Autodetachment of CH_2CN^- viewed with high resolution photoelectron imaging

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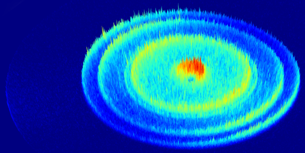
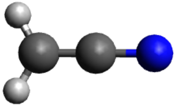


International Symposium on Molecular Spectroscopy
Champaign-Urbana IL USA, 19 June 2019

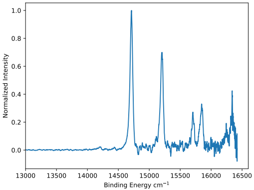
Reasons for studying the cynaomethyl anion:



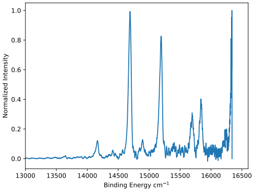
- CH_2CN^- is an important molecule in diffuse interstellar bands
- It is an excellent prototype for studying dipole bound states of negative ions:
  - Electron affinitey (EA) is well defined
  - Vibrational frequencies are well known
  - Neutral has a large dipole moment ($\sim$ 3.6 D)
  - Autodetachment resonances have been observed above threshold

Autodetachment in C_2H_3O[1]

$C_2H_3O^-$ at 609 nm

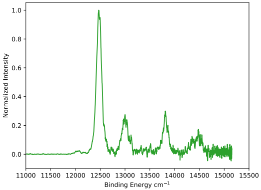


$C_2H_3O^-$ at 612 nm

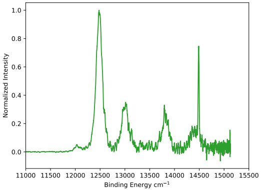


Autodetachment in CH_2CN

CH_2CN at 660 nm

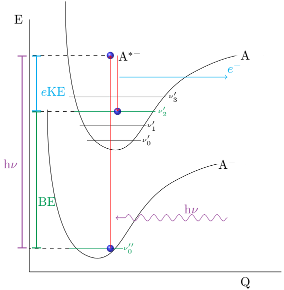


CH_2CN at 661 nm



[1] Gibson, **WF07**

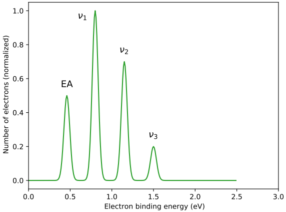
Anion photoelectron spectroscopy:



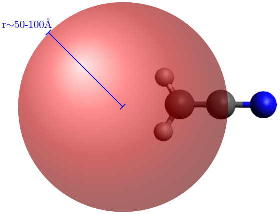
If we know the photon energy $h\nu$ and can measure the electron kinetic energy eKE, then we can calculate the binding energy BE

$$\mathrm{BE} = h\nu - \mathrm{eKE}$$

Now repeat for millions of ions, photons, electrons ...



What about excited anion states?

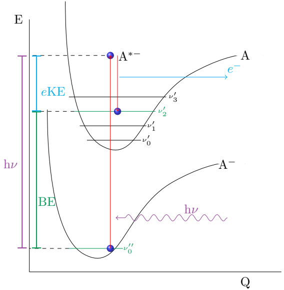


- Excited electronic states in anions are rare
- However if molecule had a permanent dipole $\gtrsim$ 2D it may support at dipole bound state (DBS)
- Analogous to Rydberg states in neutrals:
  - F $\propto 1/\mathrm{r}^2$ not $\propto 1/\mathrm{r}$
  - Only 1 or 2 states, not ∞
- Weakly bound ($\lesssim 100\mathrm{cm}^{-1}$)

Autodetachment of CH_2CN^-

What is autodetachment?

Anion photoelectron spectroscopy:



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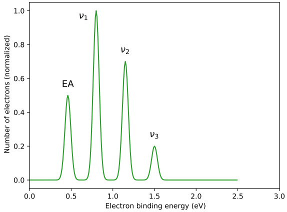
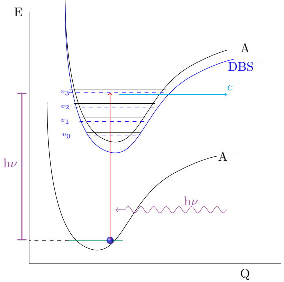
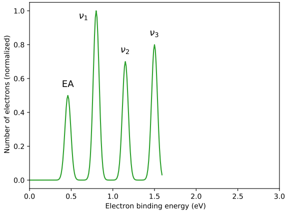


What about excited anion states?



At all photon energies we still get regular photodetachment. However, if the photon energy hv is resonant with an energy level in the DBS, this opens a new absorption channel.

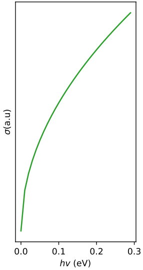
Changes the relationship between σ and hv!



Wigner threshold law

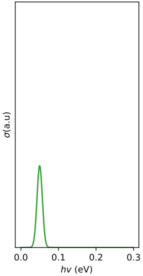
- If orbital has angular momentum ℓ, outgoing electron must have momentum $\Delta\ell \pm 1$
- Detached photoelectron experiences a centrifugal potential, $V(r) \propto \ell(\ell+1)/r^2$

$$\sigma \propto (\mathrm{eKE})^{\ell+1/2}$$



Absorption spectroscopy

- Absorption only occurs if photon energy $h\nu$ is resonant with a transition.
- The resonance width includes both Doppler broadening, and lifetime broadening, where $\Delta\nu \geq 1/2\pi\Delta\tau$



2 experiments at once!
Direct detachment + absorption -> autodetachment

Wigner threshold law

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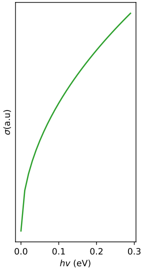

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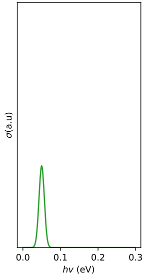
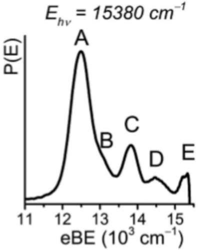
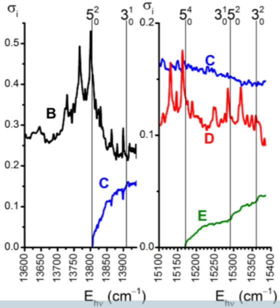


What does this look like in CH_2CN^-?

Photoelectron spectrum of CH_2C^- at 650.3 nm[2]



Cross section measurements of CH_2CN^- [2]



[2] Lyle, J. Chem. Phys. **147** 234309 (2017)

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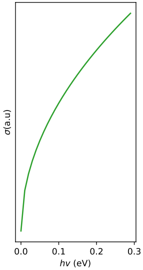

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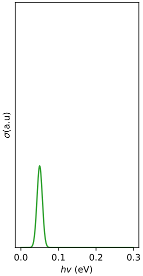
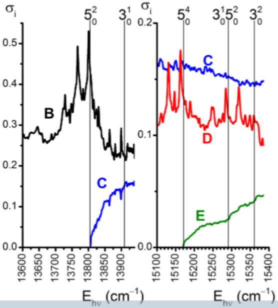


What does this look like in CH_2CN^-?

High resolution cross section measurements can map out the absorption channels to the DBS - but what about the detachment channels?

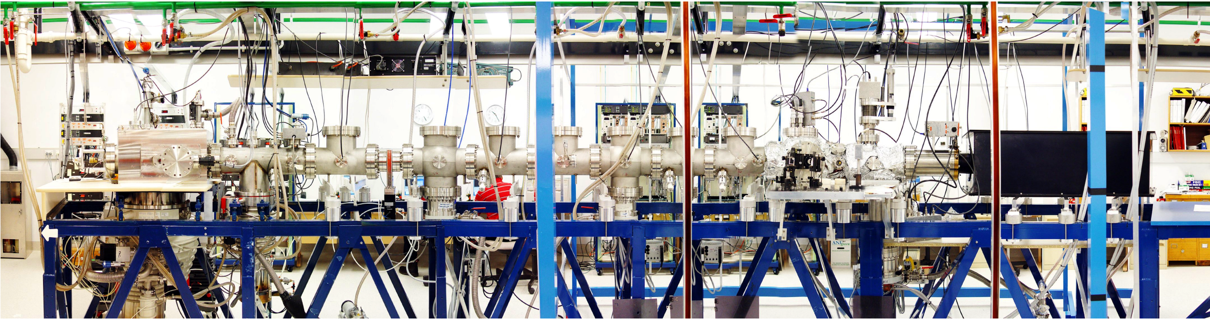
Cross section measurements of CH_2CN^- [2]

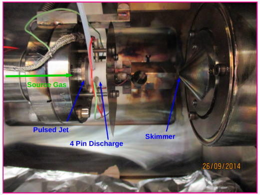


[2] Lyle, J. Chem. Phys. **147** 234309 (2017)

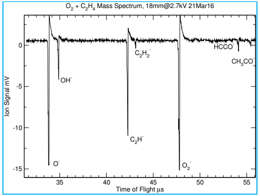
Experimental set-up

ANU photoelectron spectrometer

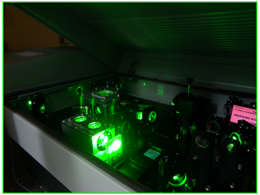




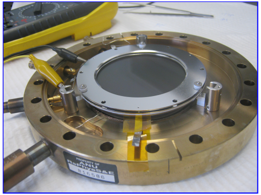
Ion Source



ToF Mass Spectrometer



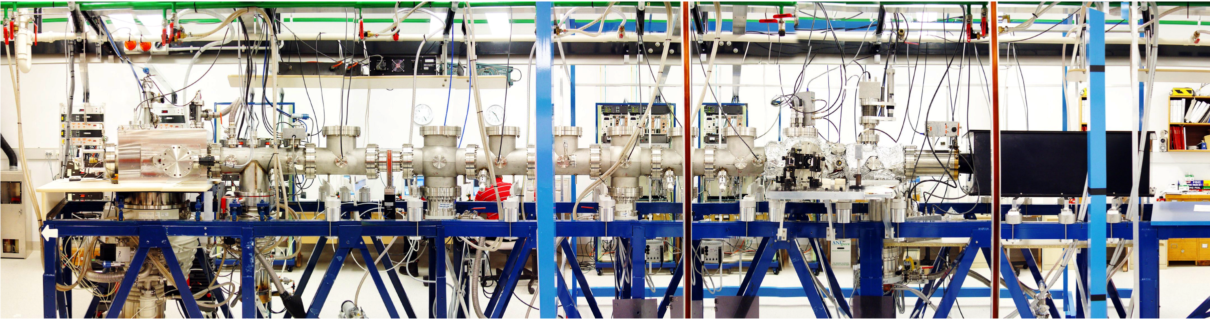
Laser-OPO



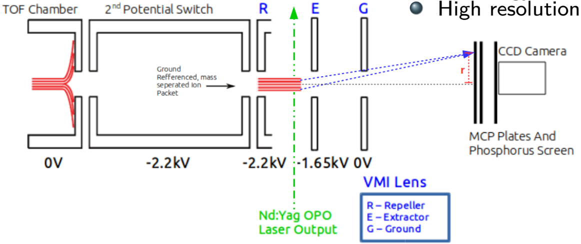
VMI Detector

Experimental set-up

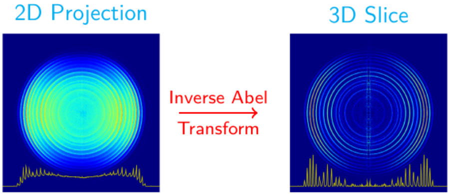
ANU photoelectron spectrometer



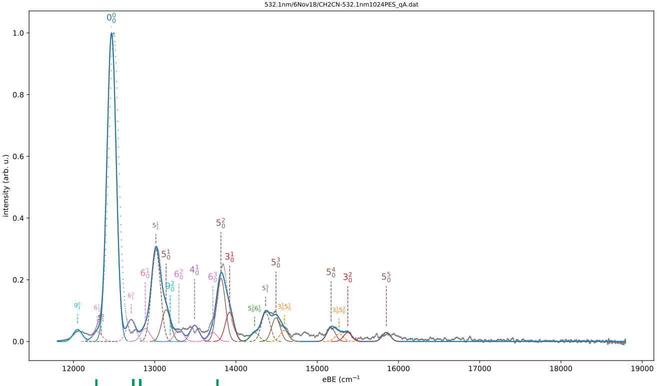
Velocity Map Imaging (VMI)



- Radial position only depends on electron velocity, r $\propto \epsilon$
- All energy and angular information from event, with $\sim$ 100% efficiency
- High resolution, $\Delta\epsilon \propto \epsilon$



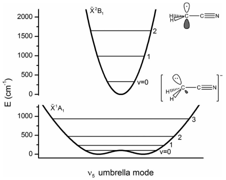
Photoelectron spectrum of CH_2CN^- at 532.1 nm



Calculated frequencies[3]

Mode	CH_2CN^- (C_s)	CH_2CN (C_{2v})
$\omega_1(a_1)$	3148	3177
$\omega_2(a_1)$	2087	2117
$\omega_3(a_1)$	1419	1453
$\omega_4(a_1)$	1061	1023
$\omega_5(b_1)$	130	640
$\omega_6(b_1)$	552	410
$\omega_7(b_2)$	3232	3289
$\omega_8(b_2)$	1015	1032
$\omega_9(b_2)$	418	361

v_5 umbrella mode



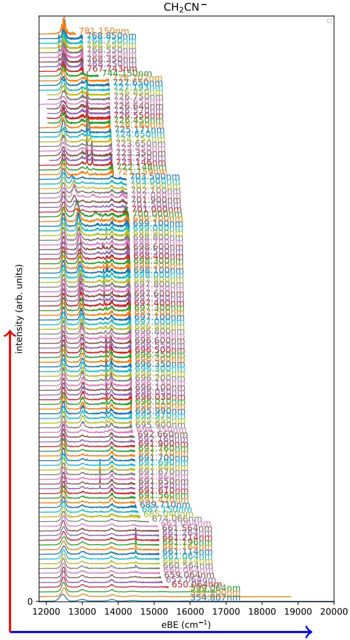
- Due to inversion doubling of the umbrella mode, $\Delta \mathbf{E} v_5 = 0 \rightarrow v_5 = 1$ is only ≈ 130 cm^{-1}
- Therefore, the $v_5 = 1$ hot band in the anion is substantially populated

Transitions of b_1 symmetry with $\Delta v =$ odd, should be totally forbidden!

[3] Weichman J. Chem. Phys. **140** 104305 (2014)

Photoelectron spectra of CH_2CN^-

Hunting for autodetachment resonances



Searching for resonances

Looking for autodetachment resonances requires a LOT of measurements

- Looking at how the intensity varies with *hv* gives us information about the absorption channels
  - $>$ 130 wavelengths measured
  - $\rightarrow$ energy structure of DBS
- By measuring a full PES at each λ, the intensity variation with eKE gives us information about the autodetachment channels
  - High resolution, $>$ 1 million electrons per λ
- By combining **both** sides of the problem, we can get a full picture of the DBS chemistry

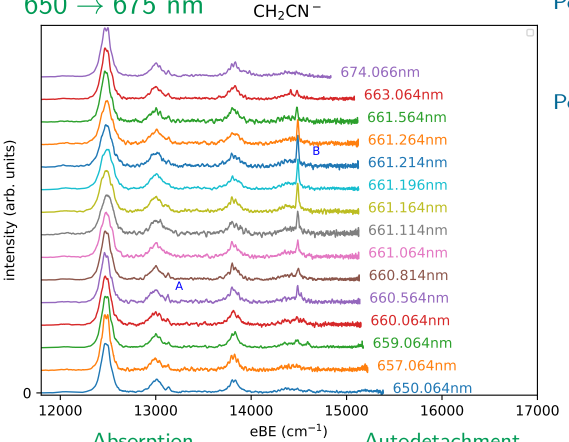
$\rightarrow$ a lot of data to try decode...

12 peaks of interest found: A-L

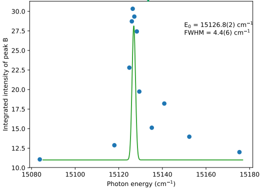
Photoelectron spectra of CH_2CN^-

Assigning resonances

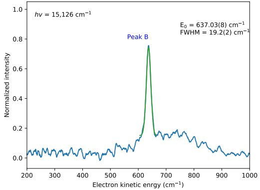
650 → 675 nm



Absorption



Autodetachment



Peak A

- Appears to be forbidden 5^1_0 transition
- Is not sensitive to *hν* - not AD

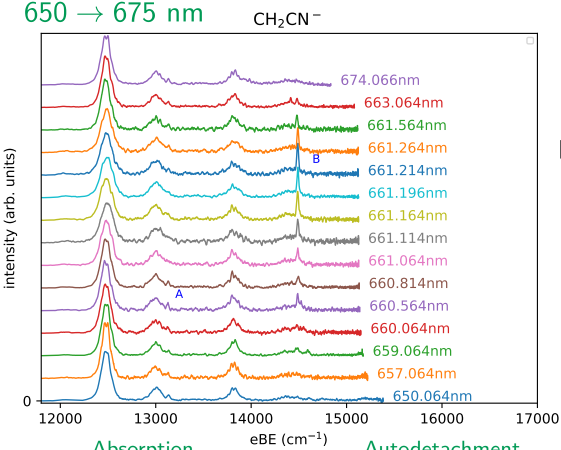
Peak B

- Very sensitive to *hν* - likely AD
- Narrow resonance suggests long lifetime

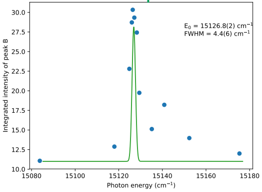
Photoelectron spectra of CH_2CN^-

Assigning resonances

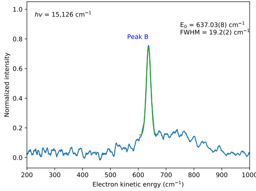
650 → 675 nm



Absorption



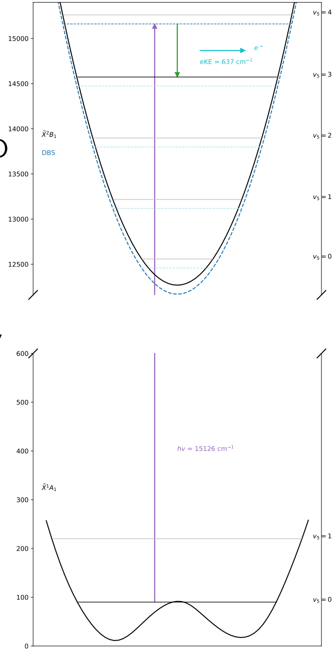
Autodetachment



By measuring both $h\nu$ AND eKE we can assign the resonance!

$$0^0 \rightarrow 5^4 \rightarrow 5^3 + e^-$$

Follows the expected propensity rules $\Delta v = \pm 1$[4]

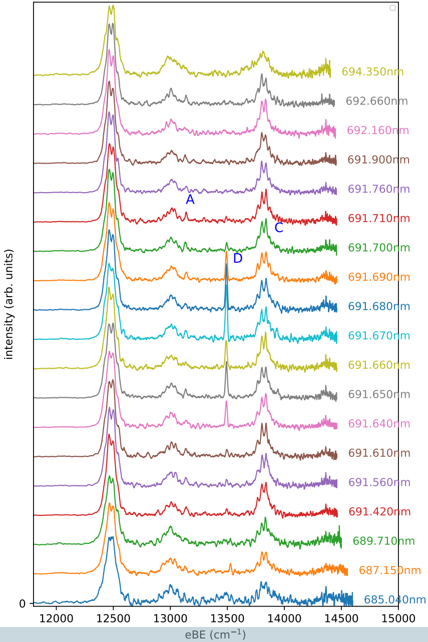


[4] Simons J. Am. Chem. Soc. **103** 3971 (1981)

Photoelectron spectra of CH_2CN^-

Assigning resonances

$685 \rightarrow 695$ nm CH_2CN^-



Peak A

- Forbidden 5^1_0 transition still present

Peak C

- Sensitive to $h\nu$, but over a larger range
- Broad structure in the eKE domain

Peak D

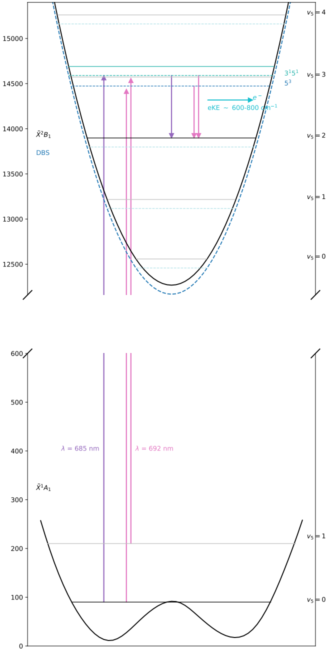
- Very sensitive to $h\nu$
- Very sharp resonance in the eKE domain

Multiple autodetachment channels to assign in peak C

$$0^0 \rightarrow 3^1 5^1 \rightarrow 5^2 + e^-$$
$$0^0 \rightarrow 5^3 \rightarrow 5^2 + e^-$$
$$5_1 \rightarrow 3^1 5^1 \rightarrow 5^2 + e^-$$

eKE range $\sim 600 - 800$ cm^{-1}

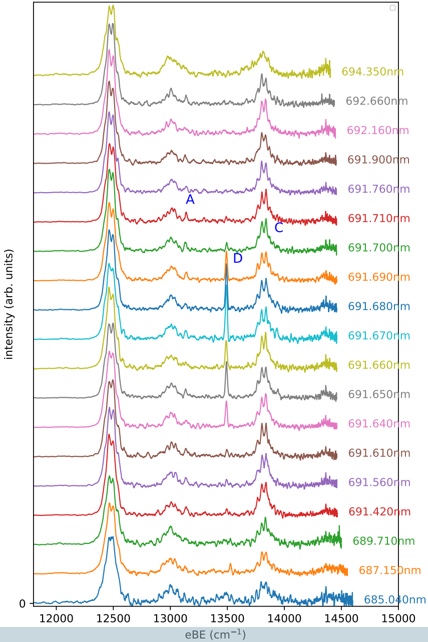
All follow $\Delta v = \pm 1$



Photoelectron spectra of CH_2CN^-

Assigning resonances

685 → 694 nm CH_2CN^-



Peak A

- Forbidden 5^1_0 transition still present

Peak C

- Sensitive to $h\nu$, but over a larger range
- Broad structure in the eKE domain

Peak D

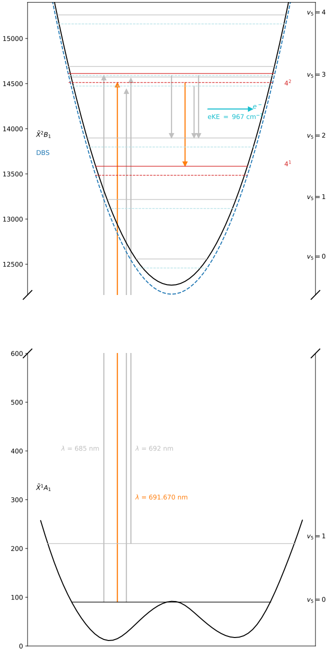
- Very sensitive to $h\nu$
- Very sharp resonance in the eKE domain

Kinetic energy of peak D does not match the main ν_5 progression

$$0^0 \rightarrow 4^2 \rightarrow 4^1 + e^-$$

eKE range $= 966 - 968\ \mathrm{cm}^{-1}$
Follows $\Delta v = \pm 1$

Very narrow resonance!

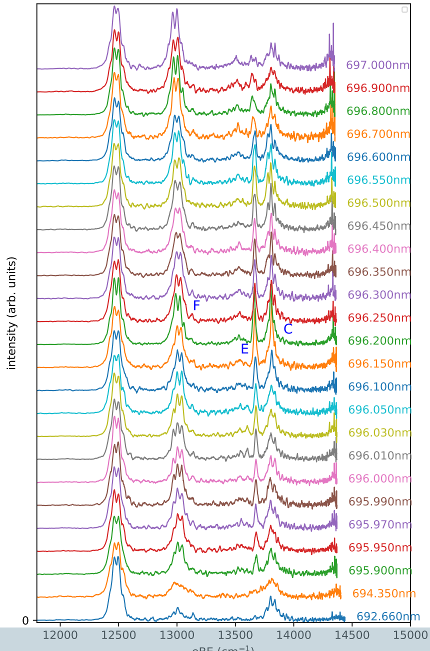


Australian National University

Photoelectron spectra of CH_2CN^-

Assigning resonances

692 $\rightarrow$ 697 nm CH_2CN^-



Peak C

- Sharp resonance sitting on top of the peak we saw last slide

Peak E

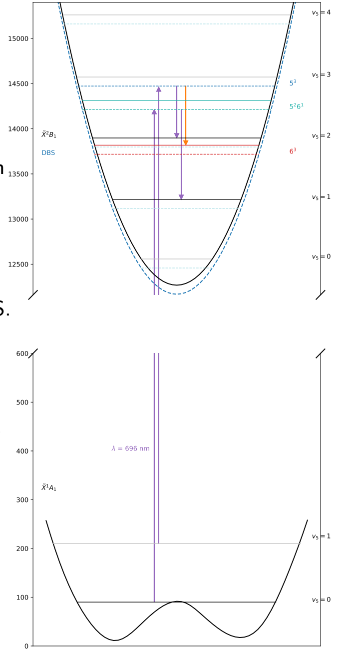
- Very sensitive to $h\nu$ range
- Very sharp resonance in the eKE domain

Peak F

- Sensitive to $h\nu$, but over a larger range
- Broad structure in the eKE domain

Absorption into 5^3 and $5^2 6^1$ bands of the DBS.
Peak C $\rightarrow 5^2$
Peak F $\rightarrow 5^1$
Peak E $\rightarrow 6^3$?

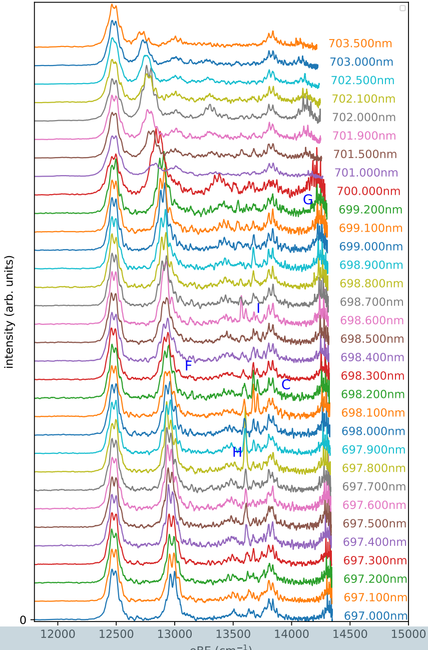
Peak E has an eKE $= 706$ cm^{-1} suggesting detachment to mode 6^3
But this would break $\Delta v = \pm 1$



Photoelectron spectra of CH_2CN^-

Assigning resonances

697 → 703 nm CH_2CN^-



Peak F

- Broad resonance F is still present
- Position of F walks with *hv*

Peak G

- Sensitive to *hv*, but over a larger range
- Broad very high resolution structure in the eKE domain
- Very small kinetic energy - likely $5^3 \rightarrow 5^2 6^1$

Peak H

- Very sensitive to *hv* range
- Very sharp resonance in the eKE domain
- Not readily assignable to an allowed autodetachment transition

Peak I

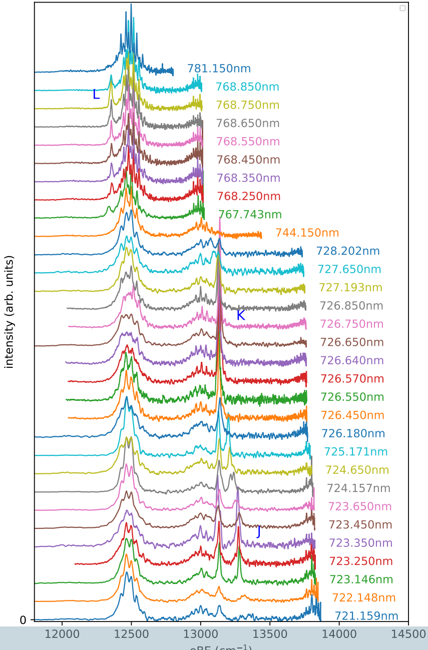
- Very sensitive to *hv* range
- Very sharp resonance in the eKE domain
- Not readily assignable to an allowed autodetachment transition

Analysis of this region is a work in progress!

Photoelectron spectra of CH_2CN^-

Assigning resonances

721 → 781 nm CH_2CN^-



Peak J

- Very sensitive to *hv*
- Very sharp resonance in the eKE domain
- Position of J walks with *hv*

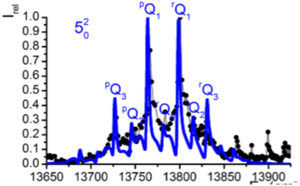
Peak K

- Sensitive to *hv*, but over a slightly larger range
- Very sharp resonance in the eKE domain
- Position of K doesn't shift with *hv*

Peak L

- Very sensitive to *hv* range
- Very sharp resonance in the eKE domain
- On the low eBE side of the origin!

High resolution cross section measurements[2]



Extra rotational structure near 13,900 cm^{-1}

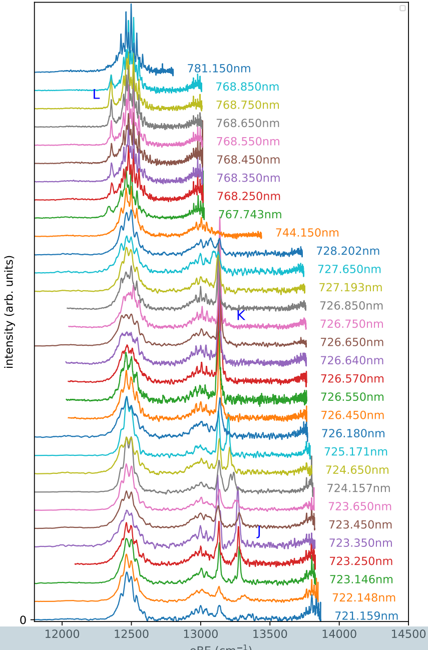
Possible absorption to DBS 3^1 ?

[2] Lyle, J. Chem. Phys. **147** 234309 (2017)

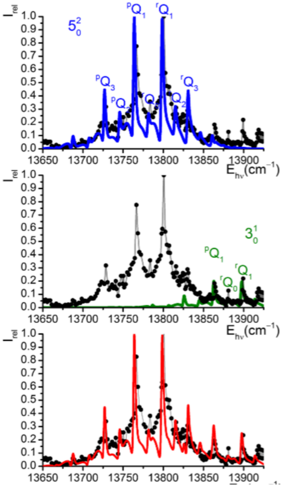
Photoelectron spectra of CH_2CN^-

Assigning resonances

721 → 781 nm CH_2CN^-

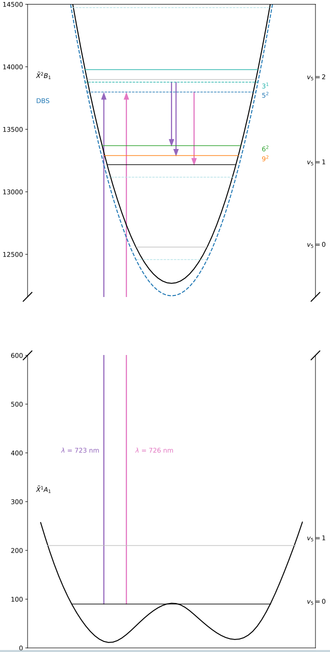


High resolution cross section measurements[2]



$\lambda = 723.146\text{nm} \sim 13830\ \text{cm}^{-1}$

$\lambda = 726.650\text{nm} \sim 13760\ \text{cm}^{-1}$

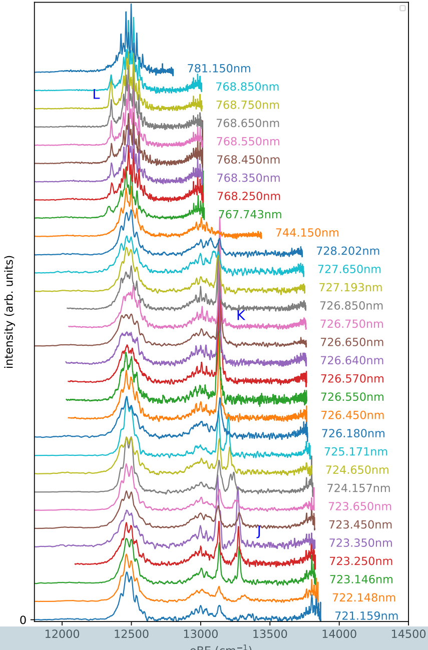


[2] Lyle, J. Chem. Phys. **147** 234309 (2017)

Photoelectron spectra of CH_2CN^-

Assigning resonances

721 → 781 nm CH_2CN^-



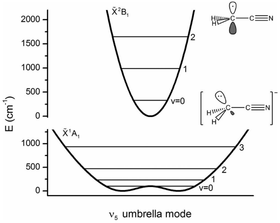
Peak L

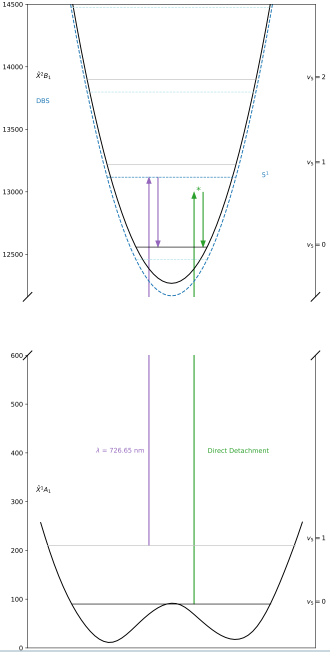
- Very sensitive to *hv* range
- Very sharp resonance in the eKE domain
- On the low eBE side of the origin!

Can we work out the transition?

- EA (CH_2CN) = 12,468 cm^{-1}
- $h\nu$ = 13,011 cm^{-1}
- eKE(0^0) = 543 cm^{-1}
- eKE(L) = 656 cm^{-1}

ν_5 inversion splitting = 113 cm^{-1}!

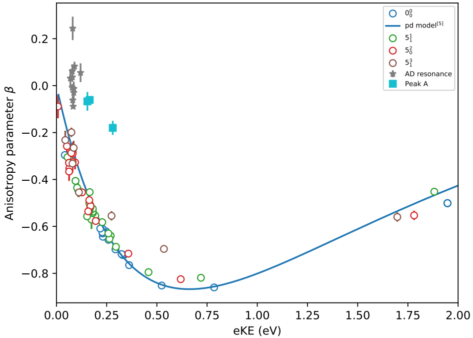




Autodetachment of CH_2CN^-

What about the anisotropies?

Anion photoelectron angular distribution



All of the direct detachment transitions follow a Cooper-Zare like *pd* mixed-character curve[5]

$$\beta_{pd} = \frac{2(1-\gamma_d)B_2\epsilon[A_1^2\epsilon^2 - 2A_1\epsilon] + \frac{2}{5}\gamma_d A_1^2\epsilon^2[1 + 6A_2^2\epsilon^2 - 18A_2\epsilon]}{(1-\gamma_d)B_2\epsilon[1+2A_1^2\epsilon^2] + \gamma_d A_1^2\epsilon^2[2+3A_2^2\epsilon^2]}$$

where the Hanstorp coefficients are defined as

$$A_1 = \frac{1}{\epsilon}\frac{\chi_{1,2}}{\chi_{1,0}} \qquad A_2 = \frac{1}{\epsilon}\frac{\chi_{2,3}}{\chi_{2,1}} \qquad B_2 = \frac{1}{\epsilon}\frac{\chi_{1,2}^2}{\chi_{2,1}^2}.$$

What about the autodetachment resonances?

- All of the autodetachment resonances appear to be near isotropic
- This provides a direct measurement of the character of the DBS orbital
- The forbidden peak A transitions also appear definitively more positive

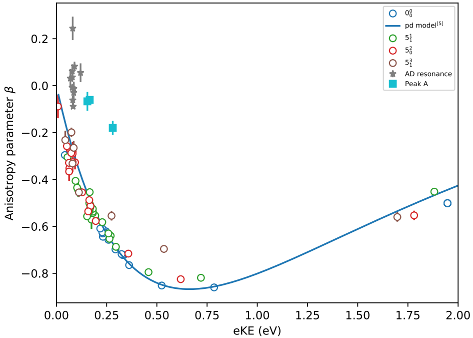
Peak A 5^1_0 transition likely a sign of Herzberg-Teller coupling!

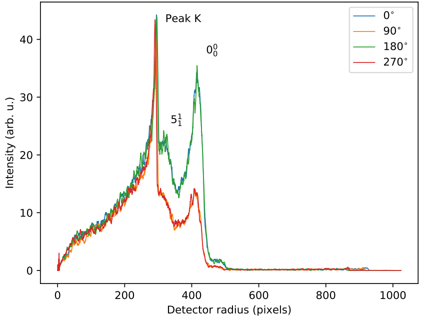
[5] Khuseynov, J. Chem. Phys. **141** 124312 (2014)

Autodetachment of CH_2CN^-

What about the anisotropies?

Anion photoelectron angular distribution





Difference in the anisotropy is very noticeable in the raw slice profiles!

What about the autodetachment resonances?

- All of the autodetachment resonances appear to be near isotropic
- This provides a direct measurement of the character of the DBS orbital
- The forbidden peak A transitions also appear definitively more positive

Peak A 5_0^1 transition likely a sign of Herzberg-Teller coupling!

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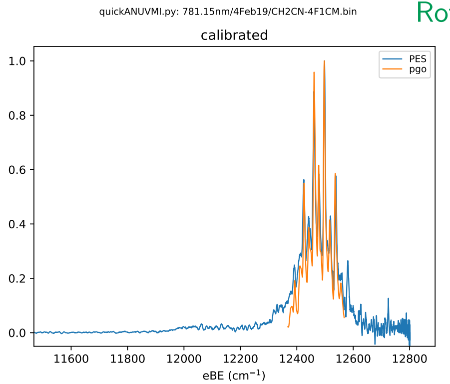
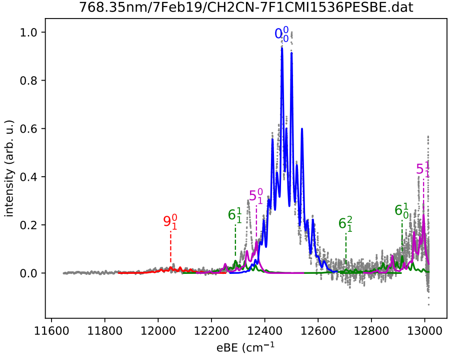
What's next?



Rotational structure



What more can we learn?

- With rotational resolution we can extract more detailed information about detachment mechanisms
- Difference resonance 'types' have been observe - broad vs narrow resonances, is this a difference in the lifetime broadening?
- Can we deduce the exact rotational transitions involved in AD?

Australian National University

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