Vibrational Excitation of Polyatomic Molecules by Slow Electrons

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    - ⋆ Threshold effects are enhanced
- For polyatomics, multiple degrees of freedom may be essential

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- Similar effects subsequently observed in polar and *non-polar* polyatomics - CO_2, CH_4, CS_2, N_2O
- Is the dipole interaction essential? Can a simple theory be developed?
  - ⋆ The nonlocal theory requires either elaborate parametrization or accurate fixed-nuclei scattering results
  - ⋆ Not feasible for polyatomics

A virtual state model for low-energy vibrational excitation

- Target must present incoming electron with an interaction on the verge of binding an extra electron
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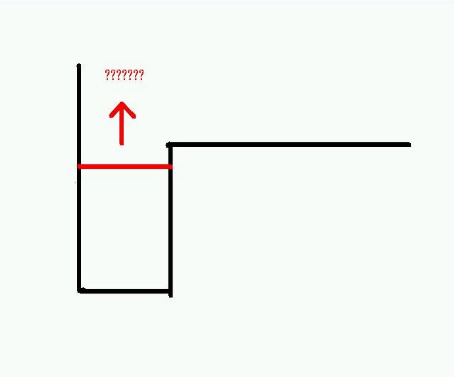
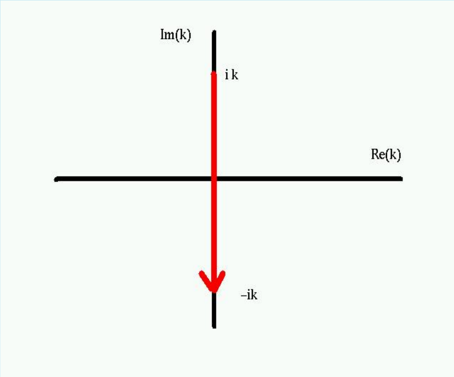
  - ⋆ Can we develop a dynamical theory to predict cross sections?

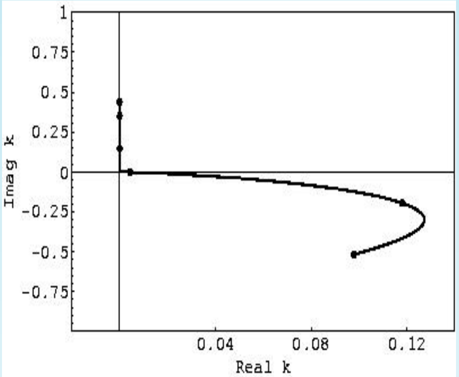
Construction of Anion Surface for Virtual States

For geometries were anion is electronically bound, quantum chemistry methods can be used

For unbound geometries, we need analytic continuation - best to work in complex momentum plane







Trajectory of virtual state in momentum plane is significantly altered by presence of dipole (right panel from HCl study by Vanroose et al.)

We can use analytic properties of electron-dipole interaction to predict shape of trajectory near threshold

Schrödinger Equation for Electron in Dipolar Field

$$\left(-\frac{\hbar^2}{2\mu}\Delta + e\frac{\mathbf{D}(\mathbf{S})\cdot\mathbf{r}}{r^3} - E\right)\psi(r,\theta,\phi;R) = 0$$

Separation in spherical polar coordinates, following Levy-Leblond '66:

$$\left[-\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{d}{d\theta}\right) + \frac{m^2}{\sin^2\theta} + 2D(\mathbf{S})\cos\theta - l_n(R)(l_n(R)+1)\right]\Theta_n(\theta;R) = 0$$

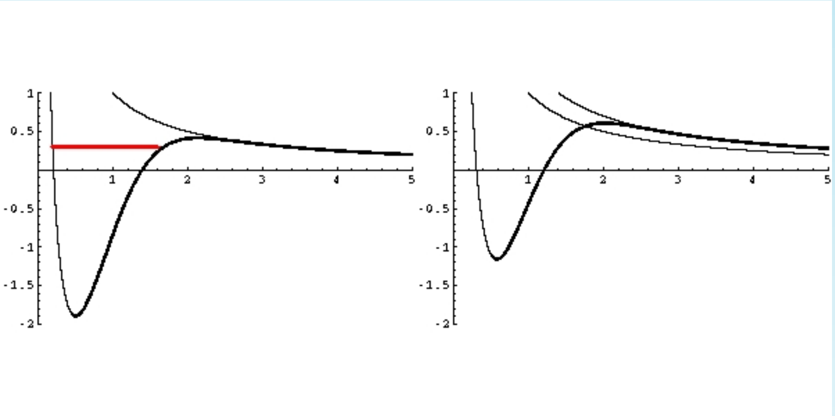
with $n \in I\!N$

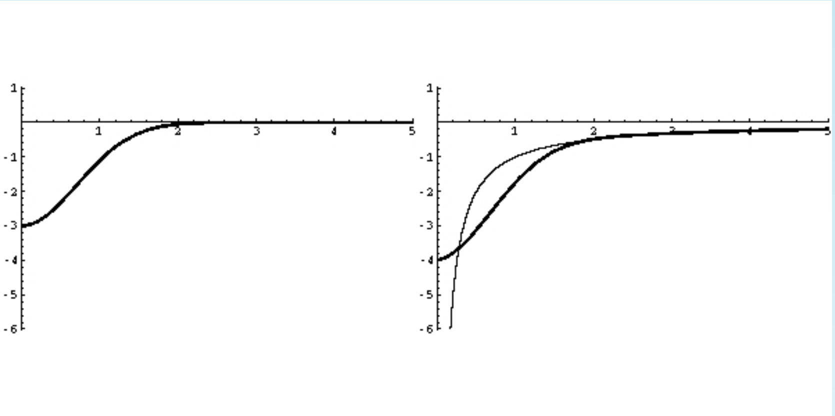
$$\left(-\frac{d^2}{dr^2} + \frac{l_n(R)(l_n(R)+1)}{r^2} - 2\mu E\right)\psi(r;R) = 0$$

$$\Theta_n(\theta;R) \neq P_n(\cos(\theta))$$

Only lowest l-eigenvalues for $m = 0$ leads to an attractive potential

Dipole makes $l \to l + \delta l$ for $l > 0$, but for s-wave scattering $l = 0 \to -\delta l$!!





$$l_0(\mathbf{S})(l_0(\mathbf{S})+1) = -\frac{2D(\mathbf{S})^2}{3} + \frac{11}{30}\left(\frac{2D(\mathbf{S})^2}{3}\right)^2 - \frac{133}{450}\left(\frac{2D(\mathbf{S})^2}{3}\right)^3 + \ldots$$

Threshold slope of virtual state trajectory follows analytic treatment of Newton

We use a double power series for the Jost function

$$\begin{aligned}\mathcal{F}_l(K,\mathbf{S}) &= a_0(\mathbf{S}) + a_1(\mathbf{S})K^2 + \ldots \\ &+ b_1(\mathbf{S})K^{2l+1} + b_2(\mathbf{S})K^{2l+3}\end{aligned}$$

where K is the electron momentum. Near threshold, a_0 and b_1 dominate. For a simple diatomic, we get

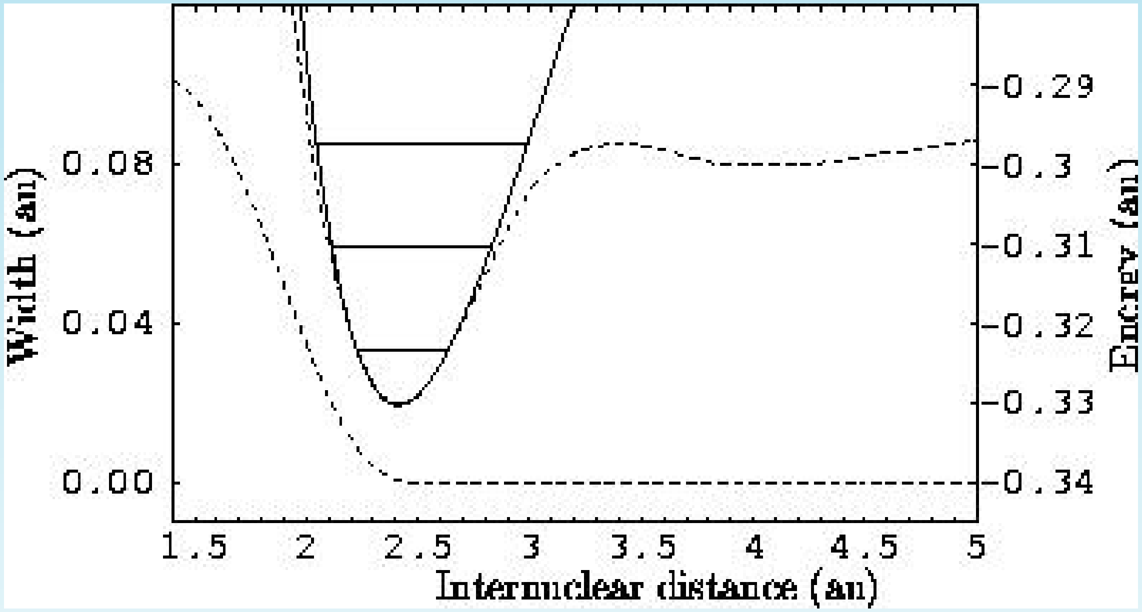
$$\rightarrow K(R) = i\alpha(R - R_0)^{1/(2l(R)+1)}$$

The (complex) electron momentum is combined with the target energy to get the anion energy the crossing region

$$V_{ion} = V_{neutral} - \frac{1}{2}\alpha^2(R - R_0)^{2/(2l(R)+1)}$$

Example: Neutral and Anion Potential Curves for HCl

R-dependent dipole moment determines l_0 which in turn determines $K(R)$
$D(R)$ and V_{HCl} are determined $ab\ initio$



Neutral and anion potential curves for HCl. Solid curve: neutral ground state with lowest three vibrational levels indicated; dashed curves: real and imaginary parts of anion curve.

A Virtual State Dynamical Model for Threshold Vibrational Excitation

- Model based on zero-range theory of Gauyacq, Dube and Herzenberg
- Assume wave function inside molecular charge cloud is independent of collision energy, (but not geometry)
- Interior wave function is dominated by virtual state pole - behaves like a Siegert state:

$$\psi(r,\mathbf{S}) \sim e^{(iK(\mathbf{S})r - l_0\pi/2)}$$

$$\frac{\partial \ln \psi}{\partial r} = iK(\mathbf{S})$$

Match Interior to Exterior Wave Function

- Outside the molecule:

$$\psi(r\,;\mathbf{S}) = h_l^-(k_0 r)\chi_0(\mathbf{S}) + \sum_n A_n h_l^+(k_n r)\chi_n(\mathbf{S})$$

where $\chi_n(\mathbf{S})$ is a target vibrational function with energy E_n and $k_n = \sqrt{2(E-E_n)}$. We match log-derivatives at $r = r_o$:

$$iK(\mathbf{S}) = \frac{k_0 h_l^-(k_0 r_o)'\chi_0(\mathbf{S}) + \sum_n k_n A_n h_l^+(k_n r_o)'\chi_n(\mathbf{S})}{h_l^-(k_0 r_o)\chi_0(\mathbf{S}) + \sum_n A_n h_l^+(k_n r_o)\chi_n(\mathbf{S})}$$

The vibrtational excitation cross sections are given by

$$\sigma_{0n} = \frac{\pi}{k_0^2}\frac{k_n}{k_0}|A_n|^2$$

Deriving a Nuclear Wave Equation

- Step 1: Use the fact that χ_n is a vibrational state of the neutral target

$$\begin{aligned} k_n \chi_n(\mathbf{S}) &= \sqrt{2(E-E_n)}\phi_n(\mathbf{S}) \\ &= \sqrt{2(E-H_{neutral}(\mathbf{S}))}\chi_n(\mathbf{S}) \end{aligned}$$

- Step 2: Use this operator identity in matching equations

$$\begin{aligned} iK(R) \quad & [h_l^-(k_0 r_o)\chi_0(\mathbf{S}) + \textstyle\sum_n A_n h_l^+(k_n r_o)\chi_n(\mathbf{S})] = \\ & \sqrt{2(E-H_{neutral})}[h_l^-(k_0 r_o)'\chi_0(\mathbf{S}) \\ & + \textstyle\sum_n A_n h_l^+(k_n r_o)'\chi_n(\mathbf{S})] \end{aligned}$$

Nuclear Wave Equation

- Assume r_o is large enough to replace $h_l^{+/-}(kr)$ by $\exp\left(+/-ikr - l\pi/2\right)$

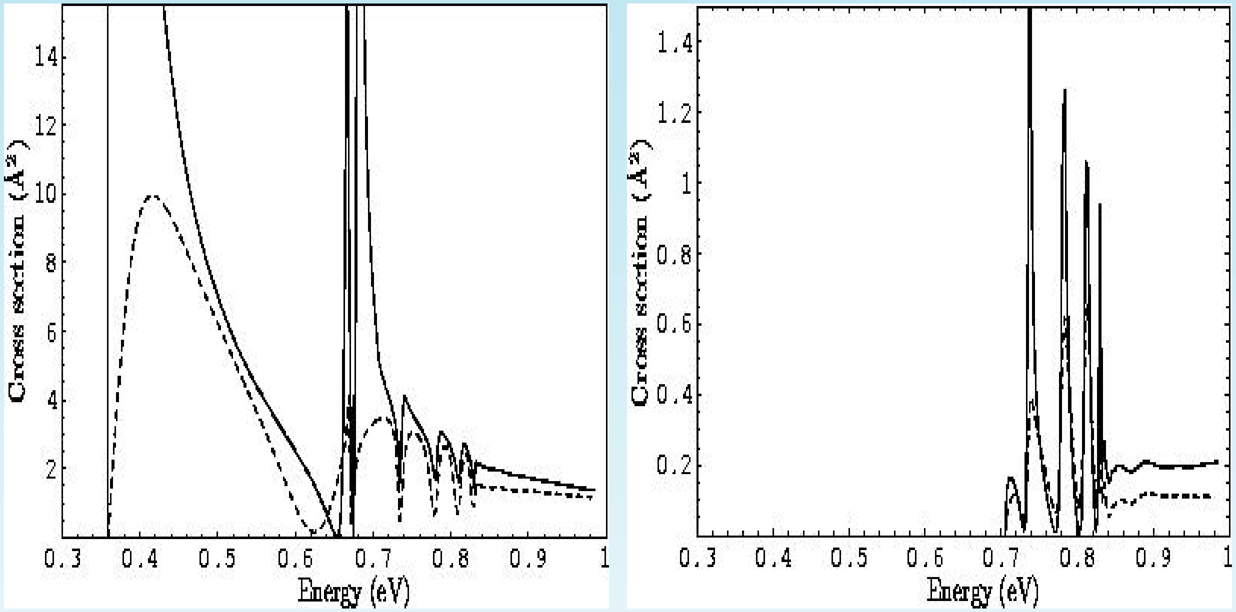
$$\left(-K(\mathbf{S}) + \sqrt{2(E - H_{neutral})}\right) \sum_n A_n e^{i(k_n+k_0)r_o} \chi_n(\mathbf{S}) = \left(K(\mathbf{S}) + k_0\right) \chi_0(\mathbf{S})$$

- Define the nuclear wave function $\Psi(\mathbf{S}) = \sum_n A_n e^{i(k_n+k_0)r_o} \chi_n(\mathbf{S})$ as $\Psi(\mathbf{S}) = \left(K(\mathbf{S}) + \sqrt{2(E - H_{neutral})}\right) \Omega(\mathbf{S})$. We arrive at:

$$\left(2(E - H_{ion}) + \left[\sqrt{2(E - H_{neutral})}, K(\mathbf{S})\right]\right) \Omega(\mathbf{S}) = \left(K(\mathbf{S}) + k_0\right) \chi_0(\mathbf{S})$$

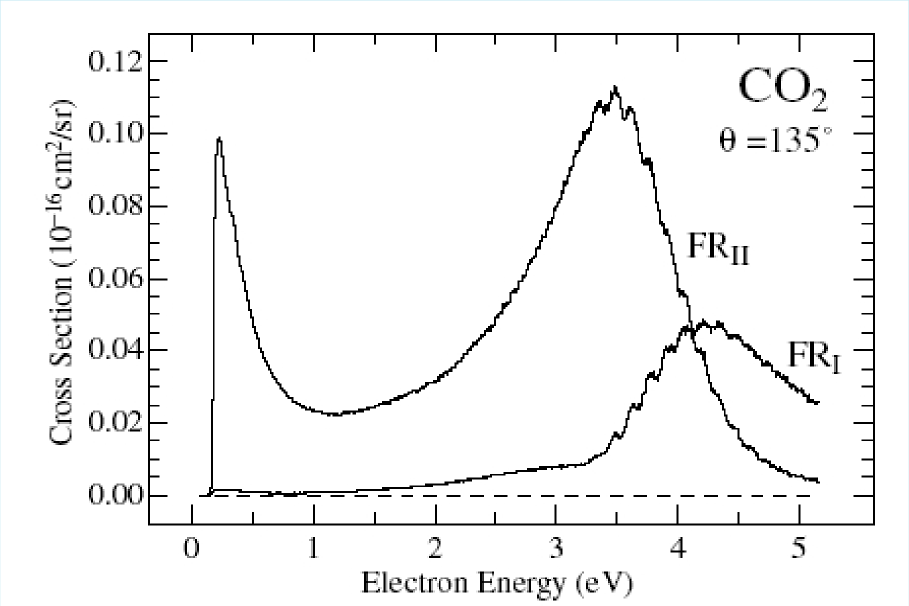
- There is no explicit dependence on r_o in the NWE!

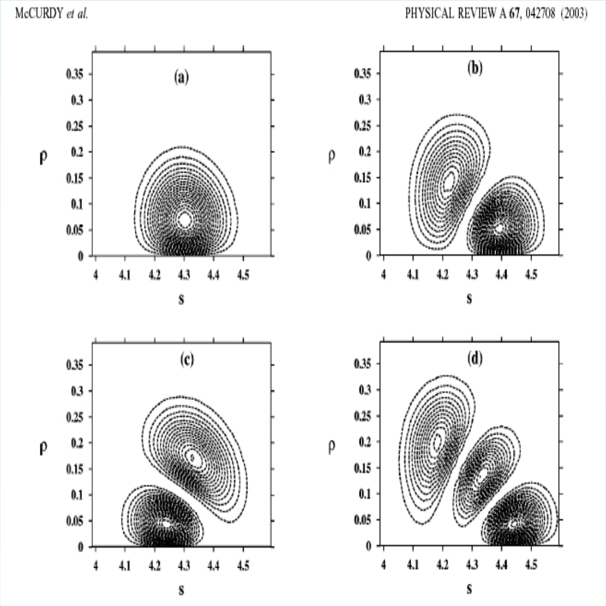
Virtual State Model Reproduces Observed Structures in e-HCl



Vibrational excitation cross sections for HCl. Left panel: $0 \rightarrow 1$ cross section; right panel: $0 \rightarrow 2$ cross section.

CO_2: Recent Experiments reveal Striking Threshold Effects

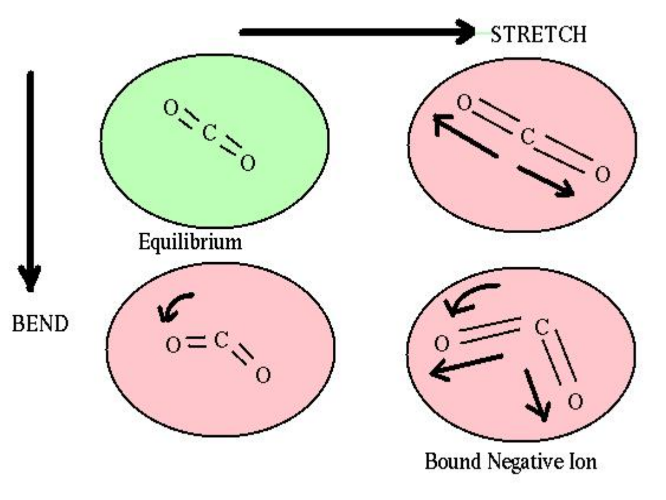


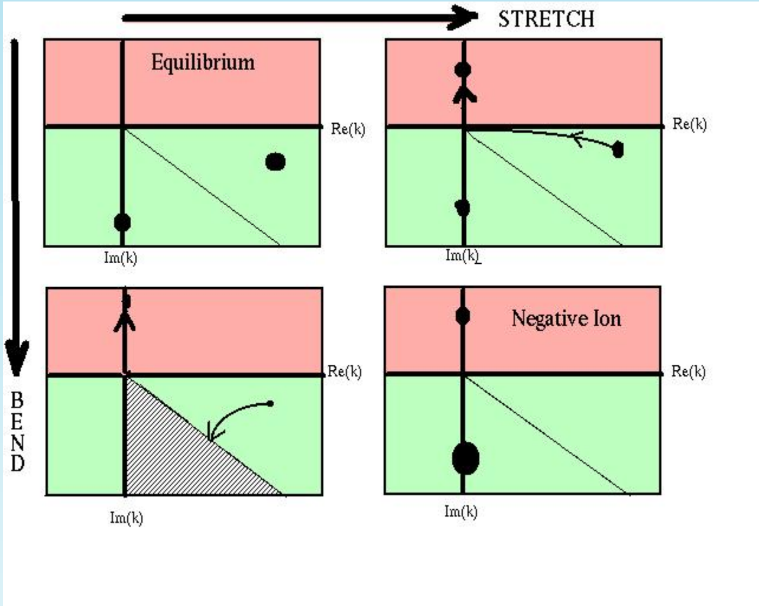


Left panel: Allan's recent expt(PRL,2001); right panels: CO_2 vibrational wave functions

Bound states, Resonances and Virtual State in CO_2^-

Is the $\mathrm{C0}_2^-$ state a resonance or virtual state??



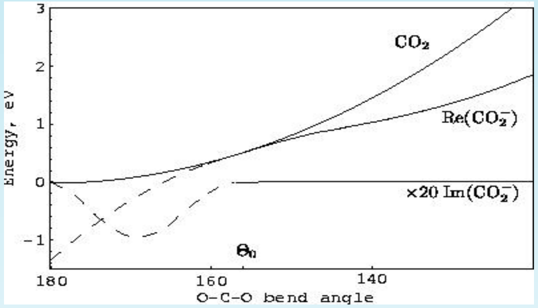


At large C-O$^-$ bond distances, anion must be triply degenerate
$^2\Sigma$ evolves into the virtual state and $^2\Pi$ becomes the RT resonance

CO_2/CO_2^- Surface Construction

- Coupled-cluster calculations produce neutral surface, dipole moment function and $^2A_1$ anion surface where it is electronically bound

- Threshold law used to analycically continue anion surface



Cuts through the potential surfaces of CO_2 and CO_2^- with the C-O bond distance fixed at 2.2 bohr. In the crossing region, around Θ_0, the difference between the curves follows a threshold law predicted by the dipole moment of CO_2.

Zero-range model results for threshold excitation of CO_2 polyads 2D Nuclear wave equation solved using finite-element DVR

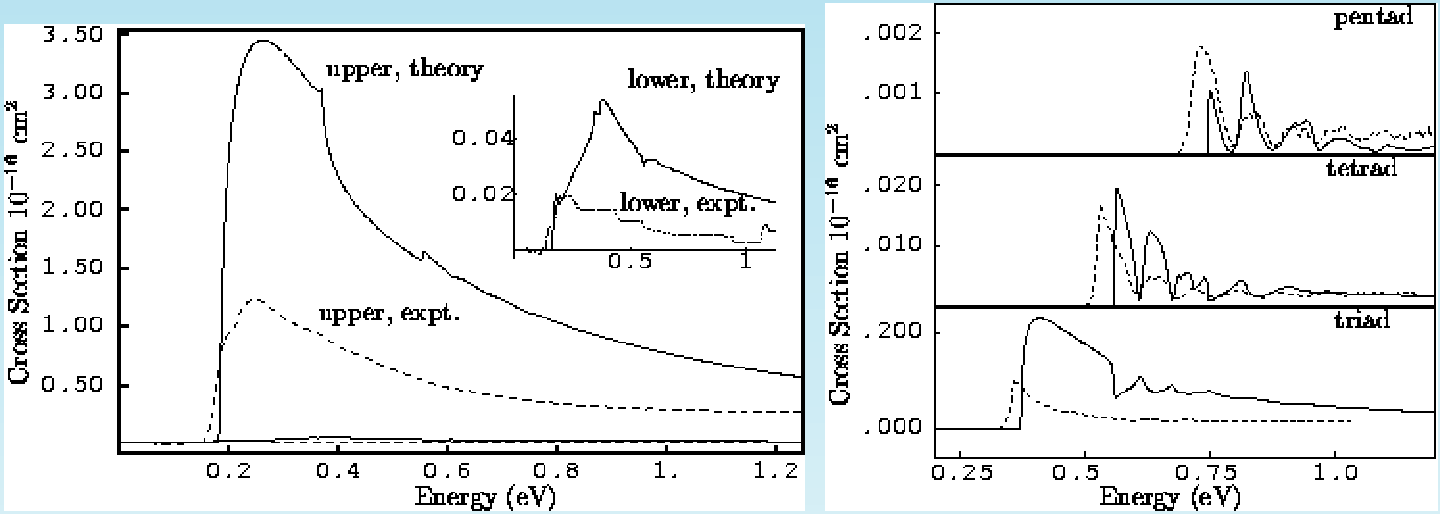


Figure 1: Excitation cross sections for the Fermi polyads in CO_2 in the threshold region. Solid lines: theory; dashed lines: experiment(Allan,2002). Left panel: dyad; right panel: triad, tetrad and pentad.

2D Virtual State Model Explains Selectivity in Fermi Dyad Excitation

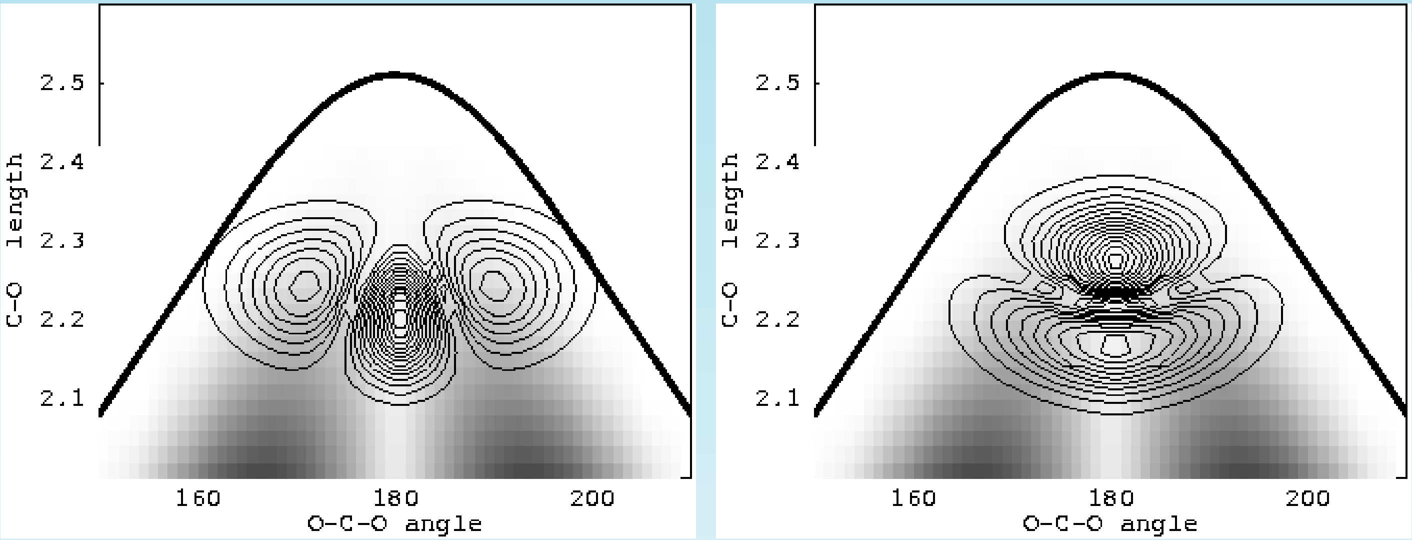


Figure 2: Contour plots of the wave functions for the two components of the Fermi dyad in O-C-O angle and C-O bond distance The thick line marks the seam where the anion and neutral surfaces cross. The imaginary part of the anion surface is zero above the seam and increases proportionately in regions indicated by the shading. Left panel: upper member of dyad; right panel: lower member of dyad.

Summary

- For many polyatomic targets, shape resonances play a dominant role vibrational excitation by electron impact
- Local complex potential model calculations in several dimensions can describe vibrational excitation cross sections
  - ⋆ Fixed-nuclei electron scattering calculations can provide required resonance parameters
- Threshold effects in vibrational excitation can be treated by zero-range theory
- Quantum Chemistry augmented with analytic continuation can provide the necessary input
  - ⋆ Elaborate fixed-nuclei scattering calculations at very low energy not required!