Electron and photon collisions with molecules large and small

From attosecond delays in CO_2 towards resonance formation in dielectric gases

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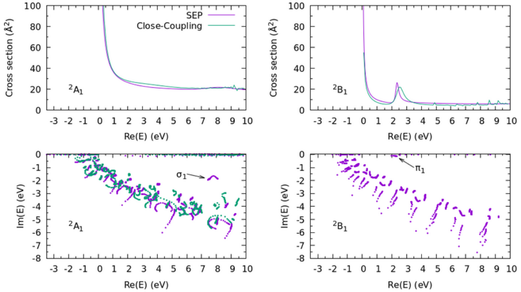
Electron-molecule collisions

$e^- + M \rightarrow M + e^-$



Elastic collisions

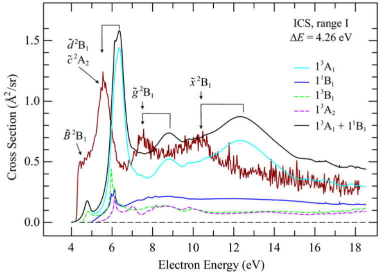
- Scattering cross sections
- Angular distributions
- Resonances

Kumar et al, JPCL 13, 11136 (2022)

Electronically inelastic collisions

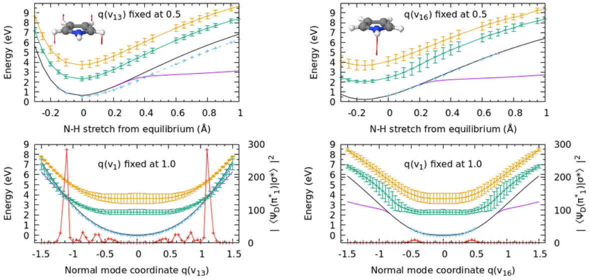
$e^- + M \rightarrow M^* + e^-$

Regeta et al, JCP 144, 024302 (2016)



$e^- + AB \rightarrow A^- + B$

$e^- + AB(v) \rightarrow AB(v^*) + e^-$



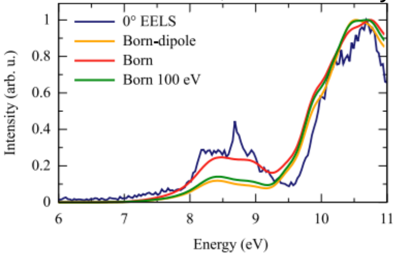
Nuclear dynamics

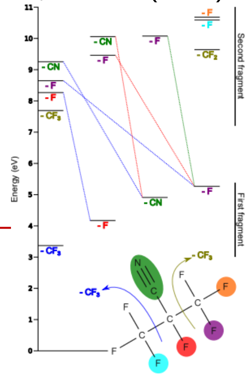
(collaboration with ITP)

- DEA
- Vibrational excitation

Fragmentation of a dielectric gas molecule Novec

T. Ovad et al, J. Chem. Phys. 158, 014303 (2023)

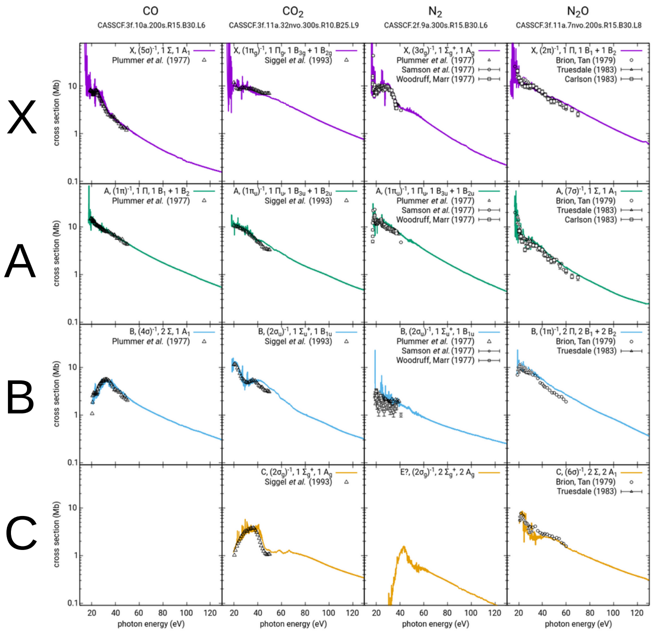




Molecular photoionization

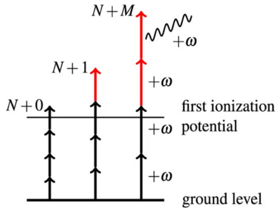
Single-photon

hv + M → M + e⁻

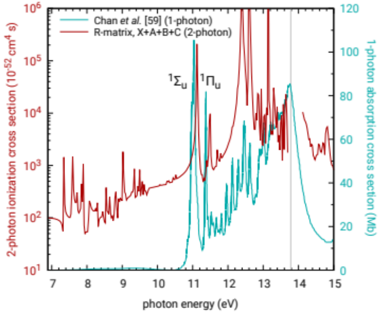


Multi-photon

n(hv) + M → M + e⁻



2-photon ionization of CO_2

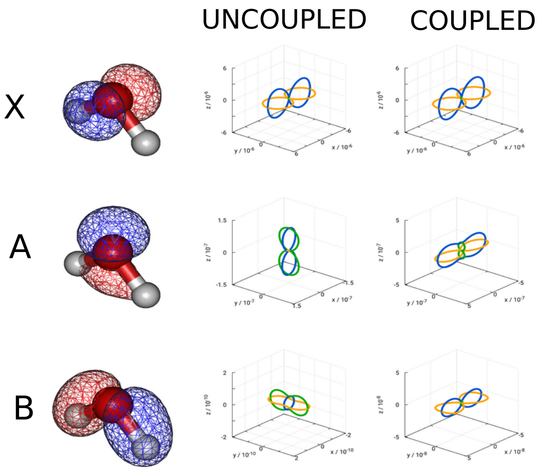


J. Benda and Z. Mašín, Sci Rep **11**, 11686 (2021)

Non-perturbative

E(t) + M → M + e⁻

Tunnel ionization of H_2O



Benda *et al*, PRA, **102**, 052826 (2020)

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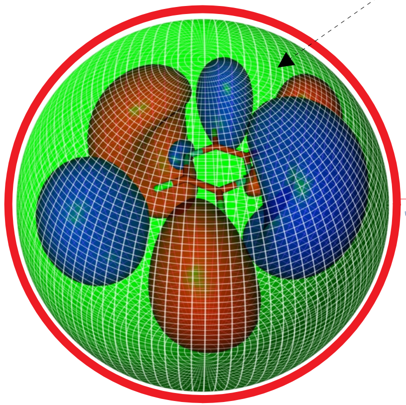
UKRmol+ code: Mašín *et al*, Comp. Phys. Comm. **249** (2020) 107092
RMT code: Brown *et al*, Comput. Phys. Commun. **250** (2020) 107062

Molecular R-matrix

R-matrix method: time-independent

Inner region (r < a):

- $(H+L)\psi_k(1,\ldots,N) = E_k\psi_k(1,\ldots,N)$
- complicated multi-electron problem
- solved using techniques similar to quantum chemistry (configuration-interaction)



R-matrix sphere
(a < 20 Bohr)

radial distance

Outer region (r > a):

- one-electron problem for the unbound electron
- solved by matching inner and outer region wavefunctions on the R-matrix sphere

Mašín *et al*, Comp. Phys. Comm. **249** (2020) 107092
J. Tennyson, Physics Reports **491**(2–3), 29–76 (2010)

UKRmol+ code

$$\mathbf{F}(E) = \mathbf{R}(E)\frac{d\mathbf{F}(E)}{dr}\bigg|_{r=a}, \quad R_{i,j}(E) = \sum_k \frac{w_{ik}w_{jk}}{E - E_k}$$

F: outer-region radial wavefunctions

R-matrix: constructed in the inner region

Analytic dependence on energy

Molecular R-matrix

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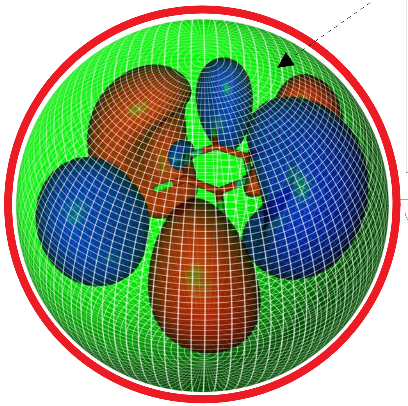

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R-matrix sphere
(a < 20 Bohr)

Mašín *et al*, Comp. Phys. Comm. **249** (2020) 107092
J. Tennyson, Physics Reports **491**(2–3), 29–76 (2010)

UKRmol+ code

- ✓ Used for decades for accurate collision data
- ✓ Multi-electron effects in continuum
- ✓ Dipole-bound and Rydberg states, Siegert states
- ✓ Variational, wavefunction-based

Types of solutions available in molecular R-matrix codes

- ✓ Scattering states
- ✓ Photoionization states
- ✓ Siegert states
- ✓ Multi-photon (perturbative) matrix elements
- ✓ Molecular R-matrix with time (RMT)

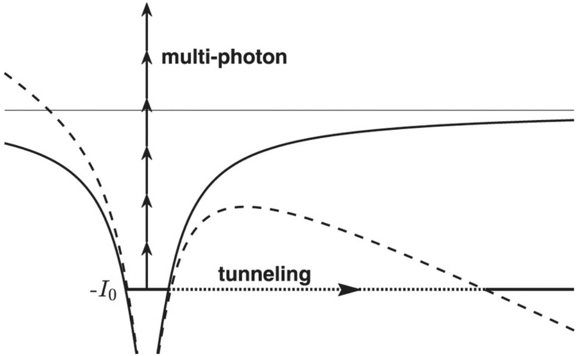


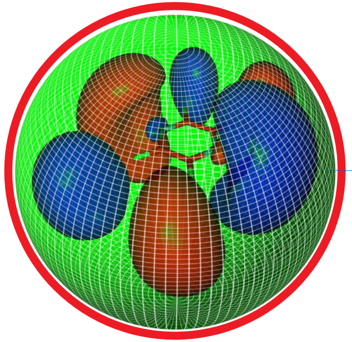
Image: N. Boroumand et al, J. Phys. B **55**(21), 213001 (2022)

- Implemented extending the atomic RMT code (QUB)

$$i\frac{d}{dt}\Psi(t)=\left(\hat{H}+r\cdot E(t)\right)\Psi(t)$$

$$\Psi_{inner}(t)=\sum c_k(t)\psi_k$$

$$\Psi_{outer}(r_i,t)=\frac{1}{r_i}\sum F_k(r_i,t)\Phi_k(\hat{r}_i)$$



Finite-difference grid in each final channel

- The same level of electronic description in TD and TI calculations
- Allows to separate the effects of the field from electronic structure

RMT code

Brown *et al*, Comput. Phys. Commun. **250** (2020) 107062
J. Benda *et al*, Phys. Rev. A 102, 052826 (2020)

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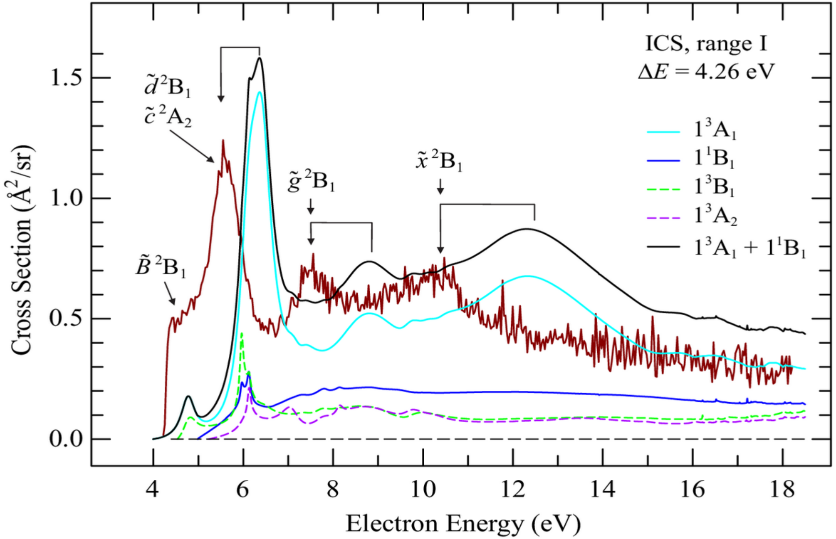
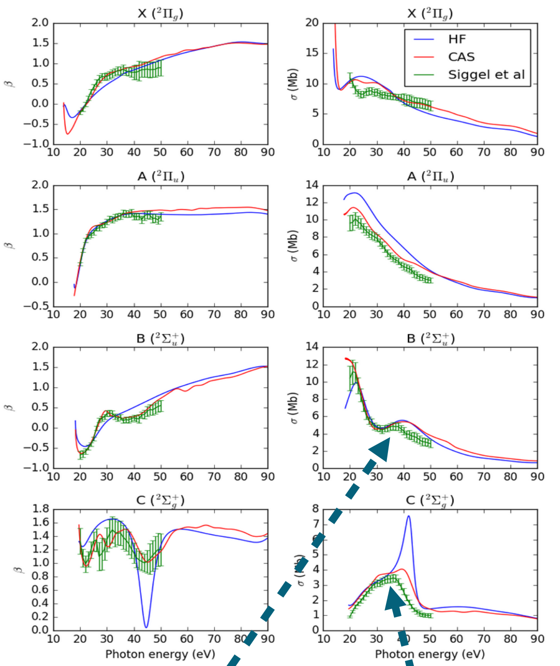
How to identify resonances in computed data?

e^- + pyrimidine

K. Regeta et al, JCP 144(2), 024302 (2016)



hv + CO_2



non-resonant (onset of p-wave)

resonant

Easy for:

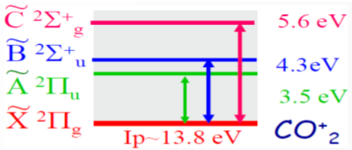
- ✓ Narrow resonances

Difficult for:

- ✘ Broad resonances
- ✘ Resonances with a mixed character

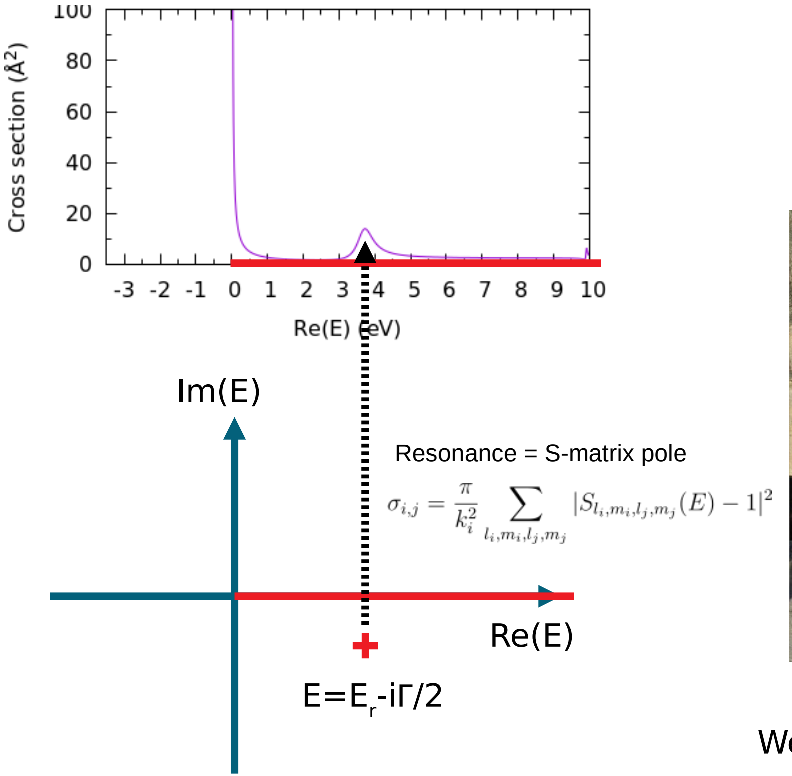
Identification requires:

- Computation of eigenphase sums, time-delays, etc.
- Running models with different levels of complexity (inclusion of polarization, excited states, etc.)
- And sometimes you’re still not 100% sure...



Z. Mašín et al, J. Phys. B 51(13), 134006 (2018)

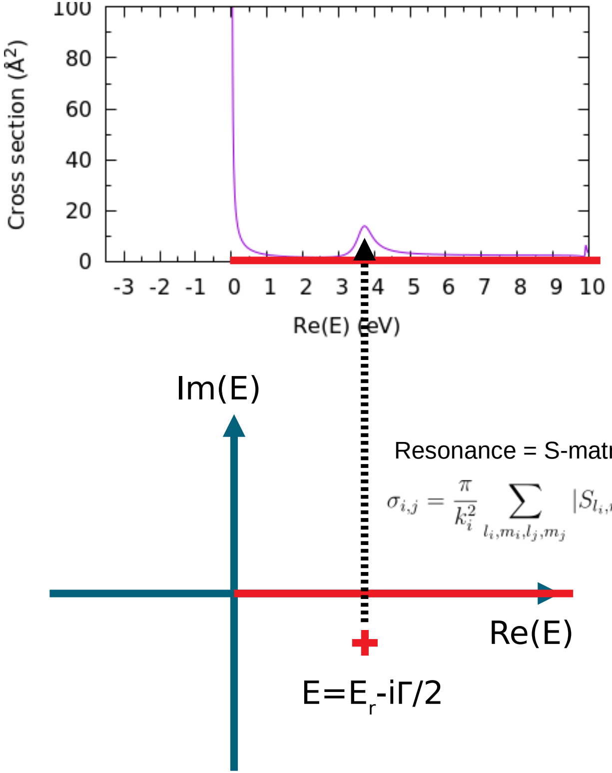
Resonances in complex plane



- Observables are only at real energies
- We see resonances indirectly

We need a way to obtain all resonant states directly!

Resonances in complex plane



Resonance = S-matrix pole

$$\sigma_{i,j} = \frac{\pi}{k_i^2} \sum_{l_i,m_i,l_j,m_j} |S_{l_i,m_i,l_j,m_j}(E) - 1|^2$$

- Observables are only at real energies
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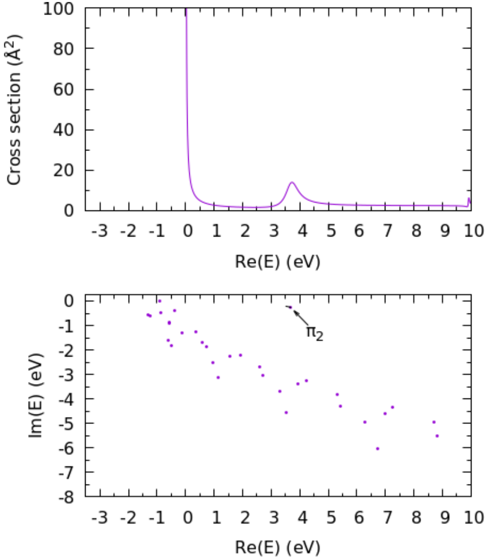


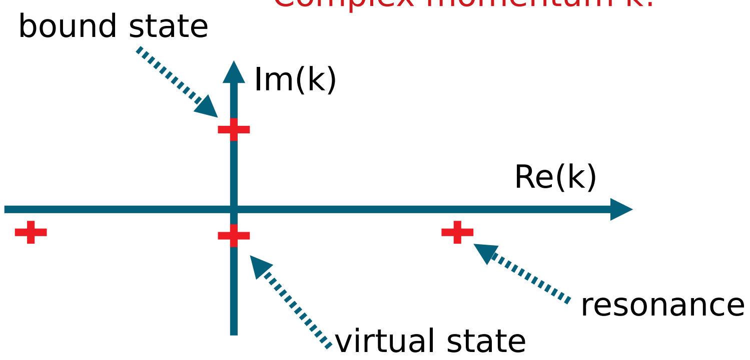
All resonant states in the complex plane

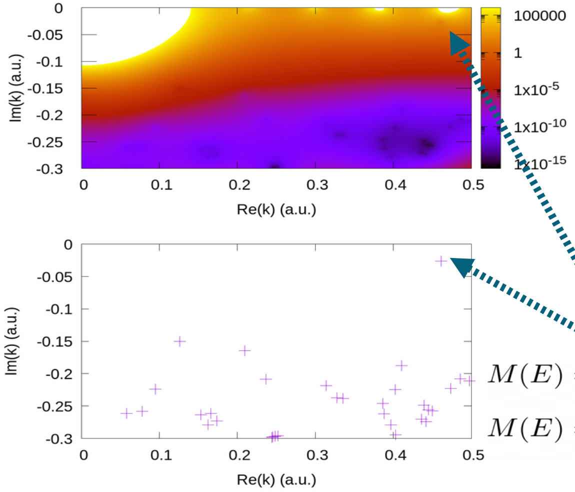
We need a way to obtain all resonant states directly!

Resonances as solutions in complex energy/momentum plane

<u>Siegert states:</u> **F** ~ exp[ikr], r→∞

Complex momentum k!





$$M(E) = 0,$$

$$M(E) = Det\left[F(r) - \mathcal{R}(E)\frac{dF}{dr}\bigg|_{r=a}\right]$$

$$\mathbf{F}(E) = \mathbf{R}(E)\frac{d\mathbf{F}(E)}{dr}\bigg|_{r=a}, \quad R_{i,j}(E) = \sum_k \frac{w_{ik}w_{jk}}{E - E_k}$$

Analytic dependence on energy

F: outer-region radial wavefunctions

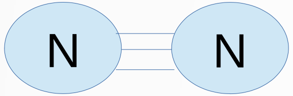
R-matrix: constructed in the inner region

C.J. Noble et al, J. Phys. B 26(18), 2983–3000 (1993)
T.P. Ragesh Kumar et al, J. Phys. Chem. Lett. 13(48), (2022)

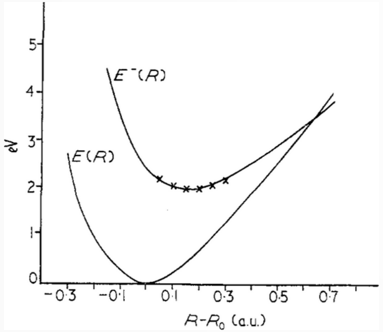
- Originally implemented by Morgan and Burke in 1988, C. Noble 1993
- Alternatives: ECS (giant resonance in Xenon; Chen et al)
- Computation of the Jost function (Rakytiansky, Elander)

Application to resonance search in prototypical molecules

$e^- + N_2$



- Prototypical system with π* resonance
- Short-range interaction only



Birtwistle, Herzenberg, J. Phys. B 4, 53 (1971)

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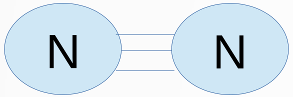

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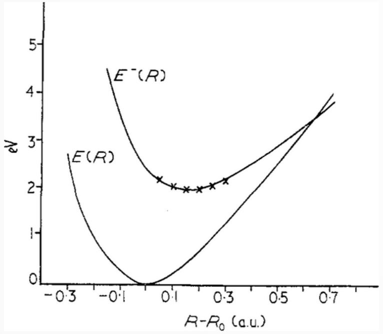
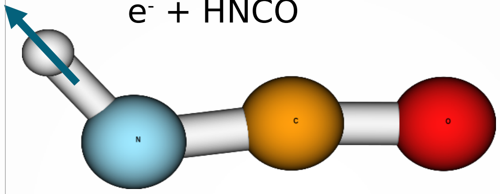
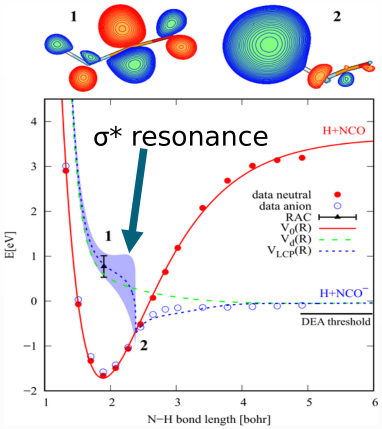


Birtwistle, Herzenberg, J. Phys. B 4, 53 (1971)

$e^- + HNCO$



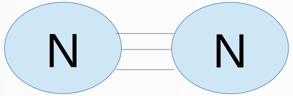
- σ* dissociative resonance confirmed
- Strong dipolar interaction



Zawadzki et al PRL, 121, 143402 (2018)

Application to resonance search in prototypical molecules

$e^- + N_2$



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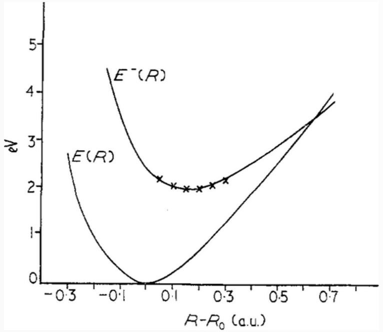

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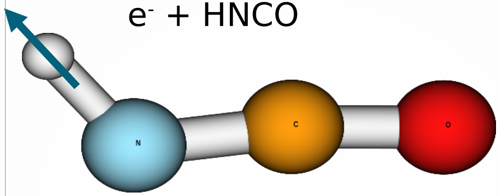

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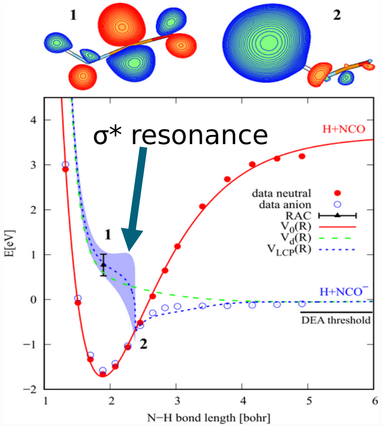
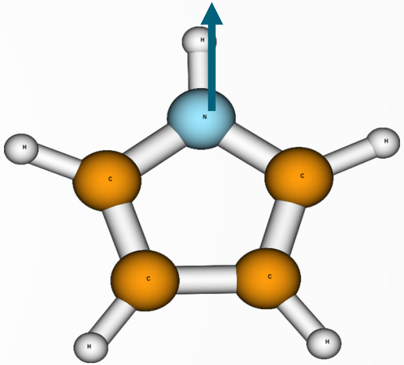


Zawadzki et al PRL, 121, 143402 (2018)

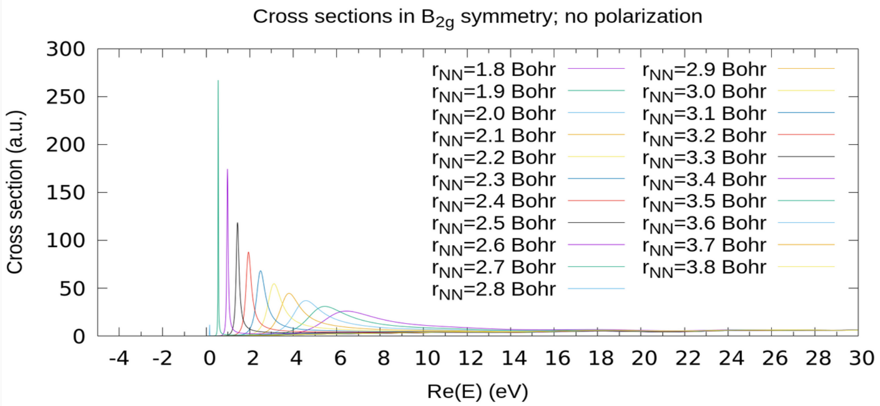
$e^- +$ pyrrole

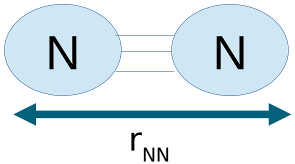


- σ* resonance present?
- Previous calculations are inconclusive
- Similar issue as in HCOOH, uracil,...
- High symmetry (C_{2v})
- Strong dipolar interaction

Kumar et al, J. Phys. Chem. Lett. 13(48), 11136–11142 (2022).

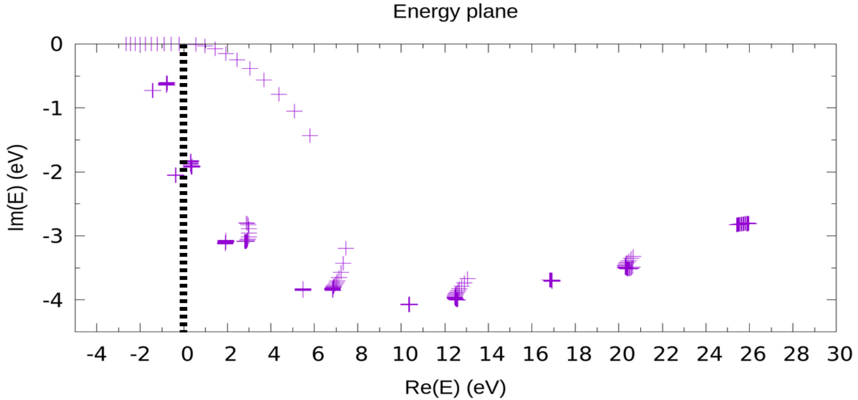
Electron collisions with N_2

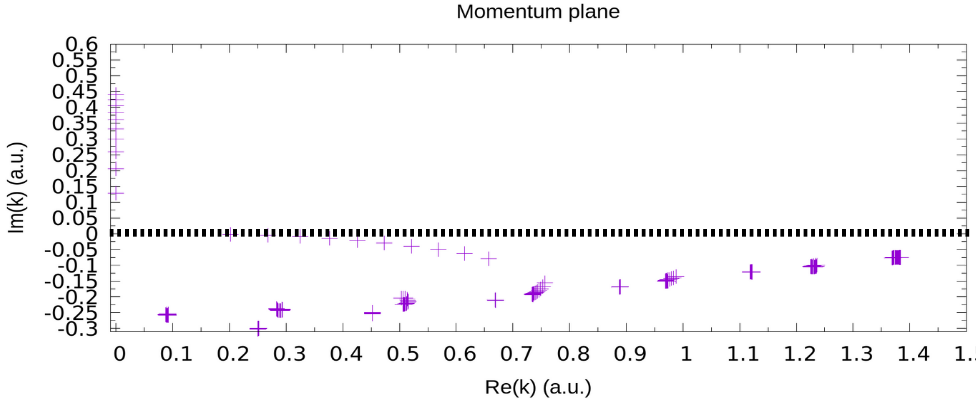




- Resonance becomes a bound state as expected (short-range interaction)
- Remaining Siegert states are weakly dependent on N-N distance
- Large number of wide Siegert states: standard property of every quantum scattering

H.M. Nussenzveig, Nuclear Physics, 11, 499-521 (1959)





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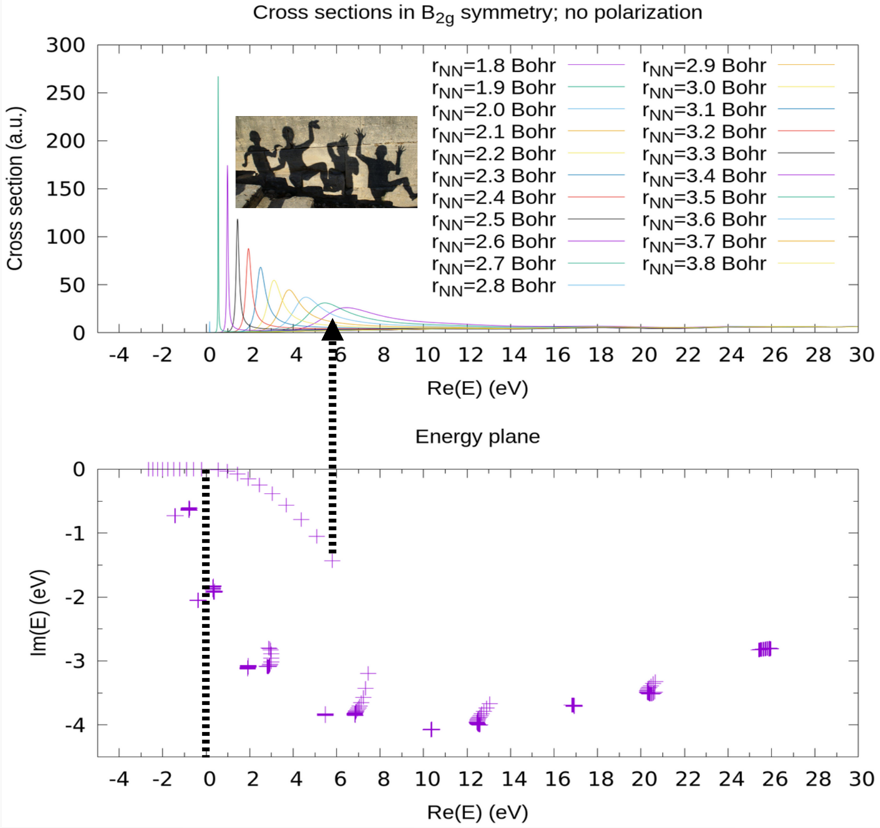

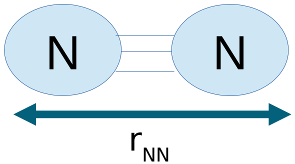

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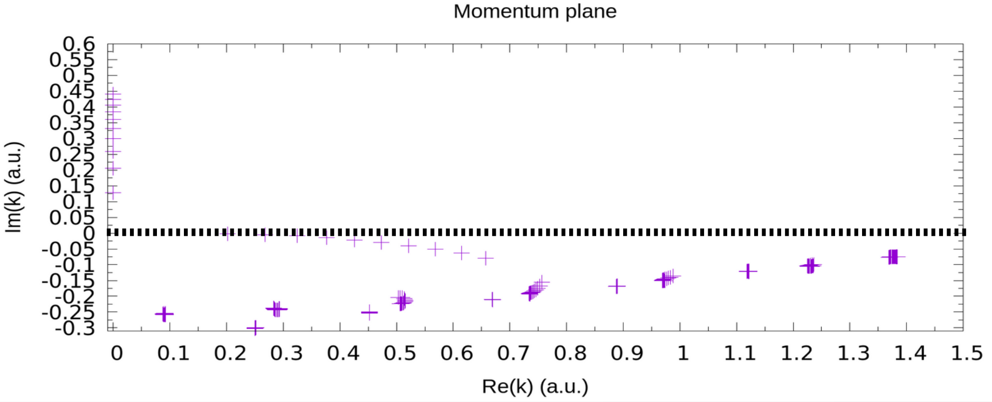

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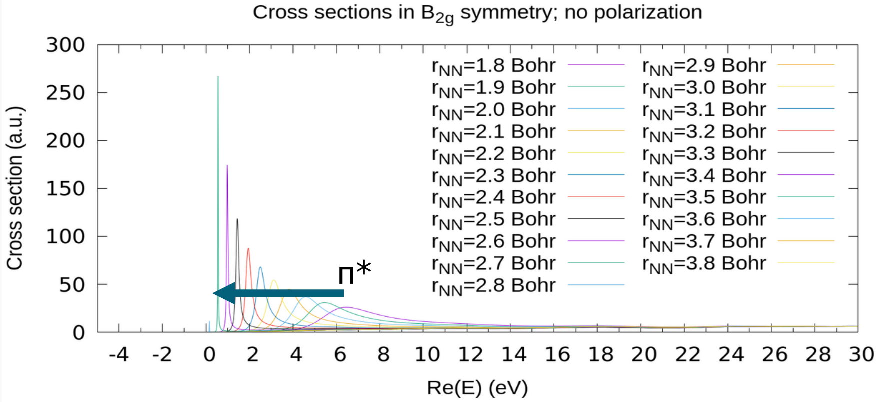

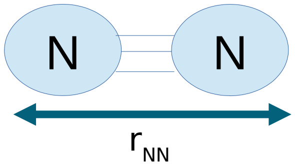

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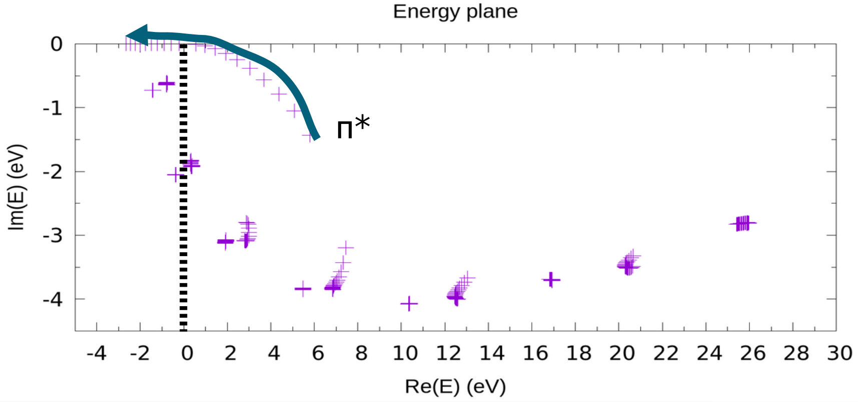
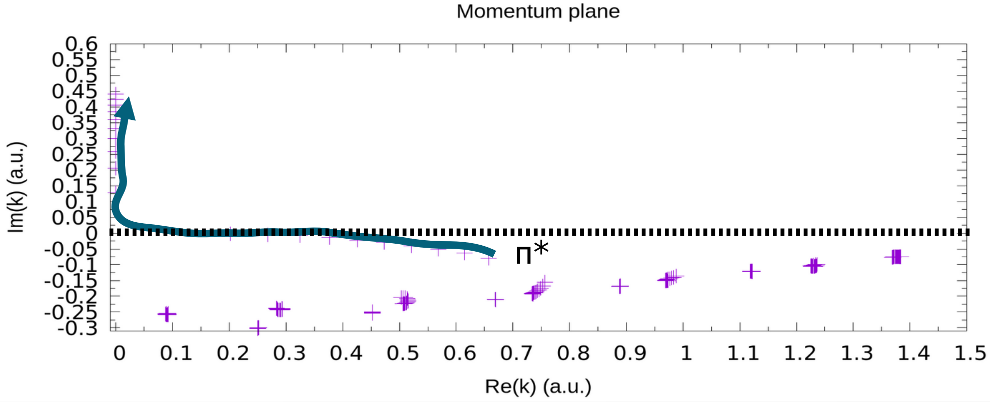
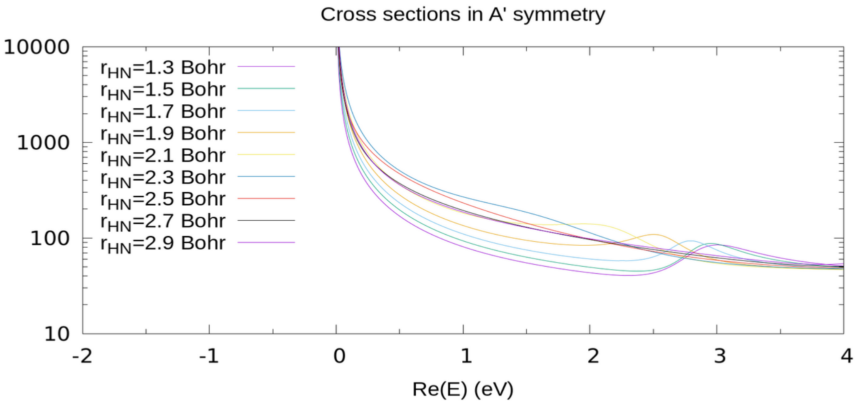


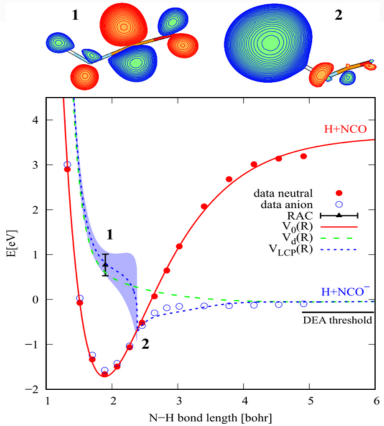


Electron collisions with HNCO

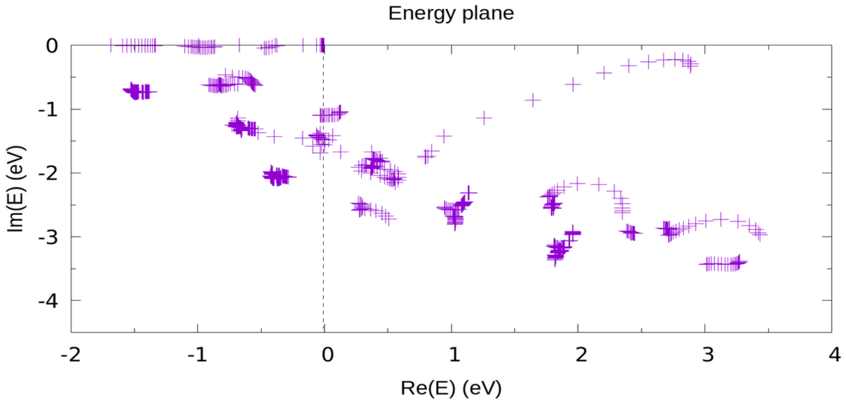


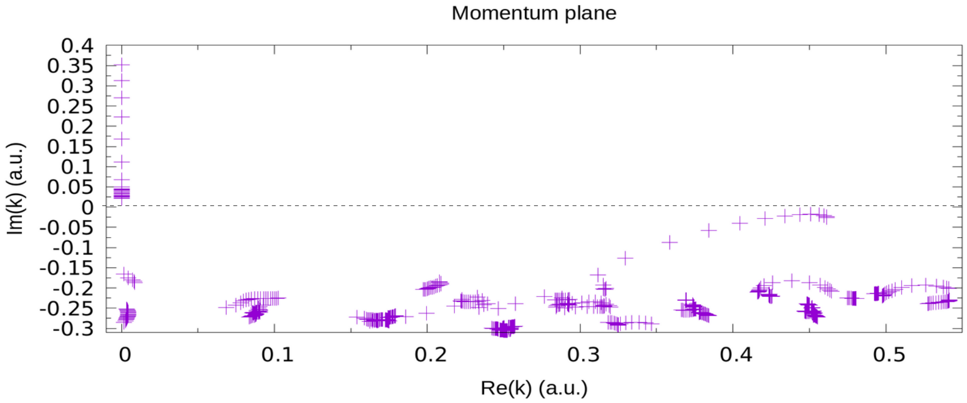
- σ* resonance moves down in energy but is disconnected from the bound state
- Valence-bound state appears suddenly
- DEA requires non-adiabatic coupling between continuum and bound state
- Dipole-bound state is found

H Estrada and W Domcke, J. Phys. B, 17, 279 (1984)

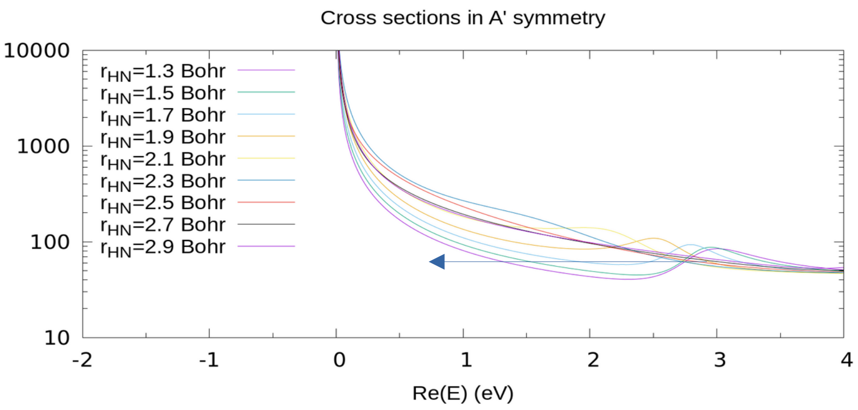


Zawadzki et al PRL, 121, 143402 (2018)





Electron collisions with HNCO



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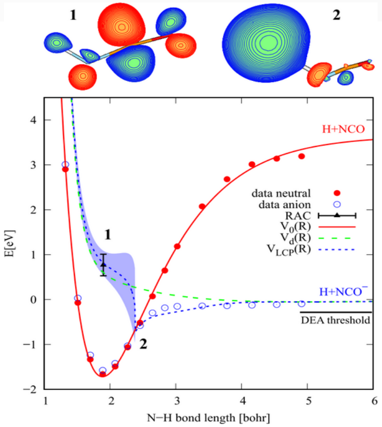

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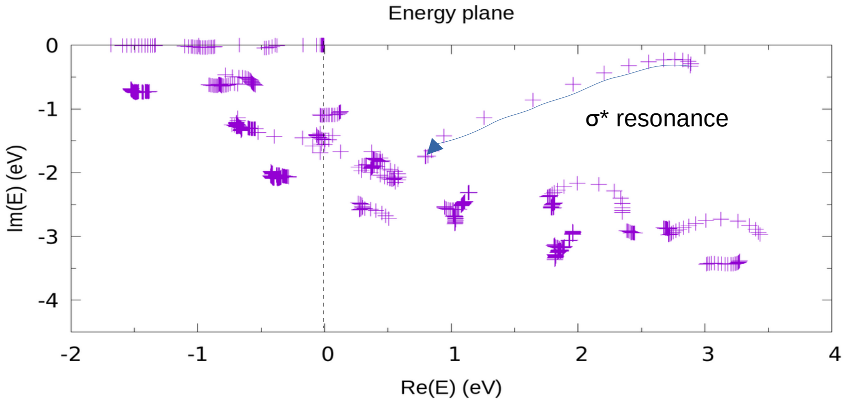
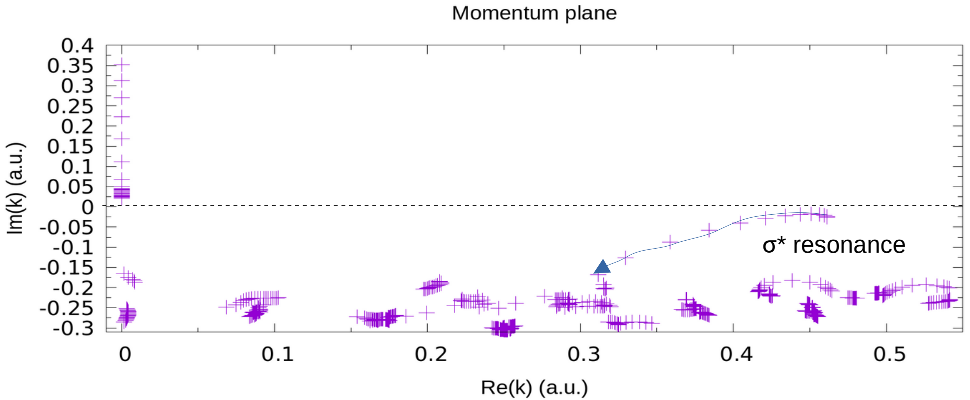
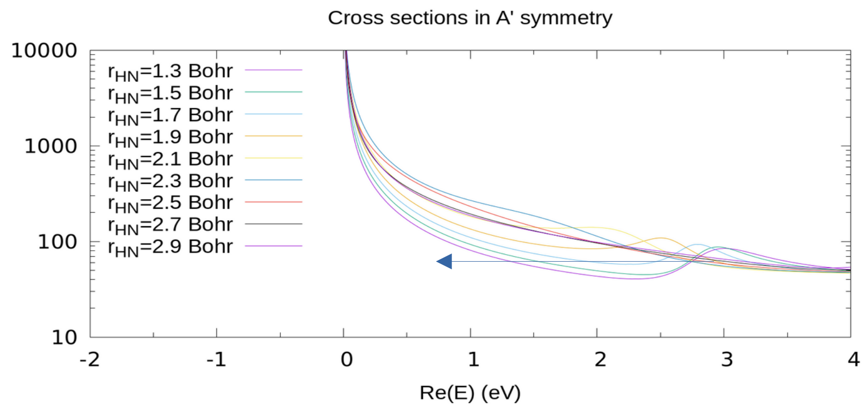


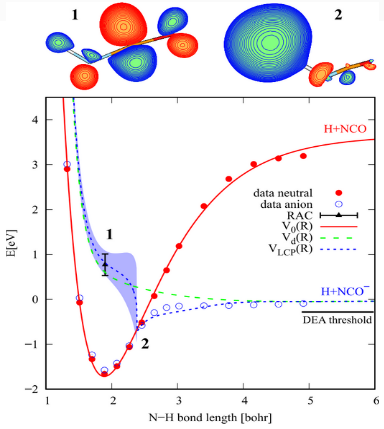


Electron collisions with HNCO

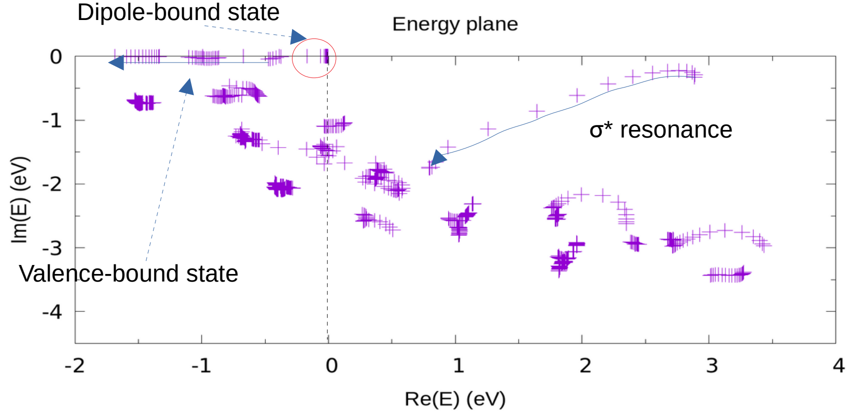


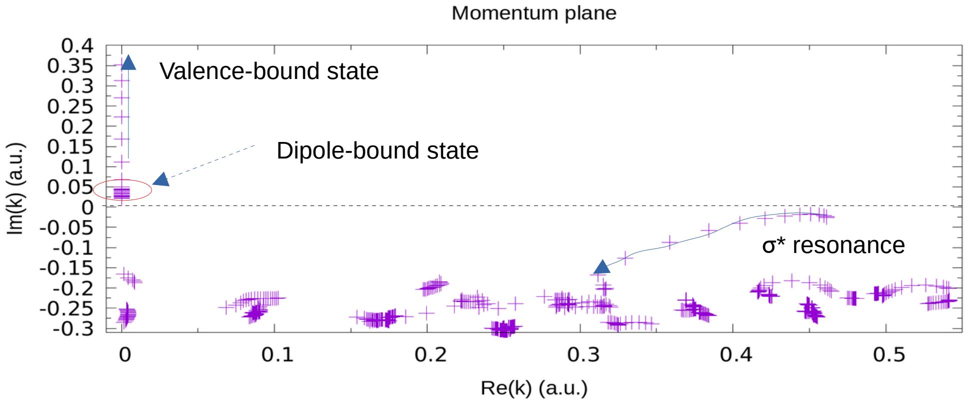
- σ* resonance moves down in energy but is disconnected from the bound state and dissolves in the continuum
- Valence-bound state appears suddenly
- DEA requires non-adiabatic coupling between continuum and bound state
- Dipole-bound state is found

H Estrada and W Domcke, J. Phys. B, 17, 279 (1984)



Zawadzki et al PRL, 121, 143402 (2018)

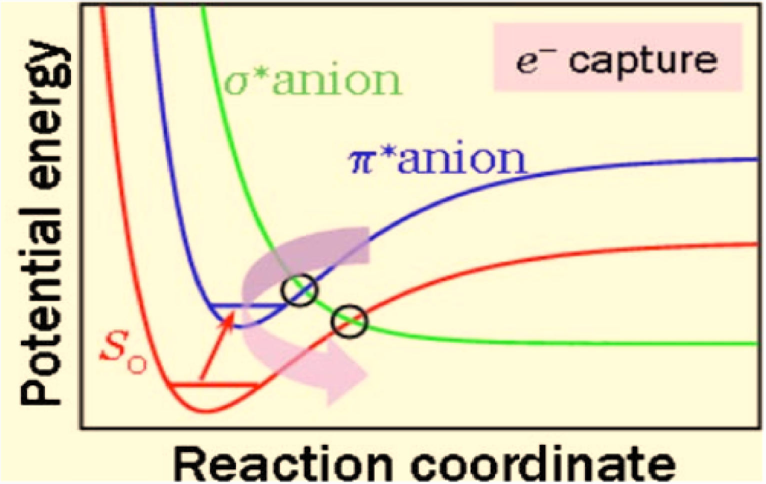




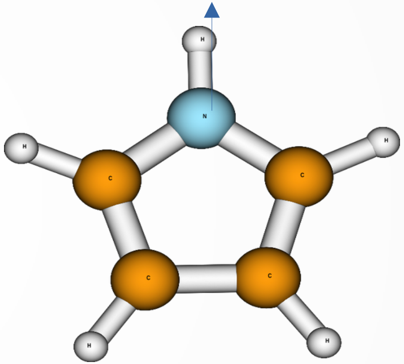
Electron collisions with pyrrole

Dissociative electron attachment

pyrrole + e- → (pyrrole)- → H+(pyrrole-H)-



de Oliveira et al, JCP, 132, 204301 (2010)

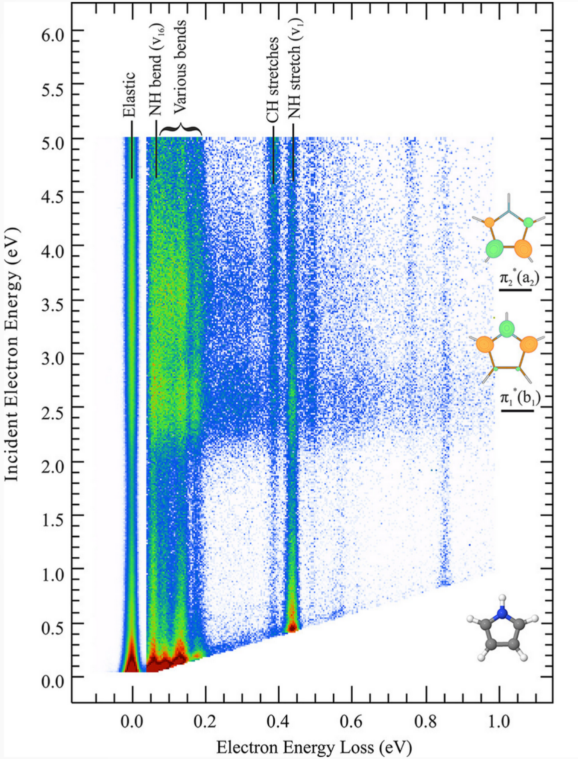


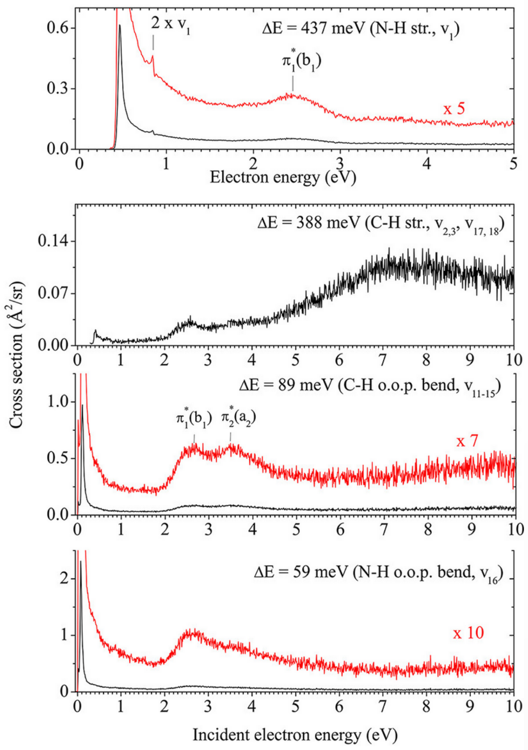
Does the σ* state exist in pyrrole? (and in HCCOH, uracil,...)

Kumar et al, J. Phys. Chem. Lett. 13(48), 11136–11142 (2022)

Electron collisions with pyrrole

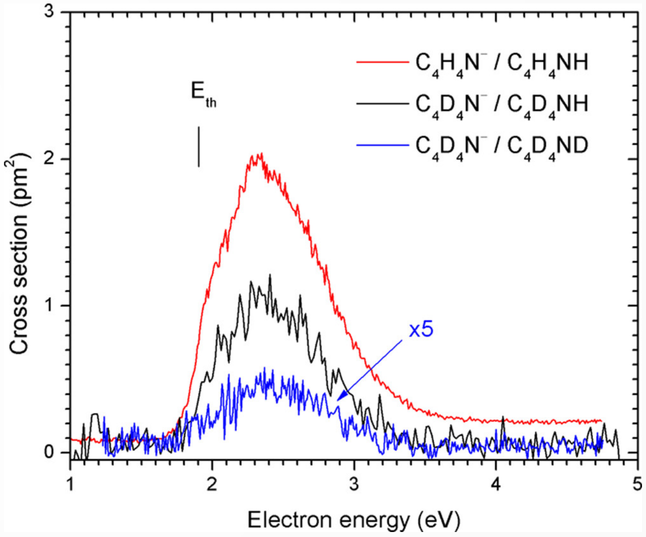
Experiment: Fedor group (Czech Ac. Sci.)





Dissociative electron attachment

pyrrole + e- → (pyrrole)- → H + (pyrrole-H)$^-$



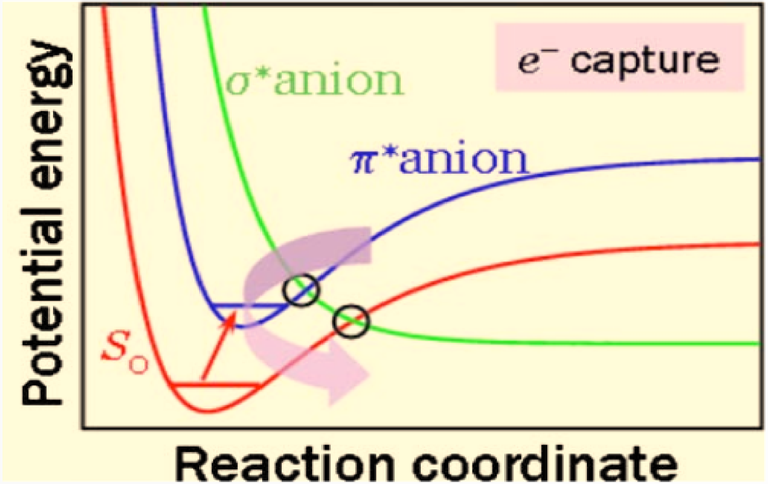
Slowing of dynamics on remote (non-dissociating) hydrogens quenches DEA!

Kumar et al, J. Phys. Chem. Lett. 13(48), 11136–11142 (2022)

Electron collisions with pyrrole

Dissociative electron attachment

pyrrole + e- → (pyrrole)- → H + (pyrrole-H)$^-$

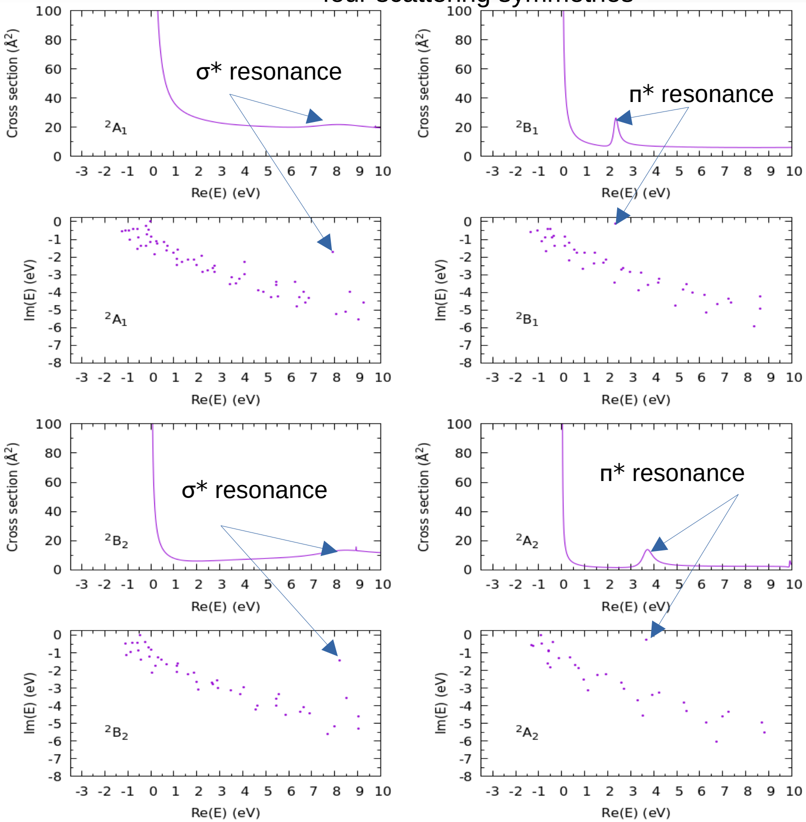


de Oliveira et al, JCP, 132, 204301 (2010)

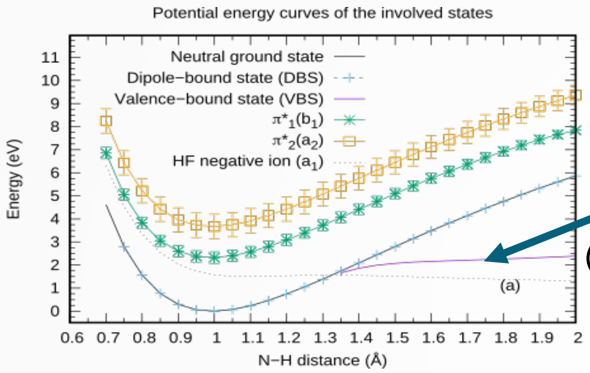
Does the σ* state exist in pyrrole? (and in HCCOH, uracil,...)

Kumar et al, J. Phys. Chem. Lett. 13(48), 11136–11142 (2022)

<u>Equilibrium geometry</u>:
four scattering symmetries

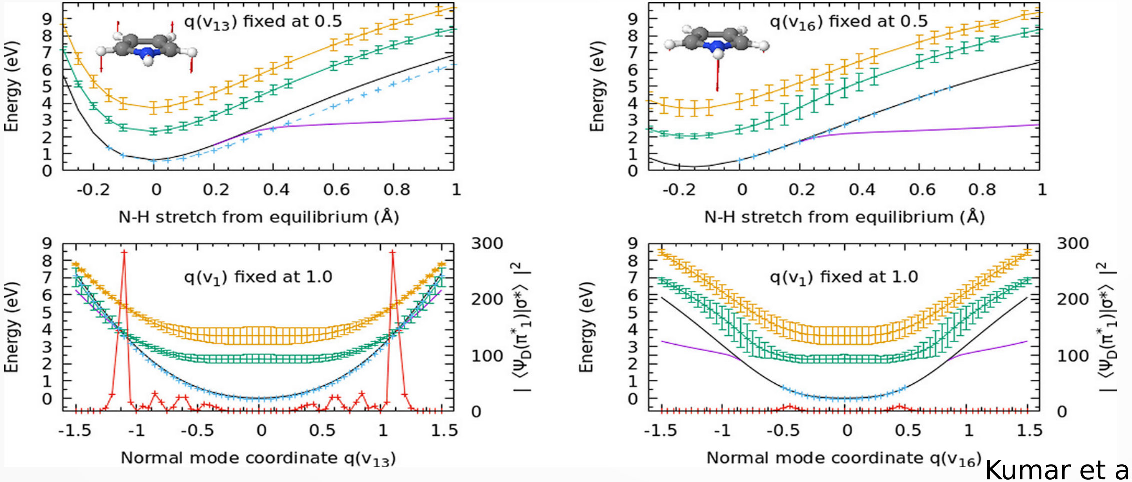


Electron collisions with pyrrole



(Pyrrole-H)⁻ + H

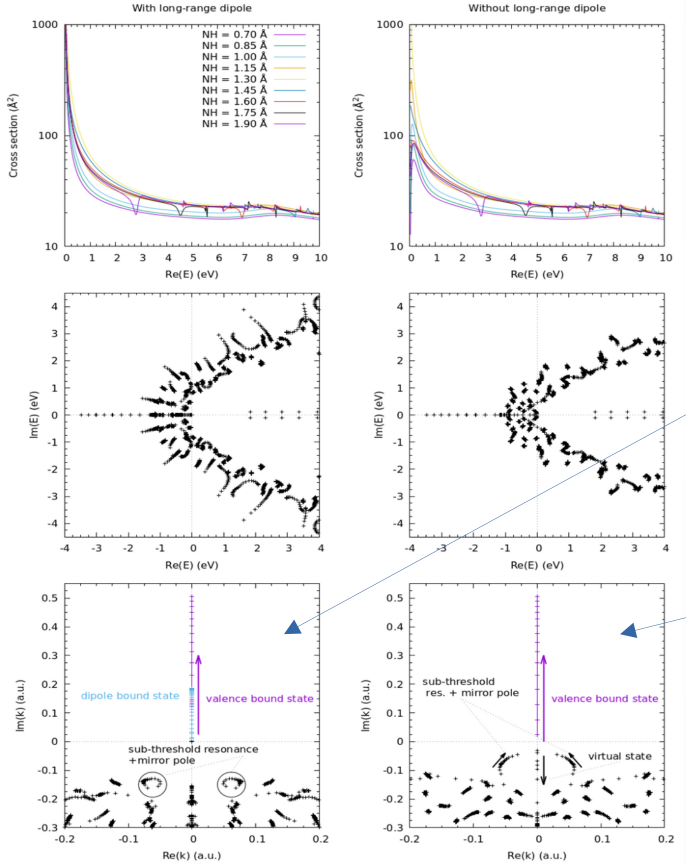
- How is the bound state connected with the continuum?
- Where has the σ* orbital gone?



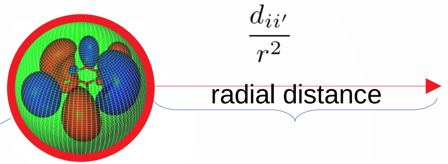
Broken symmetry:
none of the π* states become bound at reasonable geometry distortions

Kumar et al, J. Phys. Chem. Lett. 13(48), 11136–11142 (2022)

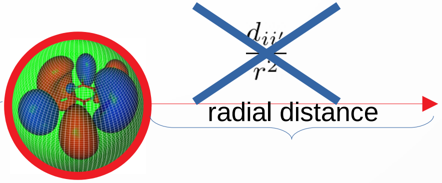
Electron collisions with pyrrole



Role of long-range dipolar interaction



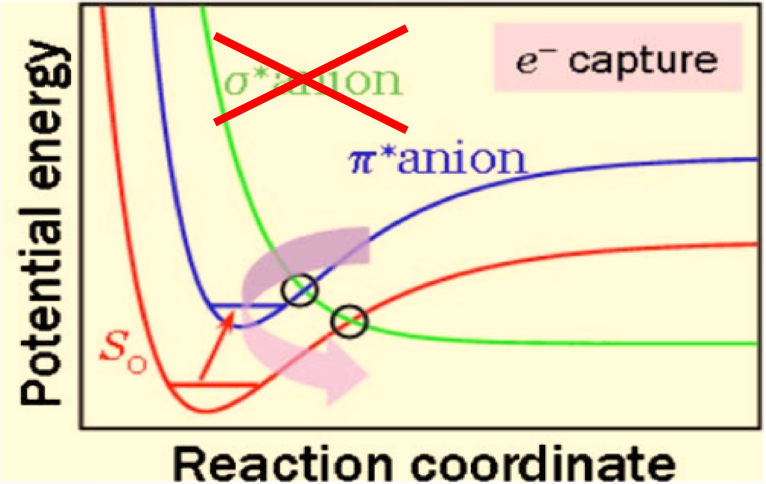
No state becomes bound

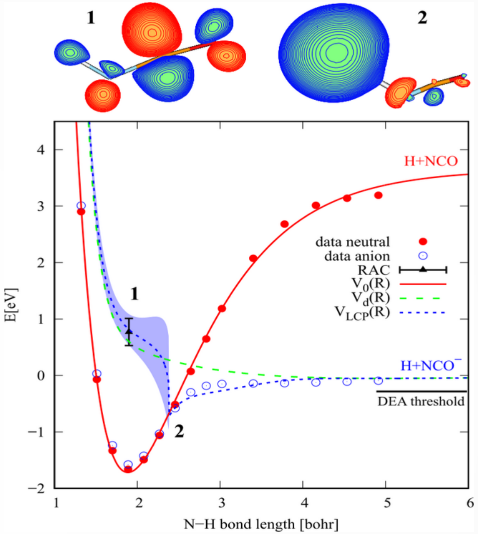


Sub-threshold resonance (virtual state) becomes bound

Kumar et al, J. Phys. Chem. Lett. 13(48), 11136–11142 (2022)

Interpretation of DEA in strongly polar molecules





- No physical state with these properties exists in pyrrole
- Sub-threshold resonance (virtual state) becoming bound
- Non-adiabatic coupling between π* resonance and the virtual state: enabled by breaking of the symmetry
- Ubiquitous mechanism in polar molecules
- Result of structure of continuum wf.

H Estrada and W Domcke, J. Phys. B, 17, 279 (1984)

- Physical resonant state vs computational parametrization
- Feshbach projection operator formalism

$$\mathcal{Q} = \sum_d |\phi_d\rangle\langle\phi_d|$$ Discrete state choice

$$\mathcal{P} = I - \mathcal{Q} = \int |\epsilon\rangle\langle\epsilon| d\epsilon.$$ Orthogonal continuum

Removal of resonances from scattering data

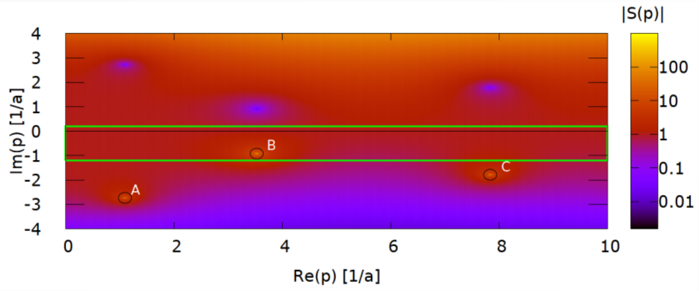
What is the effect of resonance on scattering observables?

Remove the pole from the S-matrix

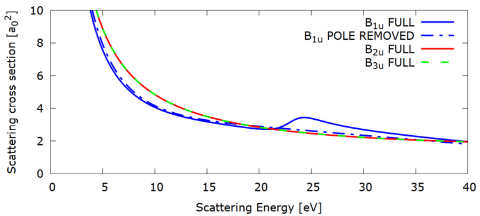
$$S^B_{ij}(E) = S_{ij}(E) - \frac{\mathrm{Res}_{E_B} S_{ij}(E)}{E - E_B}$$

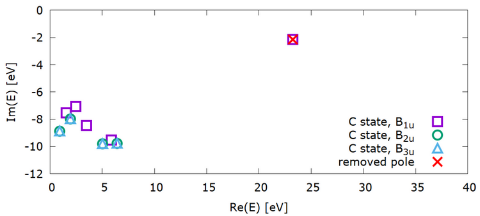
$$\mathrm{Res}_{E_B} S_{ij}(B) = \frac{1}{2\pi \mathrm{i}} \oint_C S_{ij}(E)\mathrm{d}E$$

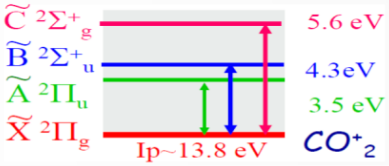
S-matrix in complex plane



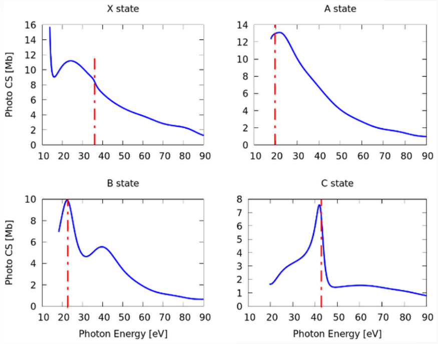
$CO_2^+(C) + e^- \rightarrow CO_2^+(C) + e^-$



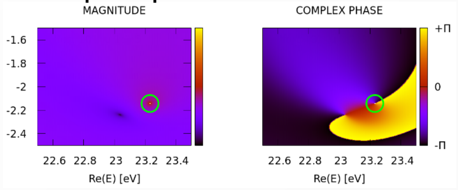




$h\nu + CO_2 \rightarrow CO_2^+(C) + e^-$



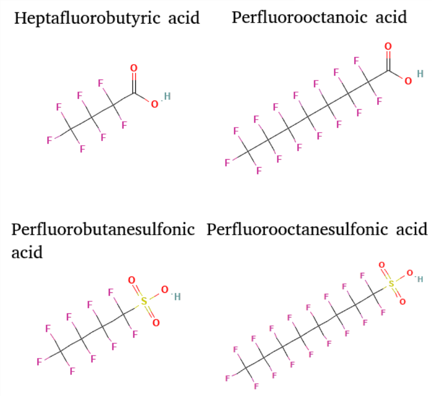
Dipole matrix element in complex plane



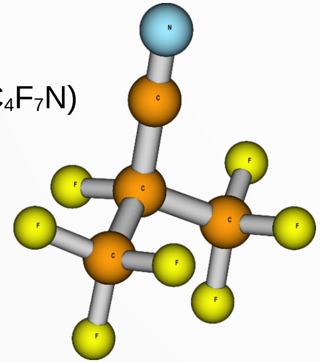
M. Konvalinka, Master thesis (2024)

Resonances in large molecules

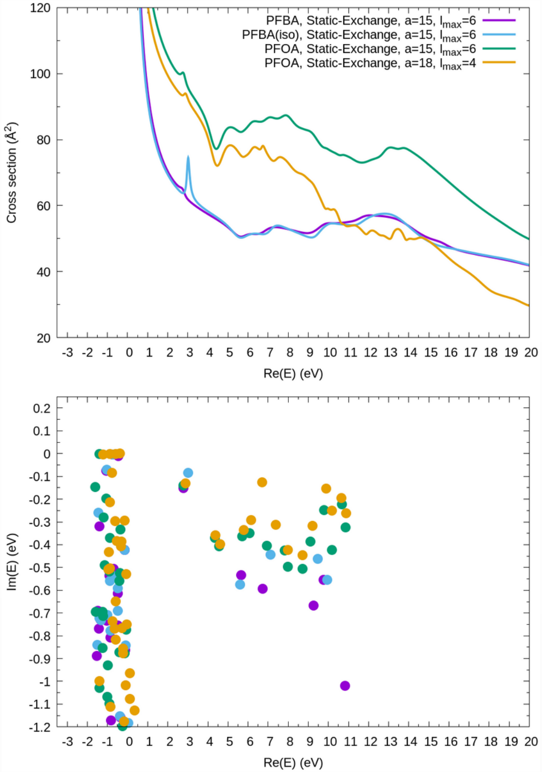
Perfluoroalkyl molecules (PFAS)



Novec (C_4F_7N)

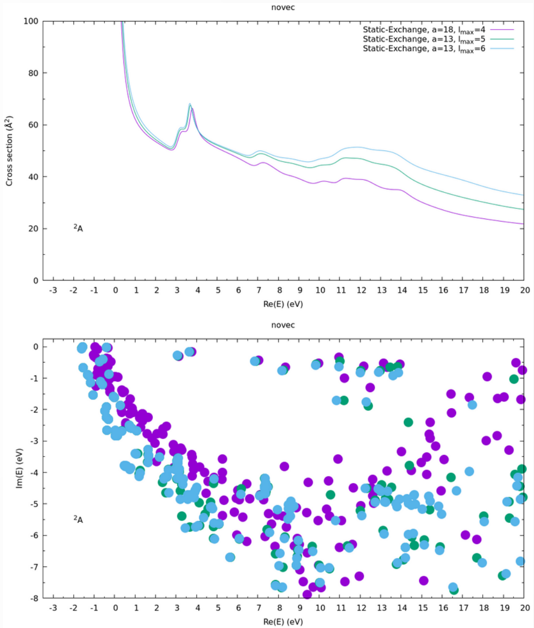


PFBA, PFOA



Sapunar et al, submitted to PCCP

Novec

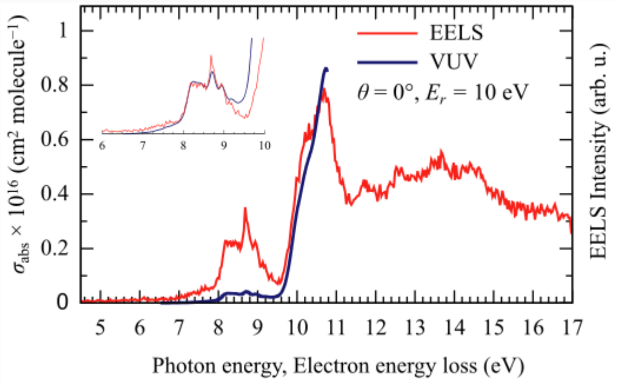


T. Ovad et al, J. Chem. Phys. 158(1), 014303 (2023)

Impact excitation cross sections

Novec – EELS, electrons vs photons

$\Delta E = E_i - E_r$



$$f^{\mathrm{Born}}_{ai,bf}(\theta,\phi) = -\frac{4\pi^2\mu}{\hbar^2}\left\langle \psi_{\mathbf{q}_f}\Phi_b \middle| V \middle| \Phi_a \psi_{\mathbf{q}_i}\right\rangle,$$
$$= \frac{2\,\mu}{|\mathbf{Q}|^2\hbar^2}\sum_{j=1}^{N_e}\langle \Phi_b | e^{-i\mathbf{Q}\mathbf{r}_j} | \Phi_a \rangle,$$

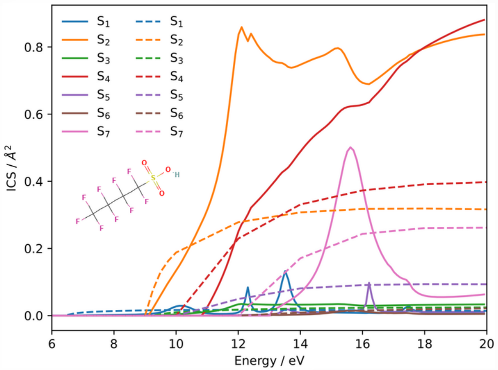
Enables use of ADC wavefunctions

$$|\Phi\rangle = \sum_{o,v} d_{ov}|\phi_o^v\rangle$$

T. Ovad et al, J. Chem. Phys. 158(1), 014303 (2023)

PFBS – Born vs R-matrix

7 lowest singlet states (CASSCF)



Born – only spin-allowed transitions

R-matrix used for triplets

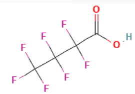
-OH and -SO_3H group loss

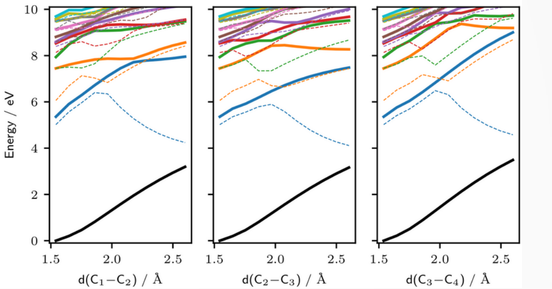
-Carbon chain breaking

Sapunar et al, submitted to PCCP

PFBA - surfaces

RI-ADC(2)/aug-cc-pVDZ





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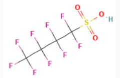

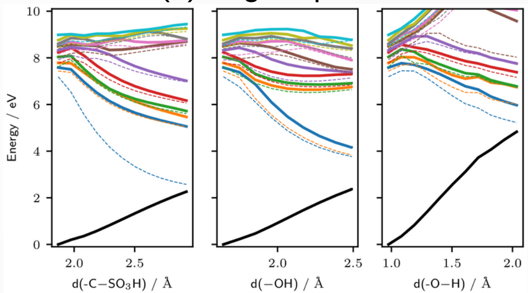

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Novec – EELS, electrons vs photons

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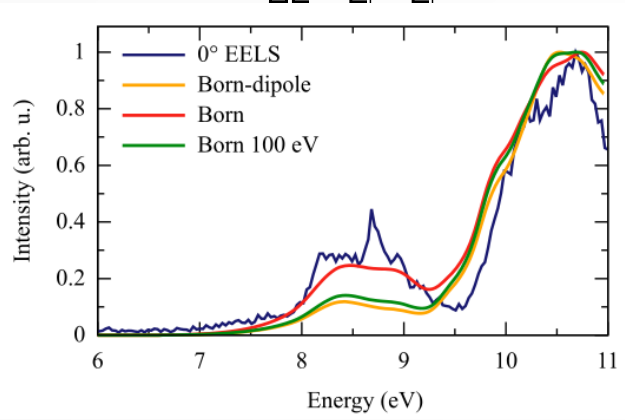

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$$|\Phi\rangle = \sum_{o,v} d_{ov}|\phi_o^v\rangle$$

T. Ovad et al, J. Chem. Phys. 158(1), 014303 (2023)

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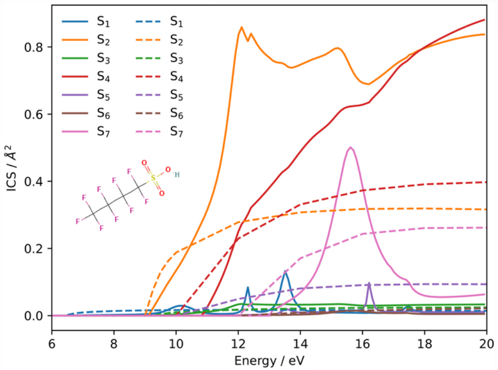

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Sapunar et al, submitted to PCCP

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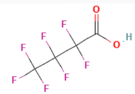
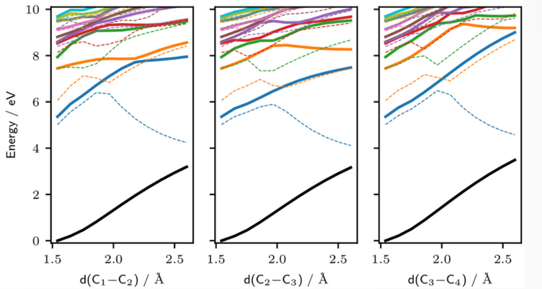
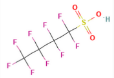
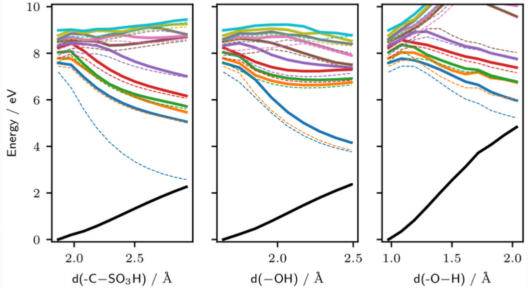




PFBS – surfaces
RI-ADC(2)/aug-cc-pVDZ



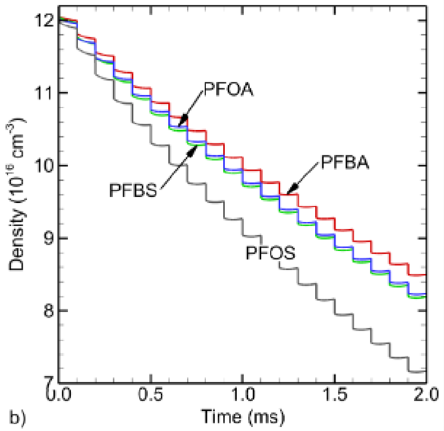


Modeling PFAS degradation in plasma

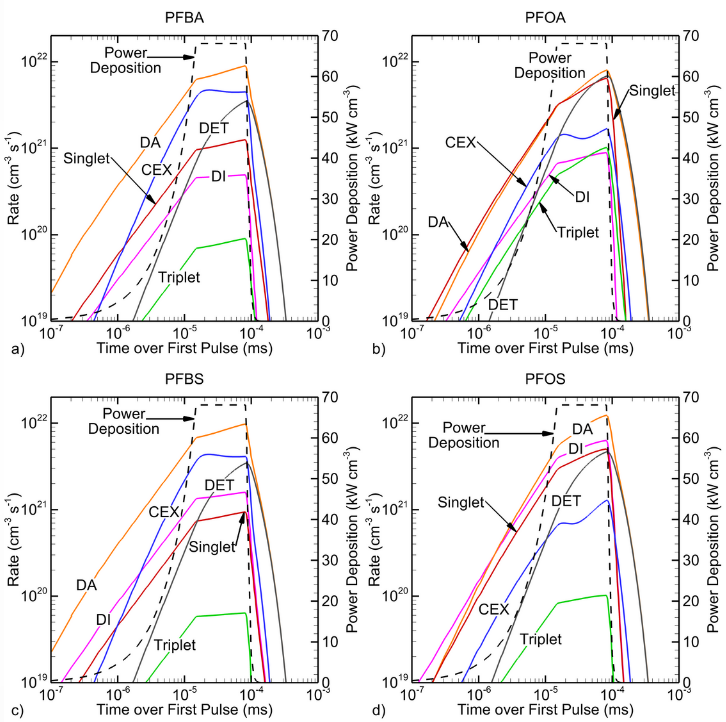
GlobalKin (0-dimensional plasma chem. model)

A. M. Lietz and M. J. Kushner, Journal of Physics D, 2016, 49, 425204.

- Repetitively pulsed Ar plasma at atmospheric pressure (dielectric barrier discharge)
- Pulse duration ~115 ns, varying envelope, Average electron temp. 6-7.5 eV
- Ar/PFAS = 99.5/0.05



Dissociative Excitation to Singlet States	e + PFBA $\rightarrow$ C_3F_7CO + OH + e
	e + PFOA $\rightarrow$ $C_7F_{15}CO$ + OH + e
	e + PFBS $\rightarrow$ HSO_3 + C_4F_9 + e
	e + PFOS $\rightarrow$ HSO_3 + C_8F_{17} + e
Dissociative Excitation to Triplet States	e + PFBA $\rightarrow$ C_2F_4 + TFA + e
	e + PFOA $\rightarrow$ C_6F_{12} + TFA + e
	e + PFBS $\rightarrow$ HSO_3 + C_4F_9 + e
	e + PFOS $\rightarrow$ HSO_3 + C_8F_{17} + e
Dissociative Ionization (DI)	e + PFBA $\rightarrow$ $C_2F_4^+$ + TFA + e
	e + PFOA $\rightarrow$ $C_2F_4^+$ + PFHxA + e
	e + PFBS $\rightarrow$ $C_2F_4^+$ + PFES + e
	e + PFOS $\rightarrow$ $C_2F_4^+$ + PFHxS + e
Charge-Exchange (CEX)	M^+ + PFBA $\rightarrow$ $HCOO^+$ + C_3F_7 + M
	M^+ + PFOA $\rightarrow$ $C_3F_5^+$ + CO_2 + HF + C_4F_9 + M
	M^+ + PFBS $\rightarrow$ $C_2F_5^+$ + C_2F_4 + HSO_3 + M
	M^+ + PFOS $\rightarrow$ $C_3F_5^+$ + C_5F_{12} + HSO_3 + M
Dissociative Attachment (DA)	e + PFBA $\rightarrow$ $C_3F_6HCOO^-$ + F
	e + PFOA $\rightarrow$ $C_7F_{14}HCOO^-$ + F
	e + PFBS $\rightarrow$ $C_4F_9SO_3^-$ + H
	e + PFOS $\rightarrow$ $C_8F_{17}SO_3^-$ + H
Dissociative Excitation Transfer (DET)	Ar^* + PFBA $\rightarrow$ $HCOO^+$ + C_3F_7 + Ar + e
	Ar^* + PFOA $\rightarrow$ $C_3F_5^+$ + CO_2 + HF + C_4F_9 + Ar + e
	Ar_2^* + PFOA $\rightarrow$ $C_3F_5^+$ + CO_2 + HF + C_4F_9 + Ar + Ar + e
	Ar^* + PFBS $\rightarrow$ $C_2F_5^+$ + C_2F_4 + HSO_3 + Ar + e
	Ar^* + PFOS $\rightarrow$ $C_3F_5^+$ + C_5F_{12} + HSO_3 + Ar + e
	Ar_2^* + PFOS $\rightarrow$ $C_3F_5^+$ + C_5F_{12} + HSO_3 + Ar + Ar + e



Short chains – slower decomposition
Carboxylic acids faster than sulfonic

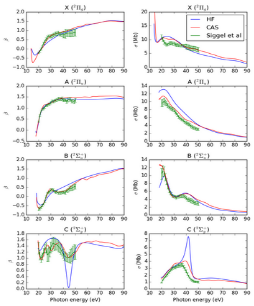
Key role of DA, but data available only up to 600 K (0.05eV)
Shape resonances – nuclear motion in continuum, missing!

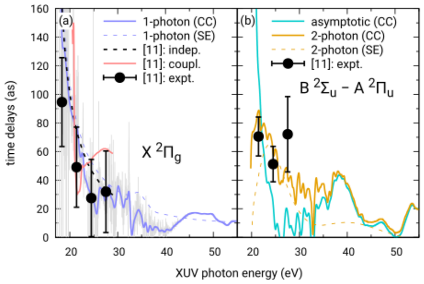
Sapunar et al, submitted to PCCP

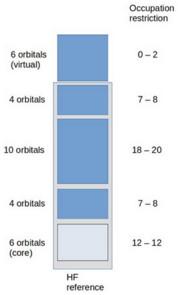
Conclusions

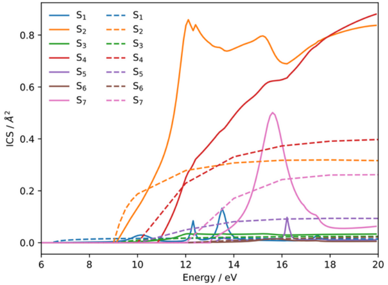
New capabilities in R-matrix

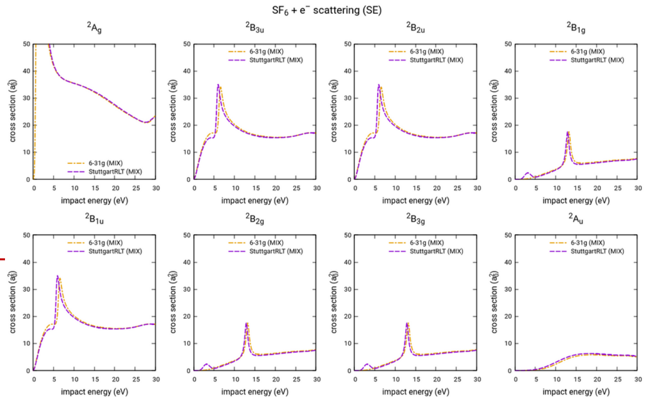
- Photoionization (1-photon, N-photon)
- Resonance analysis
- Large CI, ORMAS models
- Large molecules possible (Born approx.)
- TD calculations using RMT











Coming soon

- ECPs, efficient integral evaluation

Acknowledgments

UKRmol+

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- Karel Houfek (CUNI, Prague)
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- Prof. Mark Kushner, Mackenzie Meyer (Uni. Michigan)
- Quantemol (Harindranath B. Ambalampitiya)
- 3M

Pyrrole, novec

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- P. Slavíček (UCT)
- T. Ovad (UCT)
- J. Kočišek (CAS)
- R. Kumar (CAS)
- P. Nag (CAS)

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