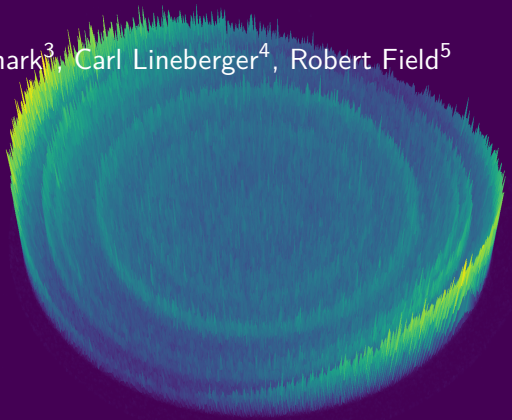
Vibronic coupling in the ground state of vinylidene $\tilde{X}^1A_1$ H_2CC

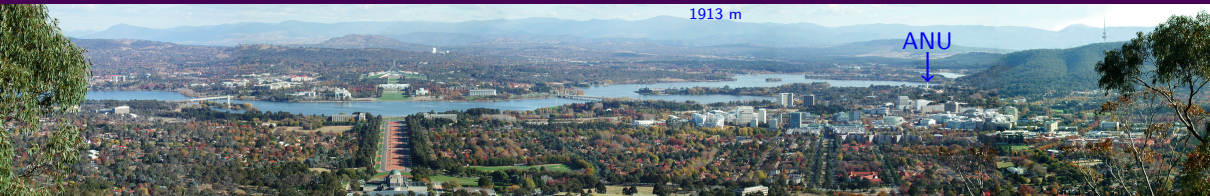
Steve Gibson[1], Ben Laws[1], Hua Guo[2], Dan Neumark[3], Carl Lineberger[4], Robert Field[5]

[1]LPC/RSPE ANU, Canberra
[2]Chem UNM, NM
[3]Chem UCB, CA
[4]Chem/Bio JILA UCol. CO
[5]Chem MIT, MA



ISMS June 20, 2017

- HR-PEI/cryo-SEVI
- H_2CC^- PES decomposition
- H_2CC^- PAD decomposition
- vibronic coupling/isomerization



Vibronic coupling in the ground state of vinylidene $\tilde{X}^1A_1$ H_2CC facilitates isomerization

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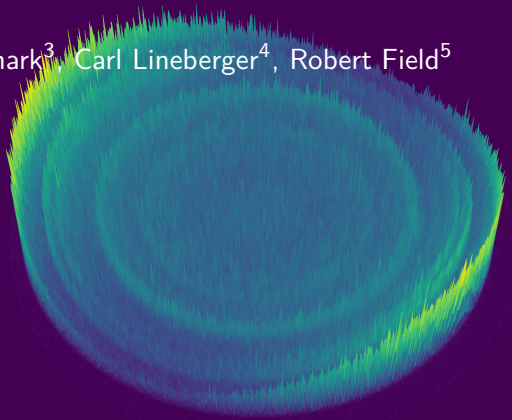

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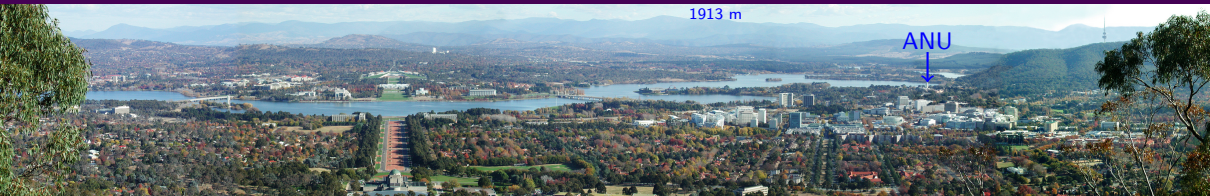
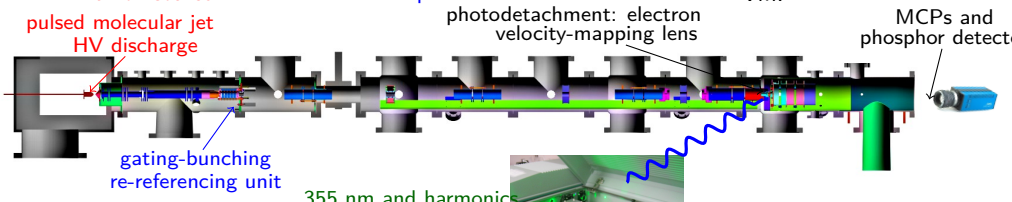
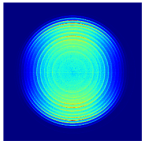


Spectrometer - photodetachment/photofragmentation





355 nm and harmonics
Nd:YAG laser

OPO laser 220 nm−1750 nm

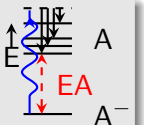
Fast beam spectrometer:
Cyr PhD Thesis (UC Berkeley 1993)

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)

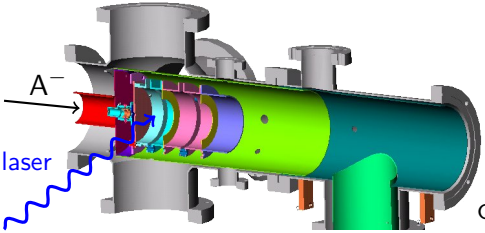
Photodetachment:

$A^- + h\nu \rightarrow A^* + e^-$

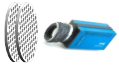


Velocity-map imaging
HR-PEI

VMI lens coaxial with ion-beam

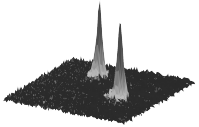


MCPs+phosphor

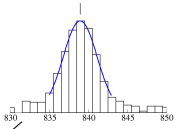


CCD camera 2048x2048 pixel

monochrome camera image



(x_i, y_i)



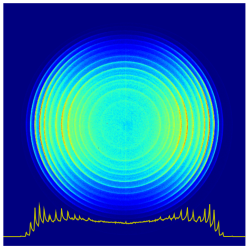
sub-pixel centroid

bin to image

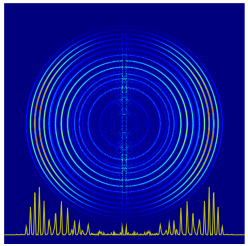
circularize Gascooke (Flind U)

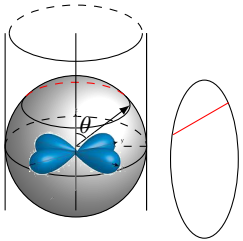
e^- trajectories

2D projection O_2^-



3D slice





$\frac{\Delta E}{E} \sim$ constant $\rightarrow e^-$ speed

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

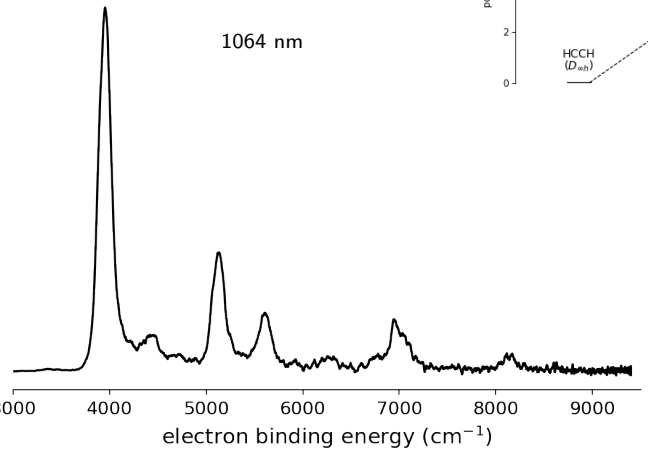
vinylidene anion H_2CC^- photodetachment

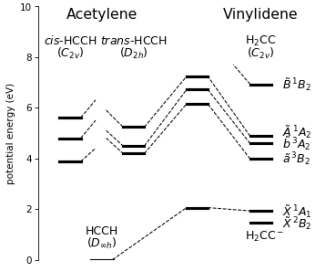
Photoelectron spectrum (HR-PEI)

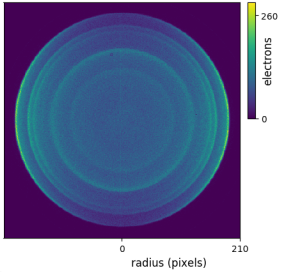
$\tilde{B}^1B_2, \ldots, \tilde{X}^1A_1$ $H_2CC \leftarrow \tilde{X}^2B_2$ H_2CC^-

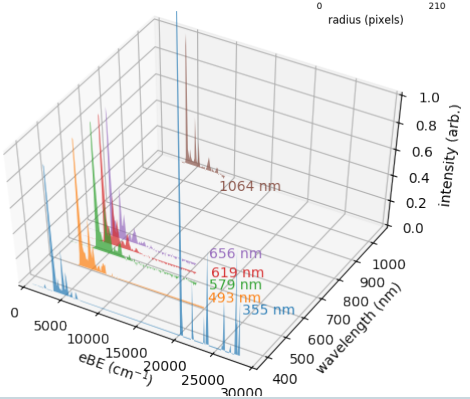
Electron affinity: 3952(48) cm^{-1}, 0.490(6)eV

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









vinylidene anion H_2CC^- photodetachment

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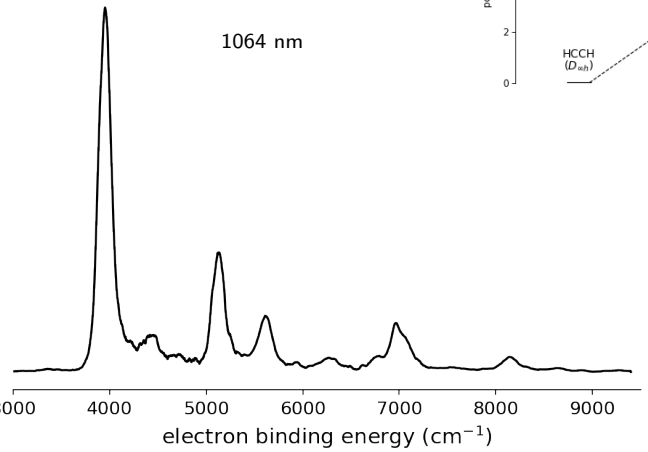
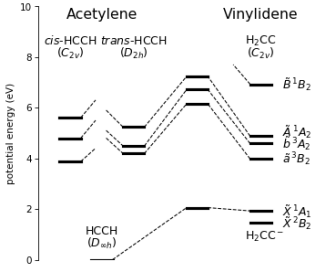
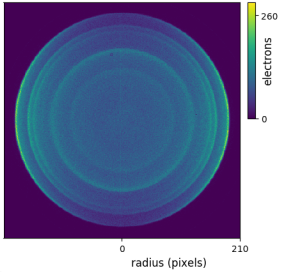
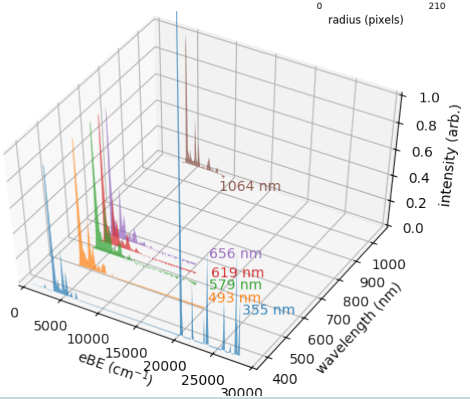






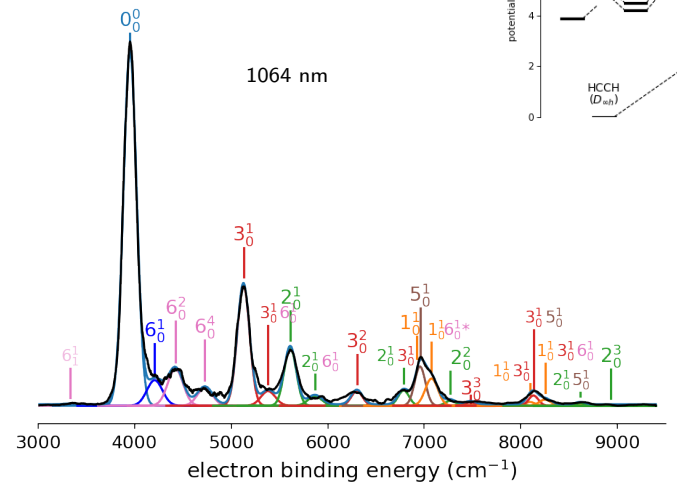


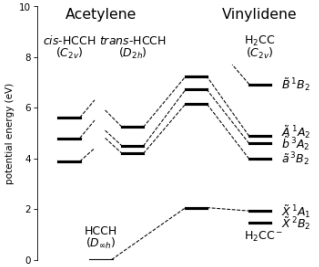
vinylidene anion H_2CC^- photodetachment

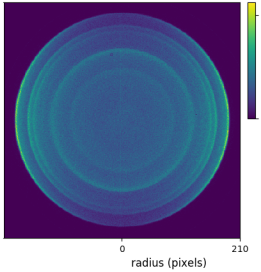
vibrational normal-mode structure

$\tilde{X}^1A_1$ $H_2CC \leftarrow \tilde{X}^2B_2$ H_2CC^-

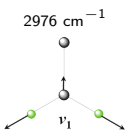
Electron affinity: 3952(48) cm^{-1}, 0.490(6)eV

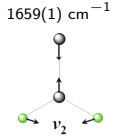


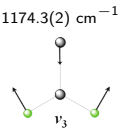




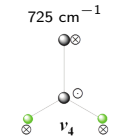
a_1

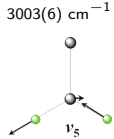


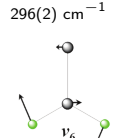




b_1, b_2

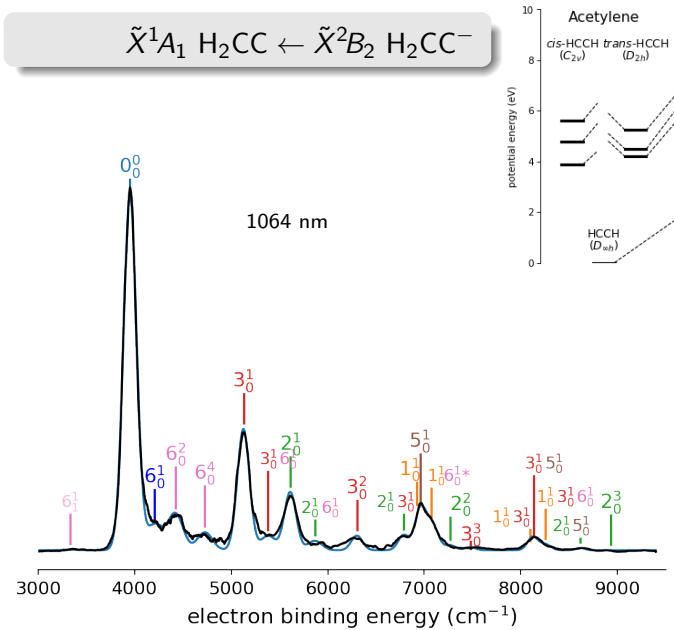


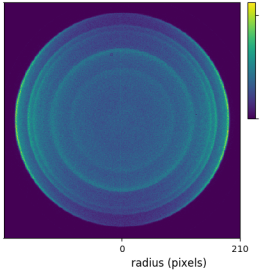




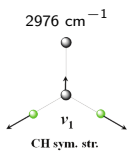
vinylidene anion H_2CC^- photodetachment

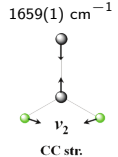
$\tilde{X}^1A_1$ $H_2CC \leftarrow \tilde{X}^2B_2$ H_2CC^-

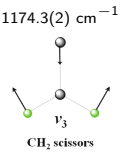




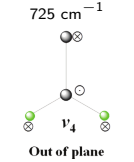
a_1

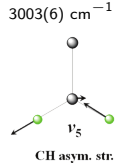


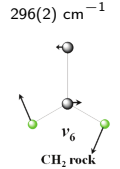




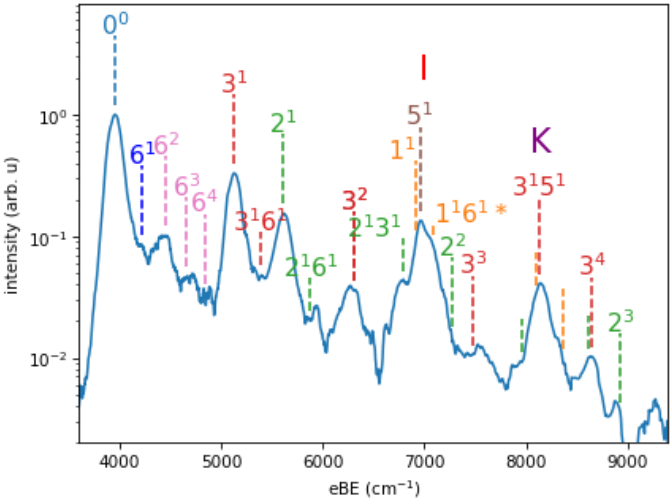
b_1, b_2





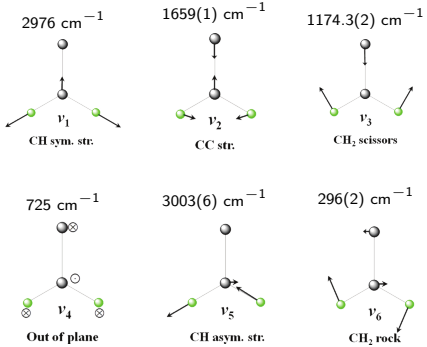


H_2CC^- PES logscale



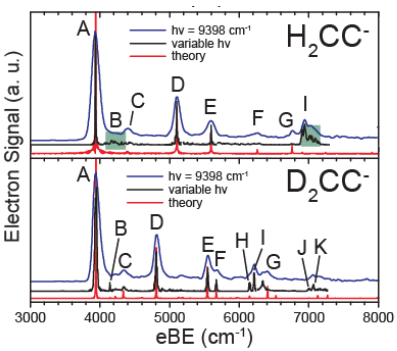
5^1, 6^{odd} are forbidden

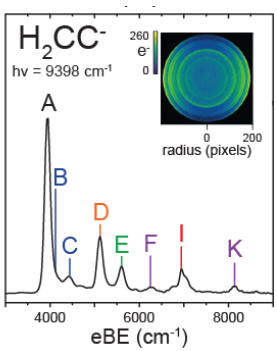
1^1 has weak vibrational Franck-Condon factor

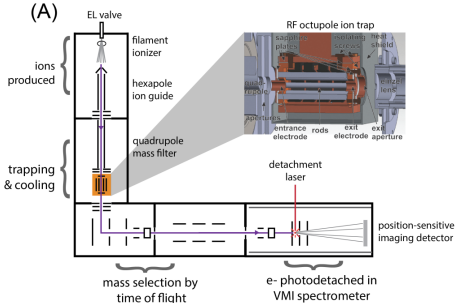


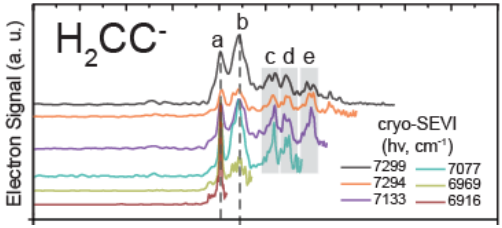
Decomposition - Neumark UCB cryo-SEVI

$\tilde{X}\ ^1A_1\,(H_2CC) \leftarrow \tilde{X}\ ^2B_2\,(H_2CC^-)$





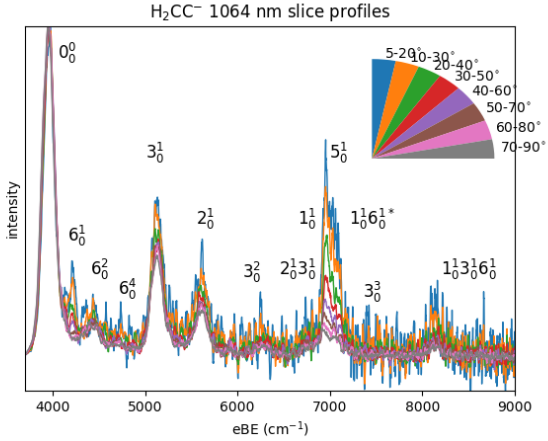


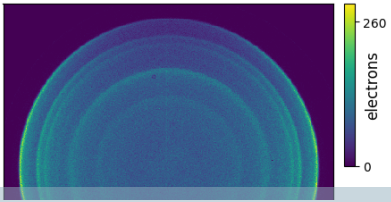


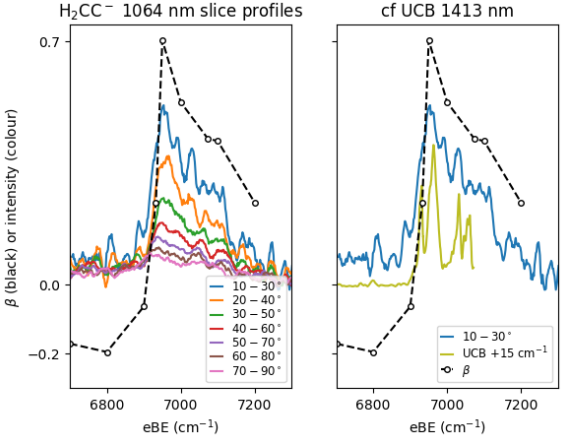
cluster of 5 close-spaced narrow peaks

H_2CC^- photodetachment

PAD - radial angular slice intensity profiles



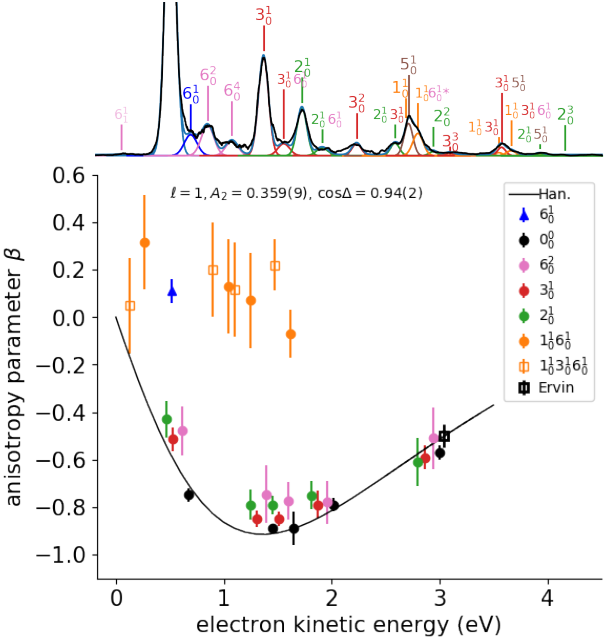


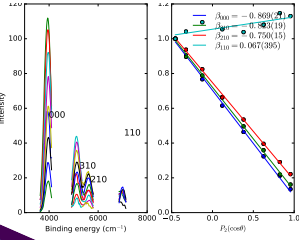


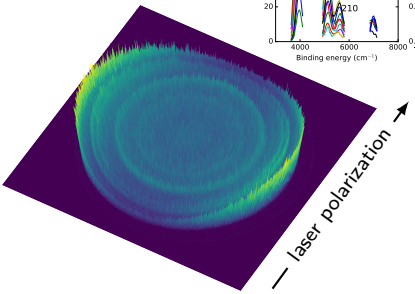
large variation of $\beta \implies$ electronic character of final state highly variable

H_2CC^- photodetachment
PAD

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







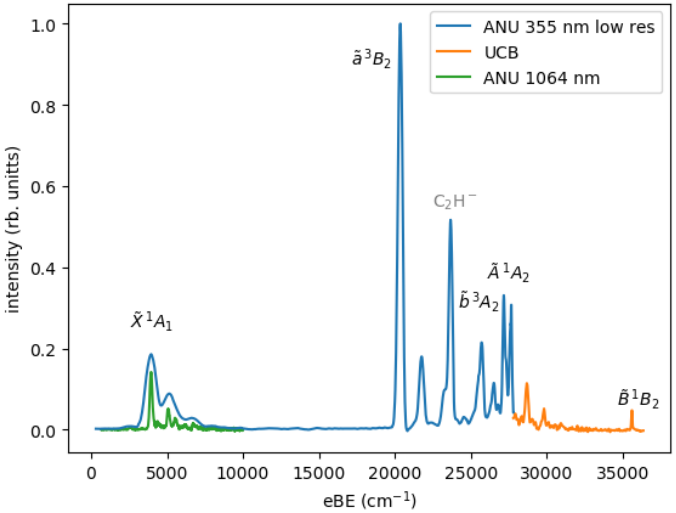
Hanstorp Phys Rev A40 670 (1989):

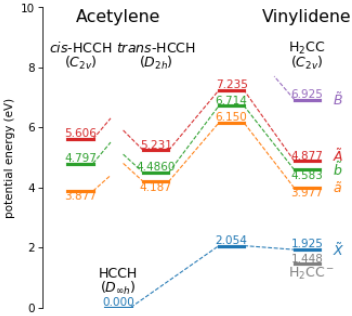
$R_d/R_s \sim A_2\epsilon$

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

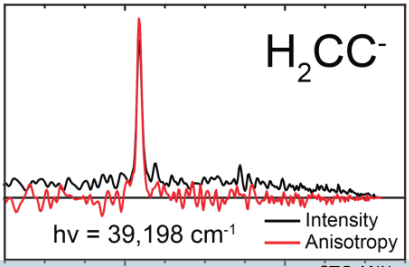
Vibronic coupling to $^1A_1$ H_2CC

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





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



- derivative vector $f^{ij}_{Q_\alpha} = \langle \psi_i(r;R) | \frac{\partial}{\partial Q_i} | \psi_j(r;R) \rangle_r$

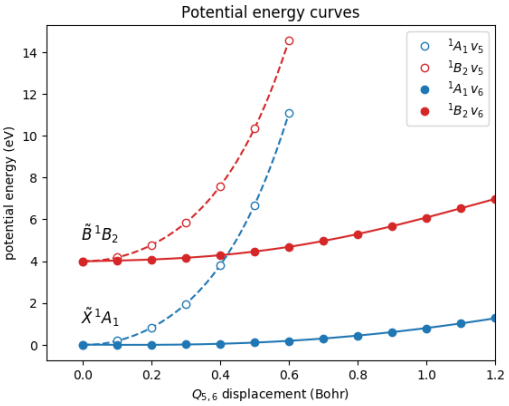
  C_{2v}: $f^{ij}_{Q_\alpha} \neq 0$ provided $\Gamma_i \otimes \Gamma_j \in A_1$

  $f^{ij}_{Q_\alpha}$ non-vanishing for b_2 vibrations: Q_5 (asymmetric CH stretch) and Q_6 (in plane rock)

- H_2CC $f^{ij}_{Q_6} = -4.08$, $f^{ij}_{Q_5} = 0.14$ (Guo UNM)

  $\psi_i(^1A_1)$ and $\psi_i(^1B_2)$ strongly coupled for mode ν_6 in-plane rocking mode

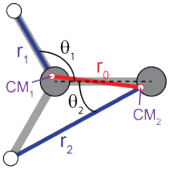
- 5^1_0 mixes with $1^1_0 6^1_0$ through *anharmonic interaction* - lowers energy of $1^1_0 6^1_0$

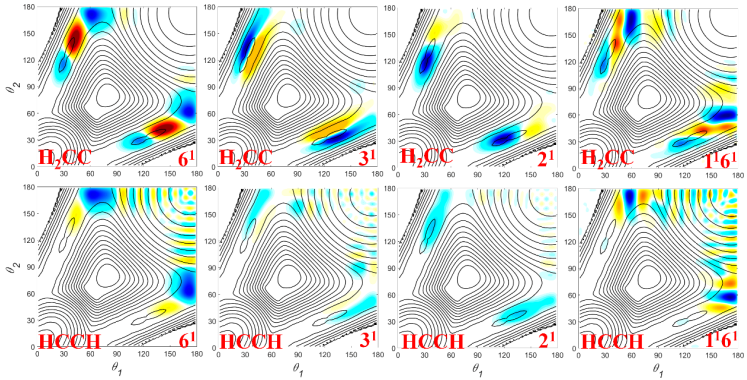


Modes harmonic except Q_6: $H_2CC\,\omega'_{e_6} = 327\text{cm}^{-1} \ll H_2CC^-\omega''_{e_6} = 876\text{cm}^{-1}$

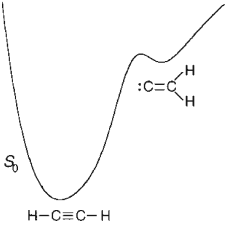
ν_6 intensity shared across many vibrational excitations

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



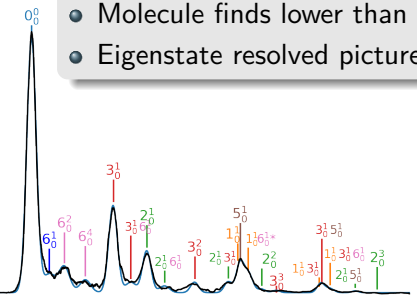


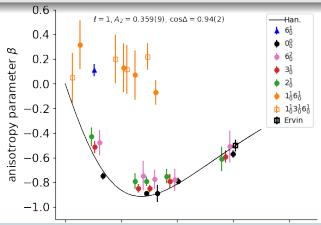
- $3^1, 2^1$ little acetylene character
- in-plane rocking mode ν_6 induces significant acetylene character
- $5^1 \sim 1^1 6^1$ manifest acetylene character
- Isomerization encoded in the spectra of vibrational states

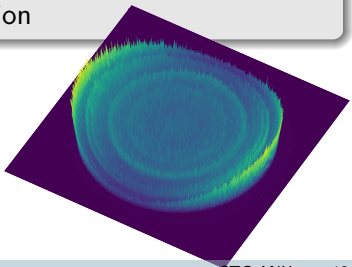


Summary and Conclusions

- H_2CC^- PES readily assigned to vinylidene vibrational normal modes
- Anomalous photoelectron anisotropy for eBE transitions $> 7,000$ 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







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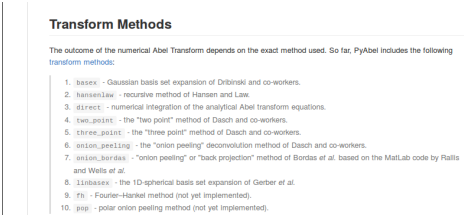
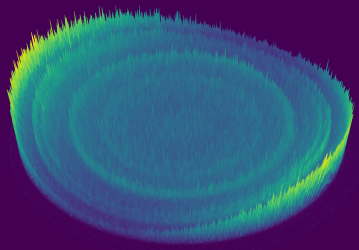
PyAbel: Abel transform software https://github.com/PyAbel



End



Appendix

- More wavefunctions

Hau Guo wavefunctions

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