Atomic and Molecular Theory Group

Vibrational excitation of weakly polar molecules by electron scattering

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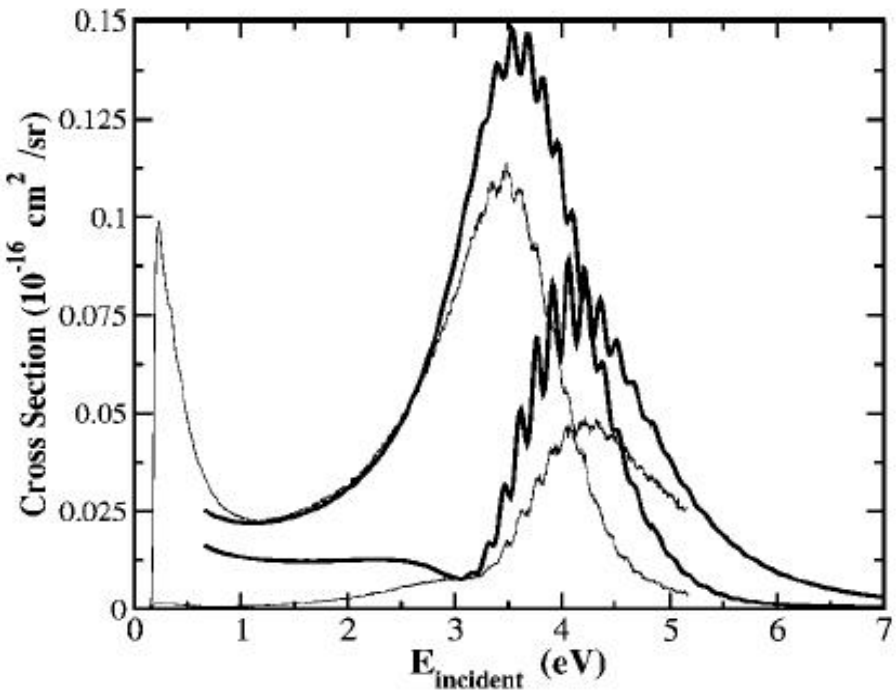
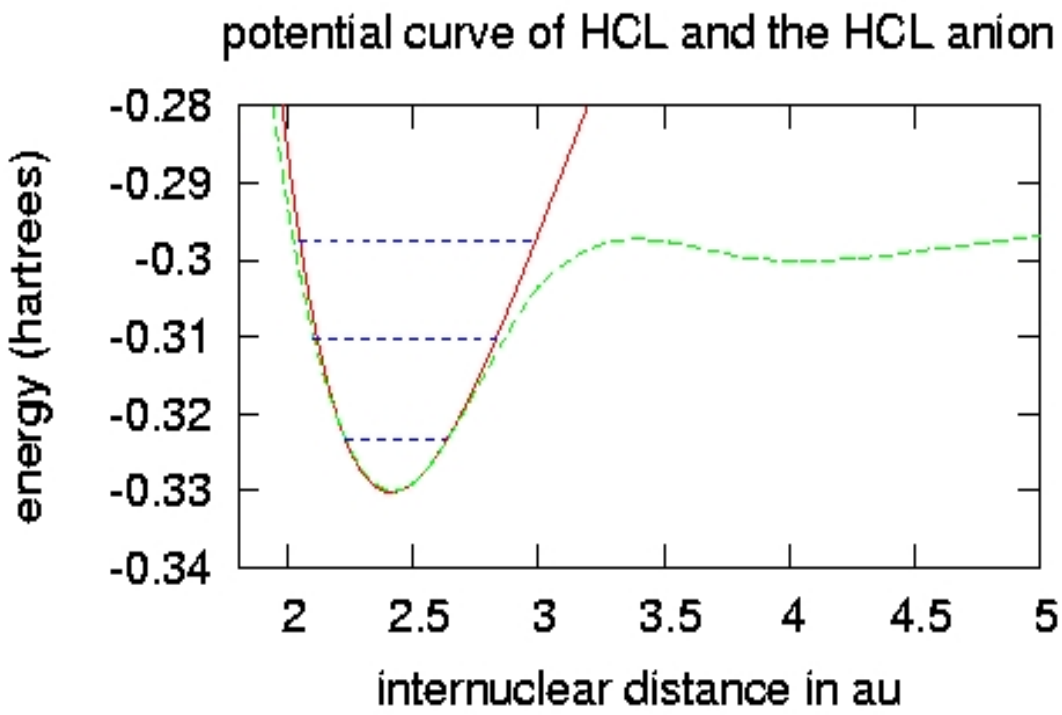
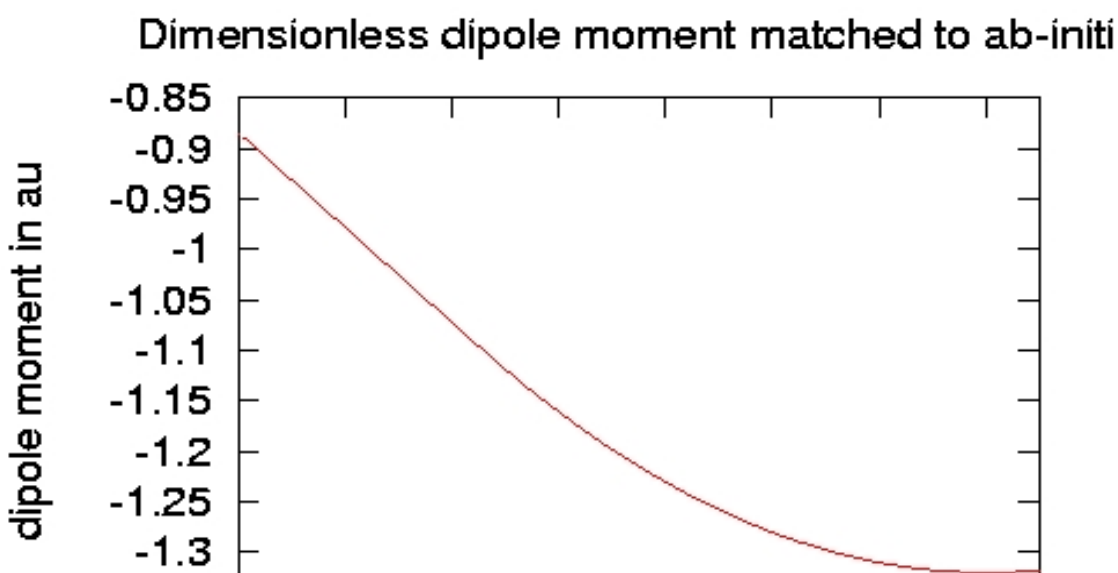
Funding: Department of Energy, Office of sciences

Vibrational excitation of fermi-dyads in CO_2



From McCurdy, Isaacs, Meijer and Rescigno, PRA **67** 042708 (2003)


potential curve of HCL and the HCL anion
energy (hartrees)
-0.28
-0.29
-0.3
-0.31
-0.32
-0.33
-0.34
2
2.5
3
3.5
4
4.5
5
internuclear distance in au


Dimensionless dipole moment matched to ab-initi
dipole moment in au
-0.85
-0.9
-0.95
-1
-1.05
-1.1
-1.15
-1.2
-1.25
-1.3

Herzenberg, Dube and Gauyacq's Matching Condition

$r < r_0$	$r > r_0$
$\psi_{el}^{N+1}(r\,;R)\Phi(R)$	$e^{-ik_0 r}\psi_{el}^{N}\Phi_0(R) + \sum_n A_n e^{ik_n r}\psi_{el}^{N}\Phi_n(R)$

where

$$k_n = \sqrt{2(E - E_n)} \tag{1}$$

$$\begin{aligned}
\psi_{el}^{N+1} &\approx \psi_{el} \times \psi_{el}^{N}(R) && (2)\\
&\approx \exp\{iK(R)r + l(R)\pi/2\} \times \psi_{el}^{N}(R) && (3)\\
&\approx \exp\{i\sqrt{2(V_{ion} - V_{neutral})}r + l(R)\pi/2\} \times \psi_{el}^{N}(R) && (4)
\end{aligned}$$

Analytic continuation of potential surface in the continuum

The $K(R)$ is a zero of the Jost function

$$\mathcal{F}_l(K(R), R) = 0 \tag{5}$$

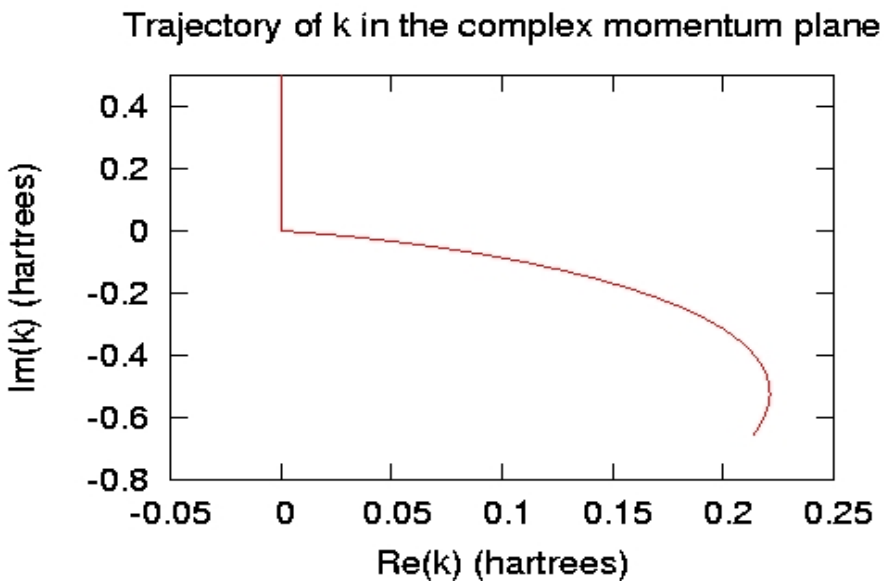
From Newton

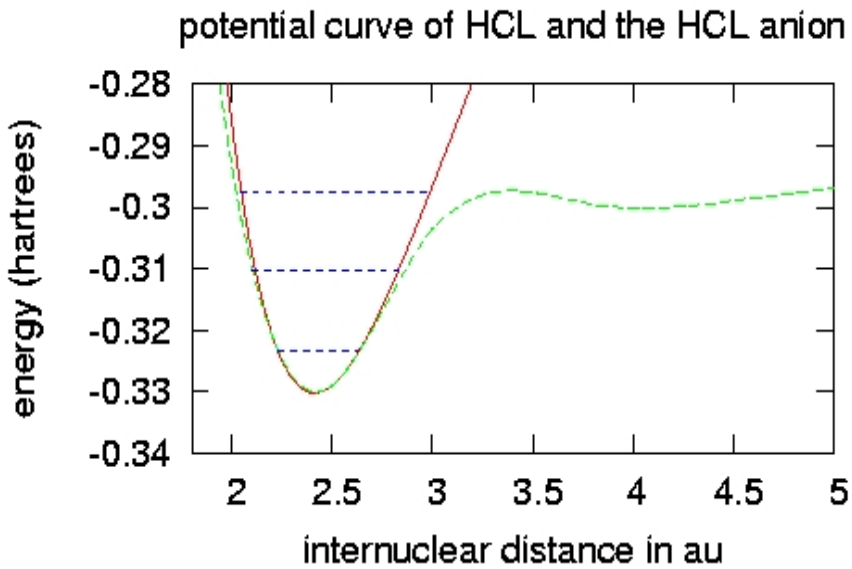
$$\mathcal{F}_l(k, R) \approx a_0(R) + a_1(R)k^2 + \ldots + b_1(R)k^{2l+1} + b_2(R)k^{2l+3} \tag{6}$$

$$K(R) = i\beta(R - R_0)^{1/(2l(R)+1)} \tag{7}$$

or

$$V_{ion} = V_{neutral} - \beta^2(R - R_0)^{2/(2l(R)+1)} \tag{8}$$


Trajectory of k in the complex momentum plane
Im(k) (hartrees)
Re(k) (hartrees)
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-0.05
0
0.05
0.1
0.15
0.2
0.25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Local "Boomerang" model

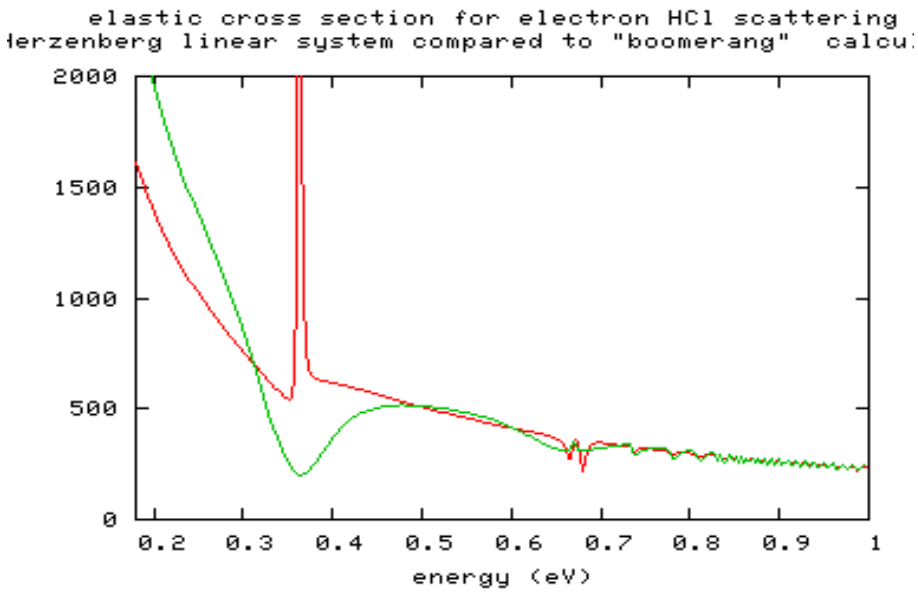
if Born-Oppenheimer approximation

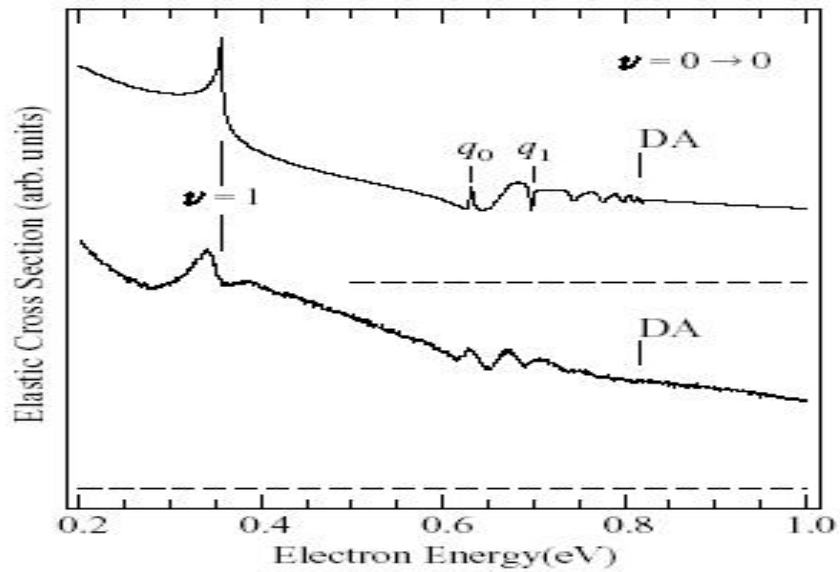
$$\left[\frac{\psi'_{el}(r;R)}{\psi_{el}(r;R)}, \sqrt{2(E - H_{neutral})}\right] = 0 \tag{9}$$

we find simplified local model

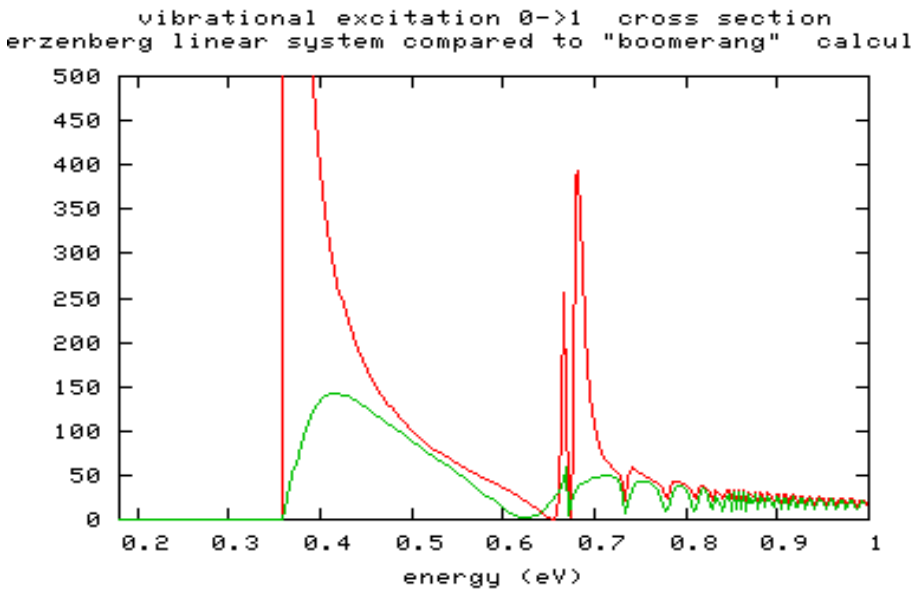
$$\sigma_{nm} \propto |\langle\phi_n|\Gamma^{1/2}\frac{1}{E - H_{ion}}\Gamma^{1/2}|\phi_m\rangle|^2 \tag{10}$$

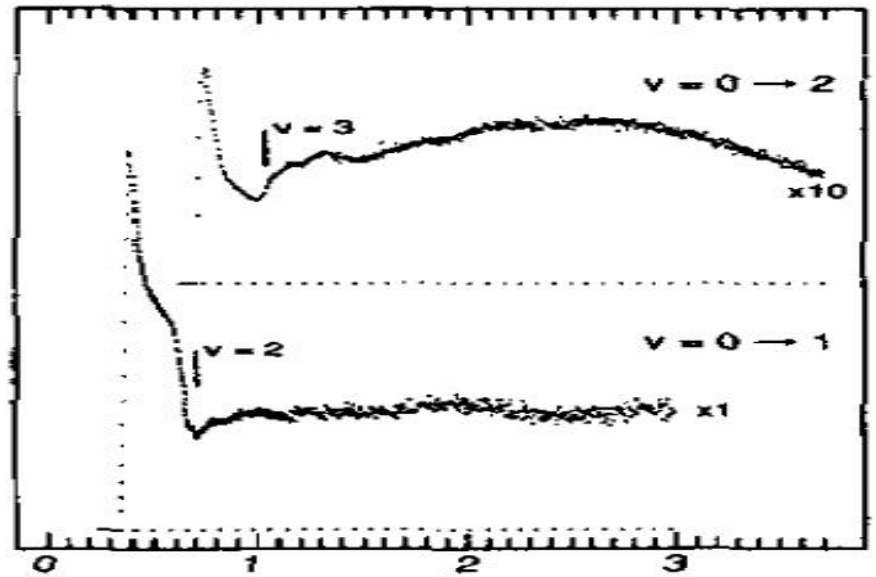
where $\Gamma^{1/2} = K(R) + k_n$





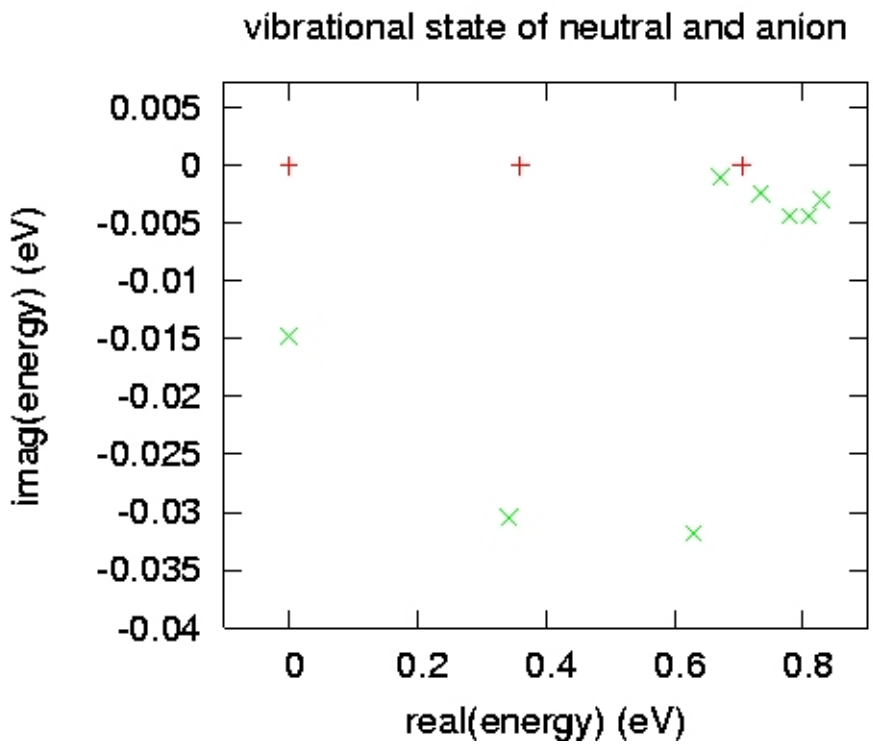
Experiment by Allan (J phys B **33** (2000) L209)

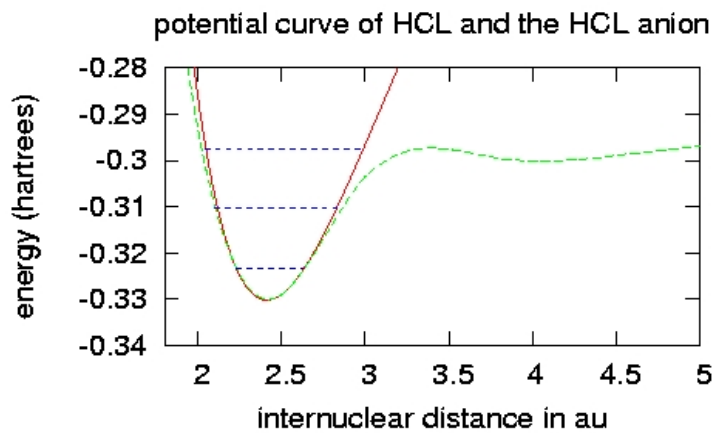




Experiment by Michael Allan

Local model shows the Vibrational excited Feshbach resonances





Conclusions

- ab-initio discussion of threshold peaks in poly-atomic molecules
- Crossing region of V_{ion} and $V_{neutral}$ is understood by the dipole moment of the neutral
- Zero-range potential model of Herzenberg, Dube and Gauyacq can be formulated as a "boomerang" model.
- The simple model gives reasonable results for HCl.