One-Electron Resonances in Electron-Molecule Scattering

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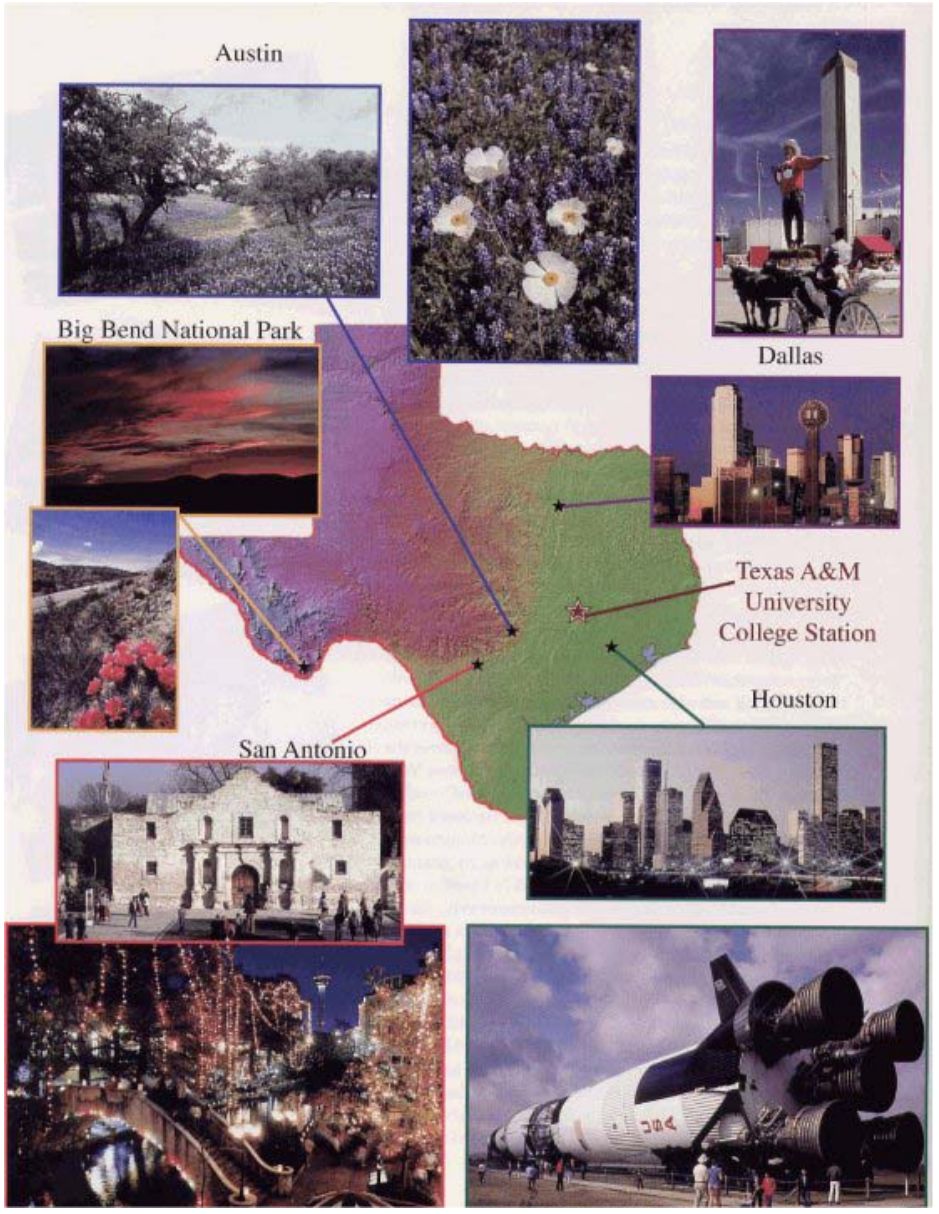


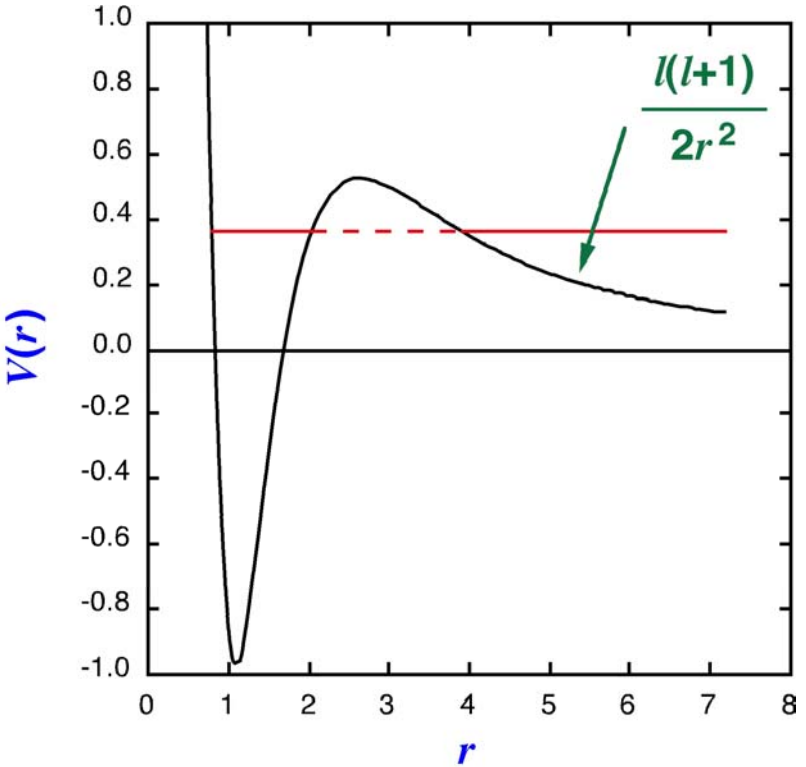
EPIC 2004, Obergurgl

Dissociation Induced by Electron Collision

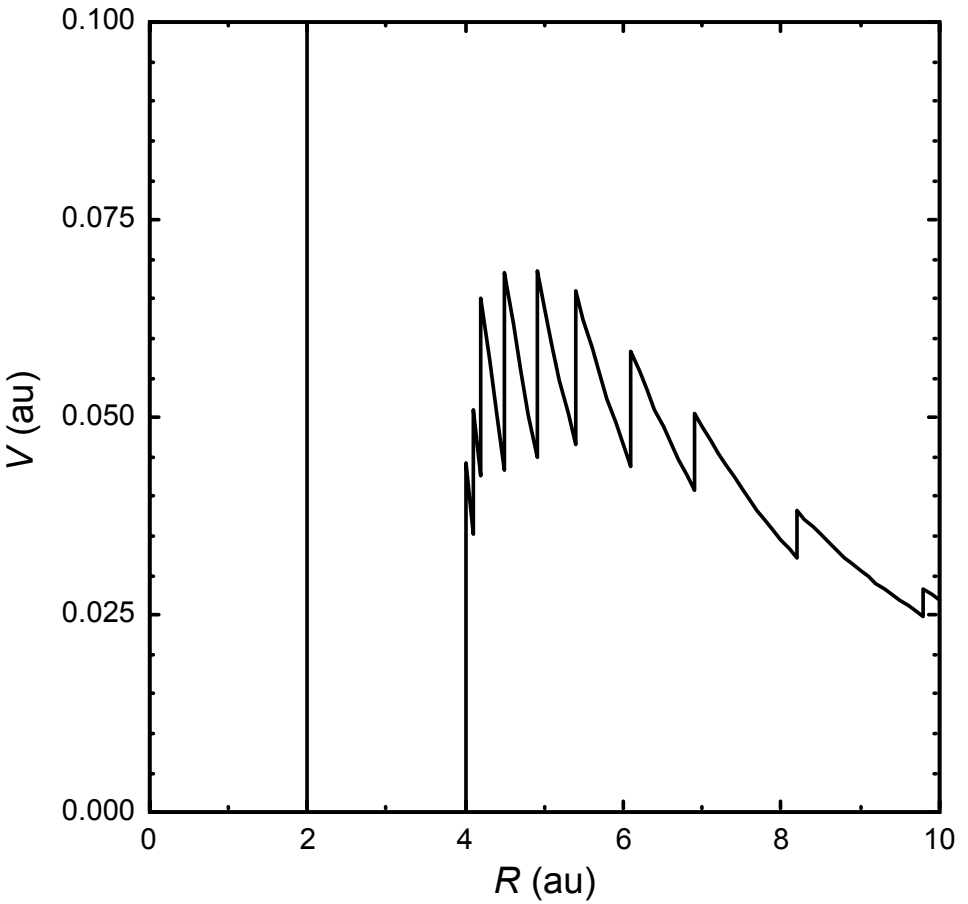
- Electronic excitation to dissociative states
- Dissociative electron attachment (DEA)
  - Enhanced by resonances which temporarily trap scattered electron (time delay)
    - One-electron resonances (shape resonances)
    - Two-electron resonances (Feshbach resonances)
  - Direct dissociation of negative ion state
    - Structure of state can be used to predict fragments
  - Predissociative negative ion state (unimolecular reaction dynamics)
    - Lowest energy products often observed

Shape Resonances in Electron-Molecule Scattering

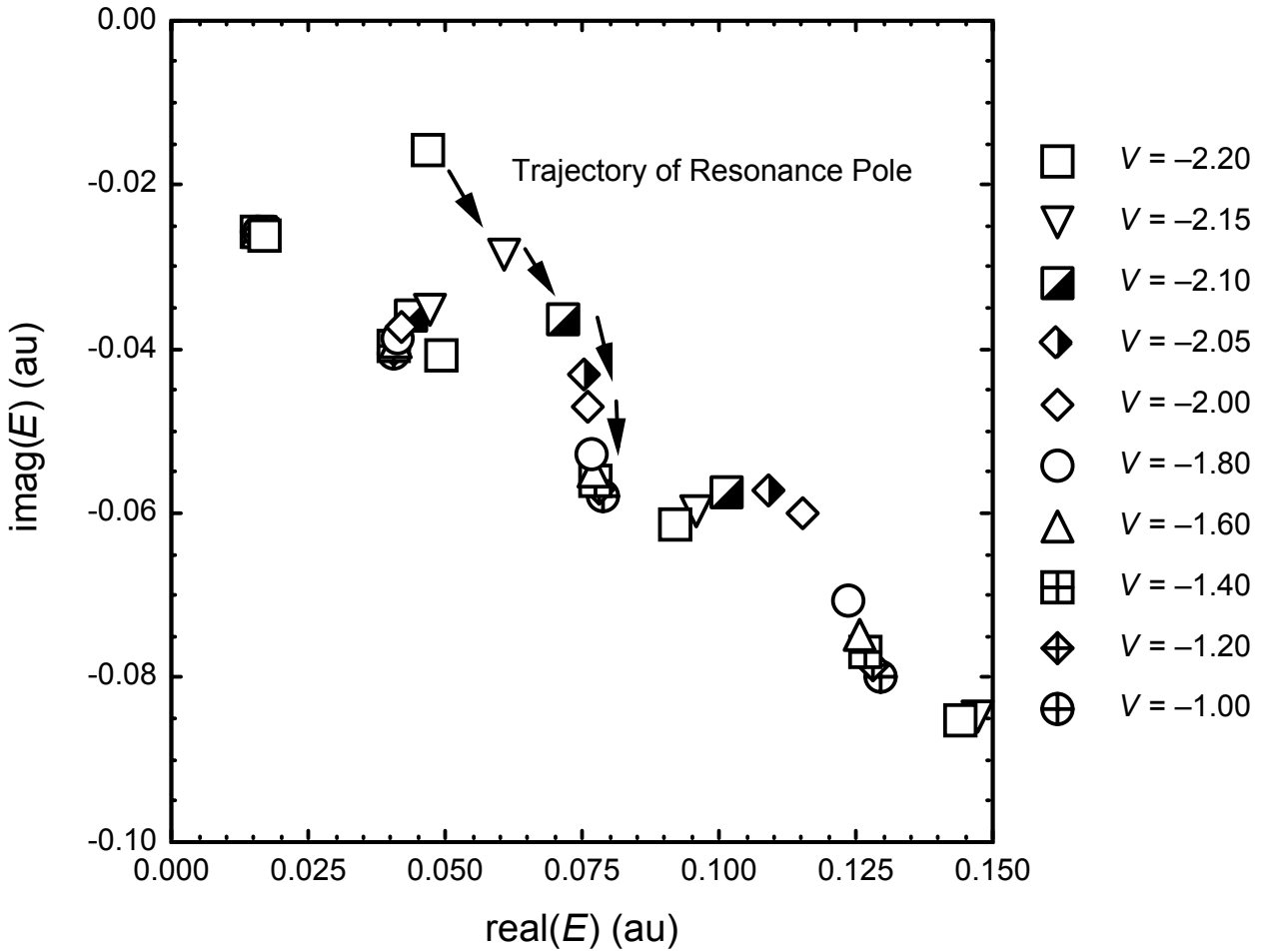
- As the molecule gets larger, the possible values of *l* increase
- For a given molecule, the larger the *l*, the higher the barrier
- Shape resonances are predicted to occur with *l* = 15 in C_{60}
- Experimental observations of shape resonances with *l* = 9 at 65 eV in the photoionizaiton of SF_6



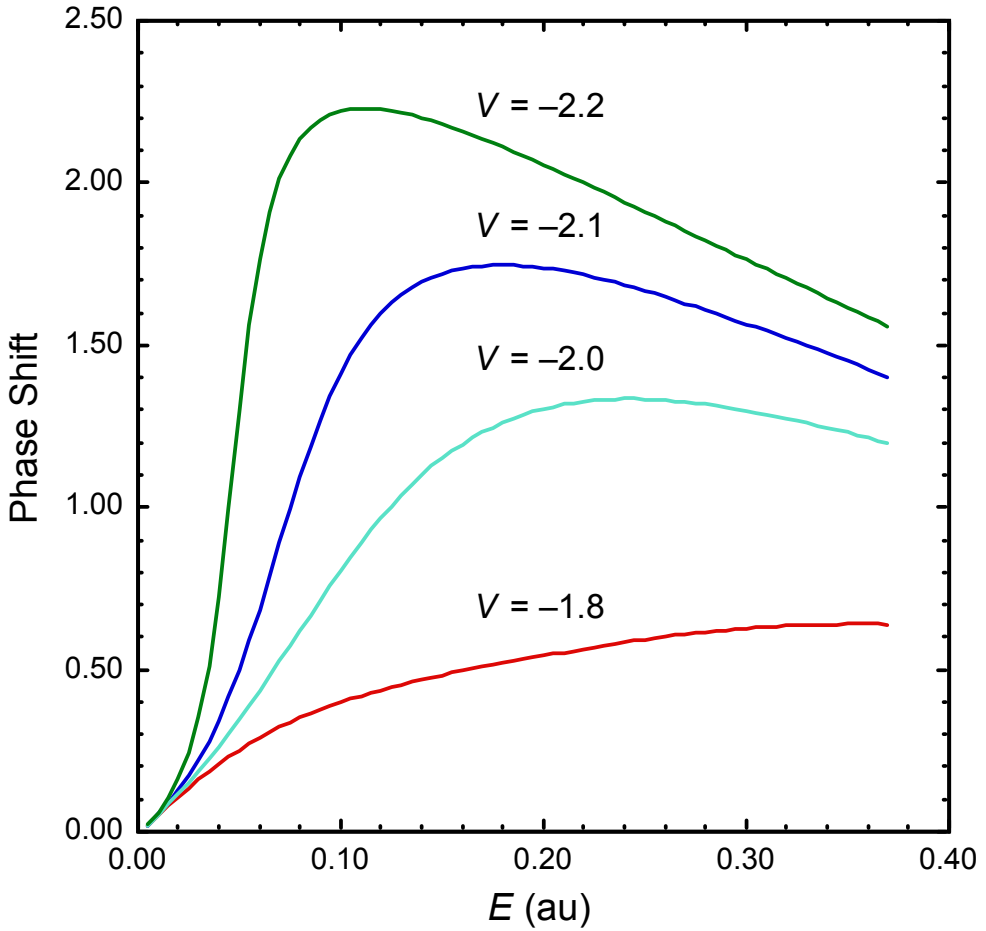
Model Potential with *l* = 2



Resonance Trajectory



Phase Shift Near a Resonance



Rising phase shift indicates a time delay in the scattering process

Model Potential

- Potential includes
  - The static potential
  - The Perdew-Zunger DFT correlation potential
  - The Hara free-electron-gas exchange (FEGE) potential
- We use approximate FEGE potential with no energy dependence.

$$V_{\mathrm{ex}}^{\mathrm{FEGE}}(\vec{r}) = \frac{2}{\pi} k_F(\vec{r}) \left(\frac{1}{2} + \frac{1-\eta^2}{4\eta} \ln \left| \frac{1+\eta}{1-\eta} \right| \right)$$

$$\eta(\vec{r}) = \left(k^2 + 2I_p + k_F(\vec{r}) \right)^{1/2} \Big/ k_F(\vec{r}) \quad \text{and} \quad k_F(\vec{r}) = \left(3\pi^2 \rho(\vec{r}) \right)^{1/3}$$

Adiabatic Angular Functions

- Full scattering equation

$$\left[\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + k^2\right] f_i(r) = \sum_j V_{ij}(r) f_j(r)$$

- Adiabatic angular functions Z, where X_i is a symmetry adapted spherical harmonic.

$$Z_p(\theta,\phi,r) = \sum_i X_i(\theta,\phi) C_{i,p}(r)$$

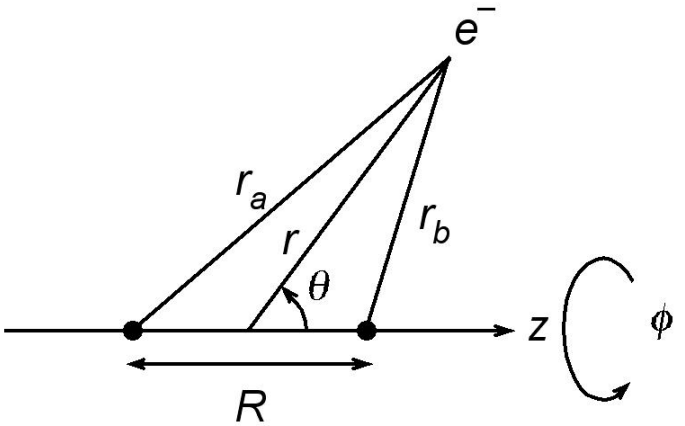
$$\sum_j \left[V_{ij}(r) + \delta_{ij}\frac{l_i(l_i+1)}{r^2}\right] C_{jp}(r) = C_{ip}(r) V_p^A(r)$$

Confocal Elliptic Coordinates

- Confocal elliptic coordinates provide the natural coordinate system for diatomic molecules

$$\xi = \frac{r_a + r_b}{R} \rightarrow \frac{2}{R} r \quad 1 \le \xi \le \infty$$

$$\eta = \frac{r_a - r_b}{R} \rightarrow \cos(\theta) \quad -1 \le \eta \le 1$$

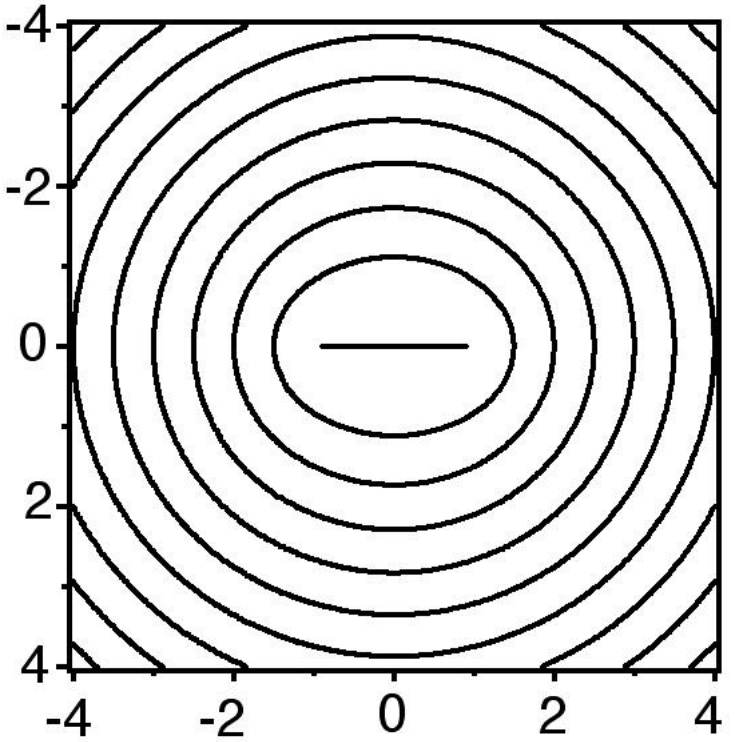


- For H_2^+ this leads to a wave function which is a product of functions of each coordinate

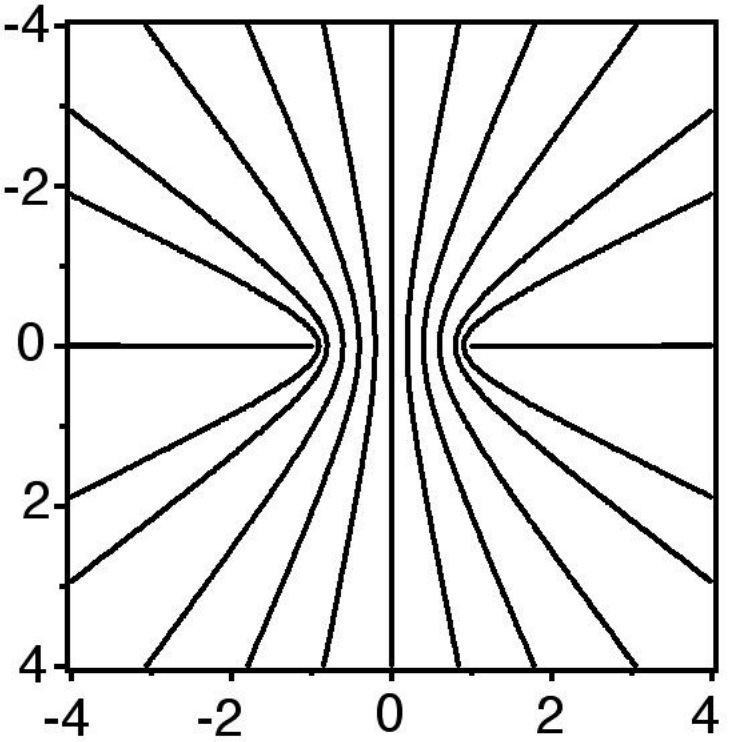
$$\psi(\xi, \eta, \phi) = L(\xi) M(\eta) \Phi(\phi)$$

R. W. Zurales, Ph. D. thesis, Texas A&M University, 1997.

Confocal Elliptic Nodes

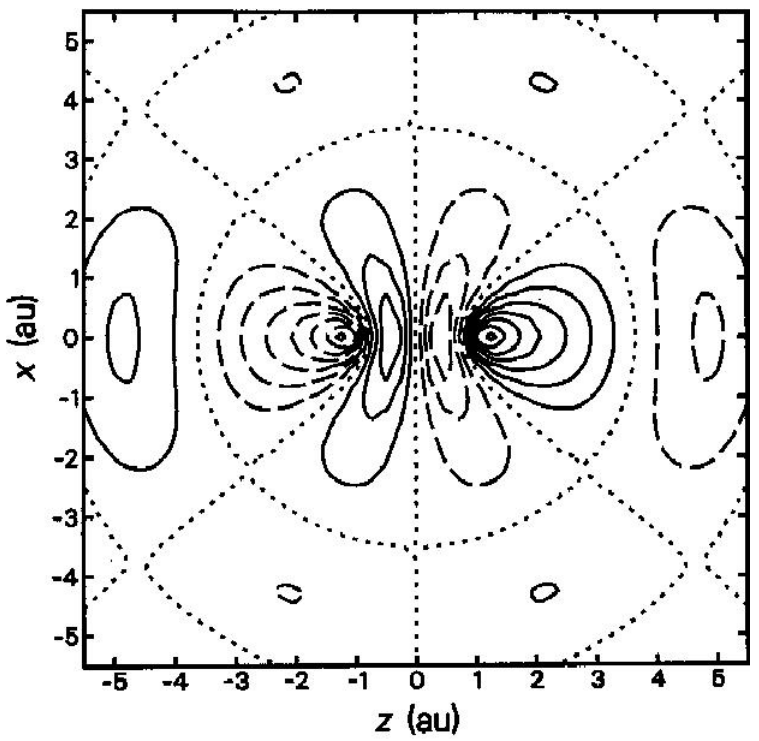


ξ Nodes



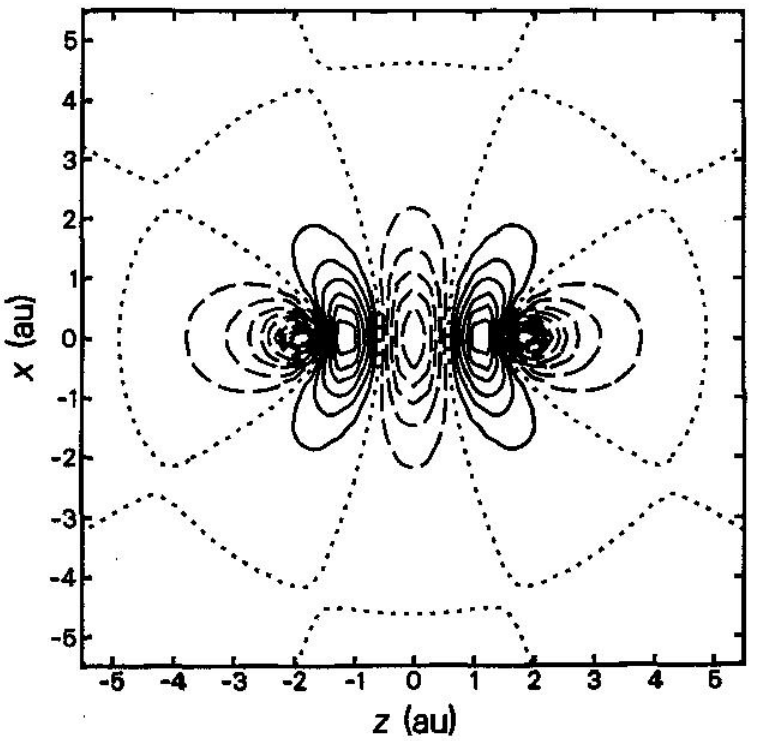
η Nodes

m = 0 Shape Resonances



N_2 σ_u l=3

Typical σ^* state

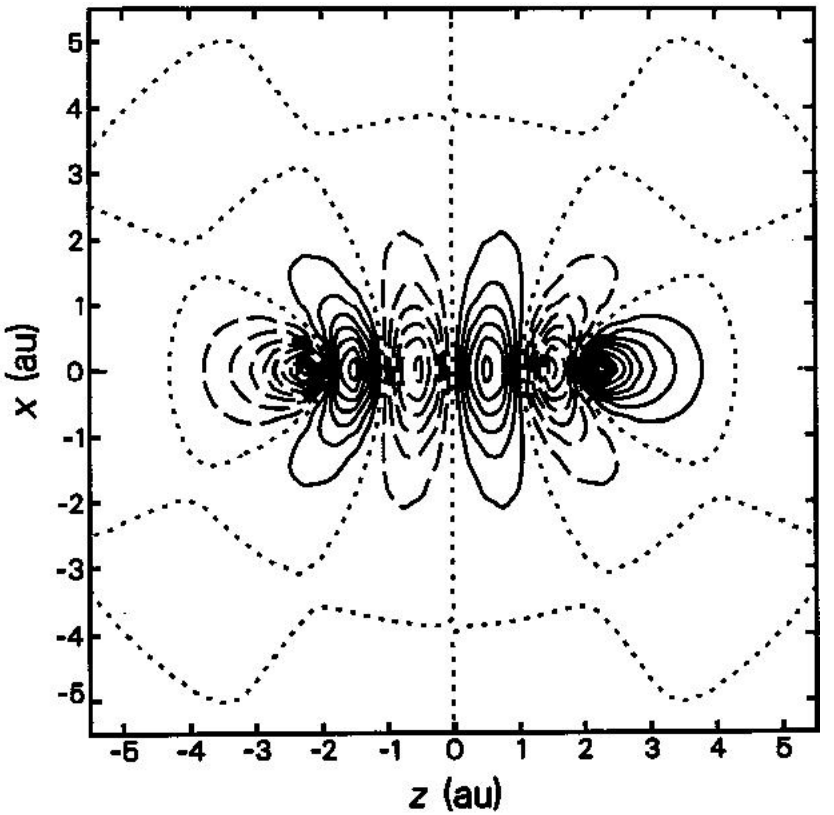


F_2 σ_g l=4

Non-valence resonant state

m = 0 Shape Resonances

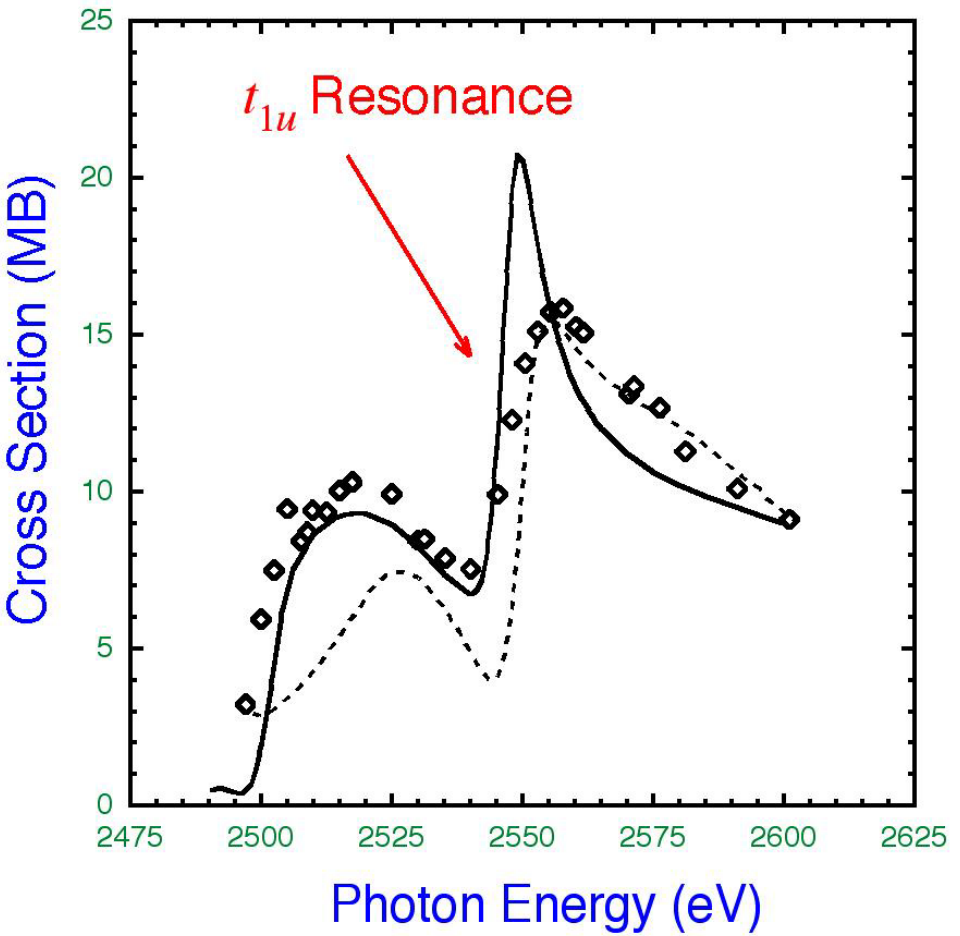
- Confocal coordinates can also be in polyatomic linear molecules
- Expected σ^* anti-bonding resonant state



CO_2 σ_u l=5

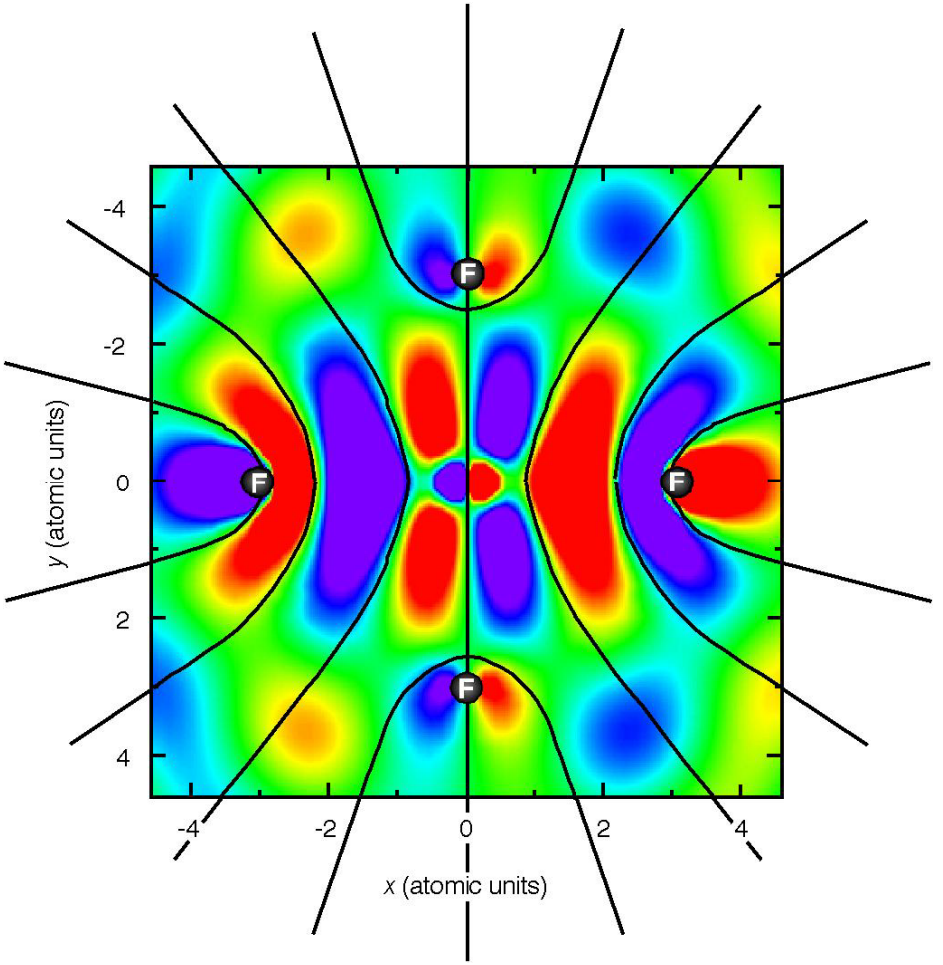
SF_6 $(1s)^{-1}$ Photoionization

- Are the confocal elliptic coordinates useful in non-linear systems?
- Shape resonance at a kinetic energy of 65 eV
- Due to a high angular momentum barrier



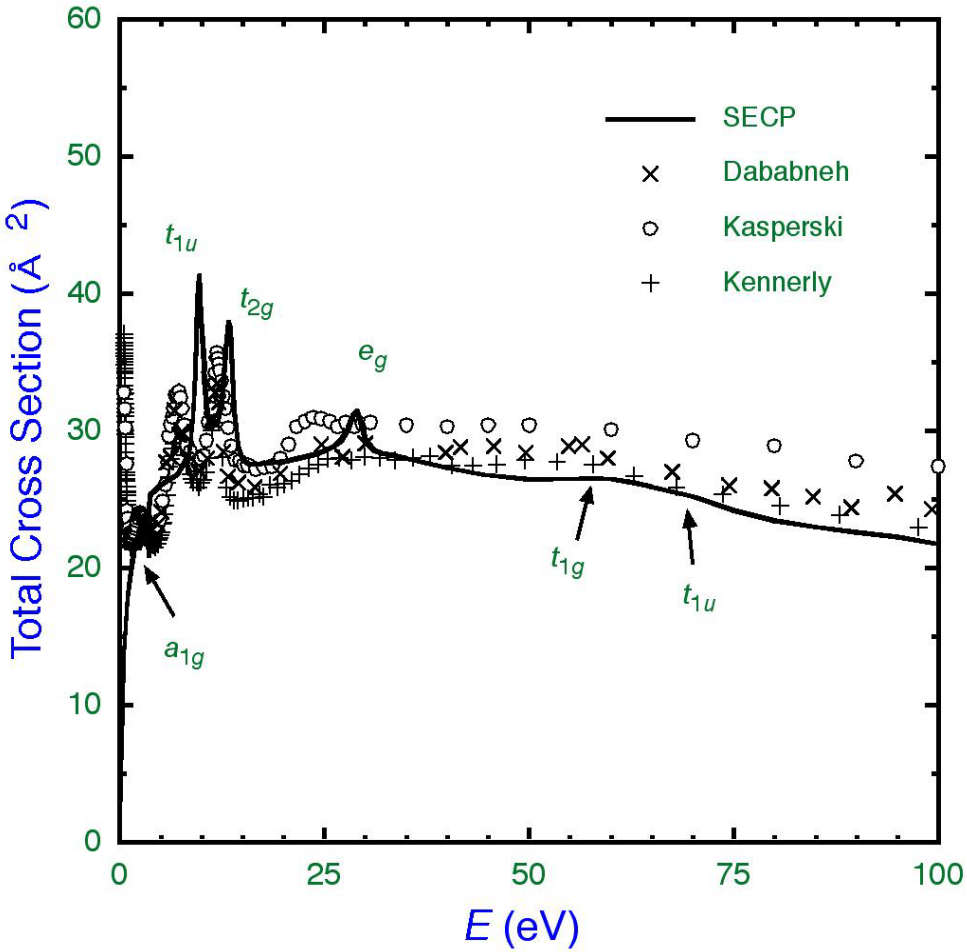
SF_6 S1$s \rightarrow t_{1u}$ Resonance at 2547 eV

- Resonant state in the plane of four of the F atoms
- Nodal lines correspond to $l = 9$ just outside the F atoms
- The tight 1*s* has a strong oscillator strength to excite this state as an *s* to *p* transition near the S atom



Electron Scattering from SF_6

- At low energy are the well known valence resonances
- At high energy are two non-valence resonances
- Much less prominent than in 1*s* photoionization



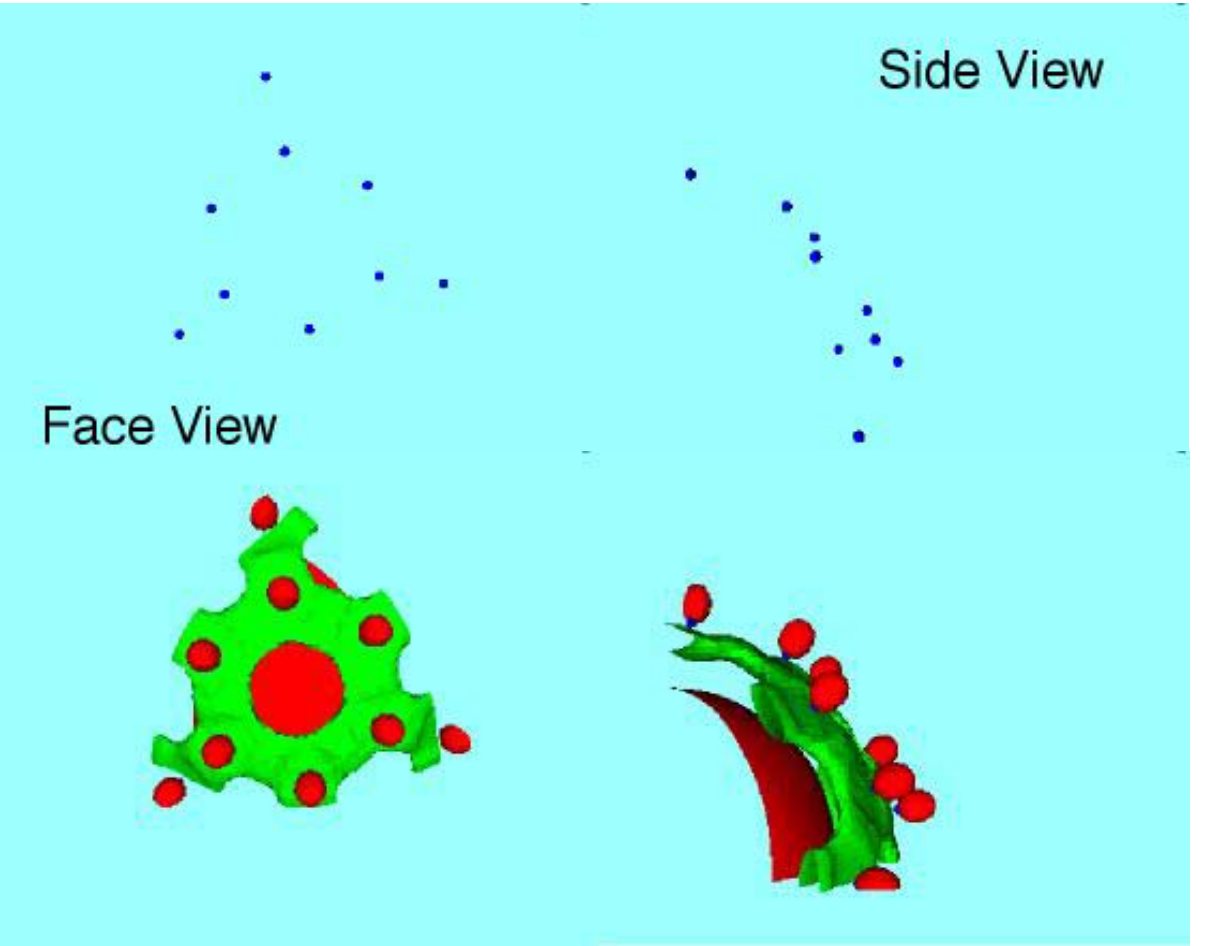
Resonances in e – C_{60} Scattering

- The adiabatic model (AM) potential yields resonance parameters that correspond to the parameters of the resonances in the full scattering potential. (All energies in eV)

Sym	E_R Full	Γ Full	E_R AM	Γ AM
h_u	2.17	0.003	3.98	0.078
a_g	2.76	0.52	3.23	0.23

a_g Resonance in e – C_{60}

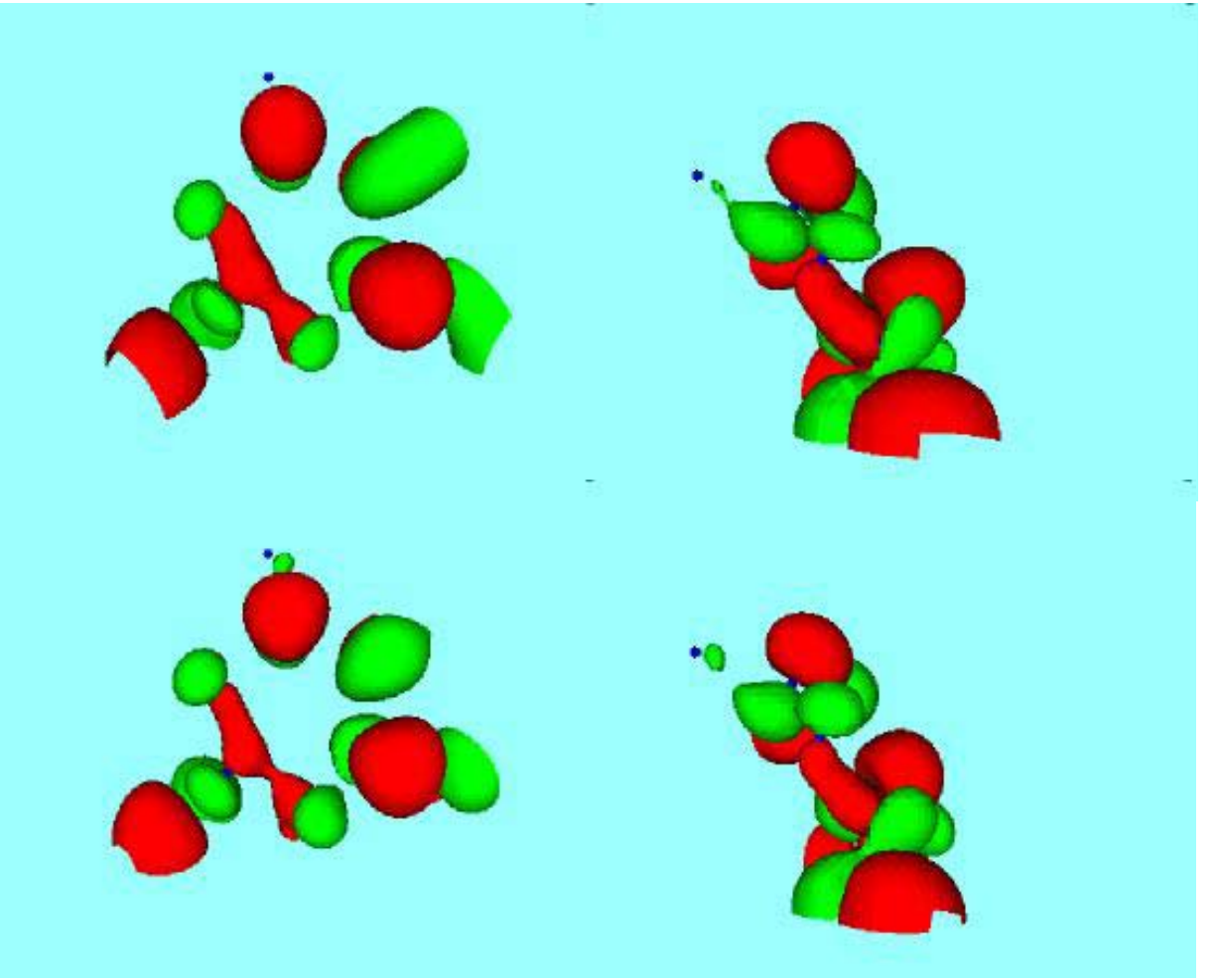
AM
E = 3.2 eV
Γ= 0.23 eV



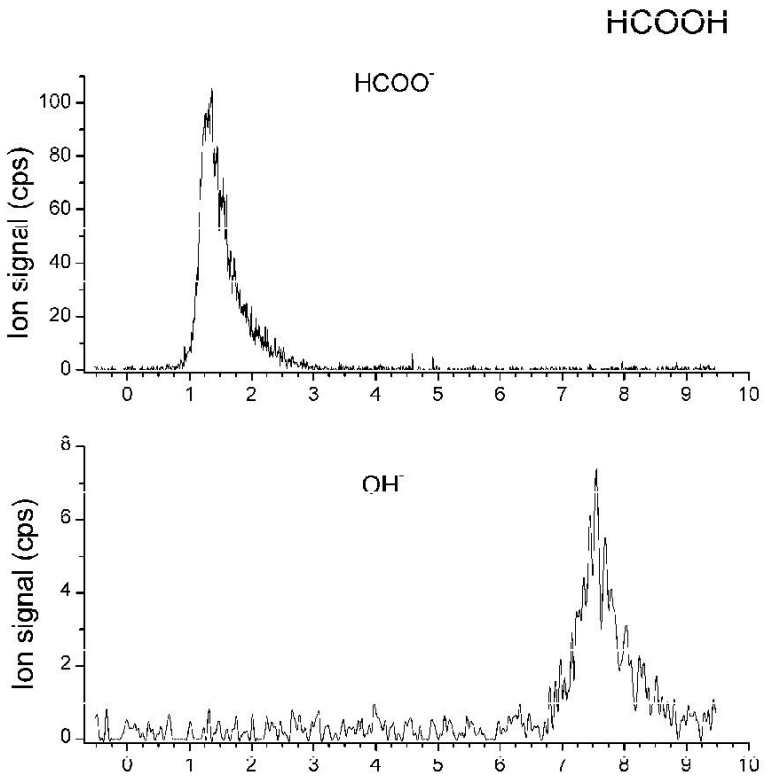
h_u Resonance in e – C_{60}

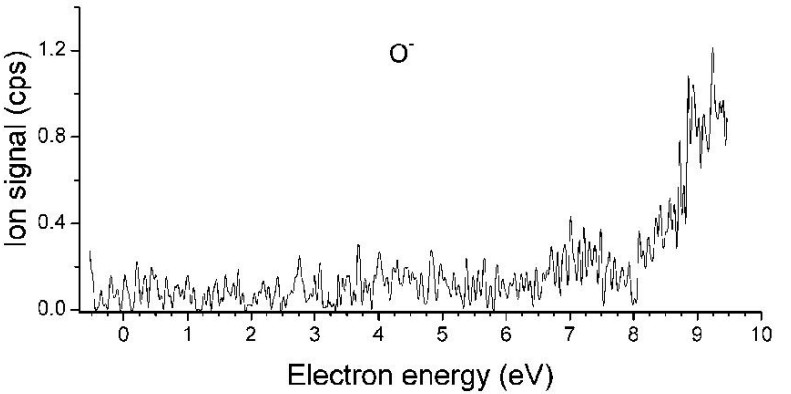
AM
E = 4.0 eV
Γ= 0.078 eV

MBS-SCF
E = 8.8 eV



Experimental Data for *e* – Formic Acid

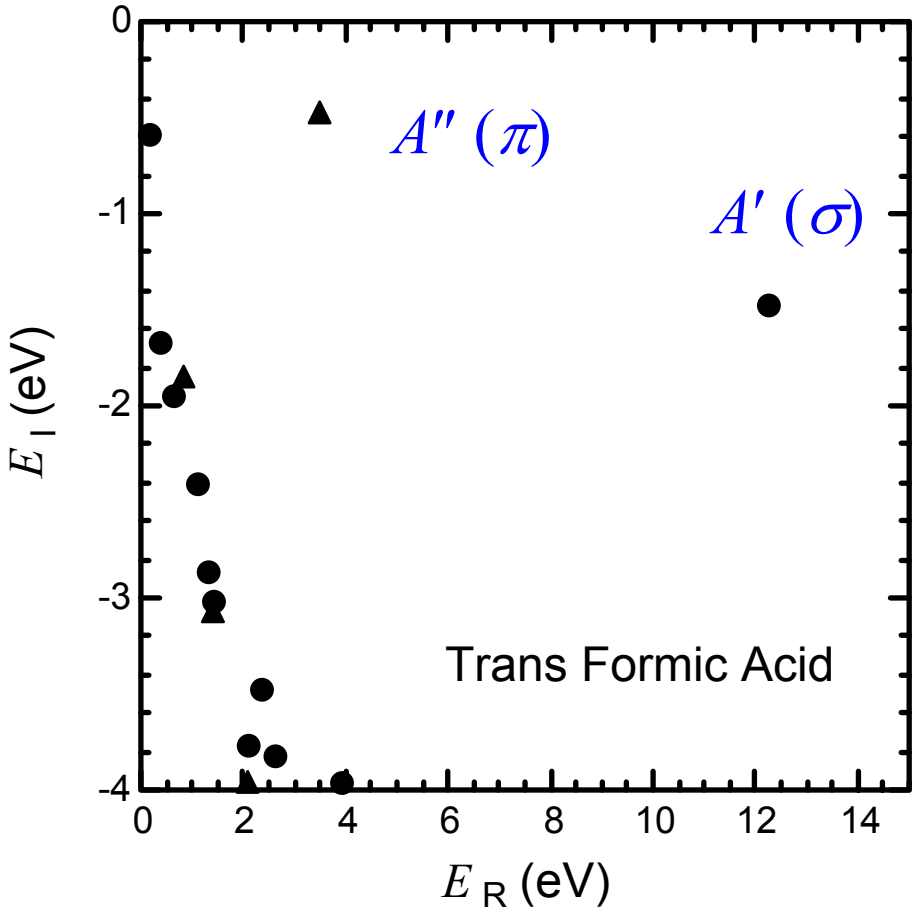




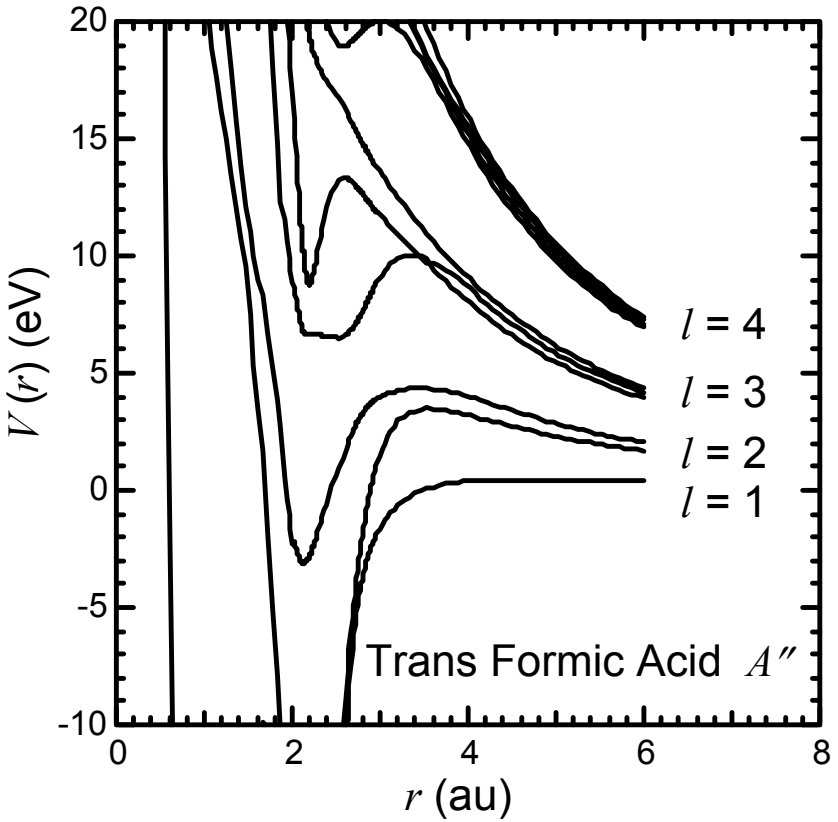
1.25 eV	Loss of H
7.5 eV	Loss of OH^-

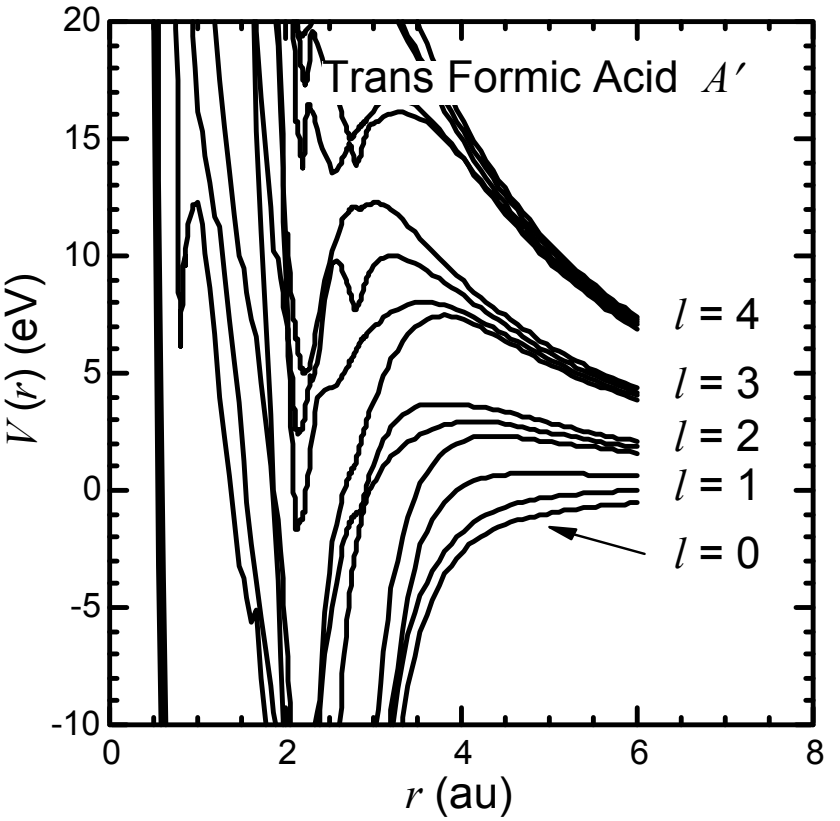
A. Pelc, Chem. Phys. Lett. 361, 277 (2002)

Location of the Poles of *S* in *e* – Formic Acid



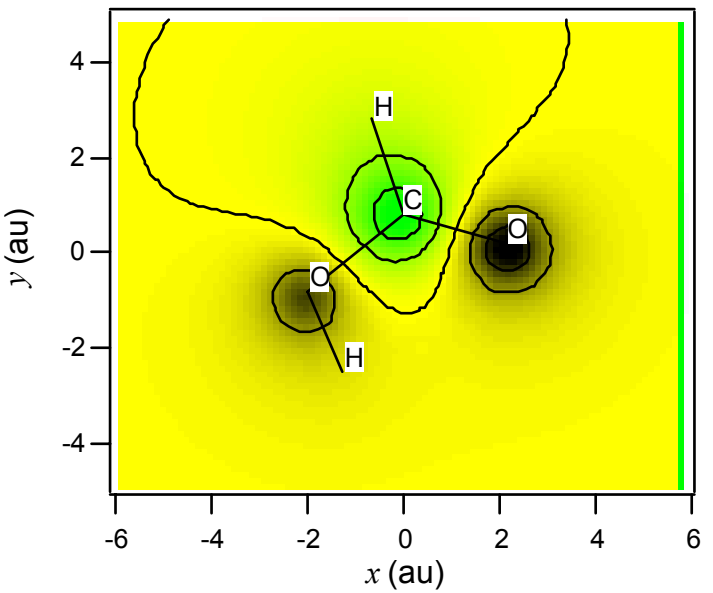
Adiabatic Model Potential in *e* – Formic Acid



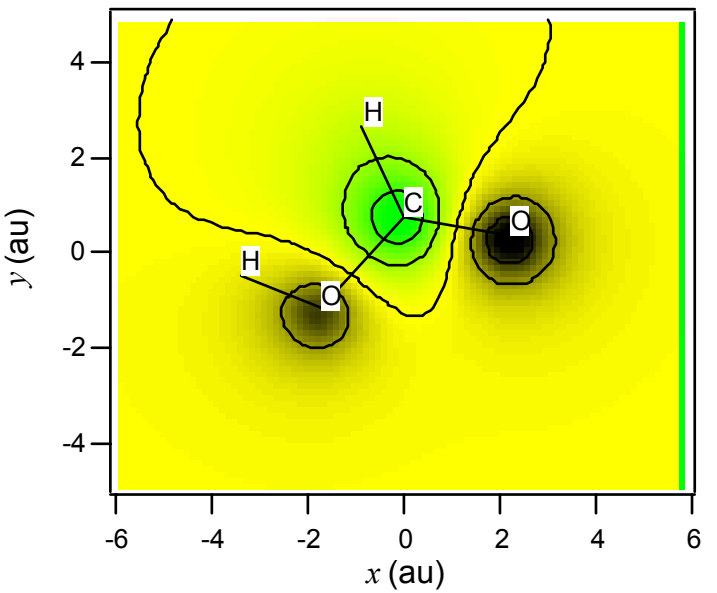


Low Energy A″ (π) Resonance in *e* – Formic Acid

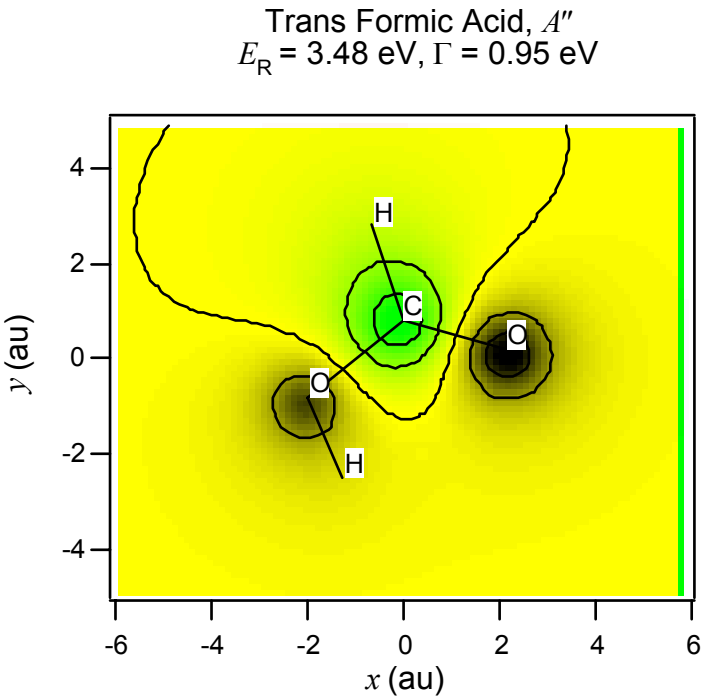
Trans Formic Acid, A''
E_R = 3.48 eV, Γ = 0.95 eV

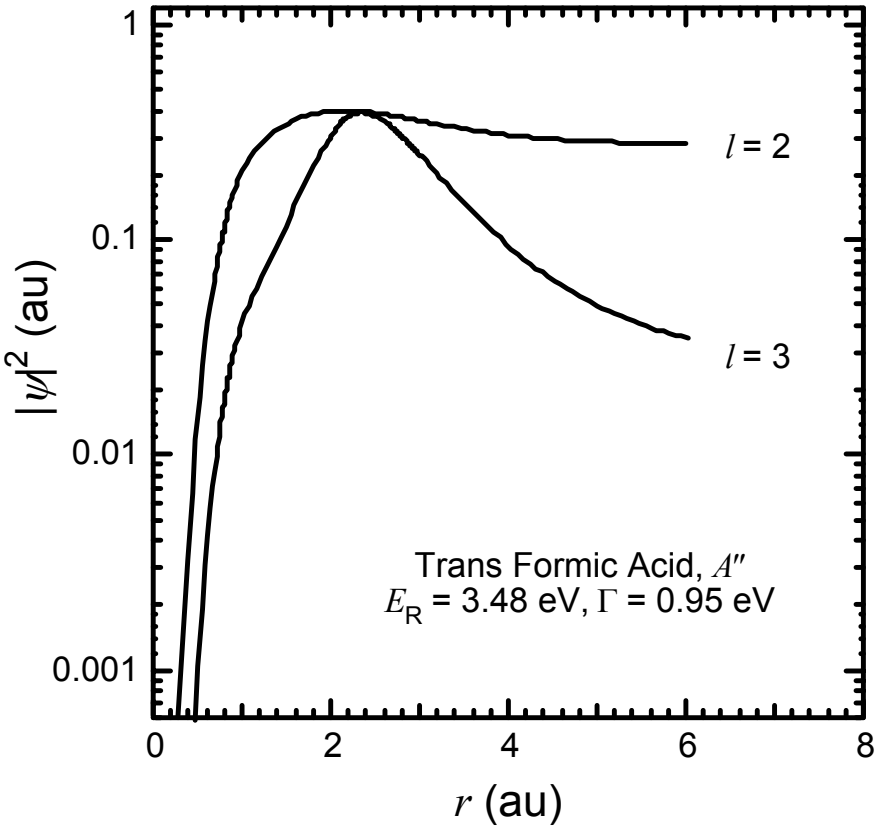


Cis Formic Acid, A''
E_R = 3.49 eV, Γ = 0.93 eV



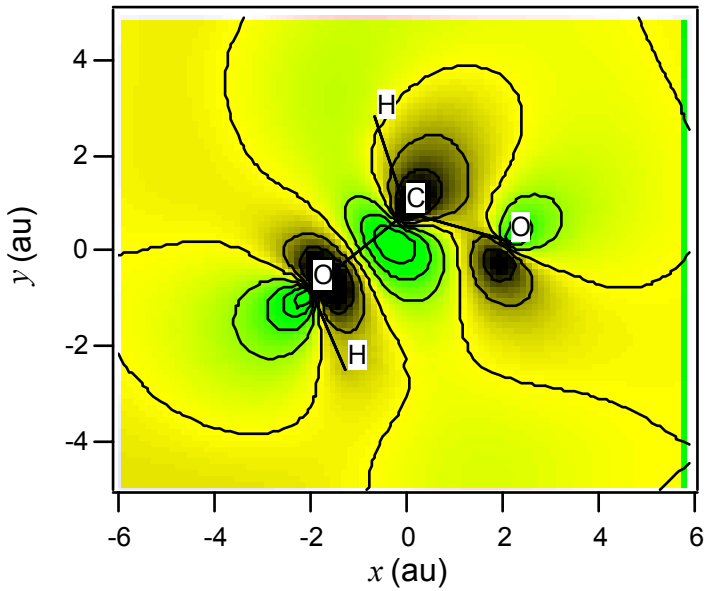
Low Energy A″ (π) Resonance in *e* – Formic Acid



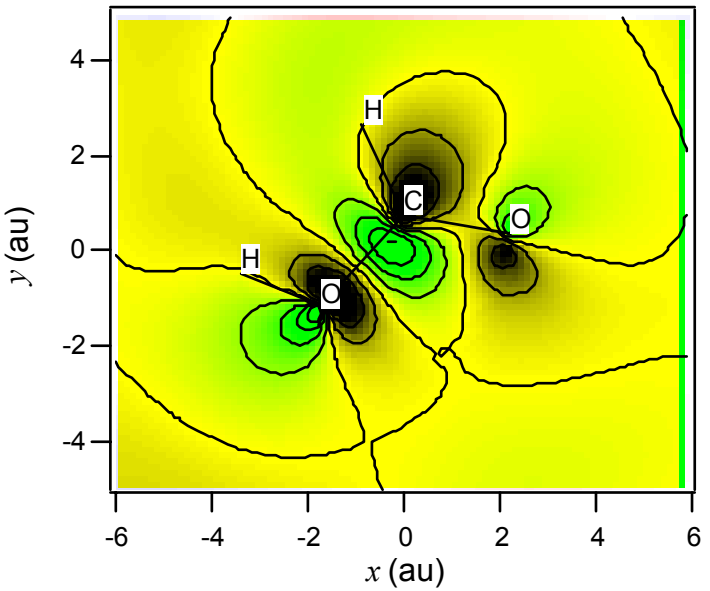


High Energy $A'(\sigma)$ Resonance in e – Formic Acid

Trans Formic Acid, A'
E_R = 12.26 eV, Γ = 2.94 eV

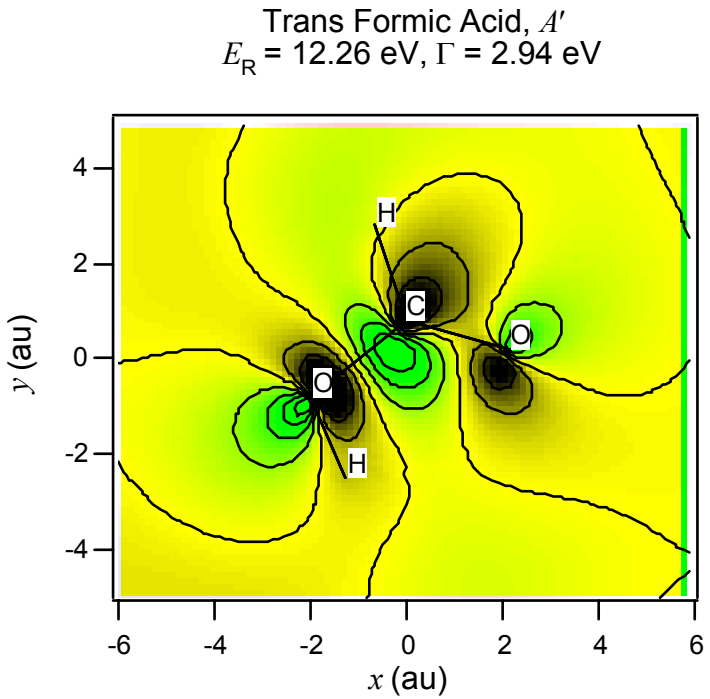


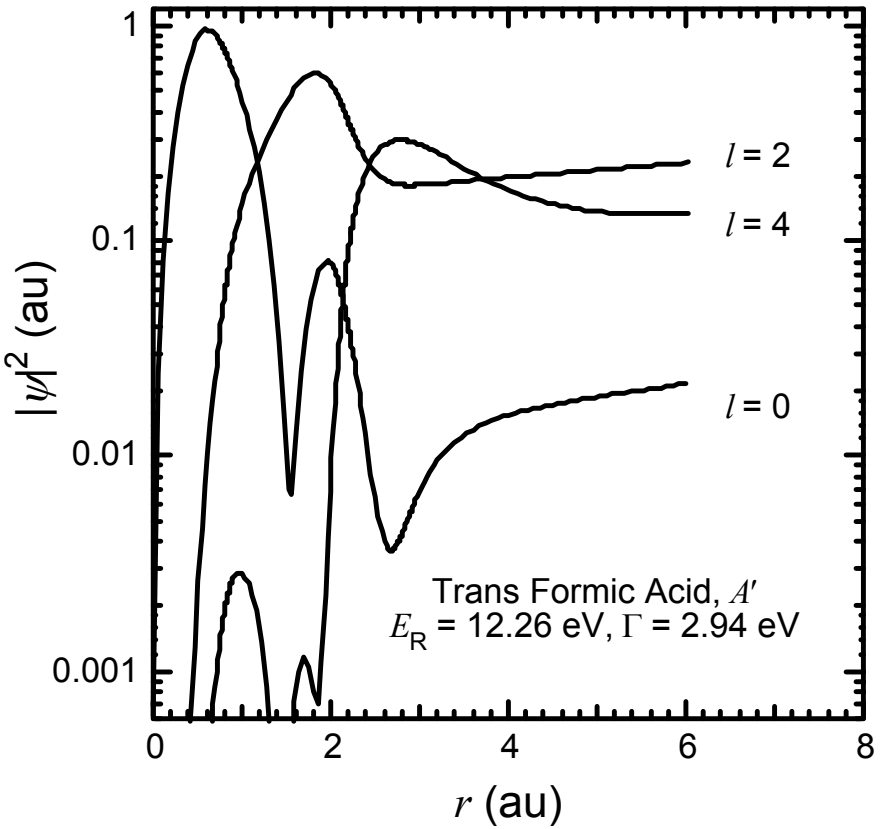
Cis Formic Acid, A'
E_R = 11.98 eV, Γ = 3.35 eV



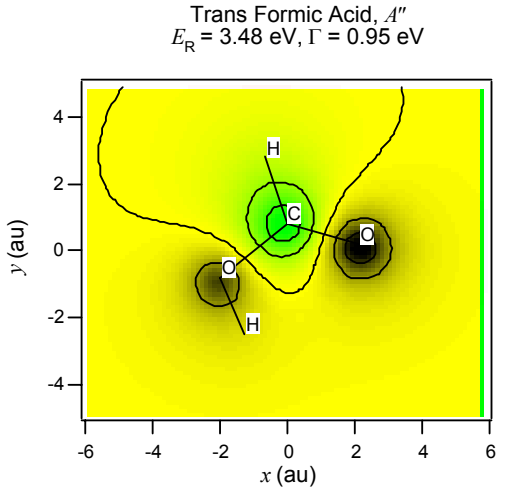
Strong C-O σ antibonding character could lead to loss of OH^-

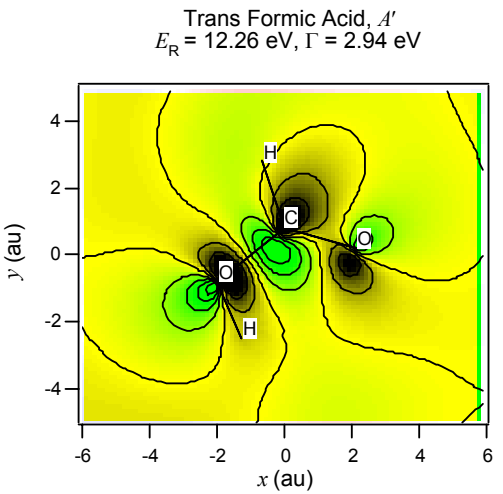
High Energy $A'(\sigma)$ Resonance in e – Formic Acid



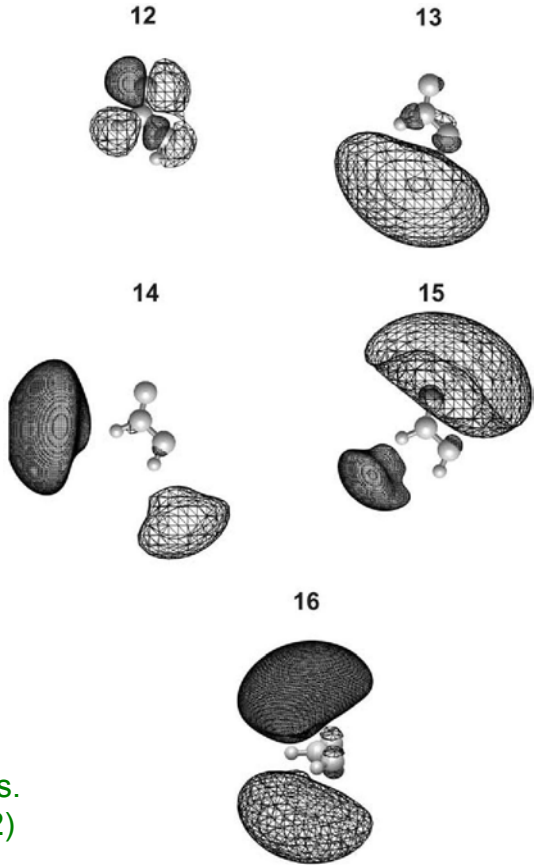


Comparison With Virtual Orbitals





MOs from aug-cc-pVTZ basis set

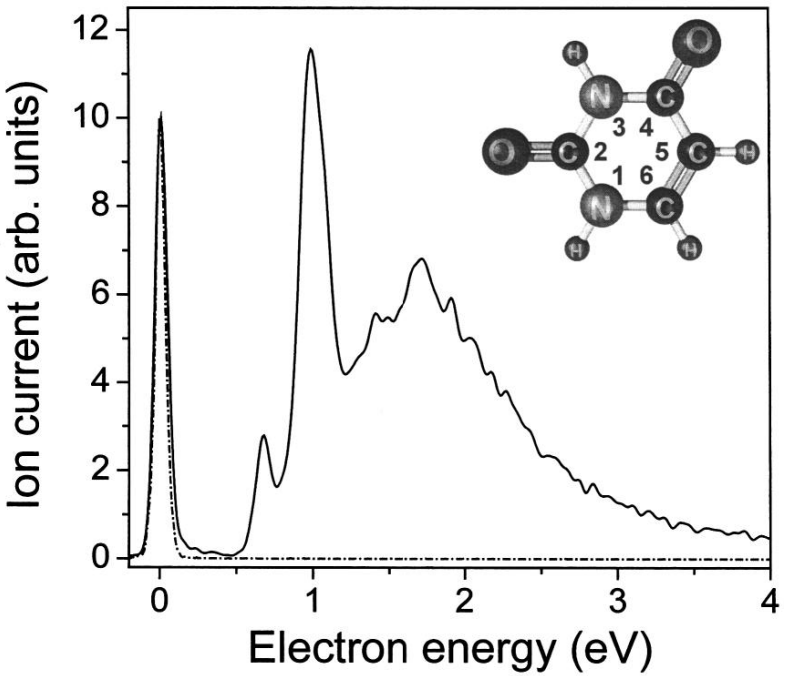


A. Pelc, Chem. Phys. Lett. 361, 277 (2002)

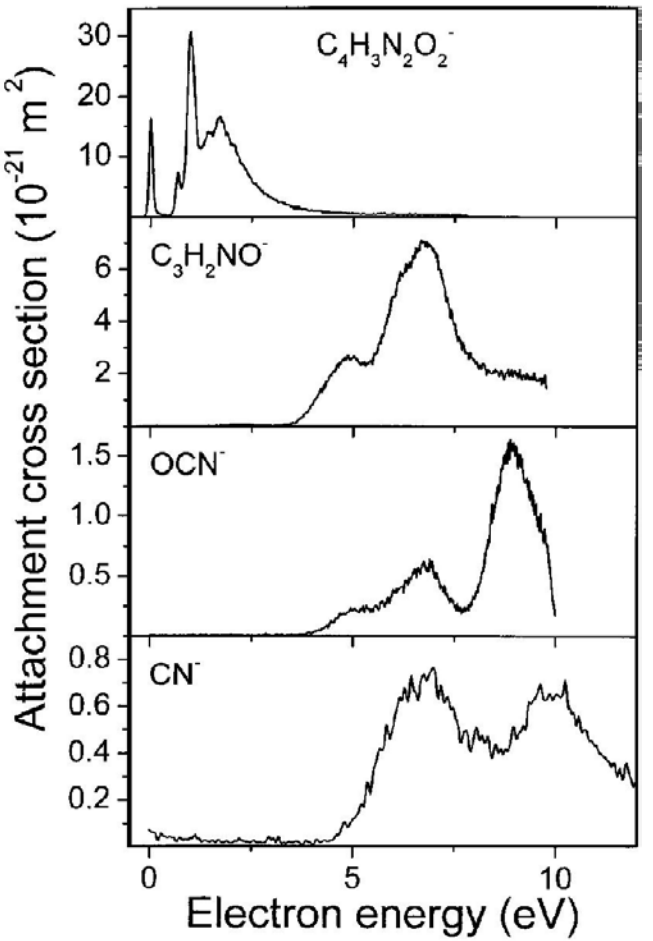
Summary for *e* – Formic Acid

- Loss of H in low energy resonance is due to A'' (π) resonance through indirect fragmentation.
- Loss of OH^- is due to A' (σ) resonance and direct fragmentation.
- Diffuse basis sets lead to virtual orbitals that do not represent resonant states.

e – Uracil Experiments

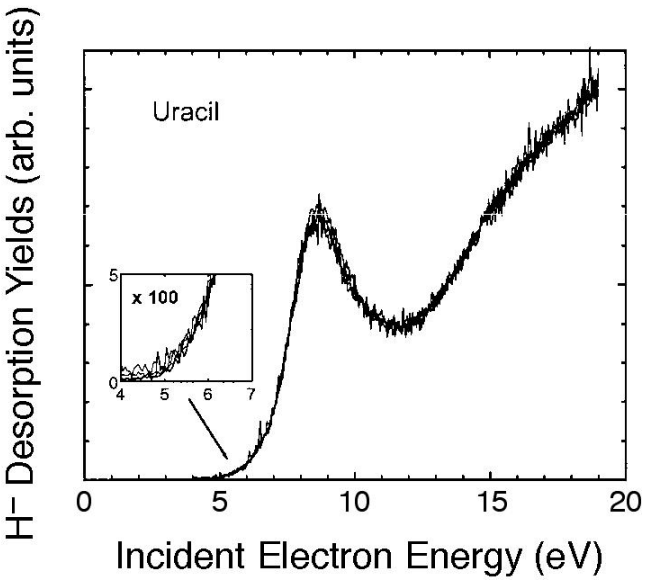


Gas phase ion yields



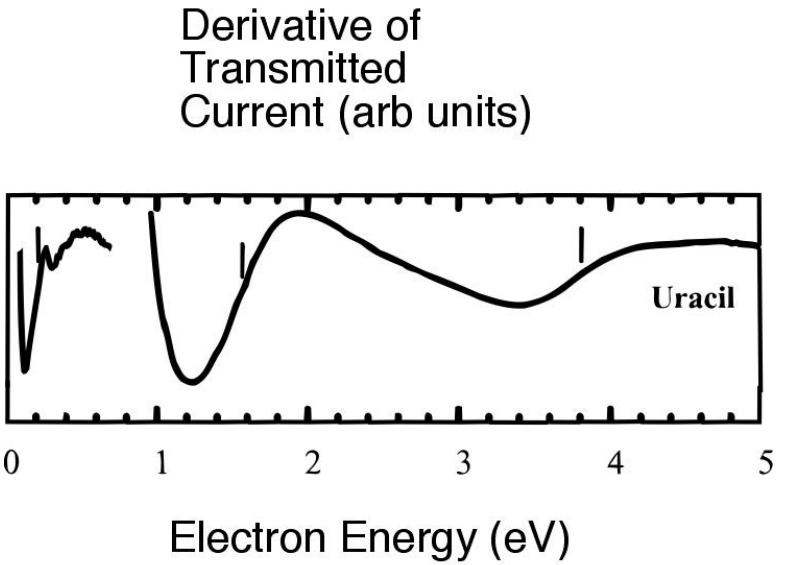
G. Hanel et al., Phys. Rev. Lett. 90, 188104(2003)

e – Uracil Experiments



H^- from Uracil on Pt

M. A. Herve du Penhoat et al.,
J. Chem. Phys. 114,5755(2001).



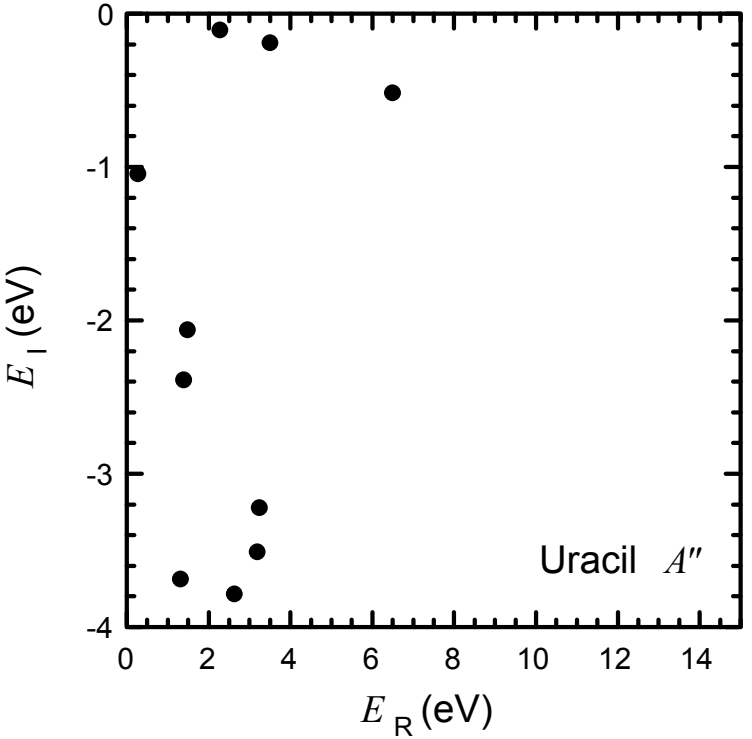
Gas phase electron transmission spectroscopy (ETS)

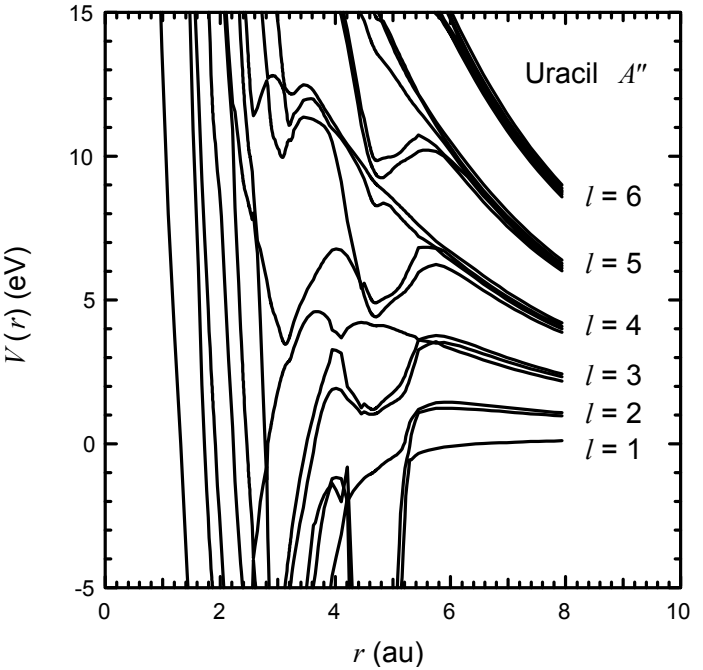
K. Aflatooni et al., J. Phys. Chem. A 102, 6205 (1998).

Summary of Experimental Data

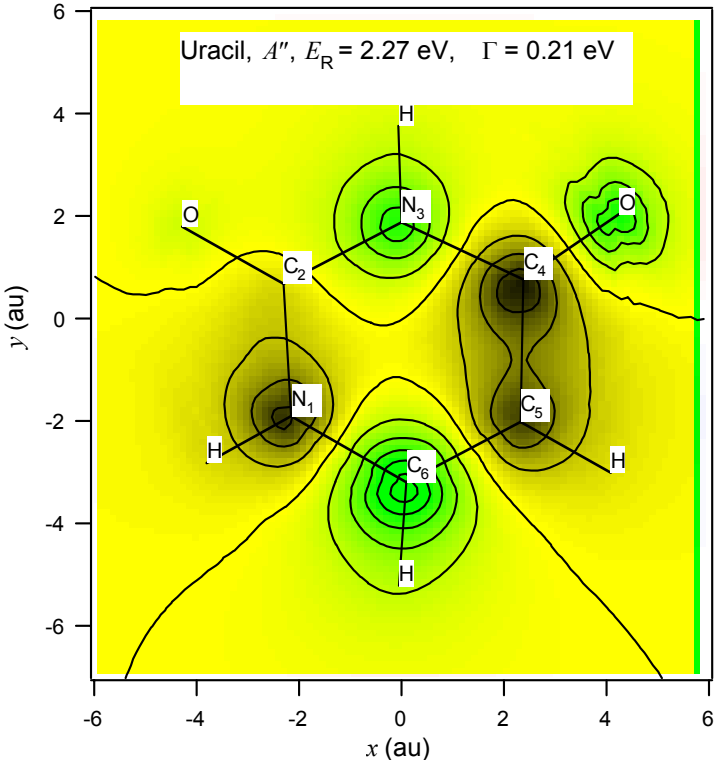
1-3 eV	Loss of H
3.8 eV	Only in ETS
5 eV	Loss of OCN^-, $OCNH_2$
7 eV	Loss of OCN^-, $OCNH_2$, CN^-
10 eV	Loss of OCN^-, CN^-, H^- (in solid)

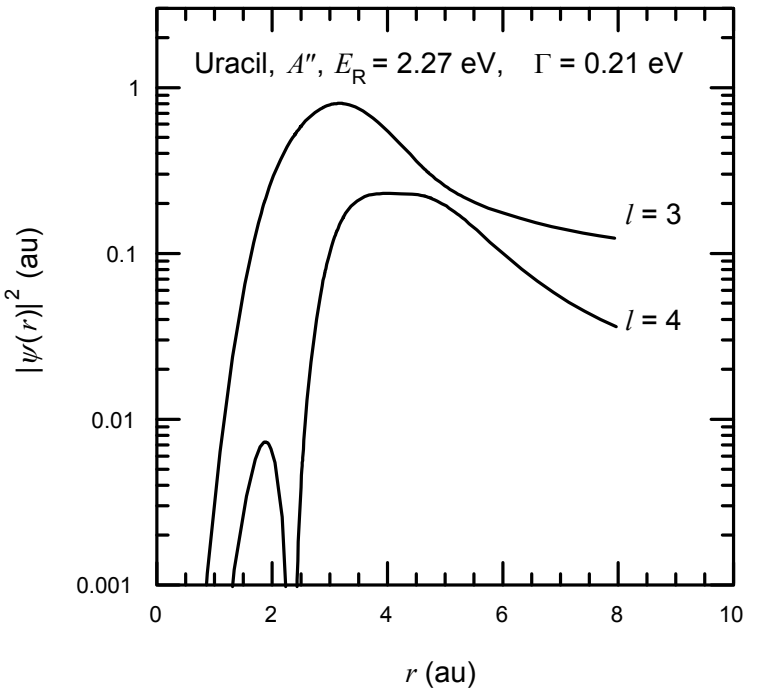
e – Uracil A″ (π) Resonance Poles



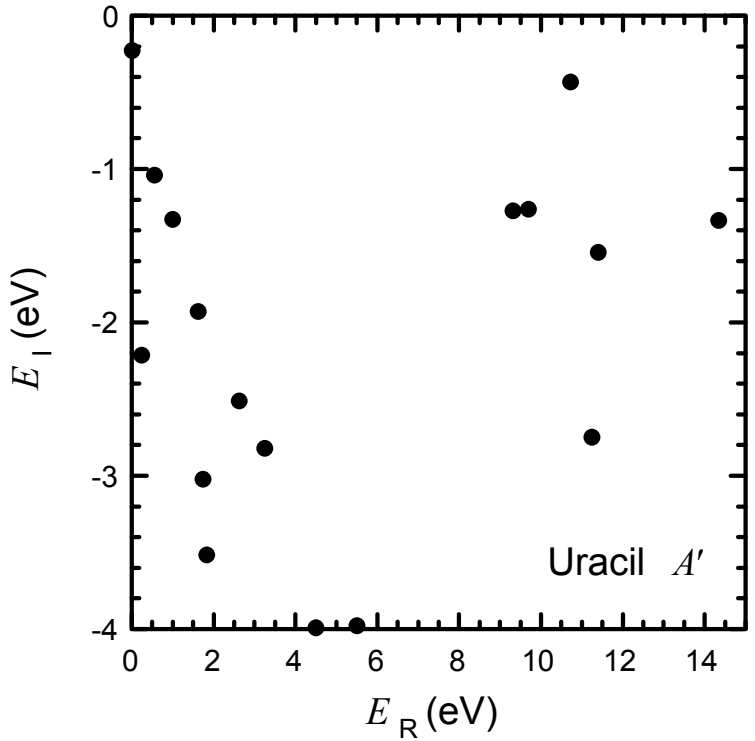


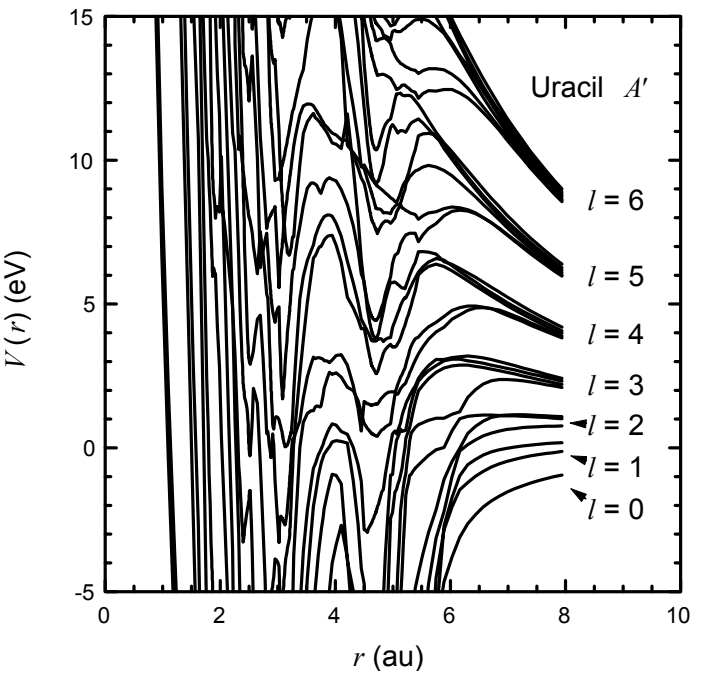
e – Uracil A″ (π) Resonances



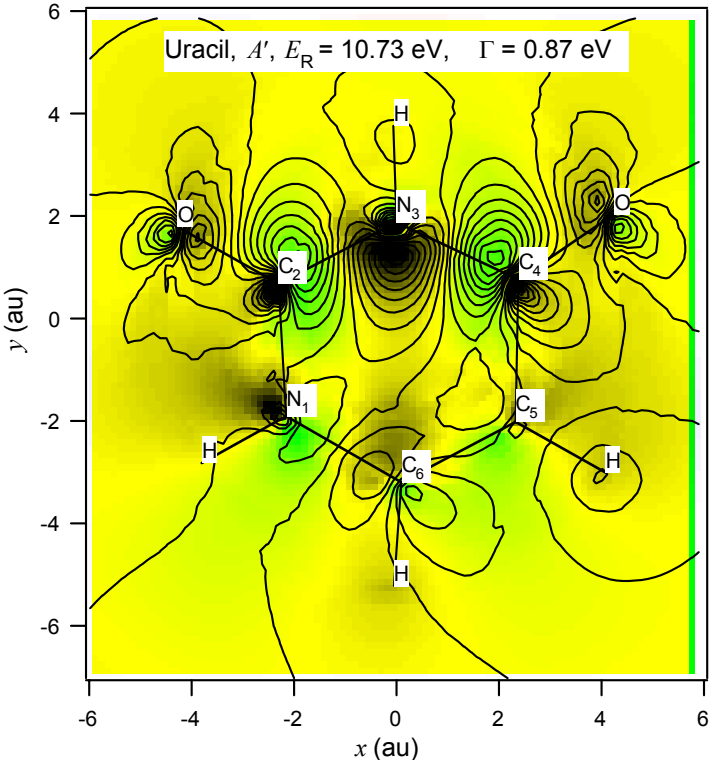


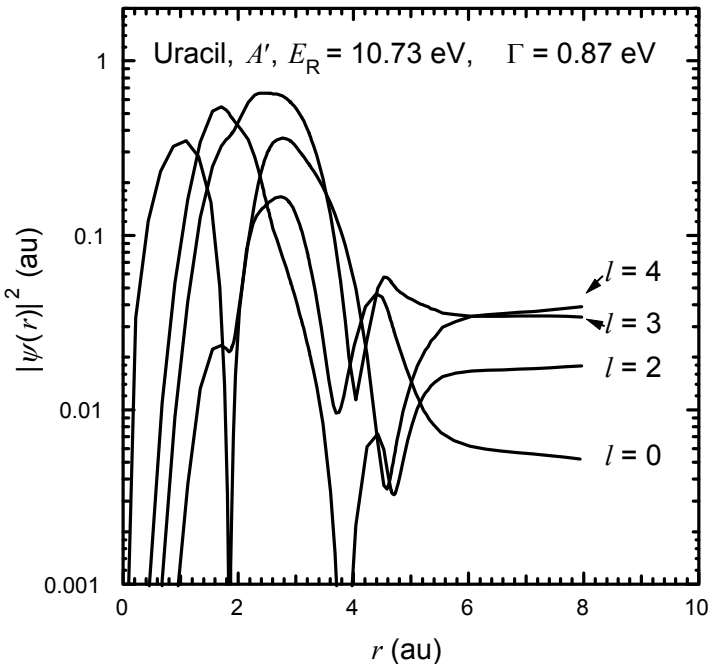
e – Uracil $A'(\sigma)$ Resonance Poles



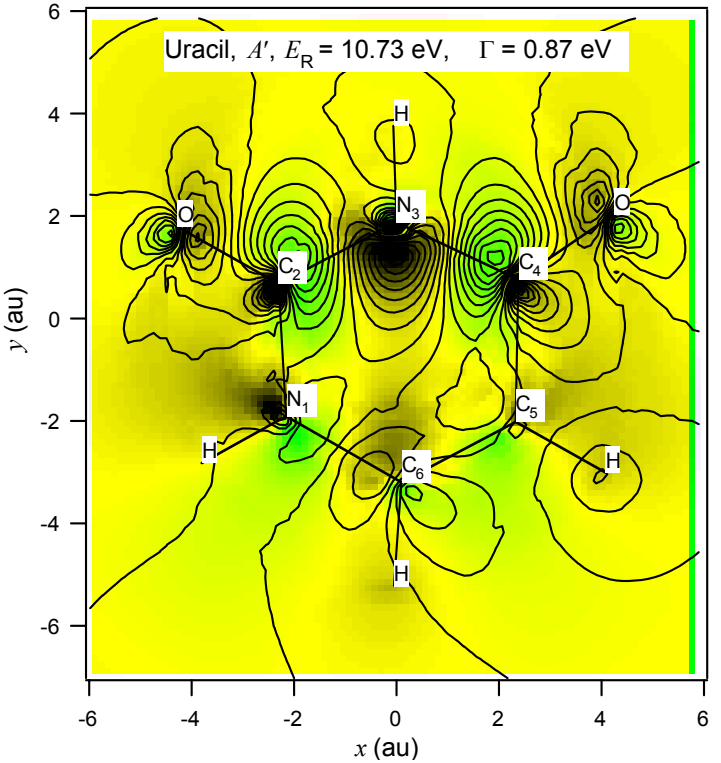


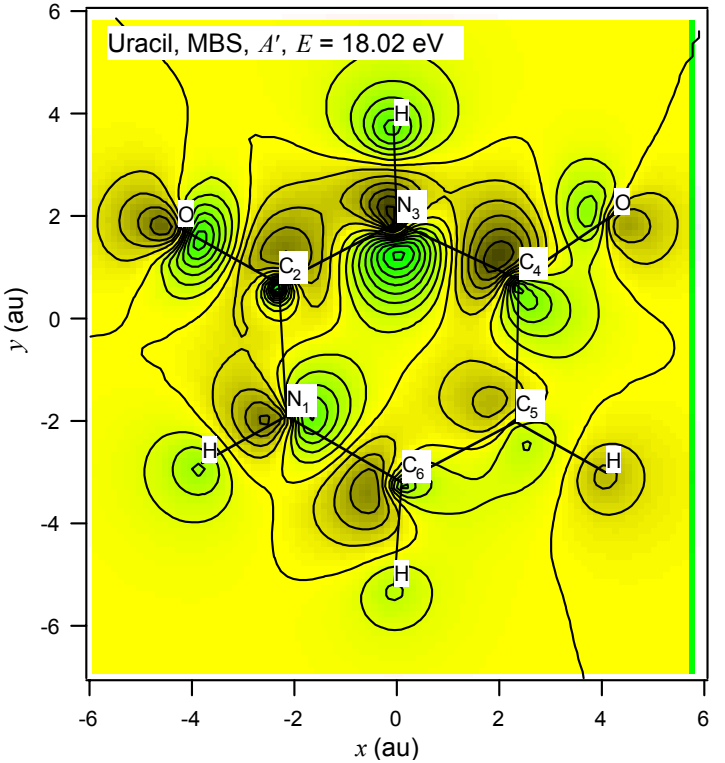
e – Uracil $A'(\sigma)$ Resonance





e – Uracil $A'(\sigma)$ MBS States

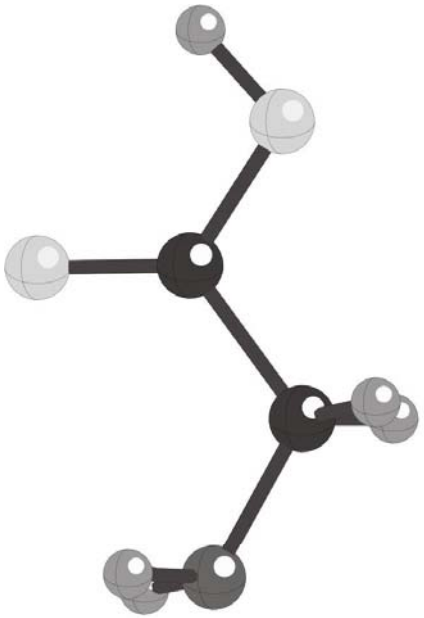




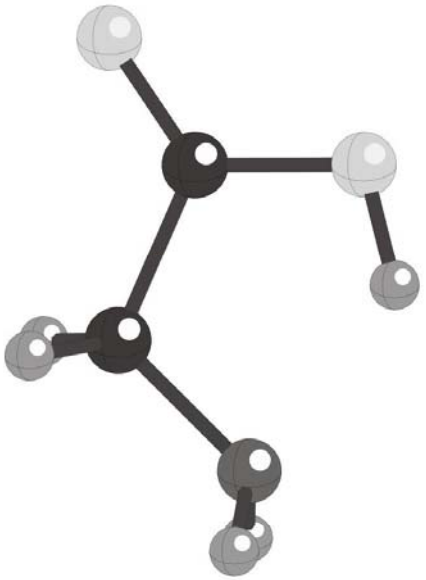
Summary for *e* – Uracil

- Low energy resonances seen in TES and H loss reactions are due to *A″* (π) resonances.
- The high energy *A′* (σ) resonance may be responsible for at least one of the DEA peaks seen.
- Strong antibonding character in the C_2–N_3 and N_3–C_4 bonds may induce first step in fragmentation process needed to obtain observed products.

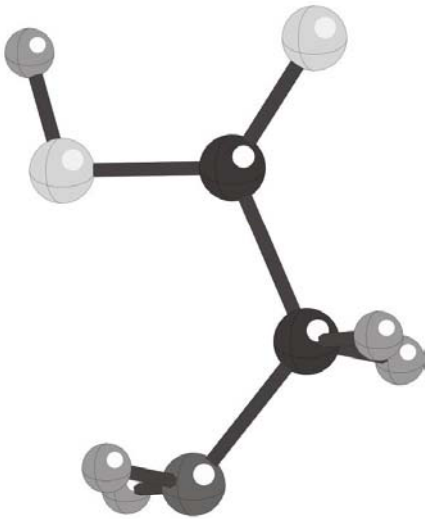
Glycine Geometries



Geometry I

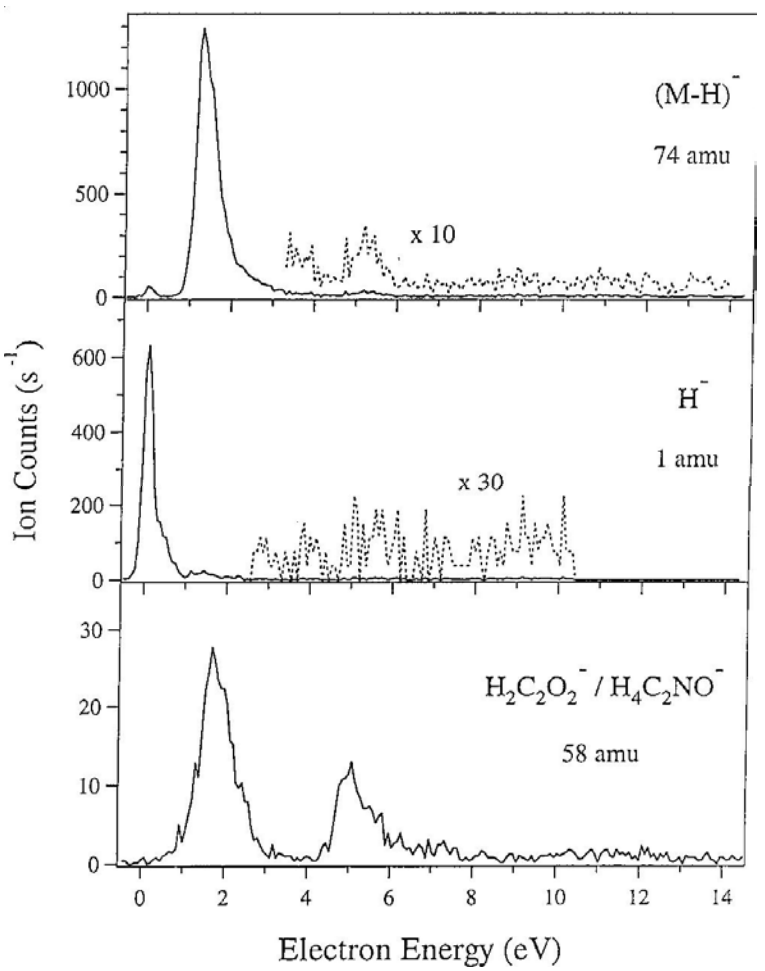


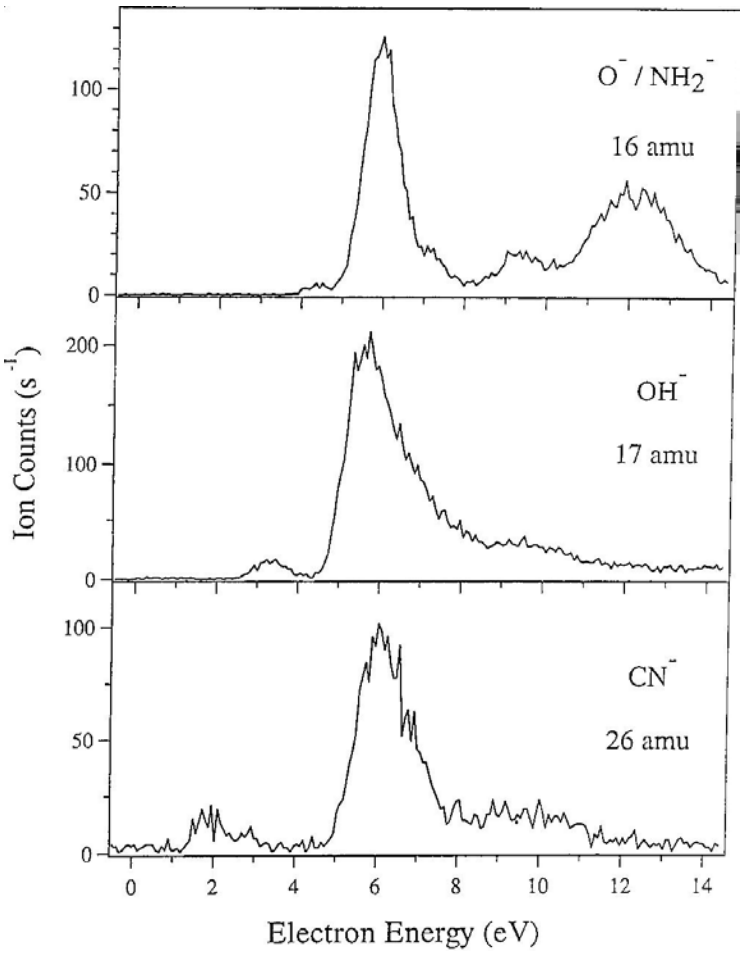
Geometry II



Geometry III

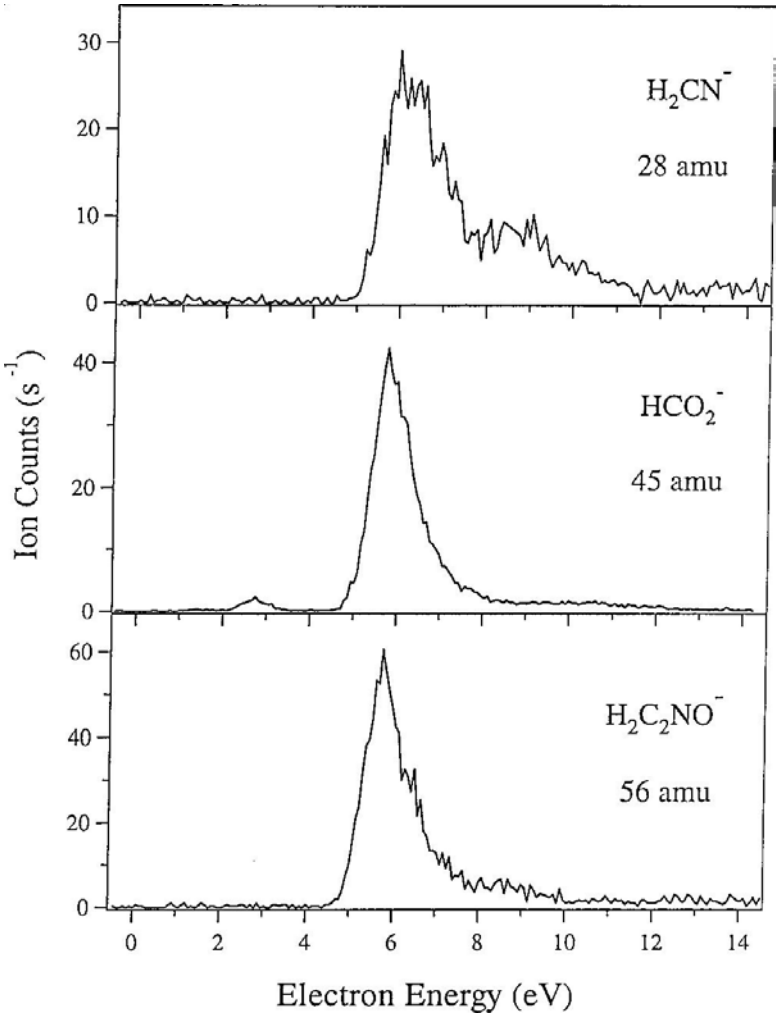
e – Glycine Experiments





S. Gohlke, J. Chem. Phys. 116, 10164 (2002)

e – Glycine Experiments

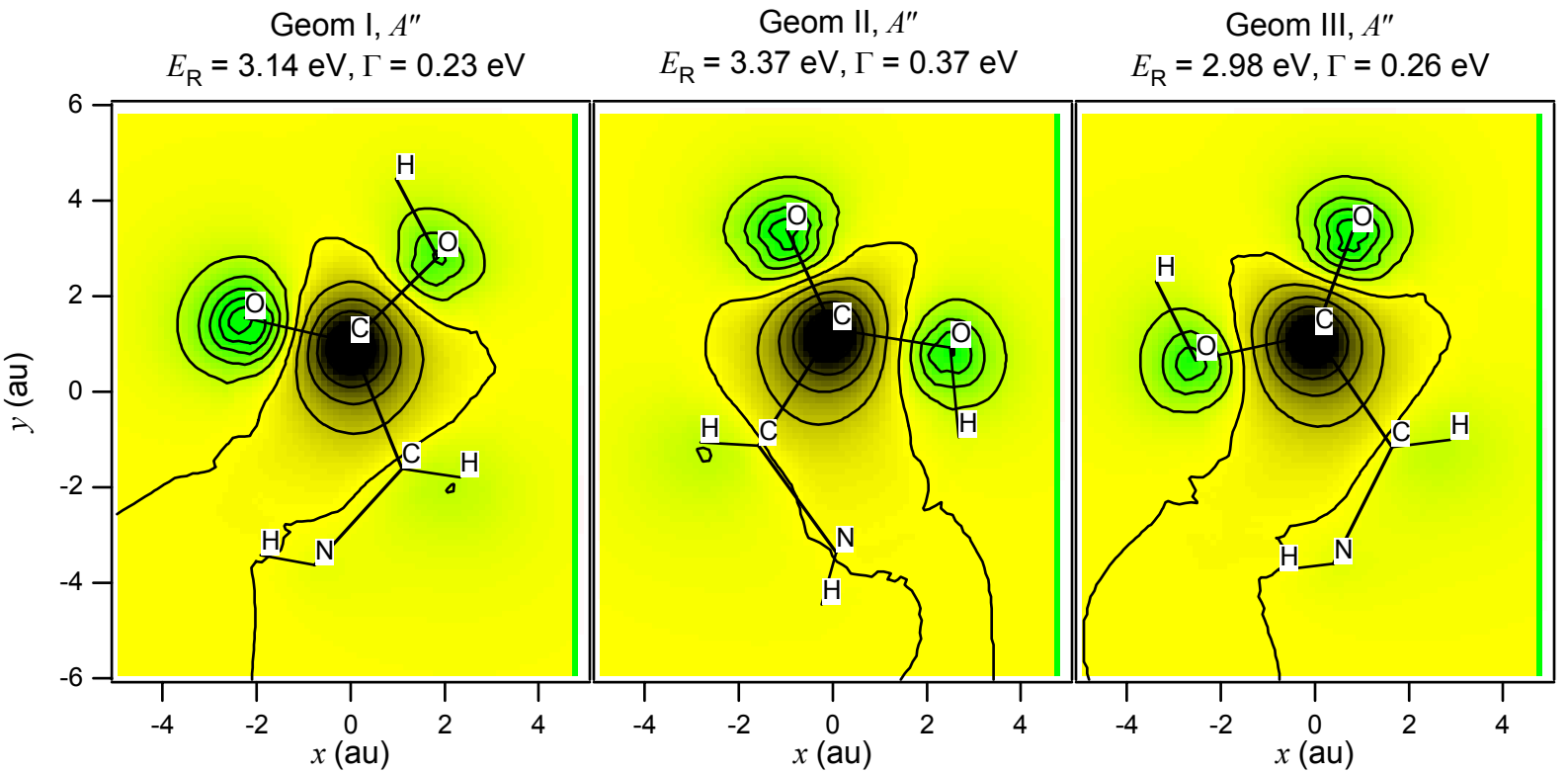


S. Gohlke, J. Chem. Phys. 116, 10164 (2002)

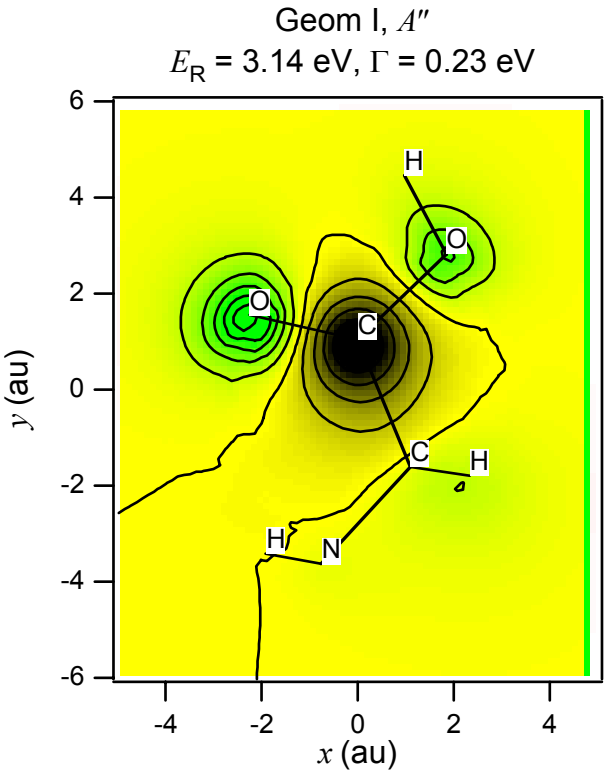
Summary of Experimental Data

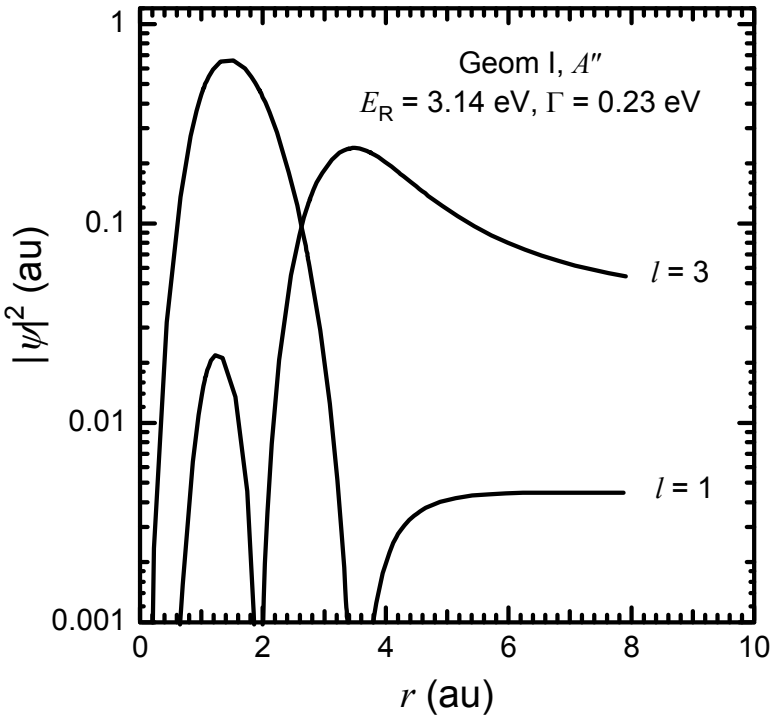
2 eV	Loss of H
5 eV	Loss of OH
6 eV	Loss of OH, NH_2^-, OH^-, CN^-, H_2CN^-, HCO_2^-, OH_3
9.5 eV	Loss of NH_2^-, OH^-, H_2CN^-
12 eV	Loss of NH_2^-

e – Glycine A″ (π) Resonance

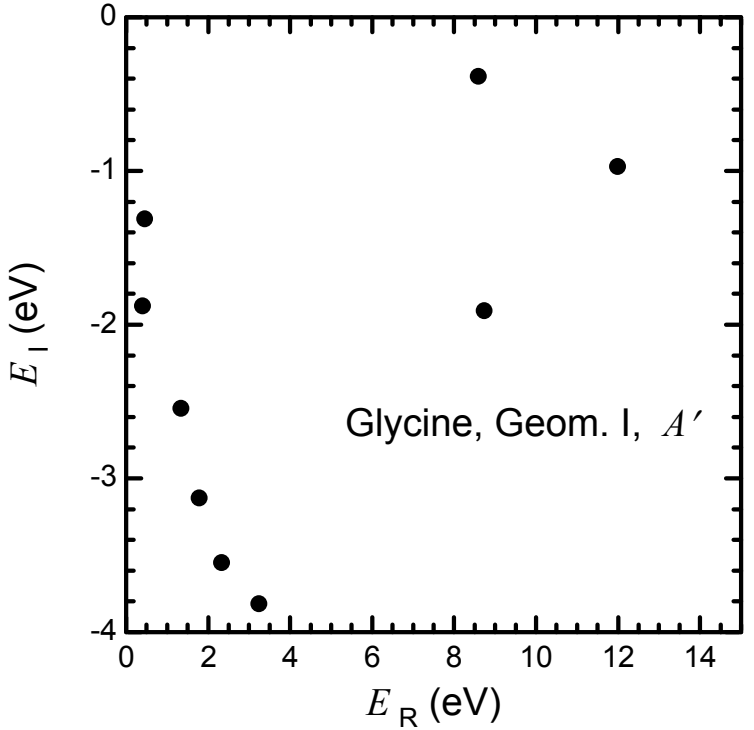


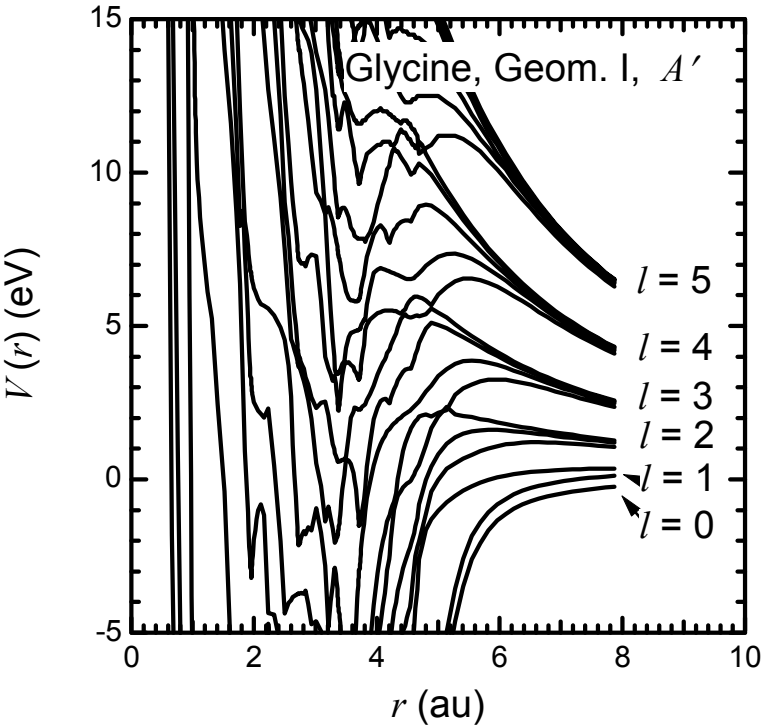
Partial Wave in e – Glycine A″ (π) Resonance



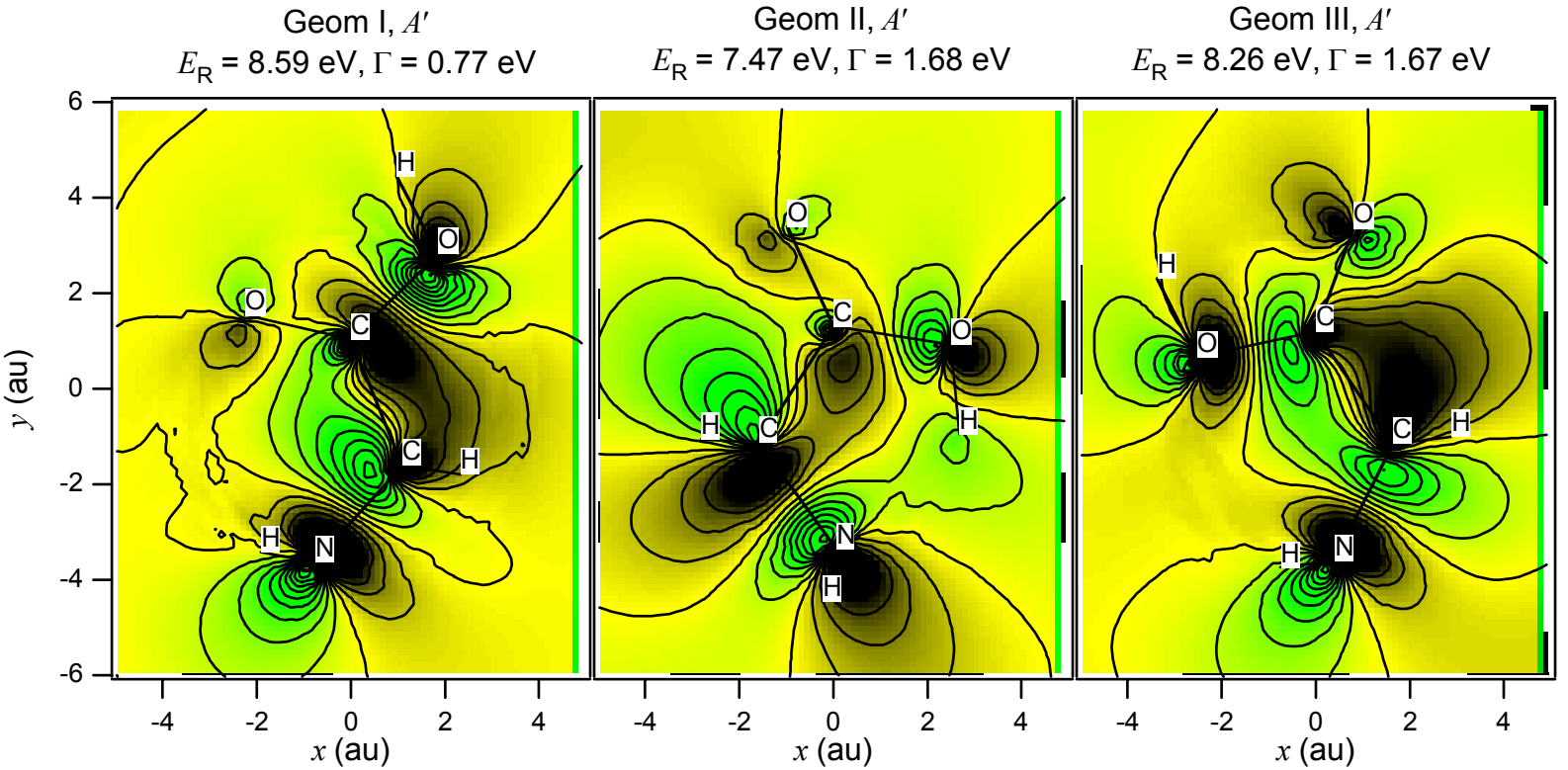


e – Glycine $A'(\sigma)$ Resonance Poles

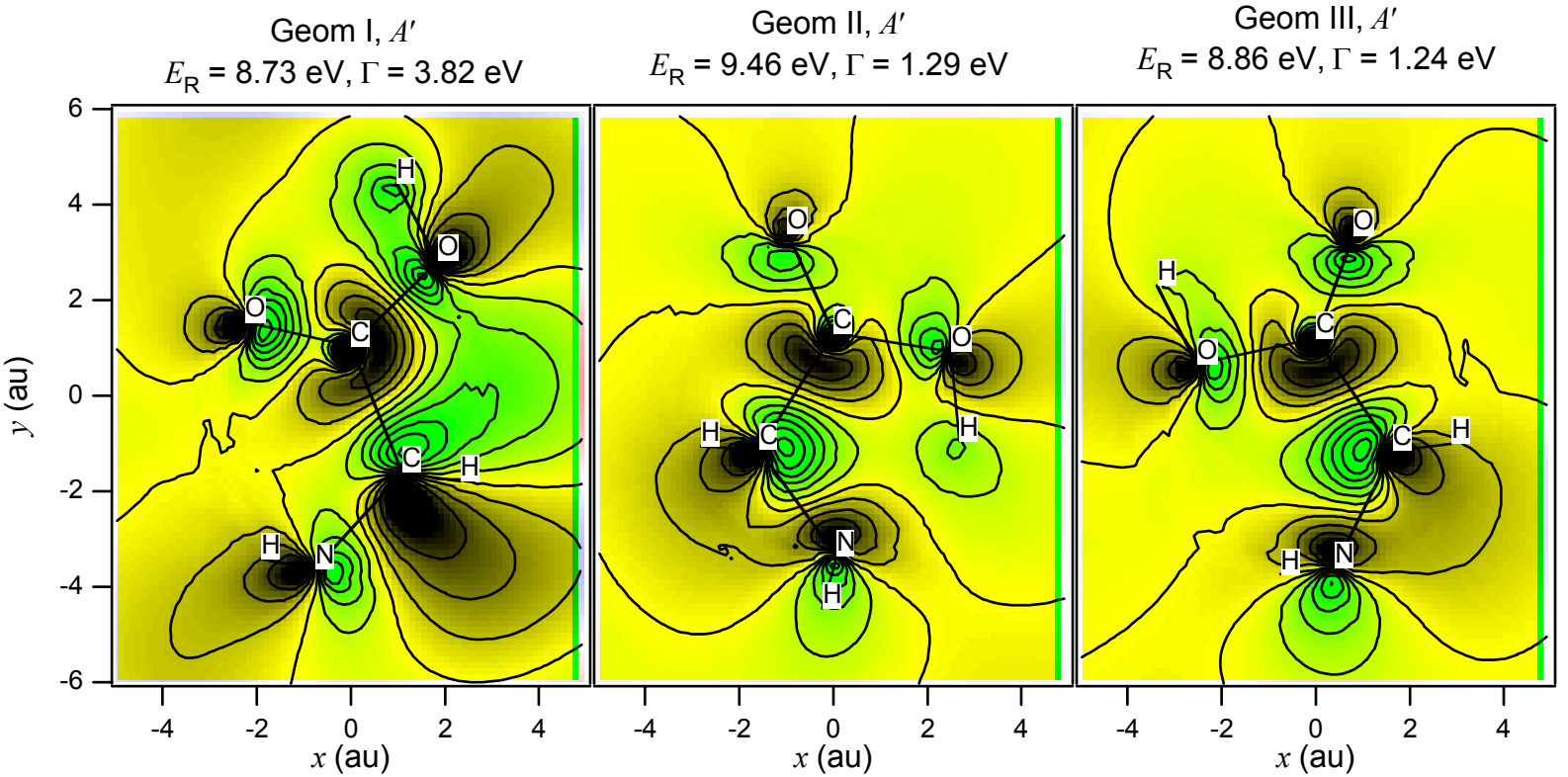




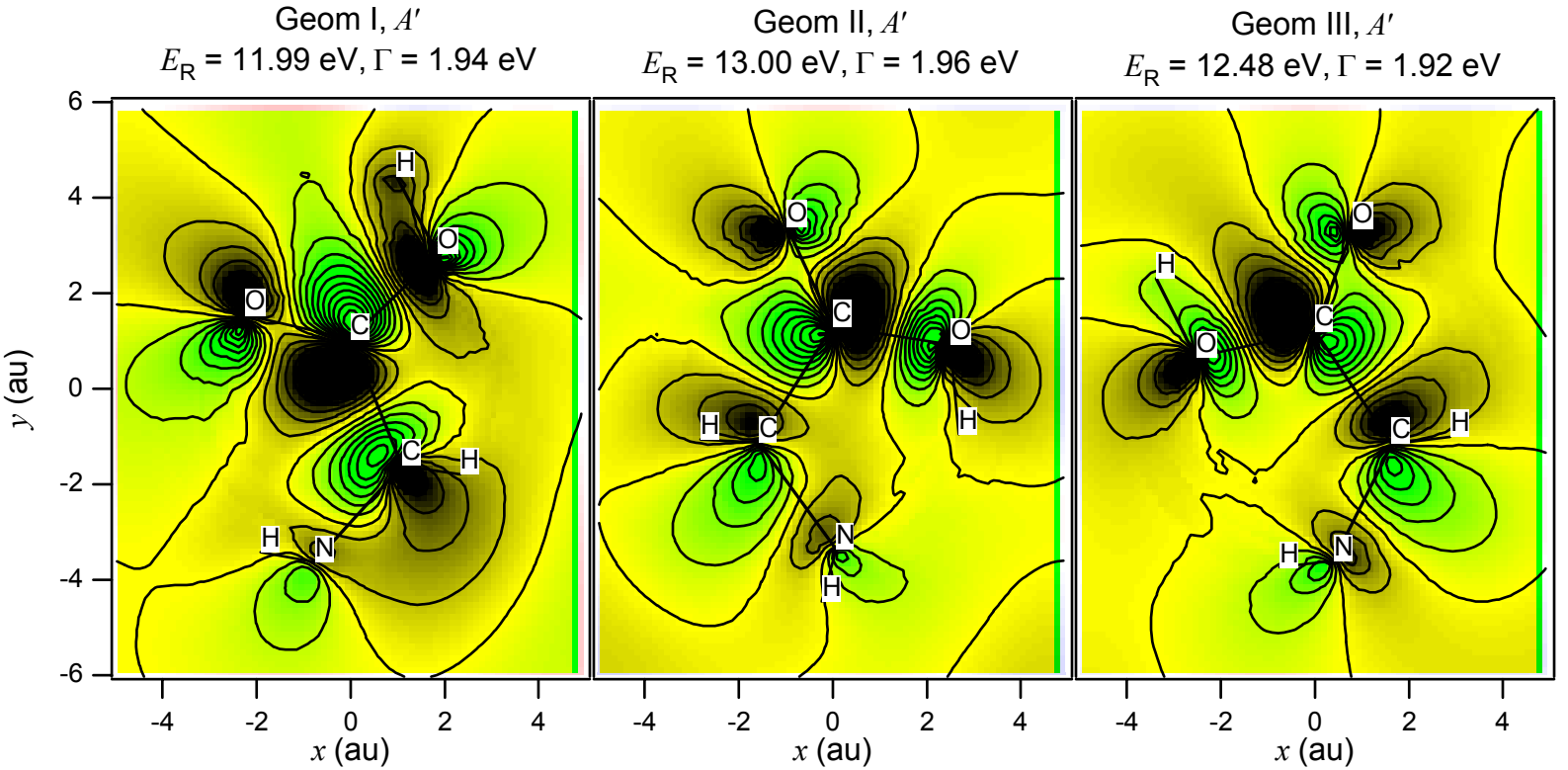
e – Glycine $A'(\sigma)$ Resonance States



e – Glycine $A'(\sigma)$ Resonance States



e – Glycine $A'(\sigma)$ Resonance States



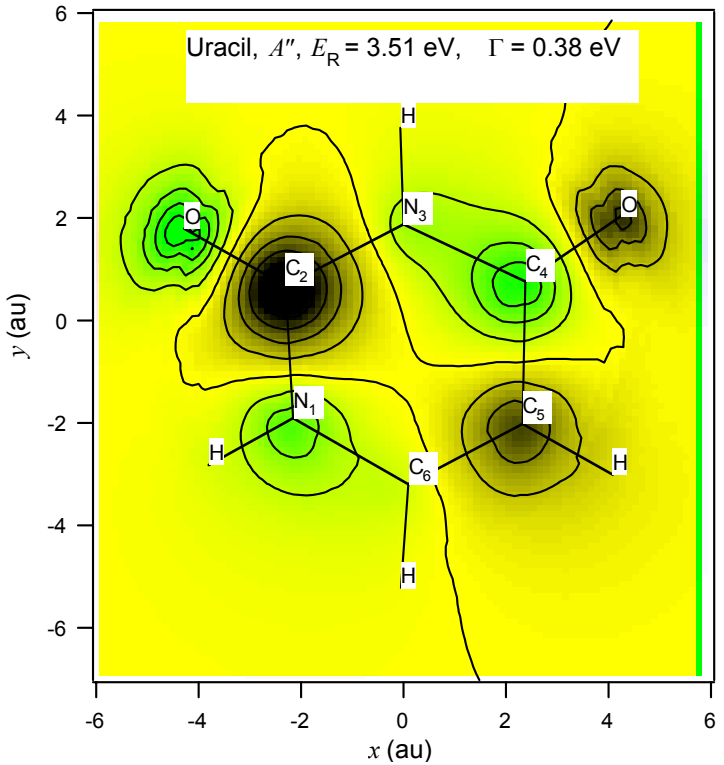
Conclusions for *e* – Glycine

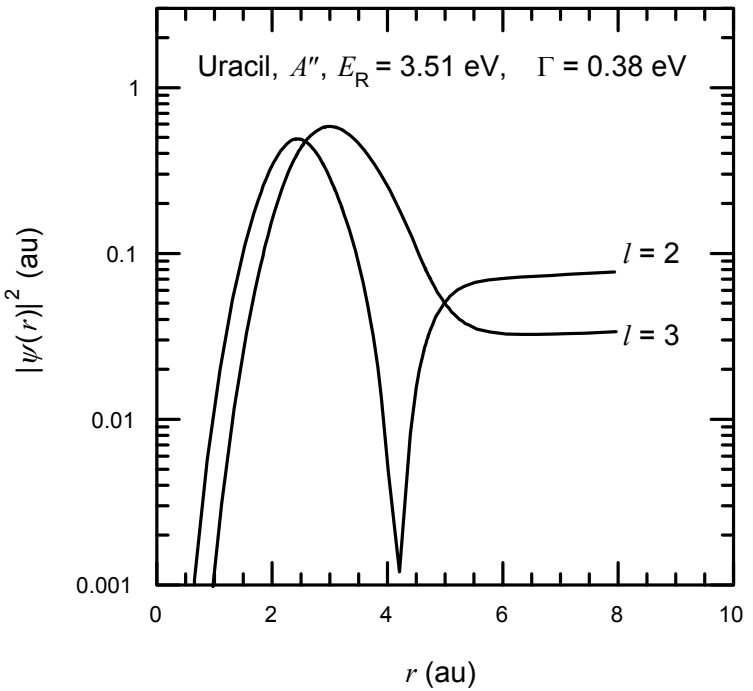
- Low energy resonances seen in H loss reactions are due to *A″* (π) resonances.
- The high energy *A′* (σ) resonance may be responsible for at least one of the DEA peaks seen.
- Strong σ^* character in the resonant state in the C–NH_2 and C–OH bonds can explain the strong OH, NH_2^-, and OH^- loss peaks.

Conclusion

- The Adiabatic Model can be used to gain a qualitative understanding of the one-electron (shape) resonances in electron-molecule scattering.
- Some resonances can be described as valence virtual orbitals, similar to virtual MBS orbitals computed with compact basis set.
- Some resonances are distinctly non-valence.
- Angular momentum barriers provide the trapping mechanism.
- Many dissociative attachment process may be due to shape resonances and subsequent direct or indirect fragmentation.

e – Uracil A″ (π) Resonances





e – Uracil A″ (π) Resonances