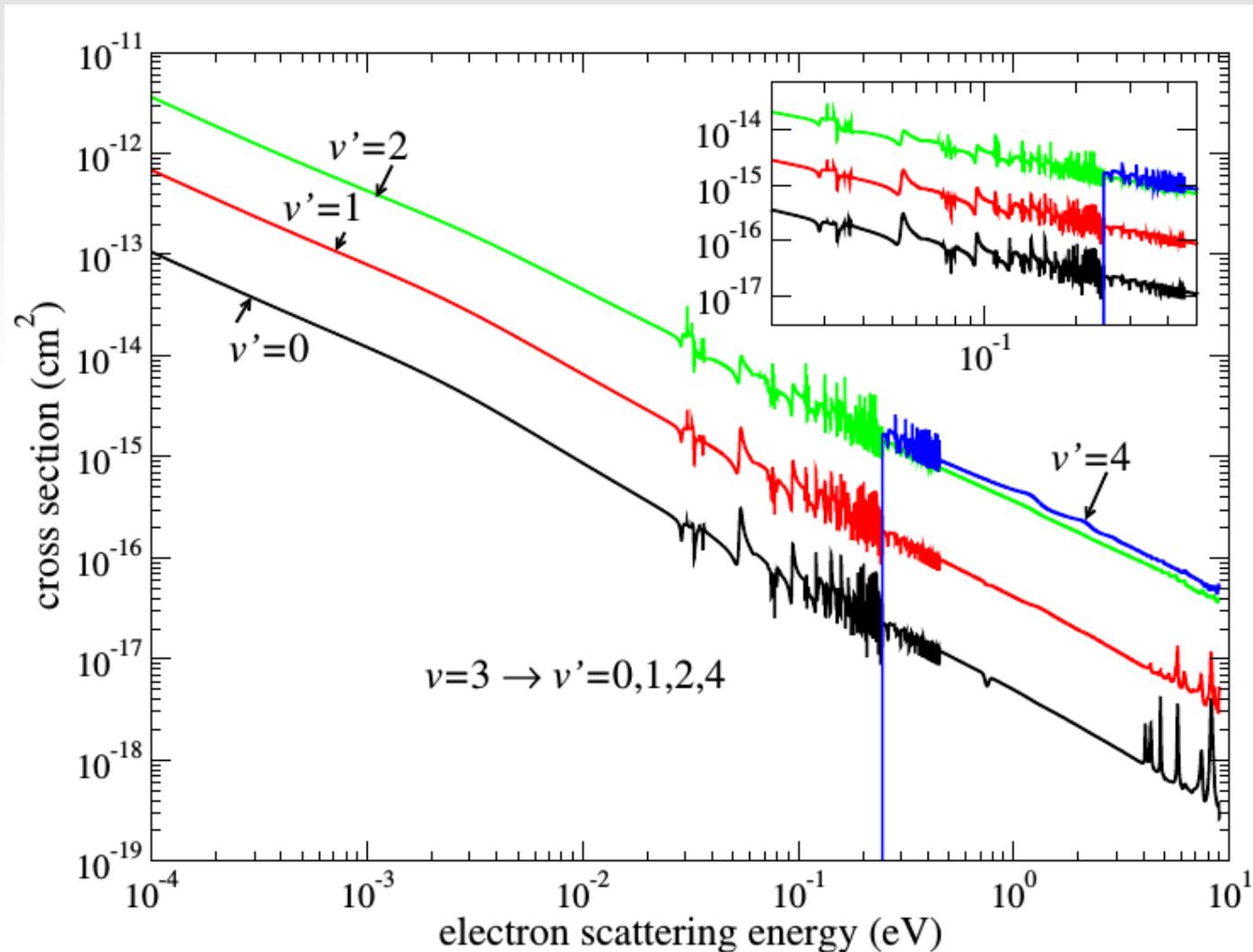
Level $\nu$	$\Delta_\nu$	$\Delta_\nu$ [26]	$B_\nu$	$B_\nu$ [25]
0	2913	2911.0007	33.527	33.558
1	2607	2604.1676	30.816	30.839
2	2300	2295.5787	28.088	28.090
3	1988	1982.0562	25.305	25.301
4	1668	1660.3559	22.425	22.402
5	1339	1327.7860	19.394	19.344
6	1000	984.3599	16.151	16.058
7	660	639.1959	12.645	12.479
8	328	327.3615	8.813	8.621

# What fixed-geometry S-matrix can tell



# Cross sections

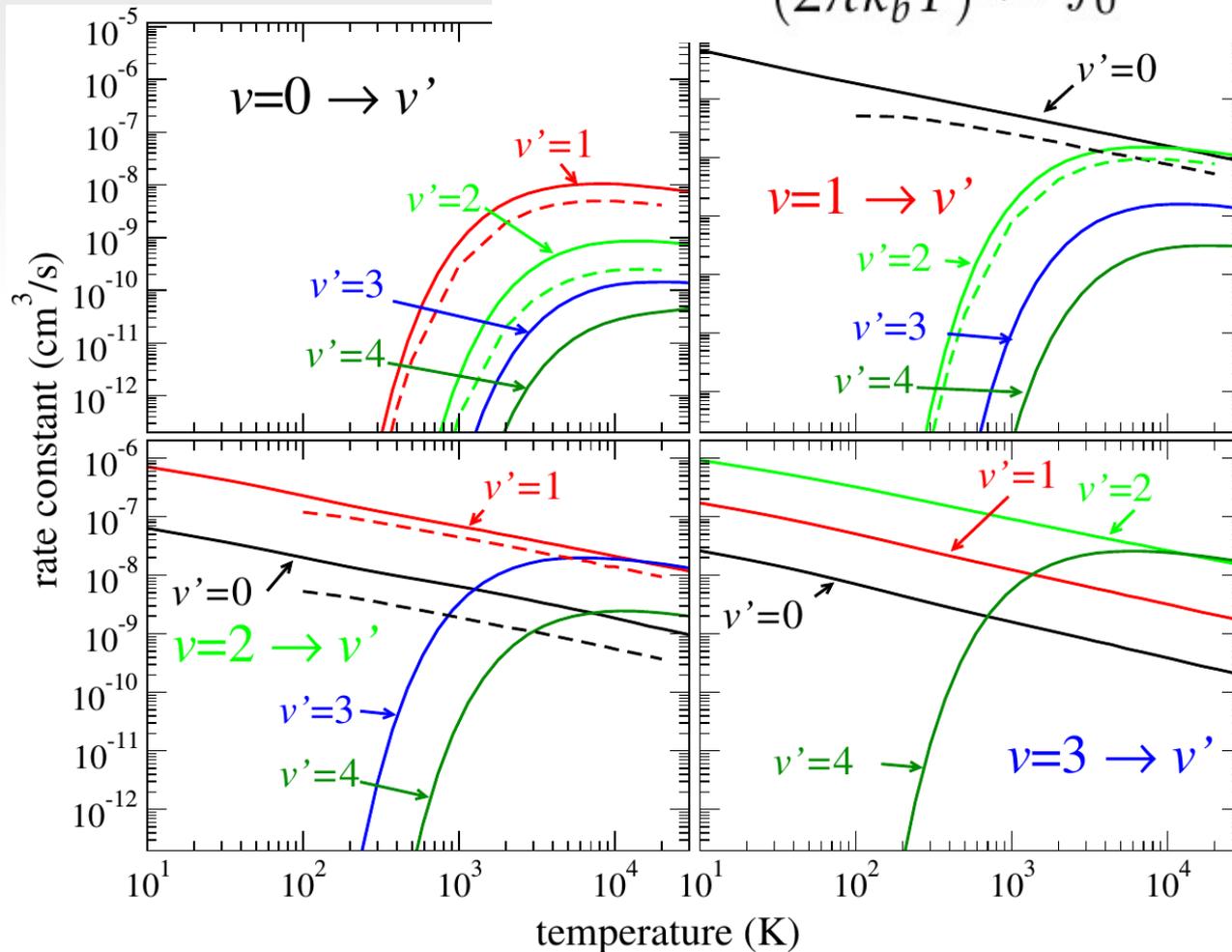
Cross sections of vibrational (de-)excitation from the vibrational level  $\nu=3$  to several other levels  $\nu$ .



# Thermally-averaged rate constants

For an environment at a thermal equilibrium, the rate constant is more appropriate to use than the cross section.

$$\alpha_{v'v}(T) = \frac{8\pi}{(2\pi k_b T)^{3/2}} \int_0^\infty \sigma_{v'v}(E_{el}) e^{-\frac{E_{el}}{k_b T}} E_{el} dE_{el}$$



# Example: Photoionization of $\text{H}_3^*$

Process of photoionization:



Several photoionization experiments with  $\text{H}_3$  molecule

Experimental spectra display a rich structure.

Theory question: can we interpret the experimental photoionization spectra?

# Main steps of the theoretical approach

The scattering matrix  $S$  for the process



is constructed

Photoionization is considered as a two-step process:

1) laser-assisted transition  $(v_i, J_i) \rightarrow (v_f, J_f)$ ;

2) ionization

Step 1) is described by dipole matrix elements

Step 2) is regarded as a half collision; represented by  $S$  matrix.

Quantum defect theory (QDT) allows us to combine calculated scattering matrix and dipole transition matrix elements to obtain a theoretical spectrum.

# Some formulas

$$e^{-}(\Lambda') + \text{H}_3^+(v_1', v_2'^{l_2'}) \rightarrow e^{-}(\Lambda) + \text{H}_3^+(v_1, v_2^{l_2})$$

Total wave function of the ion

$$\Phi_t^{n.\text{sym}} = \Phi_{g_I}^I \mathcal{R}_{N^+K^+m^+}(\alpha, \beta, \gamma) \Phi_v(Q)$$

$$\Phi_v(Q) = |v_1, v_2^{l_2}\rangle$$

Vibrational and rotational frame transformations are applied. At large distances, the  $\text{H}_3$  functions are

$$\mathcal{R}_{N^+m^+K^+}(\alpha\beta\gamma) Y_{l\Lambda}(\theta, \varphi) \mathcal{V}(v_1, v_2^{l_2}) \Phi_I$$

At short distances (where the S matrix is known)

$$|N, K, m, \Lambda; v_1, v_2^{l_2}\rangle = (-1)^{l-\Lambda} \mathcal{R}_{N^+m^+K^+}(\alpha\beta\gamma) Y_{l\Lambda}(\theta', \varphi') |Q\rangle \Phi_I$$

The rotational transformation is

$$|N^+, K^+; N, m; v_1, v_2^{l_2}\rangle = \sum_{\Lambda} C_{l, -\Lambda; N, K}^{N^+, K^+} |N, K, m, \Lambda; v_1, v_2^{l_2}\rangle$$

# Some formulas

The transformed scattering matrix is

$$\begin{aligned}
 & S_{N^+, K^+, v_1, v_2^{l_2}; N'^+, K'^+, v_1', v_2'^{l_2'}} \quad e^-(\Lambda') + H_3^+(v_1', v_2'^{l_2'}) \rightarrow e^-(\Lambda) + H_3^+(v_1, v_2^{l_2}) \\
 & = \sum_{\Lambda, \Lambda'} C_{l, -\Lambda'; N, K}^{N'^+, K'^+} \left[ \int_S \mathcal{V}(v_1', v_2'^{l_2'}; \mathcal{Q}) S_{\Lambda, \Lambda'}(\mathcal{Q}) \right. \\
 & \quad \left. \times \mathcal{V}(v_1, v_2^{l_2}; \mathcal{Q}) d\mathcal{Q} \right] C_{l, -\Lambda; N, K}^{N^+, K^+}.
 \end{aligned}$$

The e+ion function is

$$\Psi_{oi'}^{(-)} = \Phi_o(\omega) \frac{1}{i\sqrt{2}} [f_o^+(r) \delta_{o, i'} - f_o^-(r) S_{oi'}^{\dagger phys}]$$

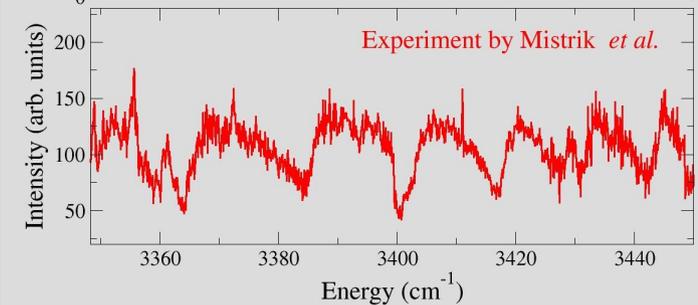
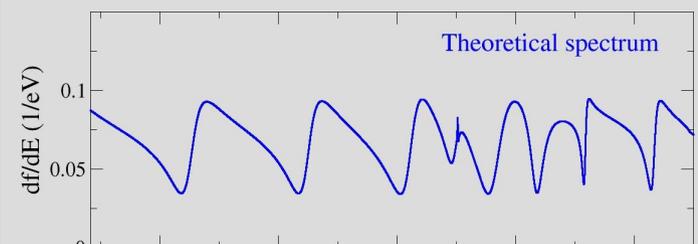
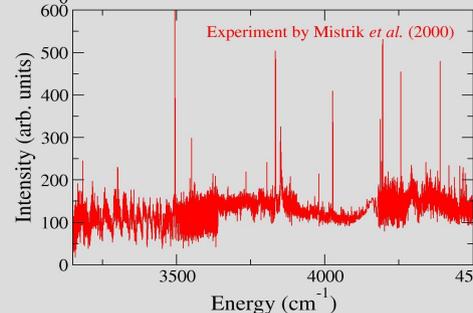
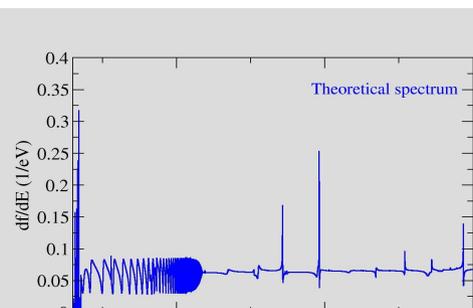
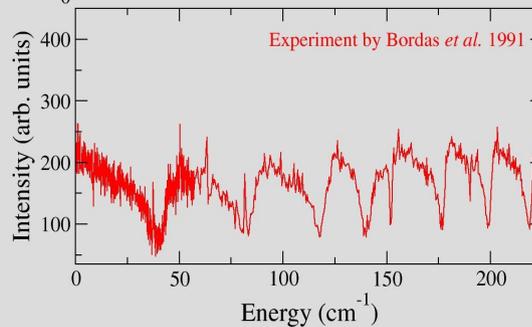
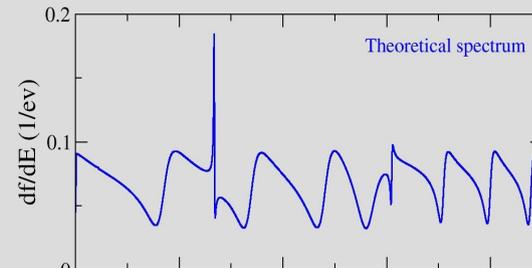
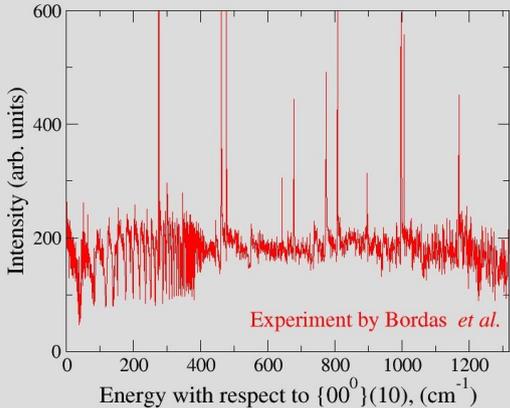
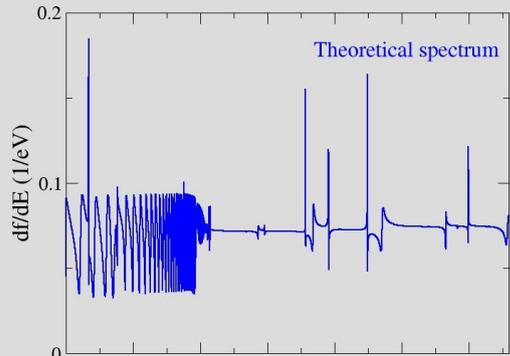
$$d_f = \langle \vec{\Psi}_f^{(-)} | \vec{\epsilon} \cdot \vec{r} | \Psi_{ini} \rangle$$

The photoionization cross section  $\sim 2\omega \sum_{f=1}^{N_o} |d_f|^2$ .

# Some results

Photoionization experiments by Bordas *et al.* (PRA 1991) and by Mistrik *et al.* (PRA 2000)

Theoretical spectra (with no adjustable parameters) are in good agreement with the experiments.



# **Photodetachment threshold law**

# Photodetachment cross section

$$\sigma_{PD} = \frac{4\pi^2\omega}{c} \left| \langle f | d_{\bar{z}} | i \rangle \right|^2$$

$$|i\rangle = \sqrt{\frac{2j+1}{8\pi^2}} D_{m_0}^{j*}(\alpha\beta\gamma) \chi_{\sigma^-} \psi_{el}^-$$

$$|f\rangle = \sqrt{\frac{2j+1}{8\pi^2}} D_{m_0}^{j*}(\alpha\beta\gamma) \chi_{\sigma} \psi_{el}$$

$$\sigma_{PD} = \frac{4\pi^2\omega}{3c} (2j+1) \left| C_{j_0 j_0}^{j_0} \right|^2 (d_0(E))^2$$

# Electronic wave function of the final state

$$\sigma_{PD} = \frac{4\pi^2\omega}{c} \left| \langle f | d_{\bar{z}} | i \rangle \right|^2$$

The final state  $|f\rangle$  of the electronic continuum is energy normalized

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right] u_l(r) = E u_l(r)$$

$$u_l^{(s)}(kr) \stackrel{kr \rightarrow \infty}{\sim} \sin\left(kr - l\frac{\pi}{2}\right) + O\left(\frac{1}{kr}\right), \quad u_l^{(s)}(kr) \stackrel{kr \rightarrow 0}{\sim} \frac{\sqrt{\pi}(kr)^{l+1}}{2^{l+1}\Gamma(l+\frac{3}{2})} \left[ 1 - \frac{(kr)^2}{4l+6} \right]$$

$$u_l^{(c)}(kr) \stackrel{kr \rightarrow \infty}{\sim} \cos\left(kr - l\frac{\pi}{2}\right) + O\left(\frac{1}{kr}\right), \quad u_l^{(c)}(kr) \stackrel{kr \rightarrow 0}{\sim} \frac{2^l \Gamma(l+\frac{1}{2})}{\sqrt{\pi}(kr)^l} \left[ 1 + \frac{(kr)^2}{4l-2} \right]$$

Energy-normalized electronic function (the radial part only)

$$\bar{u}_l^{(E)}(r) \stackrel{r \rightarrow \infty}{\sim} \sqrt{\frac{2\mu}{\pi\hbar^2 k}} \sin\left(kr - l\frac{\pi}{2} + \delta_l\right) \quad \langle \bar{u}_l^{(E)} | \bar{u}_l^{(E')} \rangle = \delta(E - E')$$

# Low-energy collisions

For small energies, the wave function near the origin is

$$u_l(r) \stackrel{kr \rightarrow 0}{\propto} u_l^{(s)}(kr) + \tan \delta_l u_l^{(c)}(kr) \\ \sim \frac{\sqrt{\pi} k^{l+1}}{2^{l+1} \Gamma(l + \frac{3}{2})} \left[ r^{l+1} + \tan \delta_l \frac{2^{2l+1} \Gamma(l + \frac{1}{2}) \Gamma(l + \frac{3}{2})}{\pi k^{2l+1} r^l} \right]$$

with

$$\tan \delta_l \stackrel{k \rightarrow 0}{\sim} - \frac{\pi}{\Gamma(l + \frac{1}{2}) \Gamma(l + \frac{3}{2})} \left( \frac{a_l k}{2} \right)^{2l+1}$$

$a_l$  are the scattering lengths.

$$|f\rangle = \frac{\sqrt{2\mu} k^{l+1/2}}{2^{l+1} \hbar \Gamma(l+3/2)} \left[ r^{l+1} + \tan \delta_l \frac{2^{2l+1} \Gamma(l+1/2) \Gamma(l+3/2)}{\pi k^{2l+1} r^l} \right]$$

# Wigner law

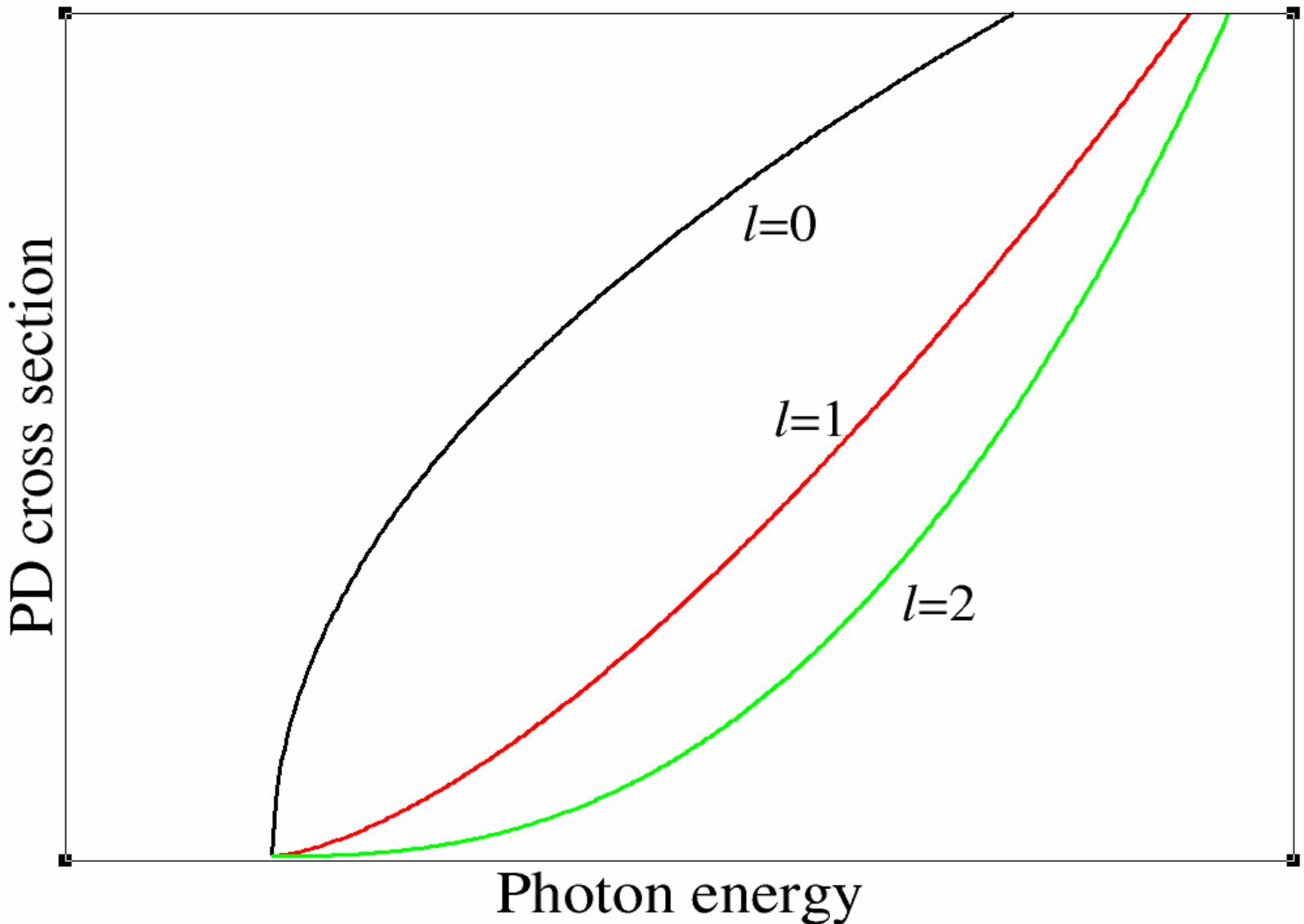
$$|f\rangle = \frac{\sqrt{2\mu} k^{l+1/2}}{2^{l+1} \hbar \Gamma(l+3/2)} \left[ r^{l+1} + \tan \delta_l \frac{2^{2l+1} \Gamma(l+1/2) \Gamma(l+3/2)}{\pi k^{2l+1} r^l} \right]$$

When  $k \rightarrow 0$

$$\sigma_{PD}^{(l)} = \frac{4\pi^2 \omega}{c} \left| \langle f | d_{\bar{z}} | i \rangle \right|^2 \sim k^{2l+1} \sim (\hbar \omega - E_{thres})^{l+1/2}$$

# Wigner law

$$\sigma_{PD} = \frac{4\pi^2\omega}{c} \left| \langle f | d_{\bar{z}} | i \rangle \right|^2 \sim k^{2l+1} \sim (\hbar\omega - E_{thres})^{l+1/2}$$



# Non-central potential

- \* In the above discussion we assumed a central potential of the interaction between the electron and the target. It is appropriate for atoms
- \* For molecules, the potential is not central, the angular momentum  $l$  of the electron is not conserved.
- \* The above arguments could still be used if one expands the electronic wave function in partial waves.
- \* Then the photodetachment cross section is

$$\sigma = \sum_{l=0} \sigma_l$$

$$\sigma_{PD}^{(l)} \sim k^{2l+1} \sim (E)^{l+1/2}$$

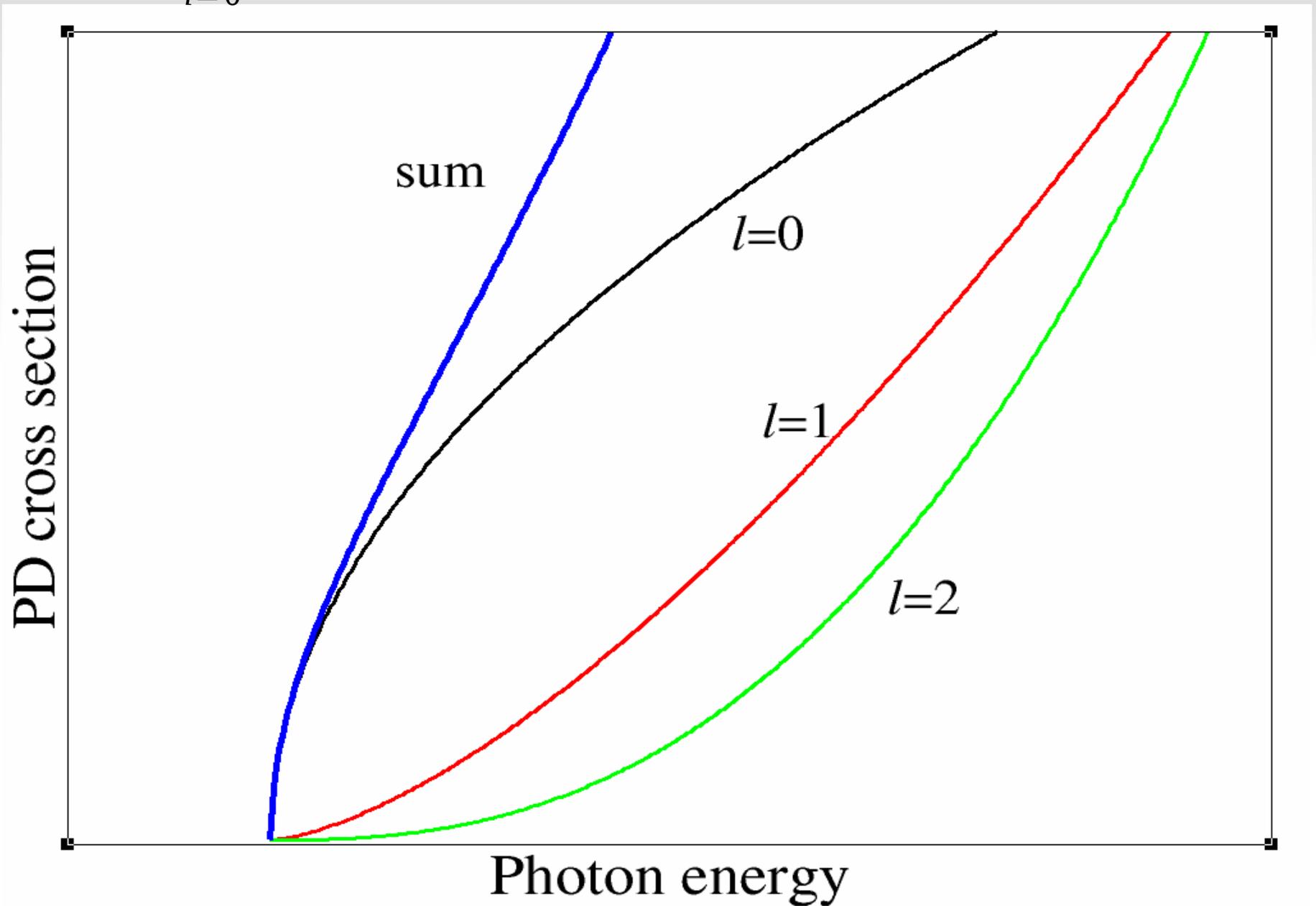
↑  
kinetic energy of the detached electron

$$\sigma(E) = A_l * k^{2l^*+1} [1 + O(k^2)]$$

$l^*$  is the smallest  $l$  for which  $\sigma_l > 0$

# Wigner law

$$\sigma_{PD}^{(tot)} = \sum_{l=0} \sigma_{PD}^{(l)}$$



# Molecular symmetry $\Gamma$ instead of partial wave $l$

- \* The wave function of the electron detached from a molecule of symmetry  $\Gamma$

$$\psi_{\Gamma}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} Y_{lm}(\hat{\mathbf{r}}) f_{lm}^{\Gamma}(r)$$

- \* If the wave function is totally symmetric (symmetry  $\Gamma$ ) in the molecular group, the s-wave component is present in the above expansion and  $l^*=0$ , s-wave photodetachment.
- \* In  $\text{CN}^-$  photodetachment, the initial state is  $\text{CN}^-(^1\Sigma^+)$ , the final state of  $\text{CN}$  is  $^2\Sigma^+$ . Therefore, the electron is detached from the state  $\sigma^+$ , . The dipole transitions  $\sigma^+ \rightarrow \sigma^+$  are allowed. Therefore,  $l^*=0$ , it is mainly s-wave photodetachment.

# Molecular symmetry $\Gamma$ instead of partial wave $l$

- \* The wave function of the electron detached from a molecule of symmetry  $\Gamma$

$$\psi_{\Gamma}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} Y_{lm}(\hat{\mathbf{r}}) f_{lm}^{\Gamma}(r)$$

- \* If the wave function is not totally symmetric and  $\Gamma$  is transformed as  $x, y$ , or  $z$  then  $l^*=1$ ,  $p$ -wave photodetachment.
- \* In  $O_2^-$  photodetachment,  $O_2^-(^2\Pi_g) \rightarrow O_2(^3\Sigma_g^-) + e^-$ . Therefore, the electron is detached from the state  $\pi_g$ . The dipole transition is not allowed into the totally symmetric state  $\sigma_g^+$ . It could be  $\sigma_u^+$  or  $\pi_g$ , i.e.  $l^*=1$ , it is mainly the  $p$ -wave photodetachment.

# Molecular symmetry $\Gamma$ instead of partial wave $l$

- \* The wave function of the electron detached from a molecule of symmetry  $\Gamma$

$$\psi_{\Gamma}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} Y_{lm}(\hat{\mathbf{r}}) f_{lm}^{\Gamma}(r)$$

- \* If the wave function is not totally symmetric and  $\Gamma$  is transformed as  $x, y,$  or  $z$  then  $l^*=1$ ,  $p$ -wave photodetachment.
- \* In  $\text{NH}_2^-$  photodetachment,  $\text{NH}_2^-(^1A_1) \rightarrow \text{NH}_2(^2B_1) + e^-$ . Therefore, the electron is detached from the state  $b_1$ , Dipole transitions  $b_1 \rightarrow a_1$  are allowed. Therefore,  $l^*=0$ , it is mainly the  $s$ -wave photodetachment.

# Molecular symmetry $\Gamma$ instead of partial wave $l$

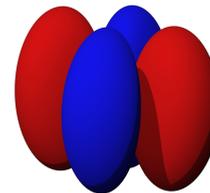
- \* The wave function of the electron detached from a molecule of symmetry  $\Gamma$

$$\psi_{\Gamma}(\mathbf{r}) = \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} Y_{lm}(\hat{\mathbf{r}}) f_{lm}^{\Gamma}(r)$$

- \* If  $l^* > 1$ , we need to check if  $\Gamma$  is transformed as products,  $xy$ ,  $xz$ ,  $yz$ ,  $z^2$ , or  $x^2 - y^2$ . If so,  $l^* = 2$ , the  $d$ -wave photodetachment.

# Simpler method

- \* One needs to identify the “effective” partial wave  $l^{\text{eff}}$  of the orbital from which the electron is detached.
- \*  $l^{\text{eff}}=0$  if the orbital is totally symmetric.
- \*  $l^{\text{eff}}=1$  if it transforms as  $x, y,$  or  $z$ .
- \*  $l^{\text{eff}}=2$  if it transforms as  $xy, yz, xz, x^2-y^2,$  or  $z^2$ .
- \* The allowed angular momentum quantum numbers of the outgoing wave are  $l=l^{\text{eff}}\pm 1$ .
- \* Then  $l^* = \min(l^{\text{eff}}\pm 1)$
- \* Example: For  $\text{O}_2^-(^2\Pi_g) \rightarrow \text{O}_2(^3\Sigma_g^-) + e^-$ , the electron is detached from the  $\pi_g$  orbital.  $\pi_g$  transforms as  $xy$  and  $yz$ ,  $l^{\text{eff}}=2$ , therefore,  $l^* = 1$ .



# The role of the permanent dipole moment

- \* For target without a charge and a dipole moment.

$$\left[ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + \frac{l(l+1)\hbar^2}{2\mu r^2} + V(r) \right] u_l(r) = E u_l(r)$$

- \* The e-dipole interaction behaves  $\sim 1/r^2$  at large distances. Therefore, the dipole moment of the target modifies the effective potential.
- \* Partial waves are mixed, and the threshold behavior is modified.
- \* A possible solution is to include the dipole interaction into the  $l(l+1)/2\mu r^2$  term.
- \*  $l(l+1)/2\mu r^2 \rightarrow \lambda(\lambda+1)/2\mu r^2$  with non-integer  $\lambda$  and the corresponding Bessel functions.

# The role of the permanent dipole moment

\* The potential of interaction

$$V_d(r, \theta) = -\frac{e d \cos \theta}{r^2} \quad \cos \theta = 2 \sqrt{\frac{\pi}{3}} Y_{10}(\theta, \varphi)$$

\* can be written as a matrix in the basis of states with definite angular momenta of the detached electron  $(l, m)$  and the target  $(j, k, m_j)$

$$|j, k, m_j, l, m\rangle$$

$$\langle j, k, m_j, l, m | V_d(r, \theta) | j, k, m_j, l \pm 1, m \rangle \neq 0$$

$$\left\langle j, k, m_j, l, m \left| \frac{\hat{l}^2}{2\mu r^2} \right| j, k, m_j, l, m \right\rangle = \frac{\hbar^2 l(l+1)}{2\mu r^2}$$

# Effective partial wave

$$\langle j, k, m_j, l, m | V_d(r, \theta) | j, k, m_j, l \pm 1, m \rangle \neq 0$$

\* The matrix is infinite. It is better to use a different basis, where the total angular momentum  $J$  is conserved.

$$\frac{\mu d k}{j(j+1)} \left( \frac{\langle j, k, l, J | \hat{l}^2 - 2\mu d \cos(\theta) | j, k, l+1, J \rangle}{(2l+1)(2l+3)} \right)^{1/2}$$

$$\langle j, k, l, J | \hat{l}^2 - 2\mu d \cos(\theta) | j, k, l, J \rangle = l(l+1)$$

\* This matrix is finite. If diagonalized, it gives eigenvalues  $\Lambda$ , which can be viewed as  $\lambda(\lambda+1)/2\mu r^2$  with non-integer  $\lambda$ .

$$\sigma(E) \sim E^{\lambda+1/2}$$

\* For OH<sup>-</sup>  $\lambda$  is about -0.2

# Large dipole moment of the target

- \* For a large dipole moment, the smallest eigenvalue becomes negative.
- \* If it is too negative, the corresponding  $\lambda$  is a complex number,  $\lambda = i\nu - 1/2$ ,  $\nu$  is a real positive number.
- \* The cross section becomes an oscillating function of  $E$ .
- \* At large distances

$$u(r) \sim N_l(k) k^{-1} \sin(kr - l\pi/2 + \eta_l)$$

$$N = \text{const} k^{\frac{1}{2}} [\sinh^2(\nu\pi/2) + \cos^2(\nu \ln k + \delta)]^{\frac{1}{2}} (1 + \text{higher order})$$

$$\tan(\eta_l - l\pi/2 - \pi/4) = -\tan(\nu \ln k + \delta) \tanh(\nu\pi/2)$$

$$\sigma \sim \text{const} [\sinh^2(\nu\pi/2) + \cos^2(\nu \ln k + \delta)]^{-1}$$

# Molecules with large dipole moments

- A **fixed in space** dipole  $\mathbf{d}$  can have an infinite number of dipole bound states if  $d > d_{\text{crit}}$ , with  $d_{\text{crit}} = 1.6243$  D. Energies of dipole bound states scale exponentially

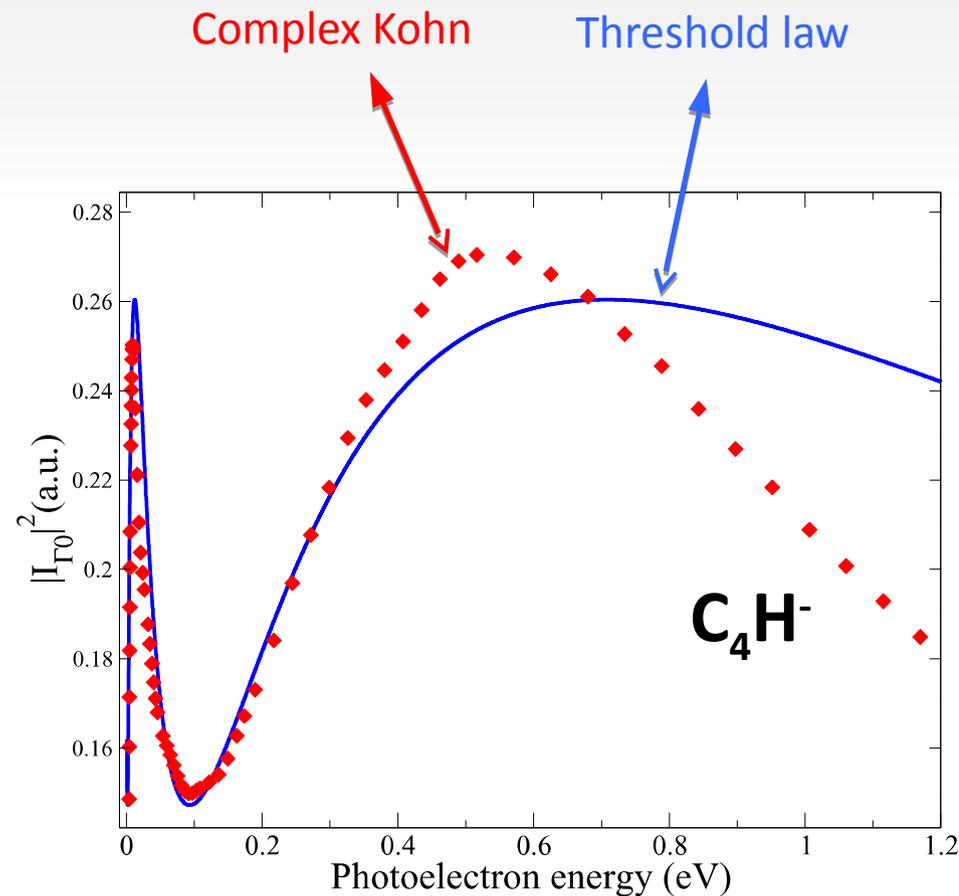
$$\frac{E_n}{E_{n+1}} \sim \text{const}, \text{ when } n \rightarrow \infty$$

$v = \sqrt{d}$

- The Wigner threshold law

$$\sigma_l \propto [\sinh^2(v\pi/2) + \cos^2(v \log k + \delta)]^{-1}$$

T. F. O'Malley, Phys. Rev. **137** (1965)



N. Douguet *et al.*, Phys. Rev. A. **90** (2014)