Decomposition of vibronic and Renner-Teller structure in C_2H and C_2D from anion high-resolution photoelectron imaging

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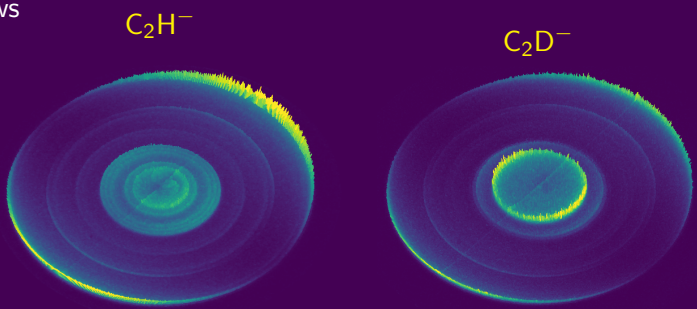
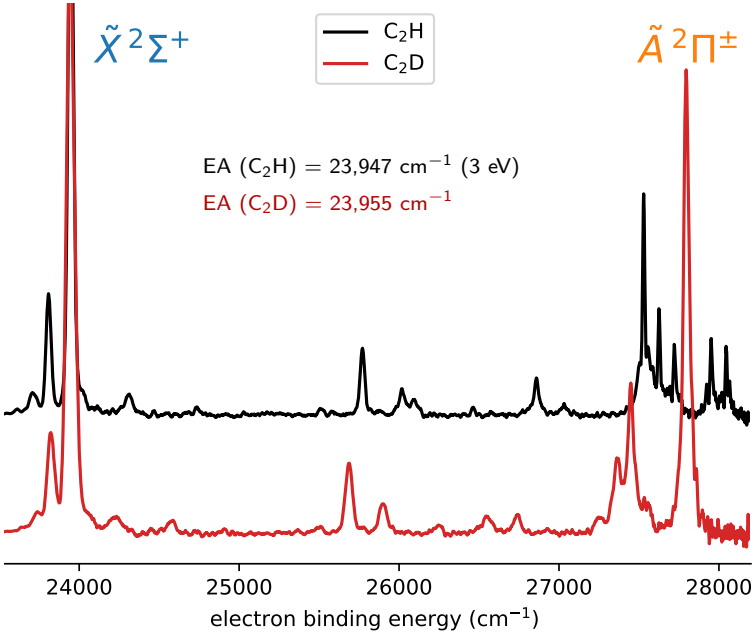
ISMS June 18, 2018

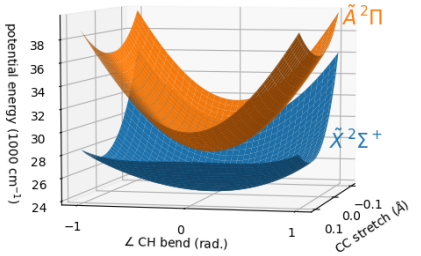
- HR-PEI
- C_2H/D^- PES
- C_2H/D^- PAD
- Theory

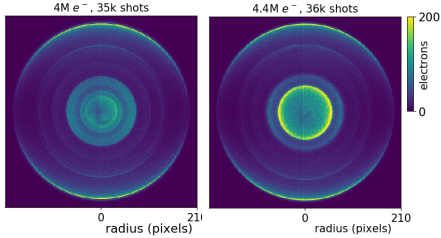


C_2H, C_2D ($\tilde{A}\,^2\Pi^{\pm}$, $\tilde{X}\,^2\Sigma^+$) $\leftarrow$ C_2H^-, C_2D^- ($\tilde{X}\,^1\Sigma^+$) photodetachment

photoelectron spectrum 355 nm - electronic structure (add one neutron)







C_2H^- C_2D^-

C_2H, C_2D ($\tilde{A}\,^2\Pi^{\pm}, \tilde{X}\,^2\Sigma^+$) $\leftarrow$ C_2H^-, C_2D^- ($\tilde{X}\,^1\Sigma^+$) photodetachment

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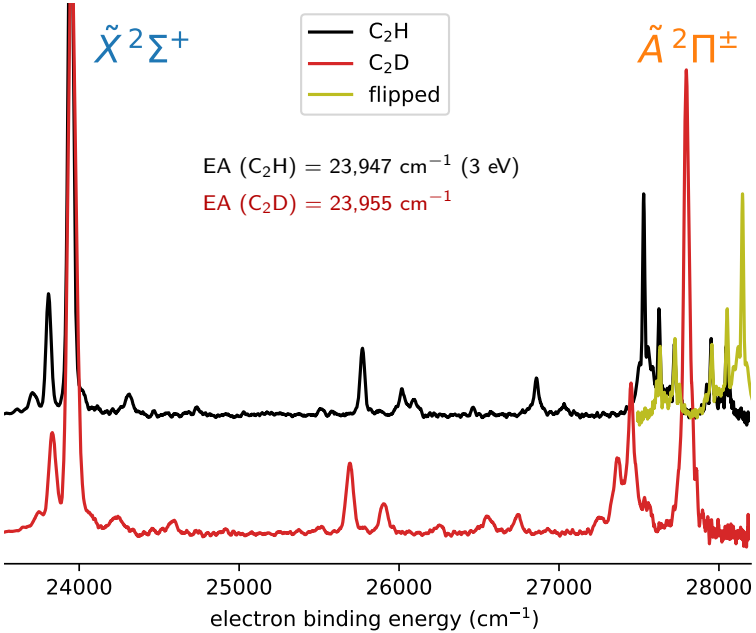
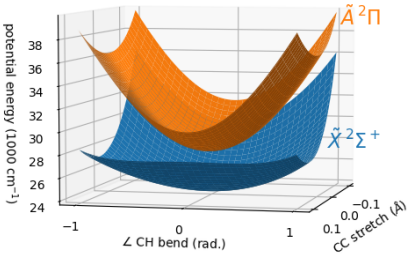
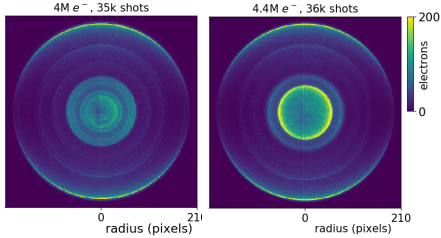






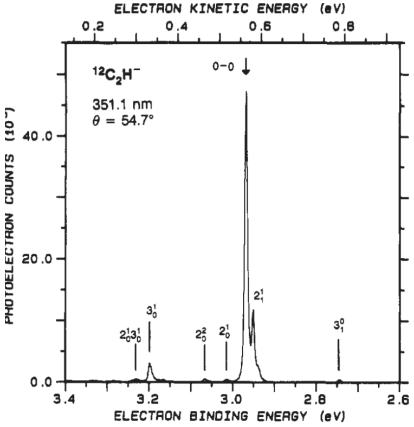
C_2H^- C_2D^-

C_2H/D^- photoelectron spectroscopy

Historical

photoelectron spectrometer

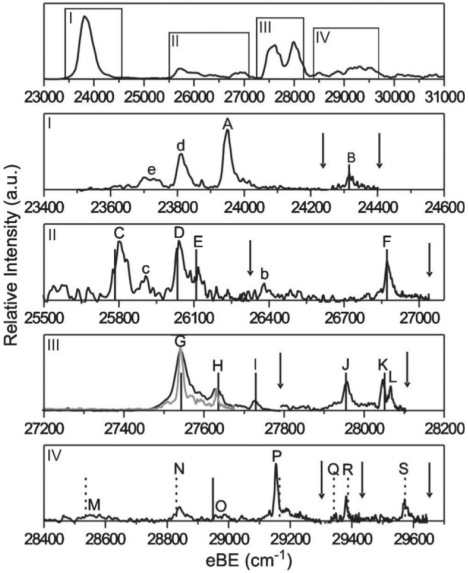
Lineberger



Ervin and Lineberger J Phys Chem **95** 1167 (1991)

& SEVI Taylor, Xu, and Neumark J Chem Phys **108** 10018 (1998)

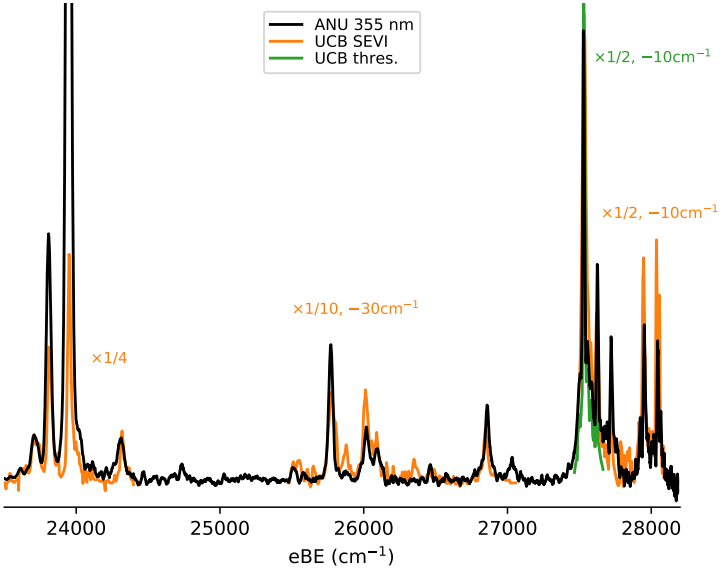
Neumark

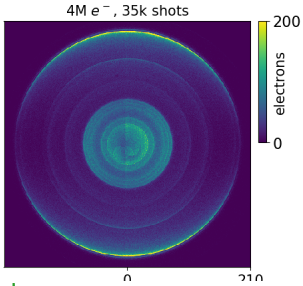


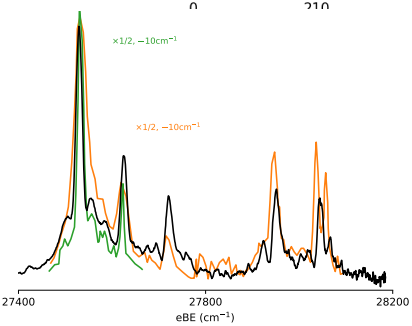
Zhou, Garand and Neumark J Chem Phys **127** 114313 (2007)

HR-PEI (ANU 355 nm) and SEVI (UCB) photoelectron spectra

$C_2H \leftarrow C_2H^- + hc/\lambda$



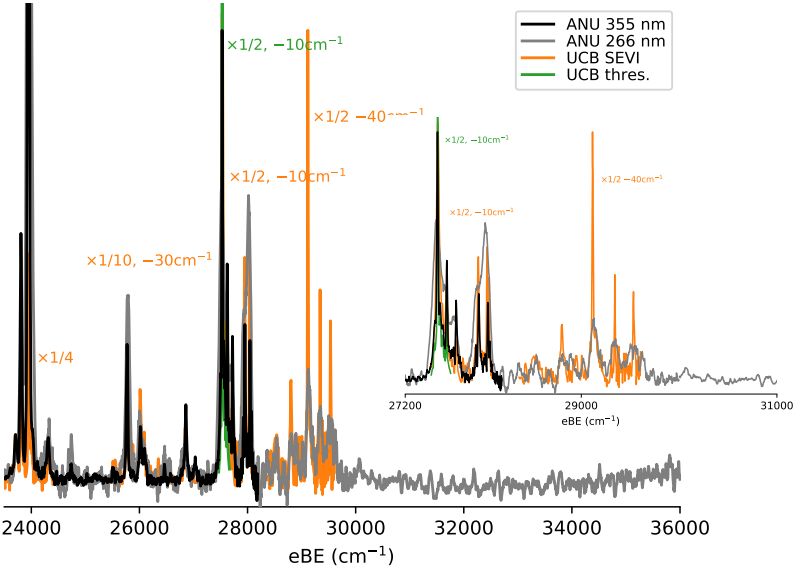


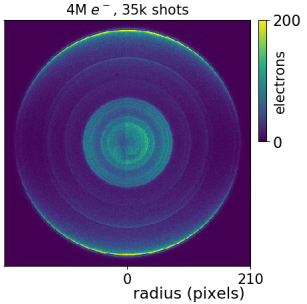


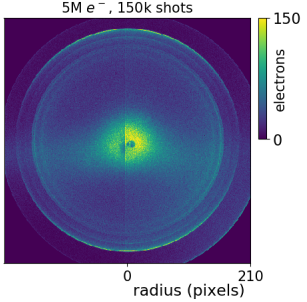
UCB (digitized) from Zhou, Garand, Neumark J Chem Phys **127** 114313 (2007)

HR-PEI (ANU 355 nm 266 nm) and SEVI (UCB) photoelectron spectra

$C_2H \leftarrow C_2H^- + hc/\lambda$

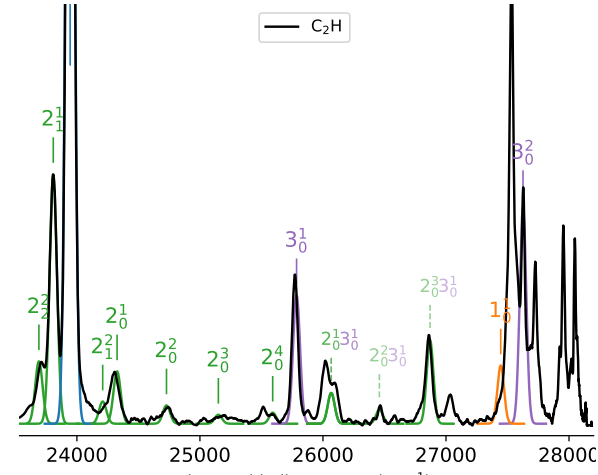


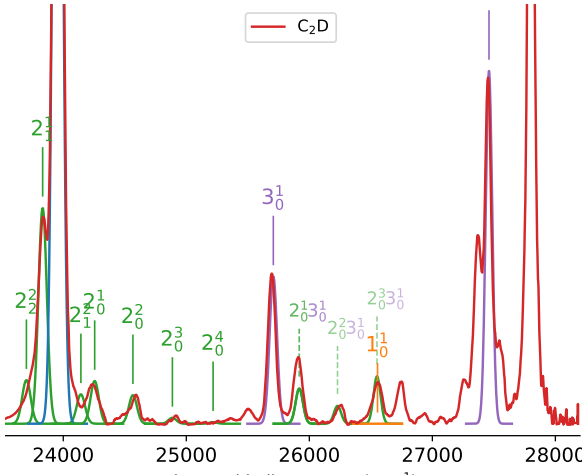




C_2H/D ($\tilde{A}\,^2\Pi^{\pm}, \tilde{X}\,^2\Sigma^+$) $\leftarrow$ C_2H/D^- ($\tilde{X}\,^1\Sigma^+$) photodetachment 355 nm

decomposition - $\tilde{X}$ vibrational structure

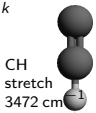


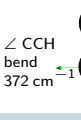


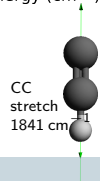
$$G_0(v_1, v_2, v_3) = \sum_i \omega_i^0 v_i + \sum_i \sum_{k \geq i} x_{ik}^0 v_i v_k + \sum_i \sum_{k \geq i} g_{ik} \ell_i \ell_k$$

$\nu_1 \sim 3500$, $\nu_2 \sim 371\,(10)$, $\nu_3 \sim 1840\,(10)$ cm^{-1}

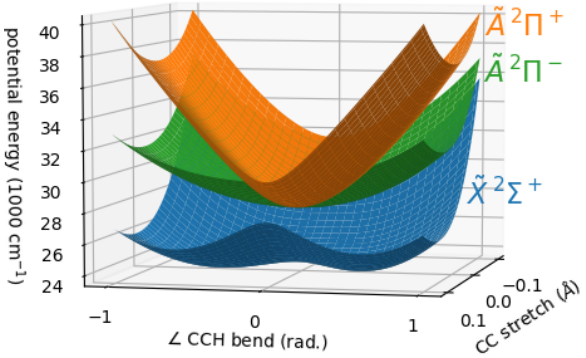
$\nu_1'' \sim 3352$, $\nu_2'' \sim 510\,(10)$, $\nu_3'' \sim 1871$ cm^{-1}



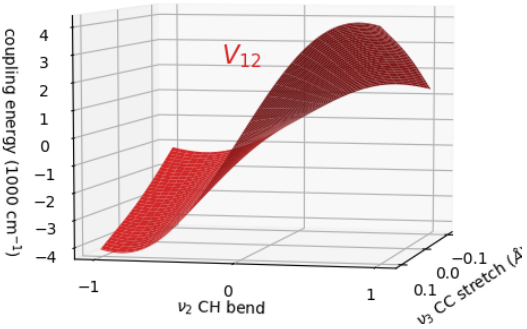




Tarroni and Carter J Chem Phys **119** 12878 (2003)



$$V_a(q_1, q_2, q_3) = \sum_{ijk} C^a_{ijk} q_1^i q_2^j q_3^k$$

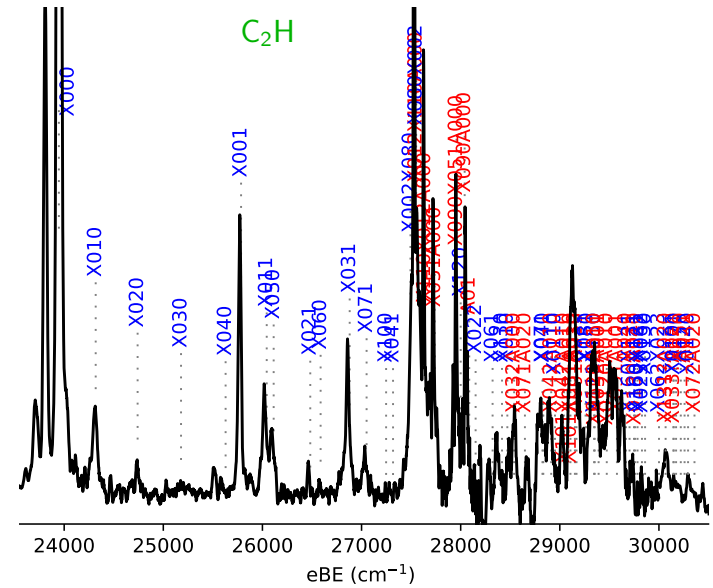


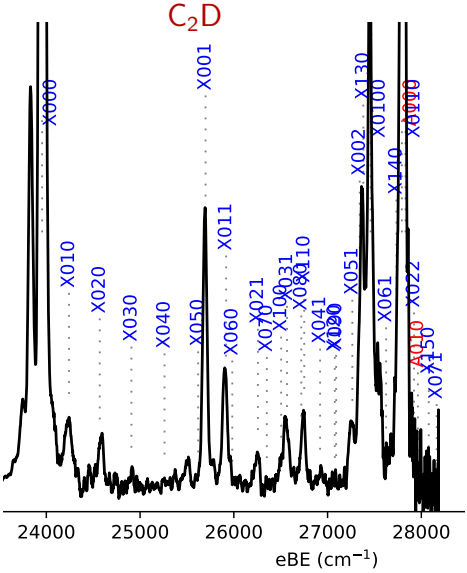
$$\begin{bmatrix} A_{\Sigma^+} & 0 \\ 0 & A_{\Pi^+} \end{bmatrix} = \mathbf{U}^T \begin{bmatrix} V_{\Sigma^+} & V_{12} \\ V_{12} & V_{\Pi^+} \end{bmatrix} \mathbf{U}$$

V_{Π^-} un-perturbed

Decomposition

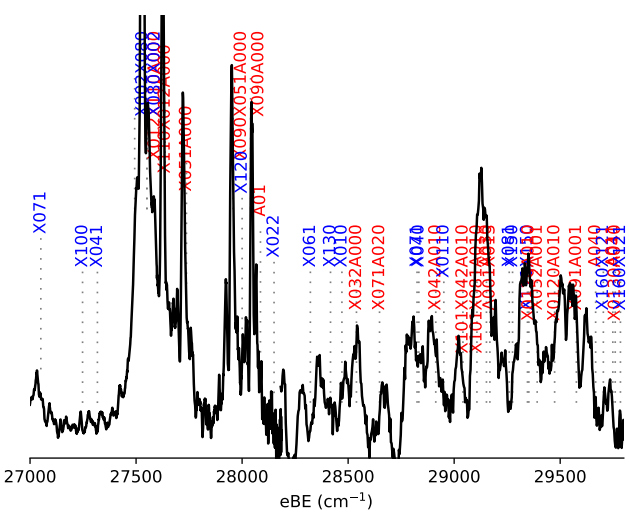
Tarroni and Carter J Chem Phys **119** 12878 (2003)

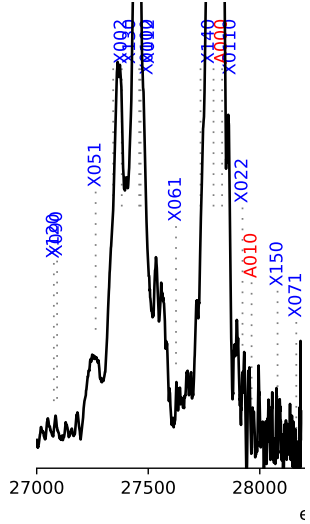




Decomposition

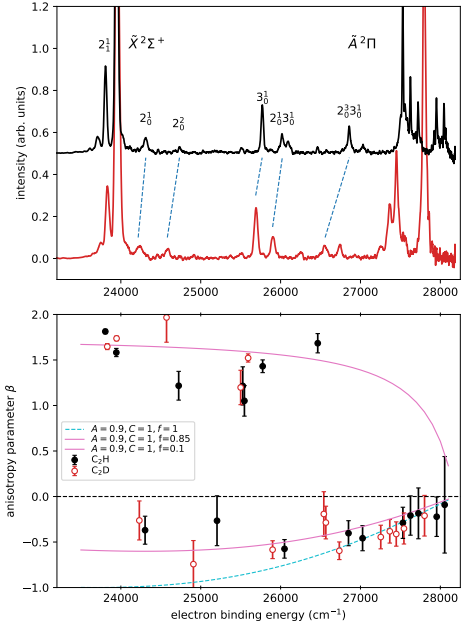
Tarroni and Carter J Chem Phys **119** 12878 (2003)





C_2H^- vs C_2D^- photodetachment

355 nm PES/PAD



$$I(\epsilon,\theta) = \frac{\sigma(\epsilon)}{4\pi}\left[1+\beta(\epsilon)P_2(\cos\theta)\right]$$

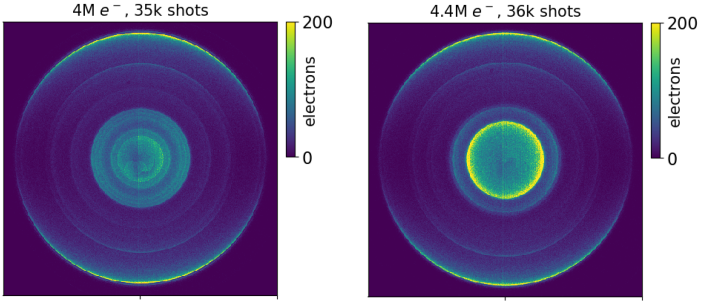
Sanov Ann Rev Phys Chem **65** 341 (2014)

$$\beta(\epsilon) = \frac{\ell(\ell-1)+(\ell+1)(\ell+2)A^2\epsilon^2 - 6\ell(\ell+1)A\epsilon\cos(\delta_{\ell+1}-\delta_{\ell-1})}{(2\ell+1)[\ell+(\ell+1)A^2\epsilon^2]}$$

$$\frac{\chi_{\ell+1}}{\chi_{\ell-1}} \sim A\epsilon \qquad \epsilon(\text{eKE}) = 10^7/\lambda - \text{eBE}$$

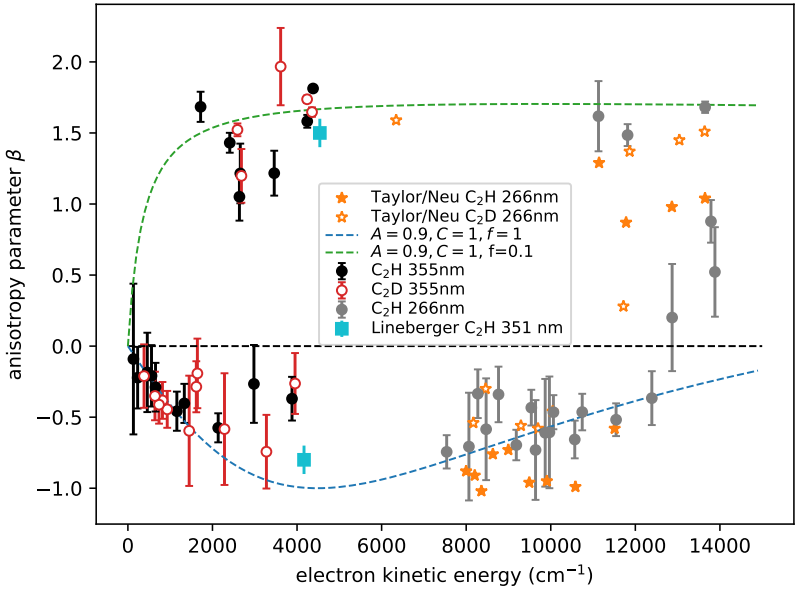
$$|sp\rangle = \sqrt{1-f}\,|s\rangle + \sqrt{f}\,|p\rangle \qquad 0 \le f \le 1$$

$$\beta(\epsilon) = \frac{2ZA\epsilon + 2(A\epsilon)^2 - 4A\epsilon\cos(\delta_2-\delta_0)}{ZA\epsilon + 2(A\epsilon)^2 + 1} \qquad Z = \frac{1-f}{f}\frac{B}{A}$$



C_2H/D photoelectron angular distributions

355 nm and 266 nm



C_2H^- ... $4\sigma^2 1\pi^4 5\sigma^2$ $\tilde{X}\,^1\Sigma^+$

C_2H ... $4\sigma^2 1\pi^4 5\sigma^1$ $\tilde{X}\,^1\Sigma^+$

... $4\sigma^2 1\pi^3 5\sigma^2$ $\tilde{A}\,^2\Pi^\pm$

$\beta_{\tilde{X}} > 0$, σ electron $\ell = 0$

$\beta_{\tilde{A}} < 0$, π electron $\ell = 1$

Summary

- New HR-PEI measurements of C_2H^- (355 nm and 266 nm) and C_2D^- (355 nm) provide continuous (in eBE) high-resolution photoelectron spectra and photoelectron angular distributions
- (known) significant spectral differences between C_2H and C_2D in region of $\tilde{A}$
- (known) photoelectron angular distributions have $\beta_{\tilde{X}} > 0$ and $\beta_{\tilde{A}} < 0$ signatures

Conclusions

- Some PES structure beyond $30,000$ cm^{-1} eBE
- C_2H and C_2D kinetic energy dependence of the anisotropy parameter is similar
- All $\tilde{A}$ region transitions have a negative anisotropy parameter, either insensitive to, or inconsistent with a mixed final-state ($\tilde{A}\tilde{X}$) wavefunction character(?)
- Unanswered question: ~ 95 cm^{-1} $\tilde{A}$ band spacing
- Not (yet) done calculation: vibronic coupling derivative transition moment calculation (see appendix slide)

Acknowledgements

People

- Robert Field (MIT)
- Brenton Lewis (ANU)
- Steven Cavanagh (ANU)

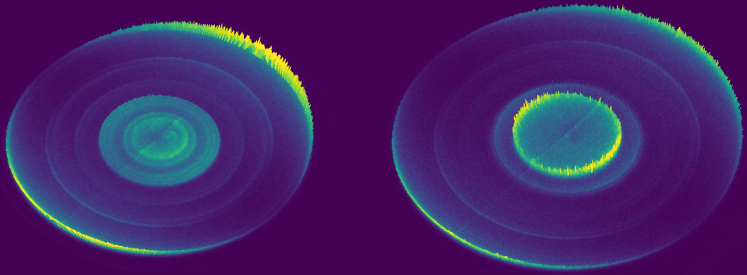
Open source software

- PyAbel - Abel transform - github.com/PyAbel
- PyDiatomic - Coupled-channel Schrödinger equation - github.com/stggh/PyDiatomic
- NWChem - computational chemistry - github.com/nwchemgit/nwchem
- Python and matplotlib - www.python.org and matplotlib.org
- Pgopher - simulate rovibrational spectra - pgopher.chm.bris.ac.uk
- ezySpectrum - stick photoelectron - github.com/iopenshell/ezSpectrum

Funding

- Australian Research Council DP160102585

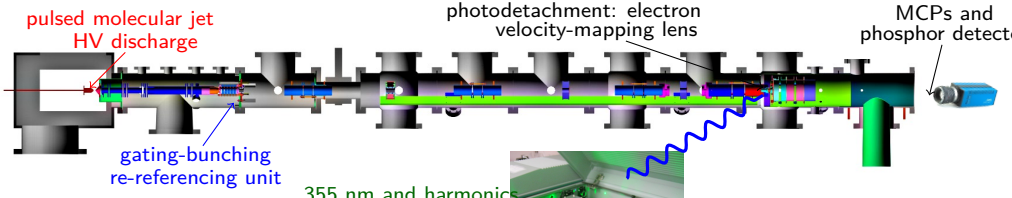
End

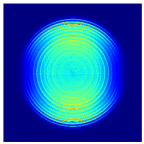


Appendix

- HR-PEI Spectrometer
- Velocity-map imaging
- pgopher - rotational structure
- $\tilde{A} - \tilde{X}$ vibronic coupling
- O^- calibration

Spectrometer - photodetachment/photofragmentation





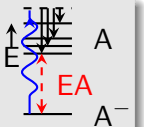
355 nm and harmonics
Nd:YAG laser

OPO laser 220 nm−1750 nm

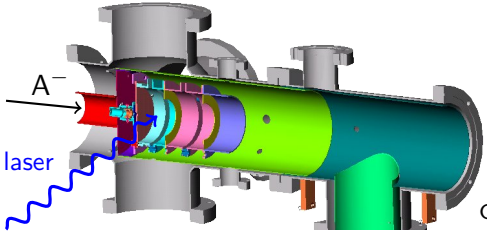
Fast beam spectrometer:
Cyr PhD Thesis (UC Berkeley 1993)
Velocity-map imaging lens:
Eppink and Parker Rev Sci Instrum **68** 3477 (1997)
Gating-bunching-rereferencing unit:
(ANU) Dedman *et al.* Rev Sci Instrum **73** 2915 (2001)

Photodetachment:

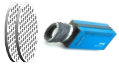
$A^- + h\nu \rightarrow A^* + e^-$



VMI lens coaxial with ion-beam

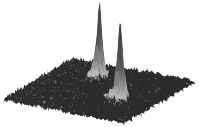


MCPs+phosphor

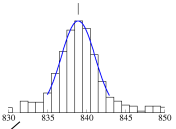


CCD camera 2048x2048 pixel

monochrome camera image



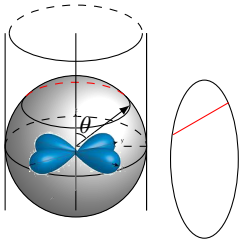
(x_i, y_i)



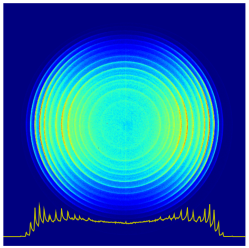
sub-pixel centroid

bin to image
circularize Gascooke (Flind U)

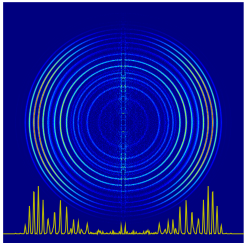
e⁻ trajectories



2D projection O_2^-



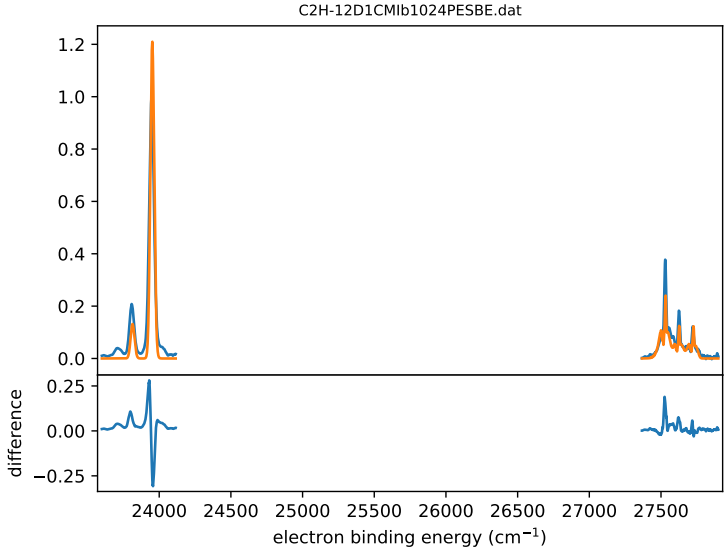
3D slice



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

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

Rotational structure



Vibronic coupling

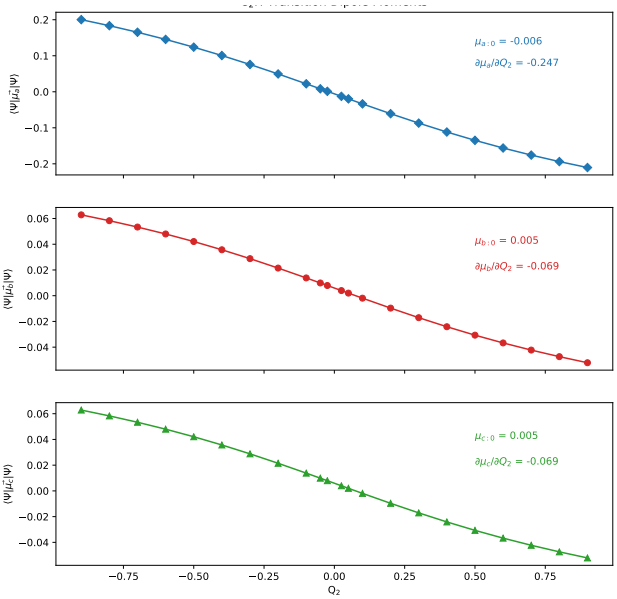
$$|\tilde{X}''\rangle = \text{anion}$$

$$|\tilde{X}\tilde{A}\rangle = |\tilde{X}\rangle + \gamma Q_2 |\tilde{A}\rangle$$

$$\mu_{(\tilde{A}\tilde{X})-\tilde{X}''} = \mu_{\tilde{X}-\tilde{X}''} \langle \psi_{\tilde{X}} | \psi_{\tilde{X}''} \rangle + \gamma \langle \psi_{\tilde{A}} | Q_2 | \psi_{\tilde{X}''} \rangle$$

cf Taylor expansion

$$\implies \left(\frac{\partial \mu_{\tilde{X}-\tilde{X}''}}{\partial Q_2} \right) = \gamma \mu_{\tilde{A}-\tilde{X}''}$$



O^- photoelectron spectra 355 nm and 266 nm
FWHM