

Vibronic coupling in the ground state of vinylidene \tilde{X}^1A_1 H₂CC

Steve Gibson¹, Ben Laws¹, Hua Guo², Dan Neumark³, Carl Lineberger⁴, Robert Field⁵

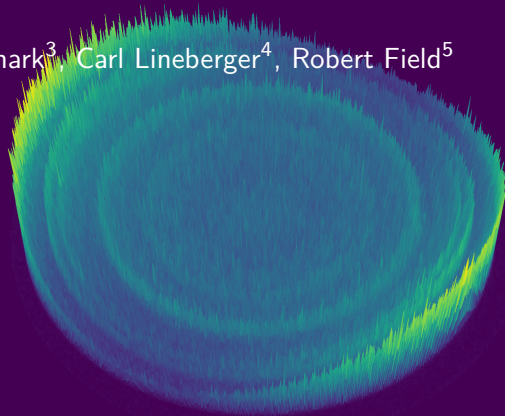
¹LPC/RSPE ANU, Canberra

²Chem UNM, NM

³Chem UCB, CA

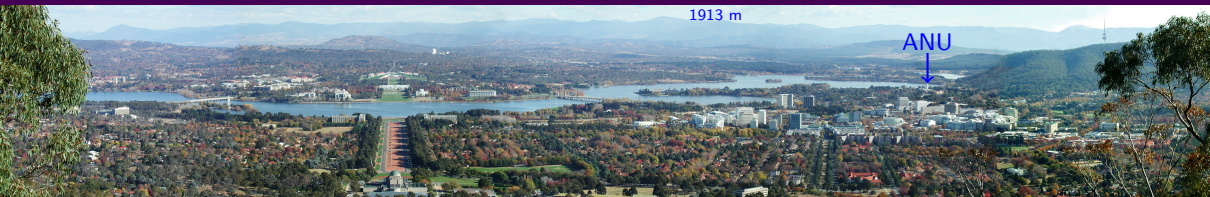
⁴Chem/Bio JILA UCol. CO

⁵Chem MIT, MA



ISMS June 20, 2017

- HR-PEI/cryo-SEVI
- H₂CC⁺ PES decomposition
- H₂CC⁺ PAD decomposition
- vibronic coupling/isomerization



Vibronic coupling in the ground state of vinylidene \tilde{X}^1A_1 H₂CC facilitates isomerization

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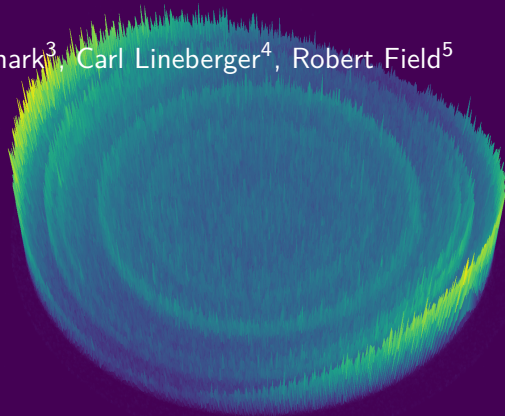
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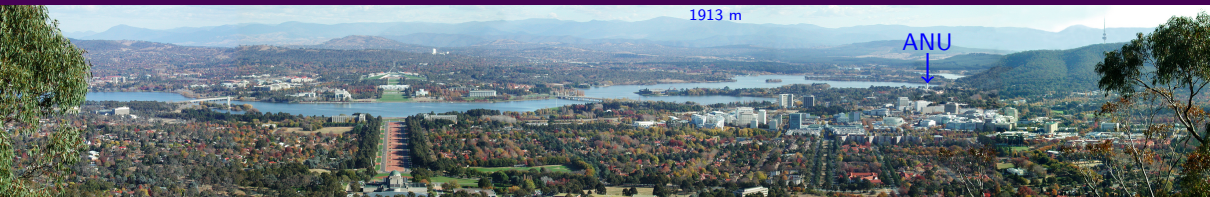
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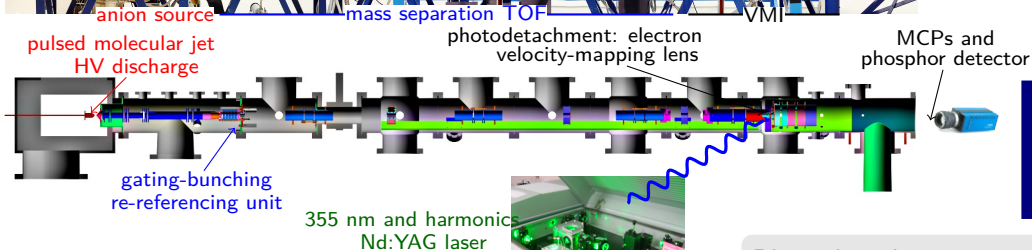
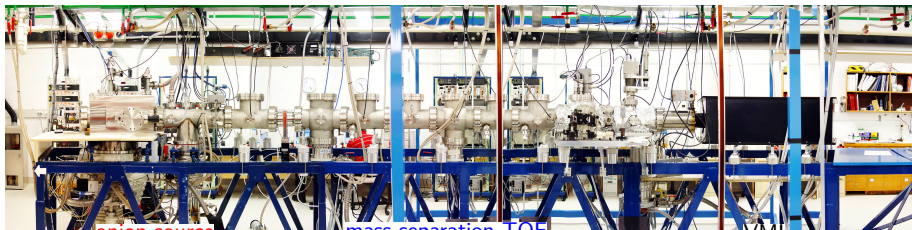


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- vibronic coupling/isomerization



Spectrometer - photodetachment/photofragmentation



Fast beam spectrometer:

Cyr PhD Thesis (UC Berkeley 1993)

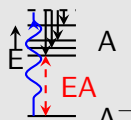
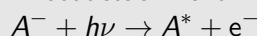
Velocity-map imaging lens:

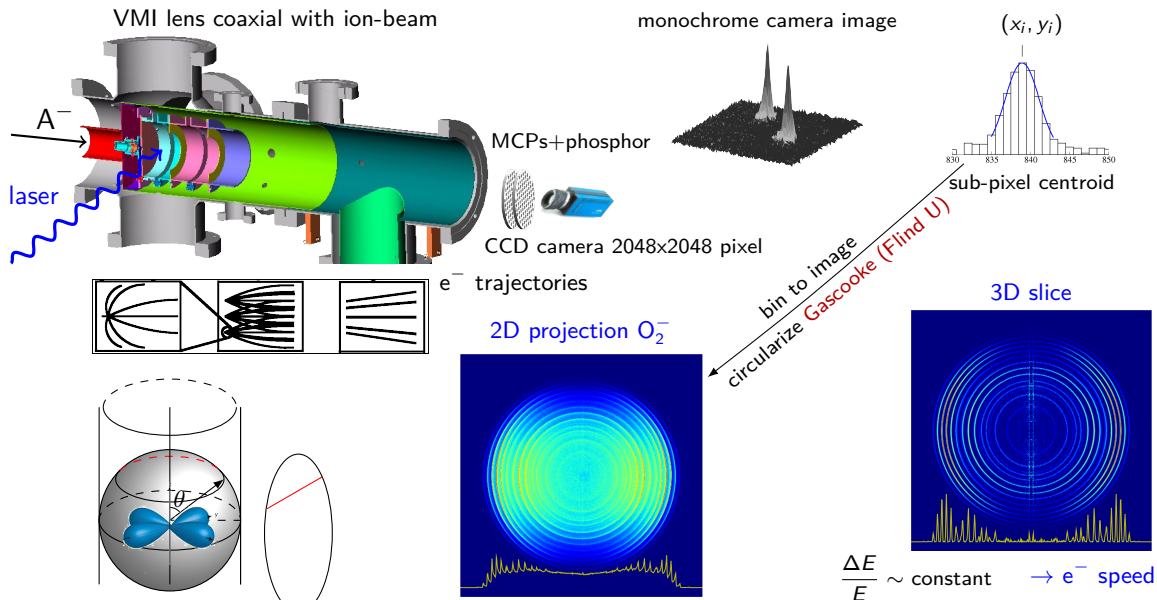
Eppink and Parker *Rev Sci Instrum* **68** 3477 (1997)

Gating-bunching-rereferencing unit:

(ANU) Dedman *et al.* *Rev Sci Instrum* **73** 2915 (2001)

Photodetachment:





Inverse Abel transformation: **PyAbel**: <https://github.com/PyAbel>

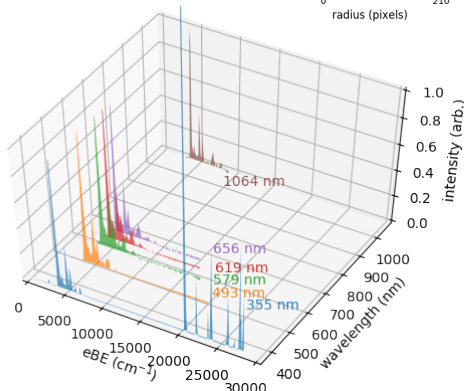
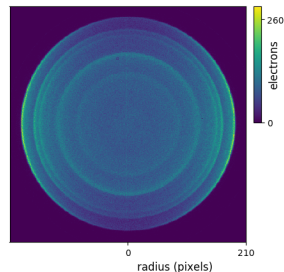
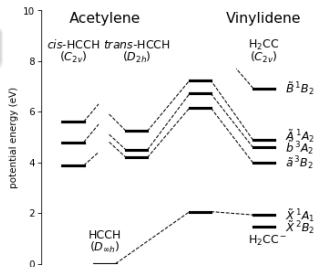
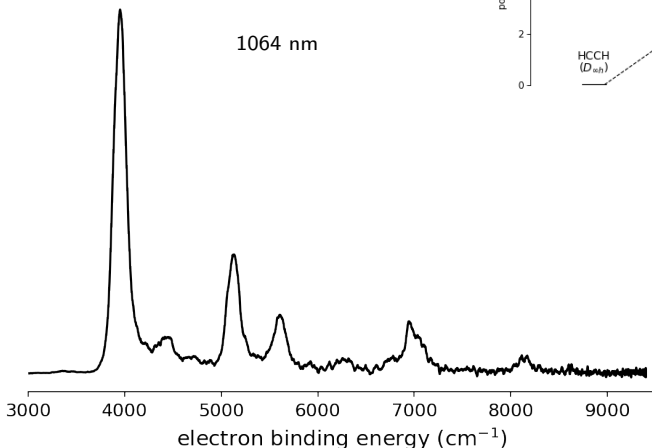
vinylidene anion H_2CC^- photodetachment

Photoelectron spectrum (HR-PEI)



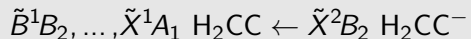
Electron affinity: $3952(48) \text{ cm}^{-1}$, $0.490(6) \text{ eV}$

Ervin *et al.* J Chem Phys **91** 5974 (1989)



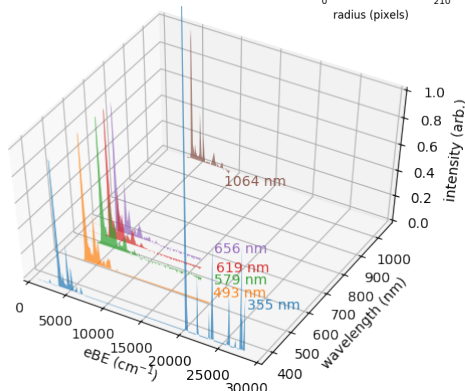
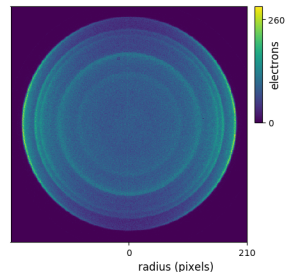
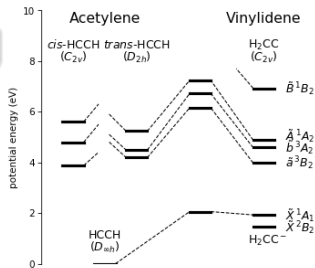
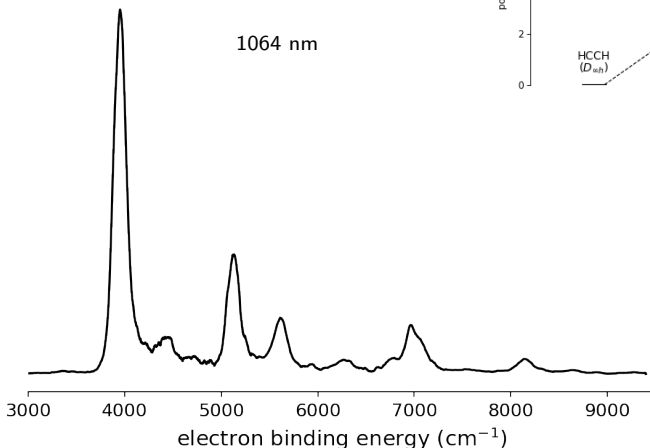
vinylidene anion H_2CC^- photodetachment

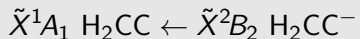
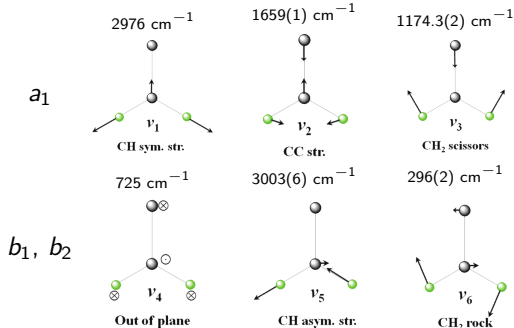
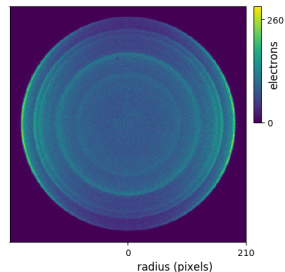
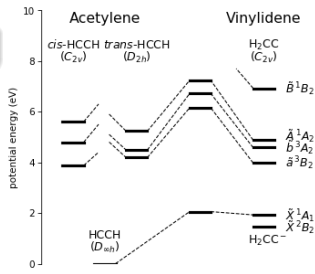
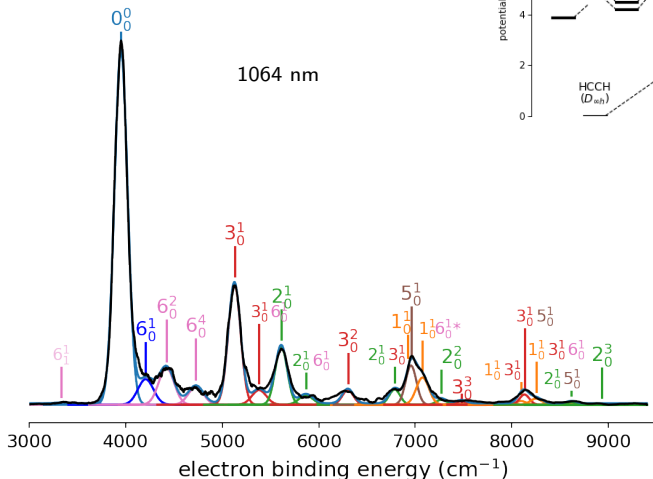
Photoelectron spectrum (HR-PEI)

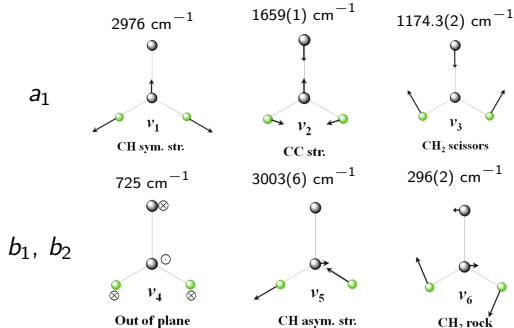
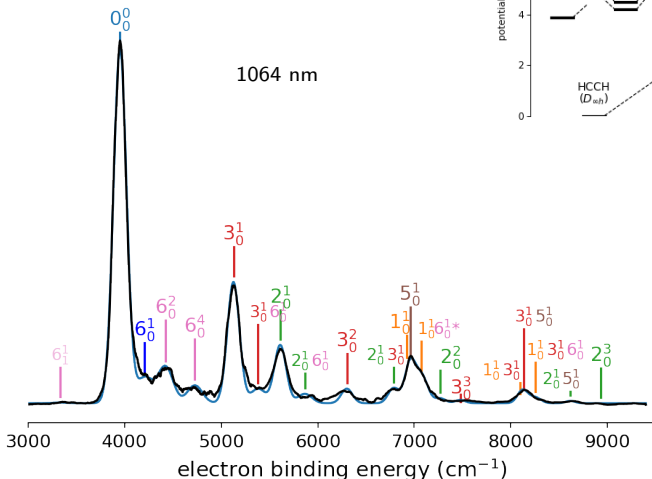
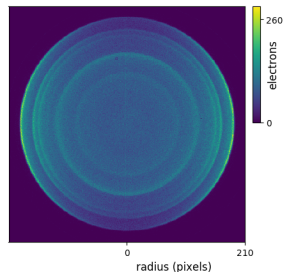
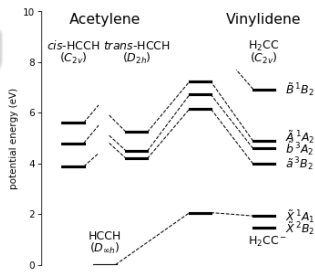


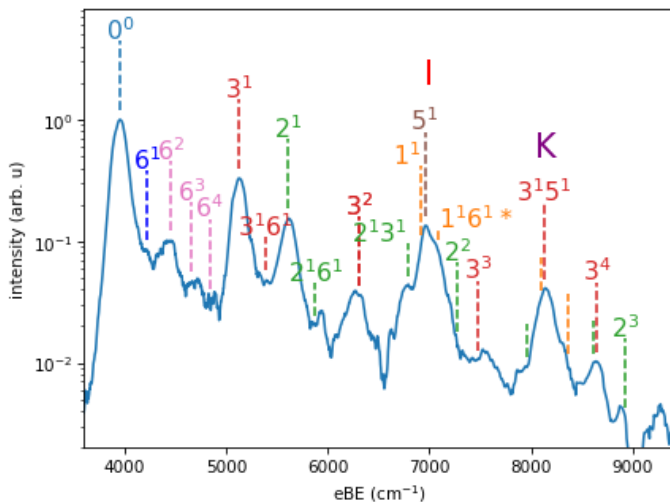
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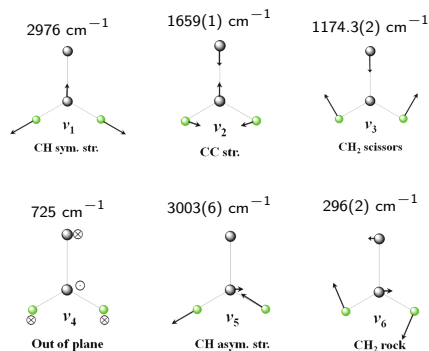


Electron affinity: 3952(48) cm⁻¹, 0.490(6)eV

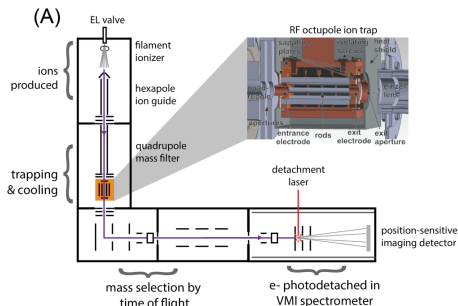
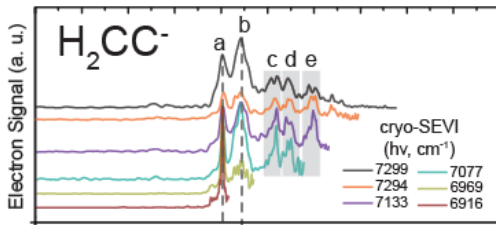
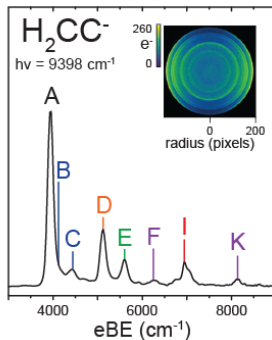
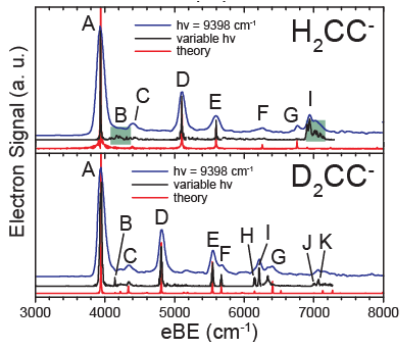
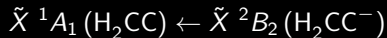




5¹, 6^{odd} are forbidden
1¹ has weak vibrational
Franck-Condon factor



Decomposition - Neumark UCB cryo-SEVI

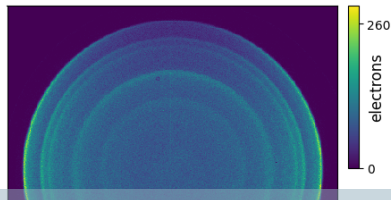
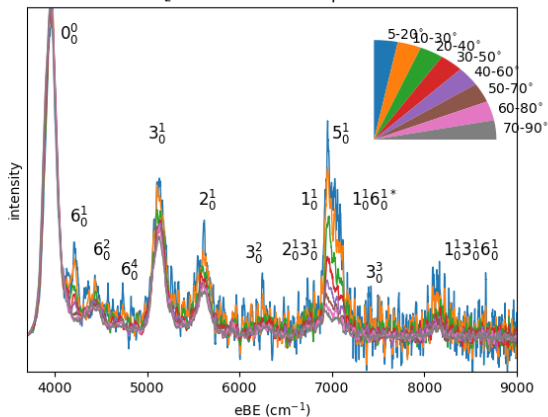


cluster of 5 close-spaced narrow peaks

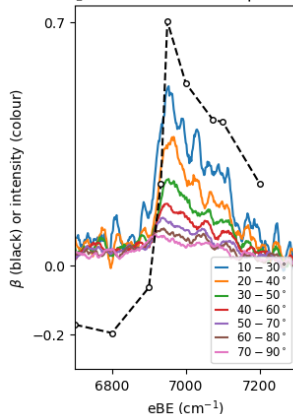
H_2CC^- photodetachment

PAD - radial angular slice intensity profiles

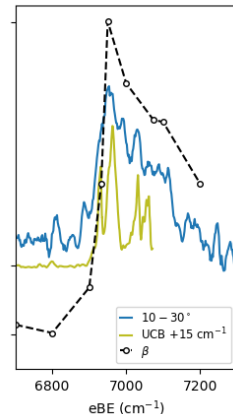
H_2CC^- 1064 nm slice profiles



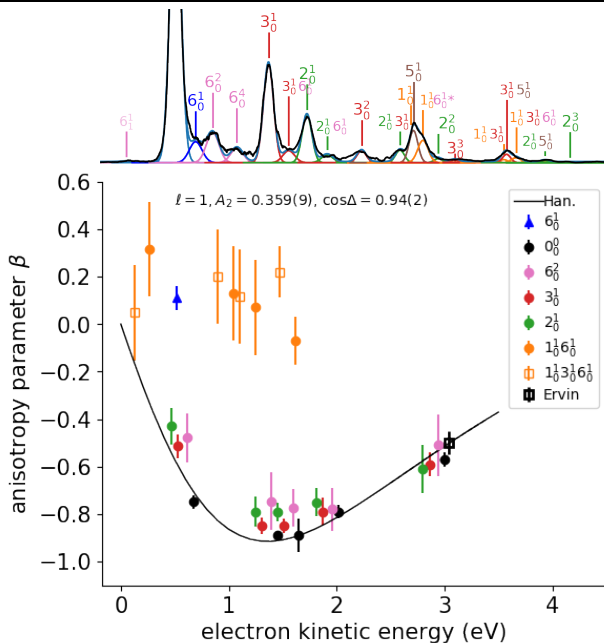
H_2CC^- 1064 nm slice profiles



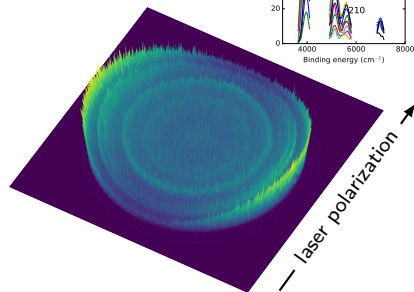
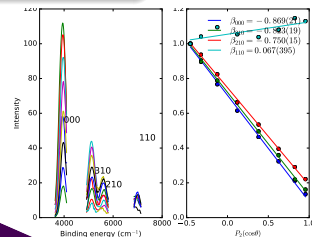
cf UCB 1413 nm



large variation of $\beta \Rightarrow$ electronic character of final state highly variable



$$I(\epsilon, \theta) \propto 1 + \beta(\epsilon) P_2(\cos \theta)$$



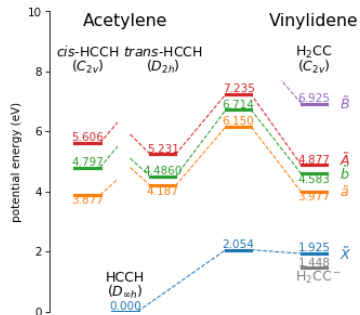
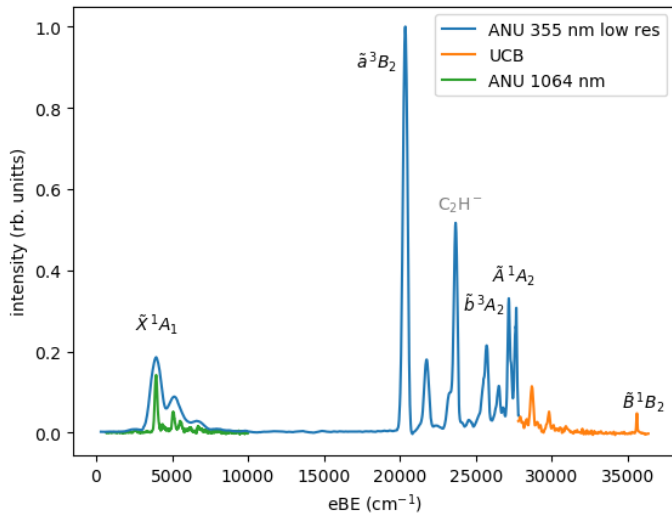
Hanstorp **Phys Rev A** 40 670 (1989):

$$R_d/R_s \sim A_2 \epsilon$$

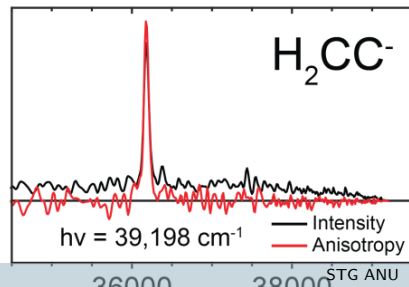
$$\beta_{\ell=1}(\epsilon) = \frac{2(A_2 \epsilon)^2 - 4A_2 \epsilon \cos \Delta}{1 + 2(A_2 \epsilon)^2}$$

Vibronic coupling to 1A_1 H₂CC

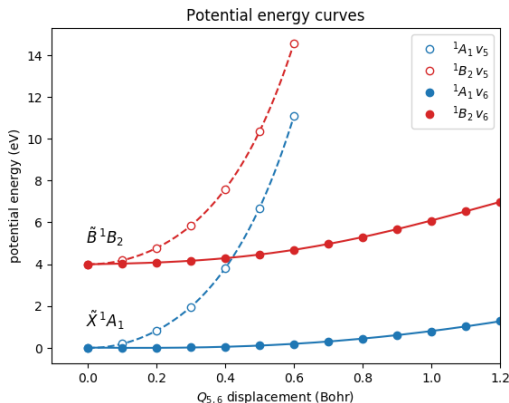
\tilde{B}^1B_2 - lowest lying state that may couple b_2 vibrational modes



$\beta_{1B_2} > 0$: Neumark UCB cryo-SEVI



- derivative vector $f_{Q_\alpha}^{ij} = \langle \psi_i(r; R) | \frac{\partial}{\partial Q_i} | \psi_j(r; R) \rangle_r$
 C_{2v} : $f_{Q_\alpha}^{ij} \neq 0$ provided $\Gamma_i \otimes \Gamma_j \in A_1$
 $f_{Q_\alpha}^{ij}$ non-vanishing for b_2 vibrations: Q_5 (asymmetric CH stretch) and Q_6 (in plane rock)
- H_2CC $f_{Q_6}^{ij} = -4.08$, $f_{Q_5}^{ij} = 0.14$ (Guo UNM)
 $\psi_i(^1A_1)$ and $\psi_i(^1B_2)$ strongly coupled for mode ν_6 in-plane rocking mode
- 5_0^1 mixes with $1_0^1 6_0^1$ through *anharmonic interaction* - lowers energy of $1_0^1 6_0^1$

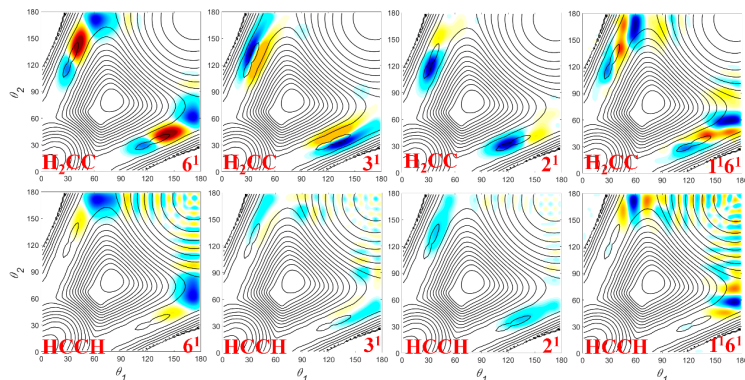
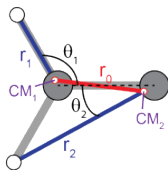


Modes harmonic except Q_6 : $H_2CC \omega'_{e_6} = 327 \text{ cm}^{-1} \ll H_2CC \omega''_{e_6} = 876 \text{ cm}^{-1}$
 ν_6 intensity shared across many vibrational excitations

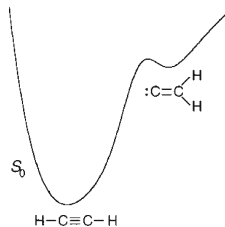
Vinylidene-acetylene isomerization

Wavefunctions - *ab initio* calculations of Hua Guo - UNM

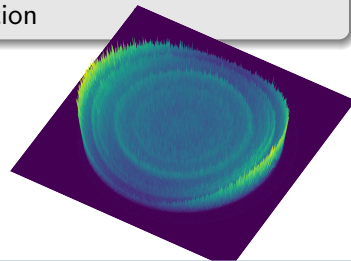
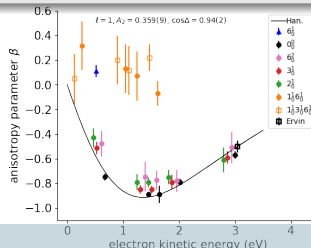
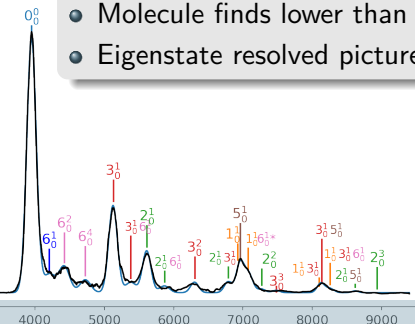
$$\psi_n^{\text{neutral}} \sim c_n^{\text{vin}} \psi_n^{\text{vin}} + c_{nm}^{\text{acet}} \psi_m^{\text{acet}}$$



- $3^1, 2^1$ little acetylene character
- in-plane rocking mode ν_6 induces significant acetylene character
- $5^1 \sim 1^1 6^1$ manifest acetylene character
- Isomerization encoded in the spectra of vibrational states



- H_2CC^- PES readily assigned to vinylidene vibrational normal modes
- Anomalous photoelectron anisotropy for eBE transitions $> 7,000 \text{ cm}^{-1}$, 1_0^1 , 5_0^1 , $1_0^1 6_0^1$ and 3_0^1 combination bands with same
- 5^1 , 6^1 Franck-Condon vibrationally forbidden (non-totally-symmetric b_2 modes)
- 6^1 appears from strong vibronic interaction \times small vibrational overlap factor with $v'_6 = 1$
- 5^1 appears from anharmonic coupling to $1^1 6^1$
- 6^n small overlaps with many odd- ν_6
- Molecule finds lower than normal isomerization path via vibronic coupling
- Eigenstate resolved picture of vinylidene-acetylene isomerization





Steve Cavanagh



Brenton Lewis

and technical assistance:

Colin Dedman, Kevin Lonsdale, Ros Tranter,
Steve Battison

Funding: ARC DP160102585

PyAbel: Abel transform software

<https://github.com/PyAbel>



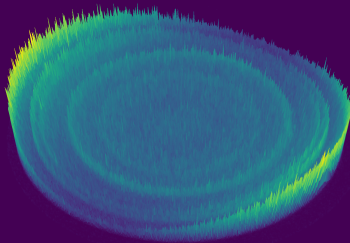
The screenshot shows the GitHub repository for PyAbel. The README file is open, displaying the title "PyAbel README" and a "BUILD INSTRUCTIONS" button. Below the title, a note states: "Note: This readme is best viewed as part of the [PyAbel Documentation](#)." The "Introduction" section follows, explaining that PyAbel is a Python package for forward and inverse Abel transforms. It describes the forward transform as taking a slice of a cylindrically symmetric 3D object and providing a 2D projection, and the inverse transform as taking a 2D projection and reconstructing a slice of the 3D distribution. It also mentions the importance of inverse Abel transforms in analyzing angle-resolved photoelectron/photocurrent spectra, plasma plumes, flames, and solar occultation. The text further states that PyAbel provides efficient implementations of several Abel transform algorithms, as well as related tools for centering images, symmetrizing images, and calculating properties such as the radial intensity distribution and the anisotropy parameters. At the bottom of the screenshot, there is a 3D visualization of a blue cylindrical object and its corresponding 2D projection, which is a color-coded intensity map.

Transform Methods

The outcome of the numerical Abel Transform depends on the exact method used. So far, PyAbel includes the following transform methods:

1. `basex` - Gaussian basis set expansion of Dribinski and co-workers.
2. `hansenlaw` - recursive method of Hansen and Law.
3. `direct` - numerical integration of the analytical Abel transform equations.
4. `two_point` - the "two point" method of Dasch and co-workers.
5. `three_point` - the "three point" method of Dasch and co-workers.
6. `onion_peeling` - the "onion peeling" deconvolution method of Dasch and co-workers.
7. `onion_bordas` - "onion peeling" or "back projection" method of Bordas et al. based on the MatLab code by Ralls and Wells et al.
8. `linbasex` - the 1D-spherical basis set expansion of Gerber et al.
9. `fh` - Fourier-Hankel method (not yet implemented).
10. `pop` - polar onion peeling method (not yet implemented).

End



Appendix

- More wavefunctions

Hau Guo wavefunctions

$$\psi_n^{\text{neutral}} \sim c_n^{\text{vin}} \psi_n^{\text{vin}} + c_{nm}^{\text{acet}} \psi_m^{\text{acet}}$$

