Electron anisotropy as a signature of mode specific isomerization in vinylidene

Steve Gibson\textsuperscript{1}, Ben Laws\textsuperscript{1}, Richard Mabbs\textsuperscript{2}, Dan Neumark\textsuperscript{3}, Carl Lineberger\textsuperscript{4}, Robert Field\textsuperscript{5}

\textsuperscript{1}LPC/RSPE ANU, Canberra
\textsuperscript{2}Chem Wash U St. Louis, MO
\textsuperscript{3}Chem UCB, CA
\textsuperscript{4}Chem/Bio JILA UCol. CO
\textsuperscript{5}Chem MIT, MA

ISMS June 20, 2016

- Historical: vinylidene-acetylene isomerization
- ANU velocity-map imaging: PES/PAD
- photodetachment of vinylidene anion $H_2CC^-$
- path forward
vinylindene-acetylene isomerization

Historical

PES


Coulomb explosion imaging

Levine et al. PRL 81 3347 (1998)

Chirped-pulse mm-wave

Jacobson & Field

ab initio

Neumark
T_{2} cryo-SEVI

Hua Guo

IR multiphoton dissociation

Suits
Spectrometer - photodetachment/photofragmentation

anion source

mass separation TOF

photodetachment: electron velocity-mapping lens

MCPs and phosphor detector

pulsed molecular jet HV discharge

gating-bunching re-referencing unit

355 nm and harmonics Nd:YAG laser

OPO laser 220 nm–1750 nm

Photodetachment:
\[ A^- + h\nu \rightarrow A^* + e^- \]

Gating-bunching-rereferencing unit:

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

Velocity-map imaging lens:
Velocity-map imaging

VMI lens coaxial with ion-beam

MCPs+phosphor

CCD camera 2048x2048 pixel

monochrome camera image

\( (x_i, y_i) \)

sub-pixel centroid

\[ \Delta E \sim \text{constant} \rightarrow e^- \text{ speed} \]

Inverse Abel transformation: **PyAbel**: [https://github.com/PyAbel](https://github.com/PyAbel)

Gascooke (Flind U)

bin to image

circularize

3D slice
$\text{O}_2^-(^2\Pi_g) + h\nu (454-900 \text{ nm}, 2.7-1.4 \text{ eV}) \rightarrow \text{O}_2 (X^3\Sigma_g^-, a^1\Delta_g, b^1\Sigma_g^+) + e^- (2.3 - 0.9 \text{ eV})$

Electron affinity: $3613(48) \text{ cm}^{-1} (0.448 \text{ eV})$

Electronic, vibration, and fine-structure resolved features

Mode $\nu'$ - dependent electron anisotropy

vinylidene anion $\text{H}_2\text{CC}^-$ photodetachment

Photoelectron spectrum

$\tilde{X}^1 A_1 \text{H}_2\text{CC} \leftrightarrow \tilde{X}^2 B_2 \text{H}_2\text{CC}^-$

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

vinylidene anion $\text{H}_2\text{CC}^-$ photodetachment
vibrational normal-mode structure

$\tilde{X}^1A_1$ $\text{H}_2\text{CC} \leftarrow \tilde{X}^2B_2$ $\text{H}_2\text{CC}^-$

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


1064 nm

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

\[ I(\varepsilon, \theta) \propto 1 + \beta(\varepsilon) P_2(\cos \theta) \]

\[ 0^0_0, 6^0_2, 3^1_1, 2^0_1, 1^1_0 \]

\[ r' = 1, A_2 = 0.34(1), \cos \Delta = 0.908(8) \]

\[ \beta_{\varepsilon=1}(\varepsilon) = \frac{2(A_2 \varepsilon)^2 - 4A_2 \varepsilon \cos \Delta}{1 + 2(A_2 \varepsilon)^2} \]


\[ R_d/R_s \sim A_2 \varepsilon \]
VMI provides 100% electron collection, excellent eBE resolution (PES) and full angular distribution (PAD).

Vinylidene anion production is very difficult - limits spectral quality.

High-isomerization barrier transitions, associated with CH symmetric stretch $1^1_0$, have anomalous electron anisotropy.

Next steps - improved anion source (Linberger), isotopologues, cryo- (Neumark), \textit{ab initio} (Guo).
Acknowledgements
Other contributors

Steve Cavanagh
Brenton Lewis

and technical assistance:
Colin Dedman, Kevin Lonsdale, Ros Tranter, Steve Battisson

Funding: ARC DP160102585

Other ISMS talks

RF10 - P1883: Ben Laws NOO^−(ONO^−)

C_2H_2^−

RJ07 - P1885: Steve Gibson O^−
Appendix

- PyAbel: Abel transforms
- Cooper-Zare angular distribution of photoelectrons
PyAbel: Abel transform software
https://github.com/PyAbel

Transform Methods

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

1. bspline - Gaussian basis set expansion of Drabinskii 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_borders - "onion peeling" or "back projection" method of Bordas et al. based on the MatLab code by Rallis and Weis et al.
8. lineas - the 1D-spherical basis set expansion of Gerber et al.
10. pop - polar onion peeling method (not yet implemented).
\[ \beta_\ell = \frac{\ell(\ell - 1) R_{\ell-1}^2 + (\ell + 1)(\ell + 2) R_{\ell+1}^2 - 6\ell(\ell + 1) R_{\ell+1} R_{\ell-1} \cos(\delta_{\ell+1} - \delta_{\ell-1})}{3(2\ell + 1)[\ell R_{\ell-1}^2 + (\ell + 1) R_{\ell+1}^2]} \]