VUV spectroscopy and photochemistry of interstellar and putative prebiotic molecules

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Colloque général PCMI 2012, 19-21 Novembre 2012.

Image courtesy of C.R. O'Dell (Vanderbilt University), Image STScI-PRC2003-06

Outline

1. Motivation
2. Photophysical properties measured by our group in relation with relevant molecules
3. 2012 Highlights
4. Concluding remarks and future perspectives

Image courtesy of C.R. O'Dell (Vanderbilt University), Image STScI-PRC2003-06

Motivation

1. Determine fundamental photophysical properties in the UV and VUV of **big molecules** (> 5 atoms) in **the gas phase**, as f(λ) in the VUV (5-30 eV):
    - Molecules already detected in ISM
    - Molecules expected to exist
    - Prebiotic or simple biomolecules
2. Deliver input data for photochemical modeling of astrophysical media (ISM, planet. Atmos. , comets)
3. Analyze and interpret space observations in the VUV
4. Help to rationalize abundance of molecules in the context of the prevailing VUV radiation fields in a specific site
5. Predict astrophysical sites of survival of prebiotic species

Image courtesy of C.R. O'Dell (Vanderbilt University), Image STScI-PRC2003-06

Photophysical properties & gas phase measurements

- Only gas phase measurements gives **intrinsic** photophyscial properties of a molecule. **Elementary photoreactions** can be studied (in contrast to matrix experiments…..)
- The condensed phase has a **large and very variable** influence on spectroscopy and elementary photoreactions, **needs dedicated experiments and theory.**
- Support by theoretical chemistry
  - In general **isolated molecules** (or small aggregates of a few molecules) are studied by theoretical chemistry. Comparison to gas phase spectroscopic results is straightforward.
- Even big molecules are observed in the gas phase (but might be formed on grains followed by UV photodesorption)

Spectral domains & photophysical processes: example of Acetonitrile CH_3CN

T = 298 K

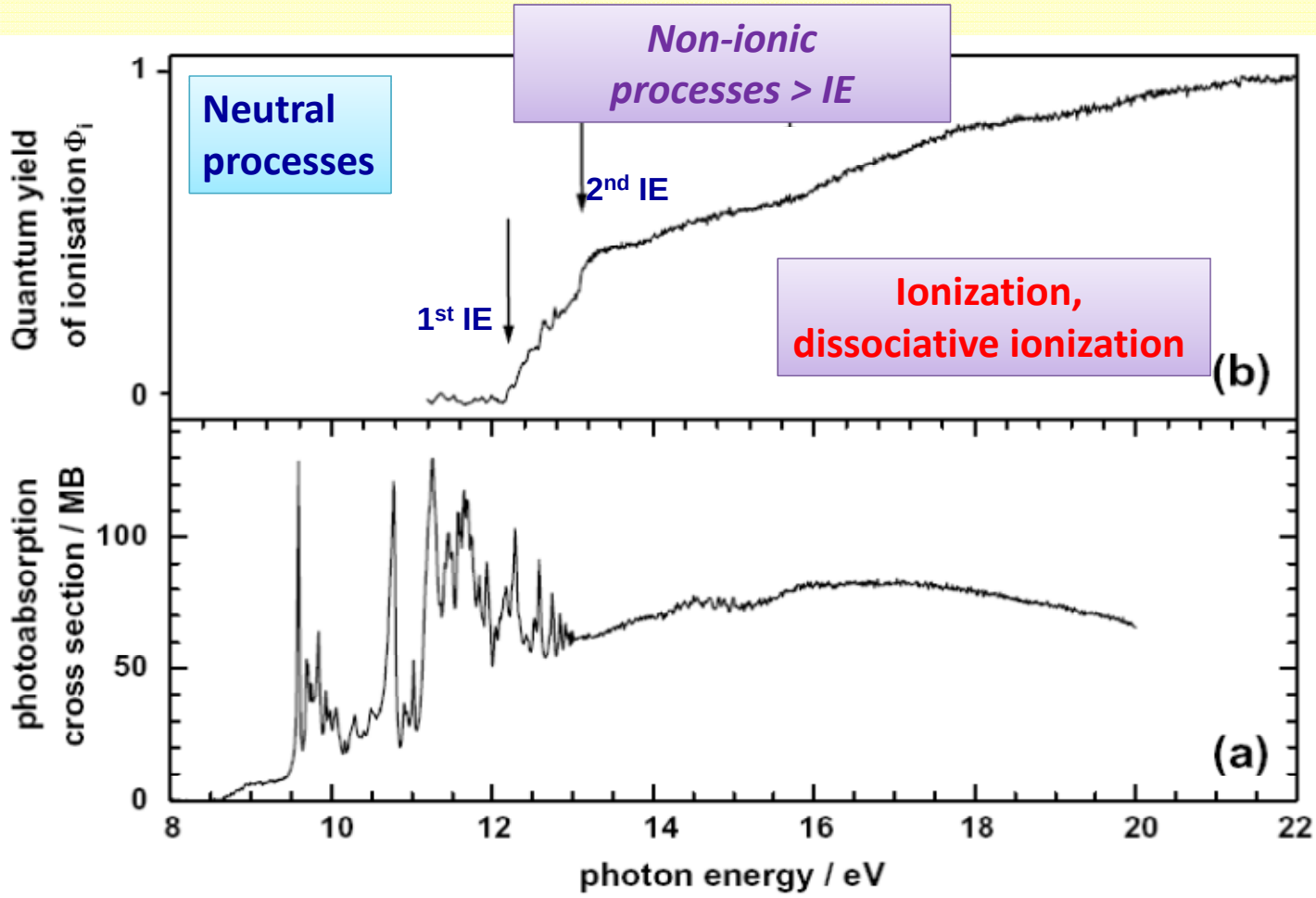
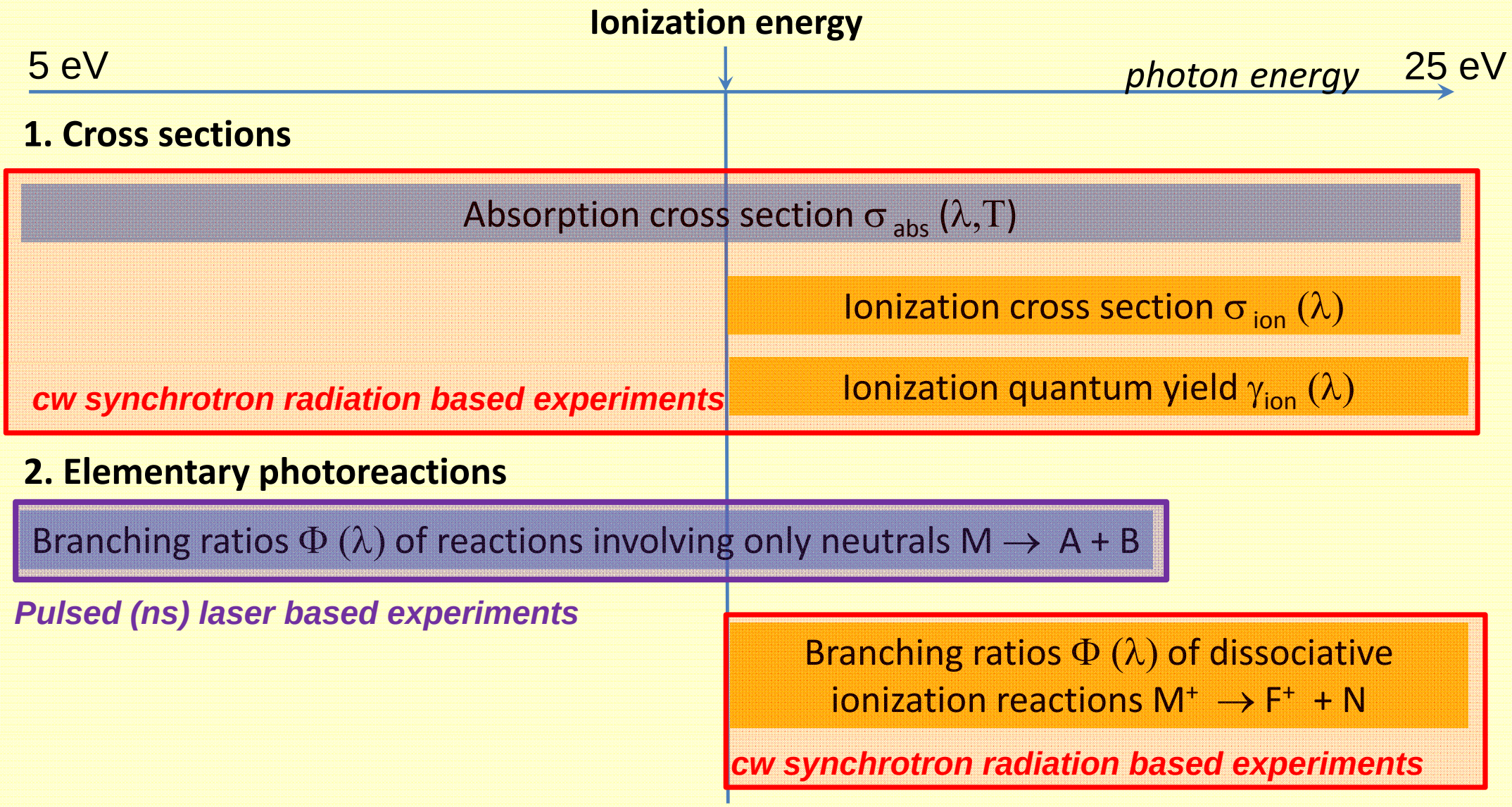


Fig. 1. (a) Absorption spectrum of acetonitrile up to 20 eV; (b) total ionization quantum yield as a function of excitation energy of acetonitrile over the range 11.2–22 eV. Vertical arrows indicate ionization limits.

Schwell et al., *Chem. Phys.* 344, 164 (**2008**)

Photophysical properties in the UV & VUV measured by our group



Photophysical properties in the UV & VUV

Cyanopolyynes & polyynes

	Synchrotron - Abs cells (T)	Synchrotron: mass spec + electr. spec. (e^- and i^+ detected in coincidence)			Pulsed ns laser experiments
	σ_{abs}	σ_{ion}	γ_{ion}	BR (Φ) dissociative Ionization	BR (Φ) photoreactions involving neutrals
HC_3N	**X** (Ferradaz, 2009), low T, **< 15 eV**	**X** (in prep.) **< 15.8 eV**	**X** (in prep.) **< 15.8 eV**	**X** (in prep.) **< 15.8 eV**	**X** (Suits et al.,2009): @ 212, 193, 157, 121.6, 106 nm
HC_5N	**X** (Fray, 2010), low T, **< 11.5 eV**	**U** *(Planned…)*	**U** *(Planned…)*	**U** *(Planned …)*	**U**
C_2N_2	**X** (Bénilan et al.) **< 11.5 eV**	**U**	**U**	**U**	**X** (can be extracted from earlier LiF work)
C_4N_2	**X** (Bénilan et al.) **< 11.5 eV**	**X** (in prep.) **< 20 eV**	**X** (in prep.) **< 20 eV**	**X** (in prep.) **< 20 eV**	**U**
C_4H_2	**X** (Ferradaz, 2009), low T, **< 15 eV**	**X** (Schwell et al., 2012) **< 19 eV**	**X** (Schwell et al., 2012) **< 19 eV**	**X** (Schwell et al., 2012) **< 19 eV**	**X** (Suits et al.,2008): @ 212, 193, 157, 121.6, 106 nm

X = Done, **U** = Unknown ; Synchrotron = Soleil (DESIRS), BESSYII (U125/2-10m NIM; 3m NIM)

Photophysical properties in the UV & VUV

Observed « big » molecules

X = Done, U = Unknown	Synchrotron - Abs cells (T)	Synchrotron: mass spec + electr. spec. (e^- and i^+ detected in coincidence)			Pulsed (ns) laser experiments
	σ_{abs}	σ_{ion}	γ_{ion}	BR (Φ) dissociative Ionization	BR (Φ) photoreactions involving neutrals
Acetic acid, CH_3COOH	**X** (Leach et al., 2006), 6-20 eV, 298 K	U	U	**X** (Schwell et al., 2006), 10-20 eV, 298 K	U
Methylformate $HCOOCH_3$	**X** (Schwell et al., 2006), 6-20 eV, 298 K	U	U	**X** (in prep.) 10.5-14 eV)	U
Glycolaldehyde, $HO\text{-}CH_2CHO$	U	U	U	Preliminary study in 2011 10-12 eV	U
Acetamide, $H_3C\text{-}C(O)NH_2$	U	U	U	**X** (Schwell et al., 2012a) **< 12.5 eV**	U
Aminoacetonitrile, H_2NCH_2CN	U (Planned 2013…)	U	U	**X** (Schwell et al, 2012b) **< 13.6 eV**	U

<u>Non-exhaustive list</u>, other interesting molecules include: **acetaldehyde, ethylcyanide, n-propyl-cyanide…..**

Leach et al, 2006: Chem. Phys. 321 (2006), nos. 1-2, 159-170; Schwell et al., 2006, P&SS 54 (2006), 1073-1085
Schwell et al., 2012a: Chem. Phys., 393 (2012) 107116; Schwell et al., 2012b: EAS publication series, in press.

Photophysical properties in the UV & VUV

Other nitriles of potential prebiotic interest, <u>to be expected</u> in the ISM….

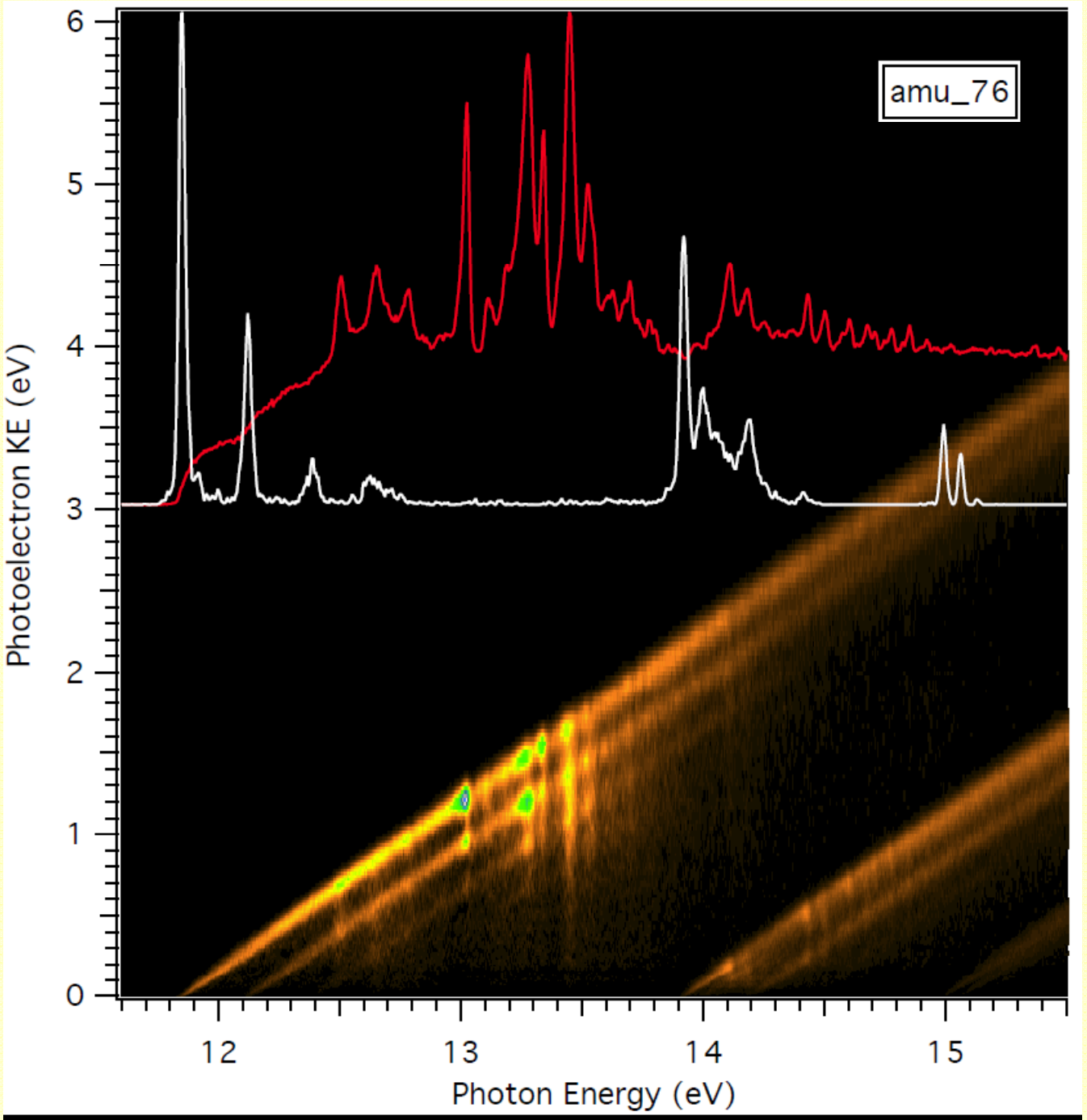
	Synchrotron - Abs cells (T)	Synchrotron + mass spec + electr. spec. (e^- and i^+ detected in coincidence)			Pulsed ns laser experiments
	σ_{abs}	σ_{ion}	γ_{ion}	BR dissociative Ionization	BR photoreactions involving neutrals
2-Aminopropionitrile* (chiral) $H_3C\text{-}CH(NH_2)CN$					
Cyanoacetaldeyde* $NC\text{-}CH_2CHO$			U		
Allenyisocyanide* H2C=C=CHNC					

* Rotational spectra have been recorded and analyzed recently by Møllendal et al. 2011& 2012. 2-Aminopropionitrile has been searched for in SgrB2(N) in 2011 for but not detected.

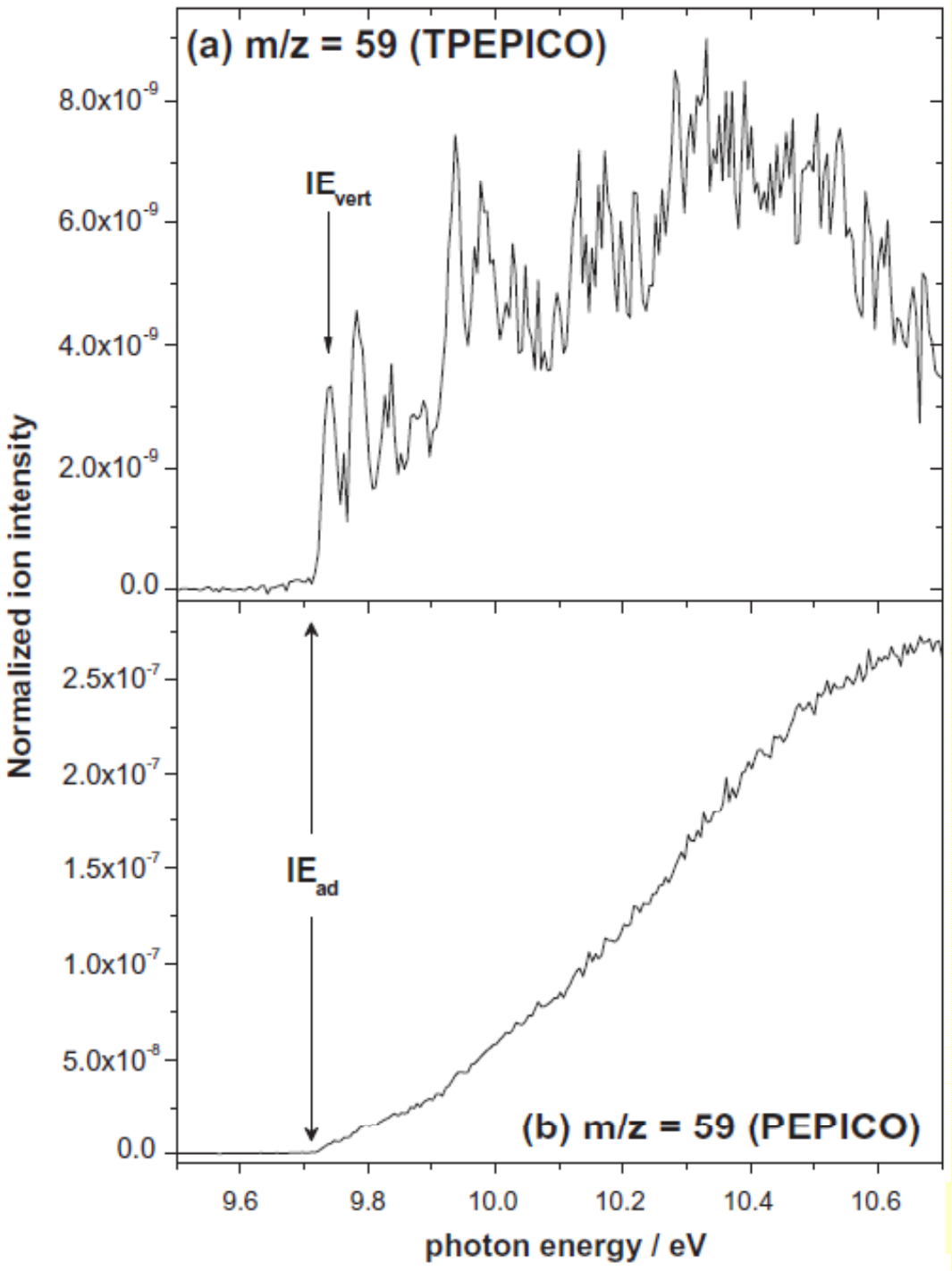
2012 Highlight: Study of C_4N_2 @ DESIRS (with Saphirs instrument).

- Red: total ion yield spectrum (calibrated: σ_{ion} can be extracted)
- White: Slow photoelectron spectrum (SPES), arbitrary units
- 3D color code: Number of photoelectrons formed with certain kinetic energy @ photon energy E. This kind of plots indicates, for example, the relaxation pathways of autoionizing Rydberg states.

Manuscript in prep.



2012 Highlight: Acetamide PEPICO & TPEPICO spectra



a) Take **only** threshold electrons (E_{kin} (e^-) = 0) for e^- / i^+ coincidence measurements
   - TPEPICO - PIE spectrum (5 meV resolution)
   - Analyse ion structure states from vibronic progressions observed >> **spectroscopy**

b) Take **all** photoelectrons formed for e^- / i^+ coincidence measurements
   - PEPICO – PIE spectrum
   - **Total ion yield ∝ ionization cross section**

Schwell et al., Chem. Phys. Vol. 393, p. 107 (2012).

Concluding remarks and perspectives for future work SEE ALSO POSTER

- Cyanopolyynes and polyynes, at lot of UV –VUV data available now, but to be completed. ***SEE POSTER***
- Absorption spectra often limited to 11.5 eV because of the window material
  - Development of **a semi-open gas cell** using a *"nid d'abeille"* as optical path delimiter @ LISA (2013).
- σ_{ion} difficult to determine for non-gaseous compounds (at 298 K).
- Branching ratios of **elementary photoreactions involving neutrals**
  - A lot of data are missing for many important molecules
  - Work planned in **collaboration with UC Davis**, chem. Dep. (W.M. Jackson, C.Y. Ng), *Time-sliced velocity map ion imaging & widely tunable VUV laser sources* ***SEE POSTER***
- Many spectroscopic studies exist but quantitative data are often not measured or difficult to extract
- Fundamental spectroscopy should is important too and must stay an aim of our studies.
- Ionization and dissociative ionization for fragile (bio-) molecules : an **aerosol source for soft vaporization** has been developed @DESIRS (integrated in the SAPHIRS setup), open to users.
- **Support by quantum chemistry calculations** is necessary for
  - Analysis and comprehension of fragmentation pathways
  - Understanding of absorption and photoionization efficiency spectra

Acknowledgement

VUV spectroscopy of interstellar and planetary atmosphere molecules

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Hans-Werner Jochims†
- Jean-Claude Guillemin (ENSC Rennes)

VUV spectroscopy at high temperatures, application to hot jupiter atmospheres

- Franck Selsis, Michel Dobrijevic, Eric Hébrard, Oivia Venot (U Bordeaux, Lab. d'Astrophysique)

VUV spectroscopy of biomolecules using aerosol-SlowPEPICO and SlowPES

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- GdR Exobiologie (<2009)
- LISA, groupes de spectoscopie et astrophysique (continuously)
- Université Paris Est Créteil (UPEC), 2012

Fundamental photophysical properties needed for astrochemical modeling

$$J(\lambda) = \int_{\lambda_1}^{\lambda_2} \Phi(\lambda) \times \sigma(\lambda) \times S(\lambda) \times d\lambda$$

- $J(\lambda)$: Photolysis rate, integrated over a certain wavelength domain [$s^{-1}.nm^{-1}$]
- $\sigma(\lambda)$: Absorption cross section [cm^2]
- $\Phi(\lambda)$: Quantum yield (**branching ratio**) of a particular fragmentation channel (*yielding neutral fragments*)
  - Φ depends on λ, especially for bigger molecules
  - $\Phi(\lambda)$ can be very low close to the thermochemical threshold
- S(λ) Stellar irradiance [$photons.s^{-1}.cm^{-2}$]

Beyond ionization energy:

Photo-ionization rate

$$J_{ion}(\lambda) = \int_{\lambda_1}^{\lambda_2} \gamma_{ion}(\lambda) \times \sigma(\lambda) \times S(\lambda) \times d\lambda$$

Quantum yield of ionization

σ_{ion} : ionization cross section

Dissociative ionization

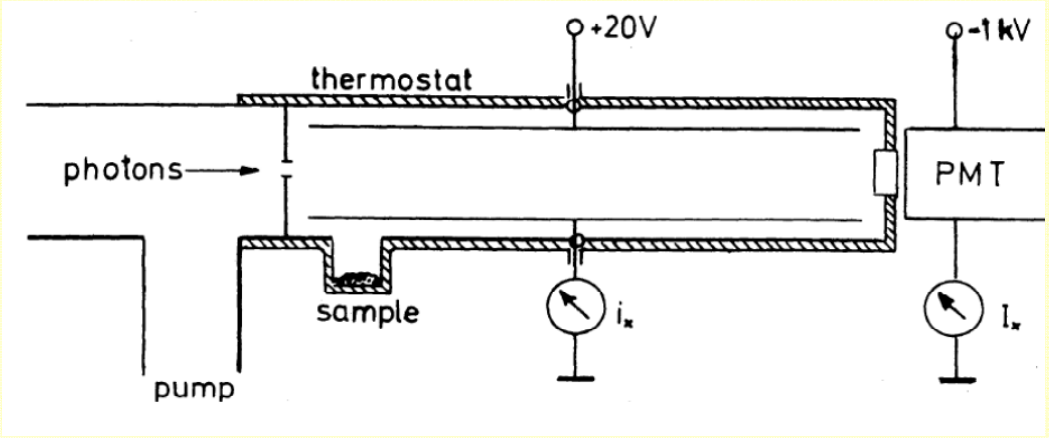
$$\gamma_{ion} = \gamma_{F1+} + \gamma_{F2+} + \ldots.$$

Fundamental photophysical properties

$$J(\lambda,T)=\int_{\lambda_1}^{\lambda_2}\Phi(\lambda,T)\times\sigma(\lambda,T)\times S(\lambda)\times d\lambda$$

- Basic photophysical properties are also **temperature dependent**
- Lot of work….

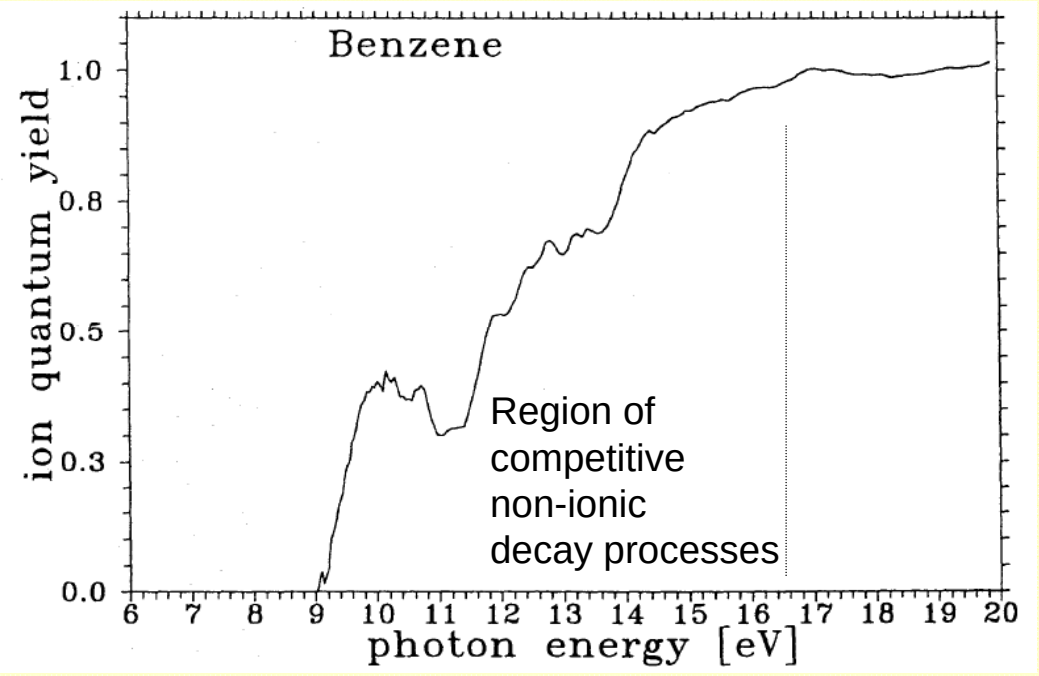
Experimental Techniques: *quantum yield of ionization*

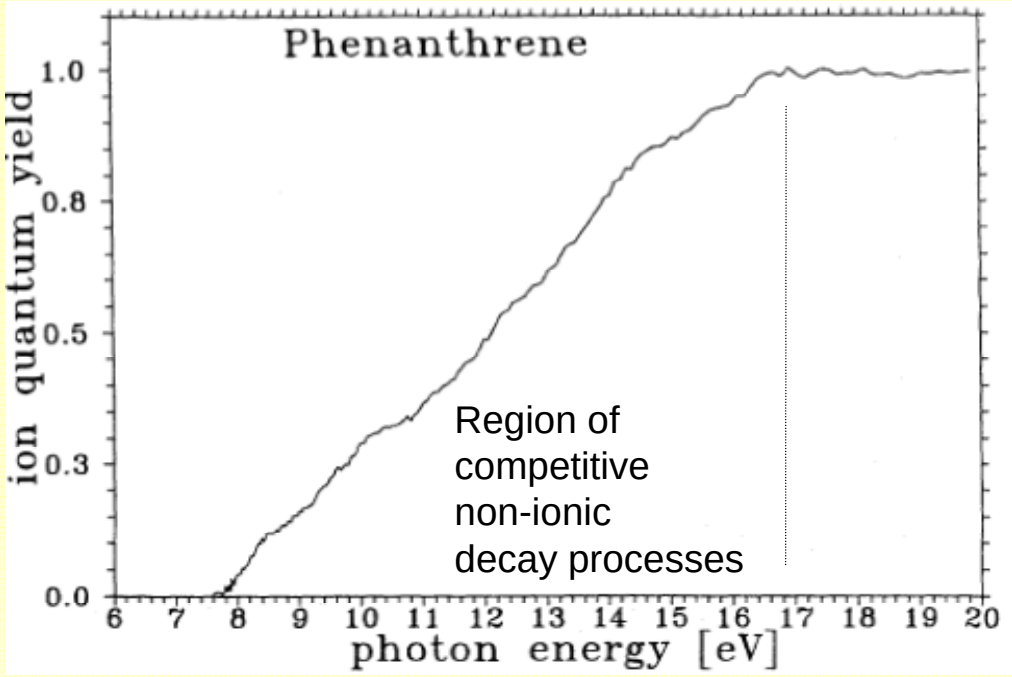


$$\gamma_{ion}(\lambda) = \Sigma \text{ (ions)} \,/\, \Sigma \text{ (photons absorbed)}$$

$$\gamma_{ion}(\lambda) = k \{ i_x(\lambda) \,/\, [I_0(\lambda) - I_x(\lambda)] \}$$

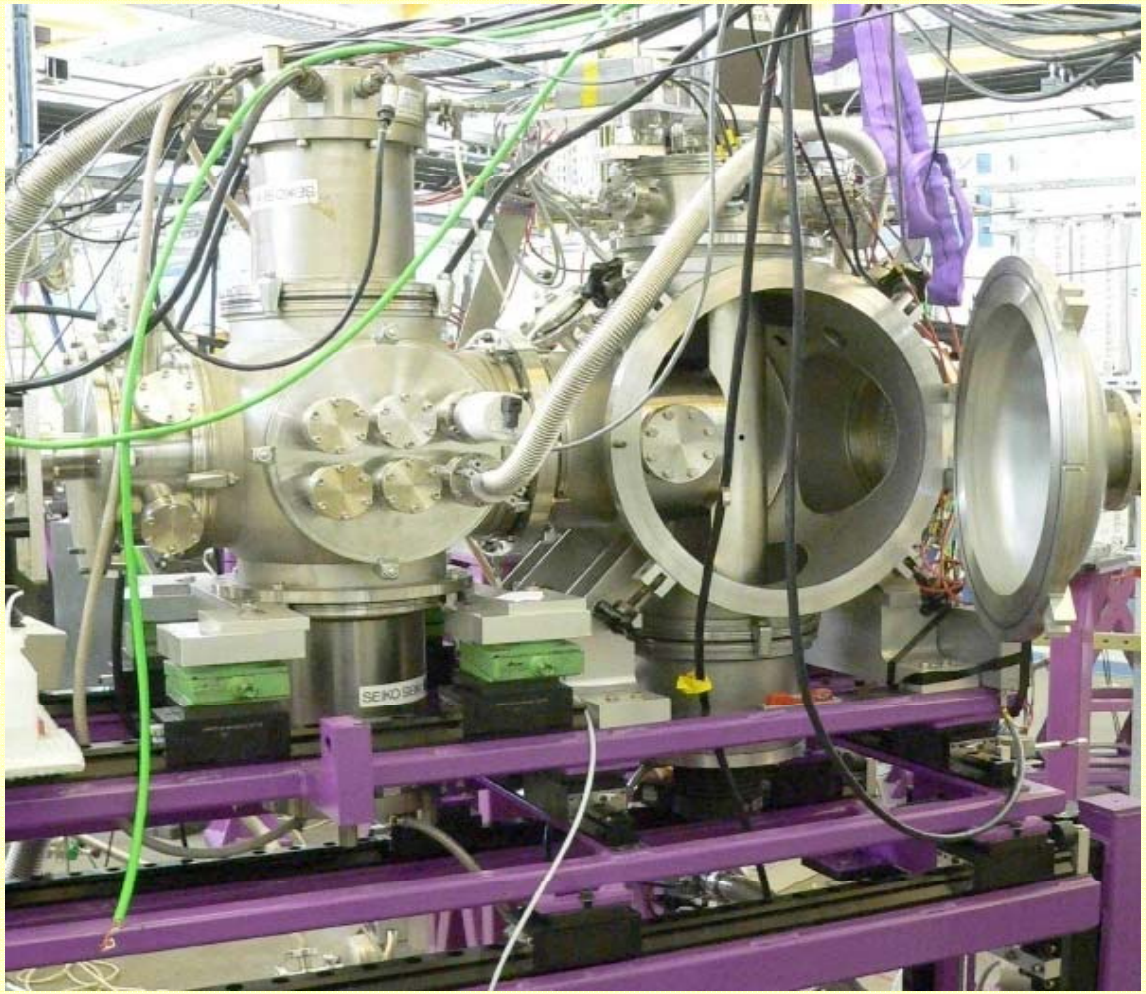
$$\gamma_{ion}(\lambda) = \sigma_{ionization}(\lambda) \,/\, \sigma_{absorption}(\lambda)$$

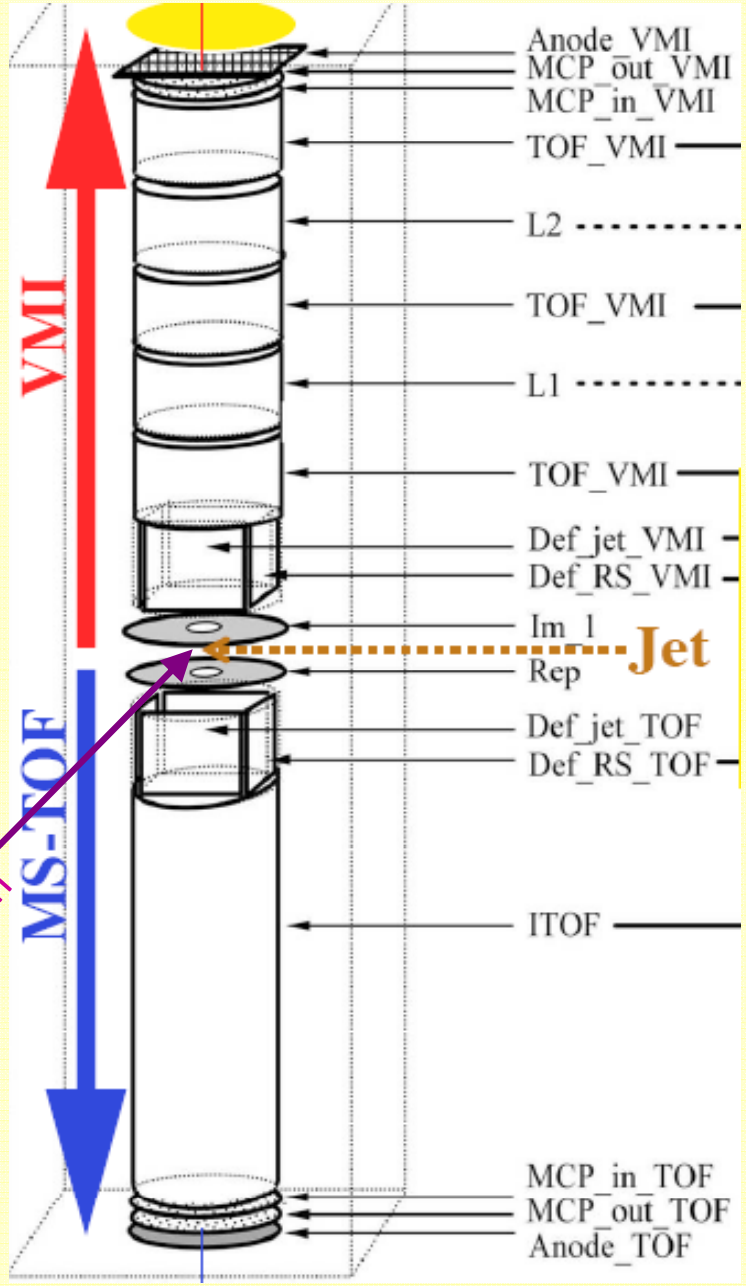




Jochims et al., *Astron. & Astrophys.*, vol. 314, 1003 (**1996**).

Experimental Techniques: *SAPHIRS molecular beam multipurpose chamber (DESIRS/Soleil)*





- Threshold Photoelectron spectroscopy (velocity map imaging)
- ToF mass spectrometry
- Electron / ion coincidence detection (PEPICO)
- VUV tunabiliy of DESIRS (5-35 eV)
- Jet-cooled molecules

Garcia et al., *Rev. Sci. Instr.* 80, 023102 (**2009**)

Recent experiments using SAPHIRS: *Acetamide*

- ISM detection 2006:
  - Hollis et al., *Astrophys. J.*, 643, L25-L28 (**2006**):

    « Largest interstellar molecule with a peptide bond »

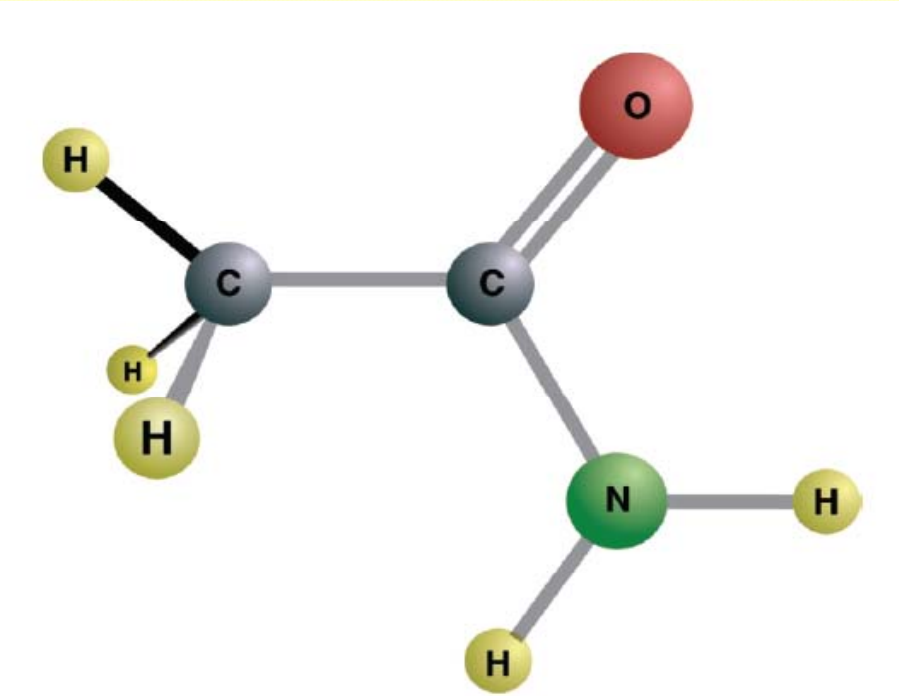
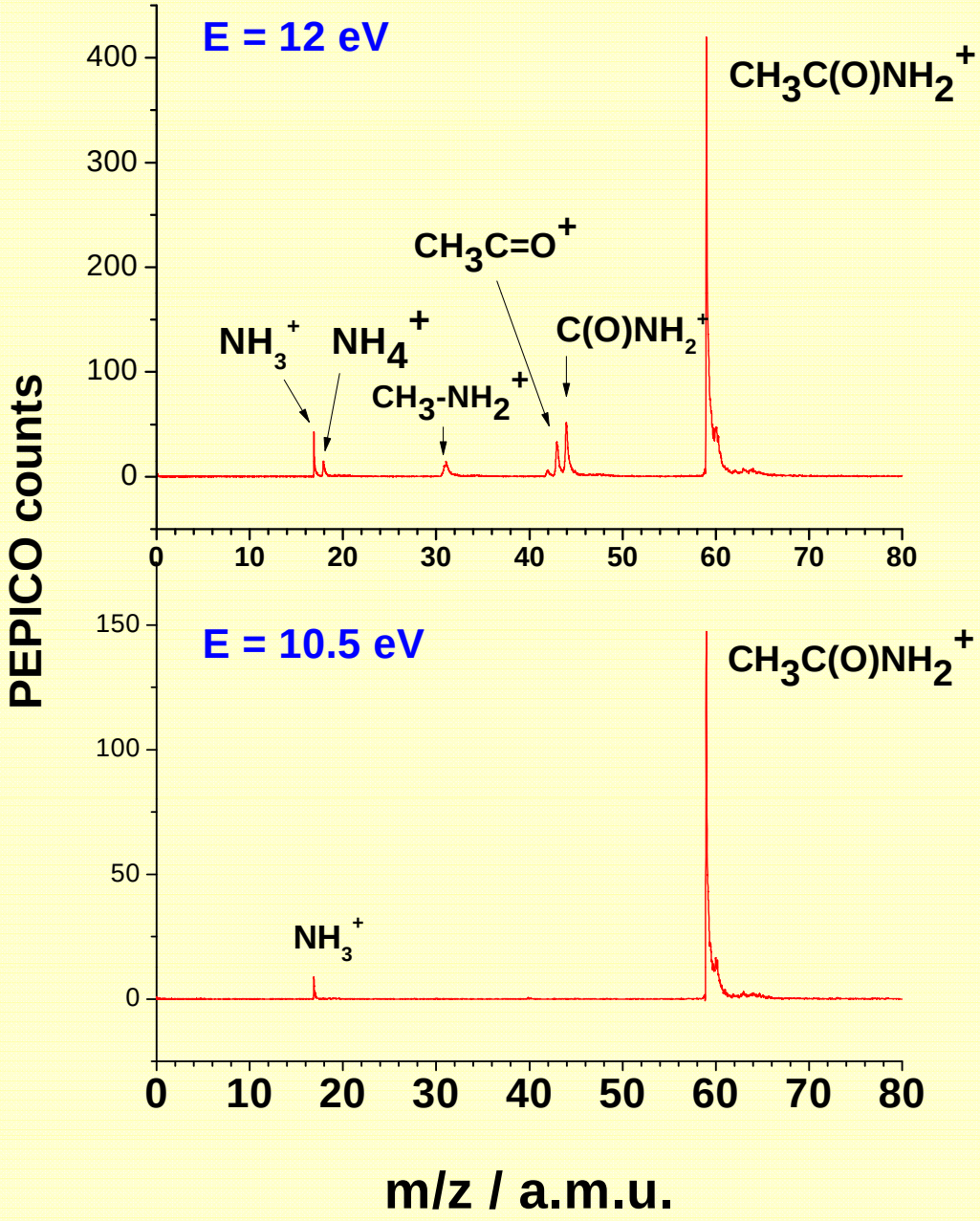
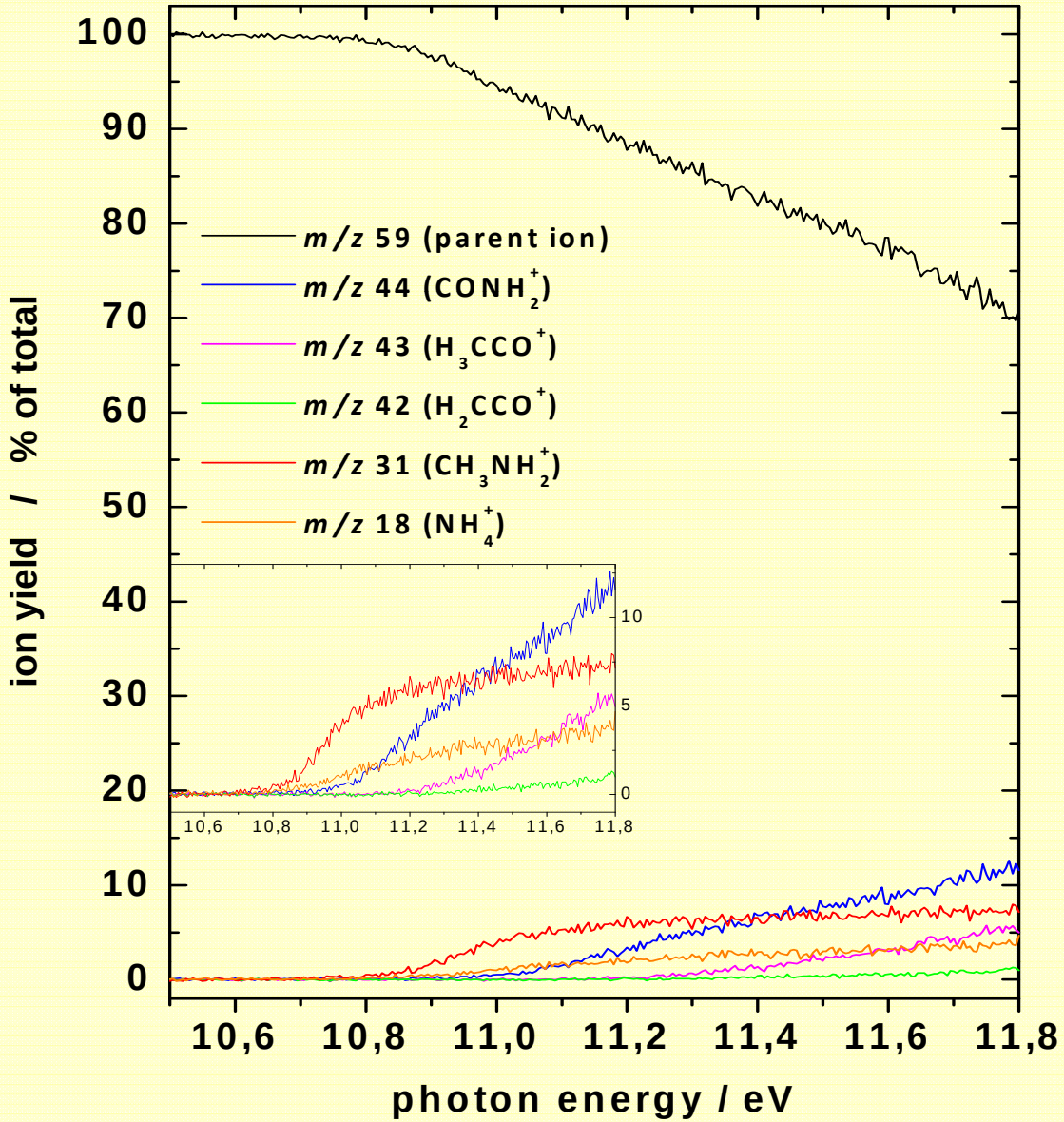


FIG. 1.—Schmatic diagram showing the molecular structure of acetamide.

Dissociative ionization of acetamide

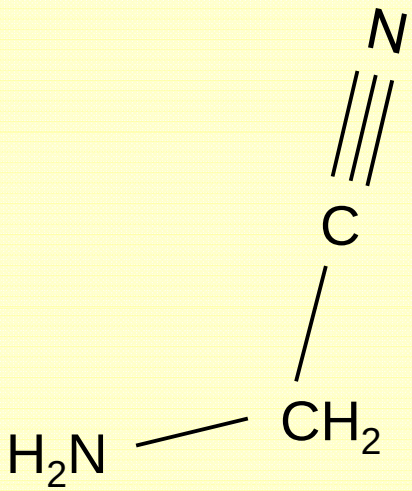




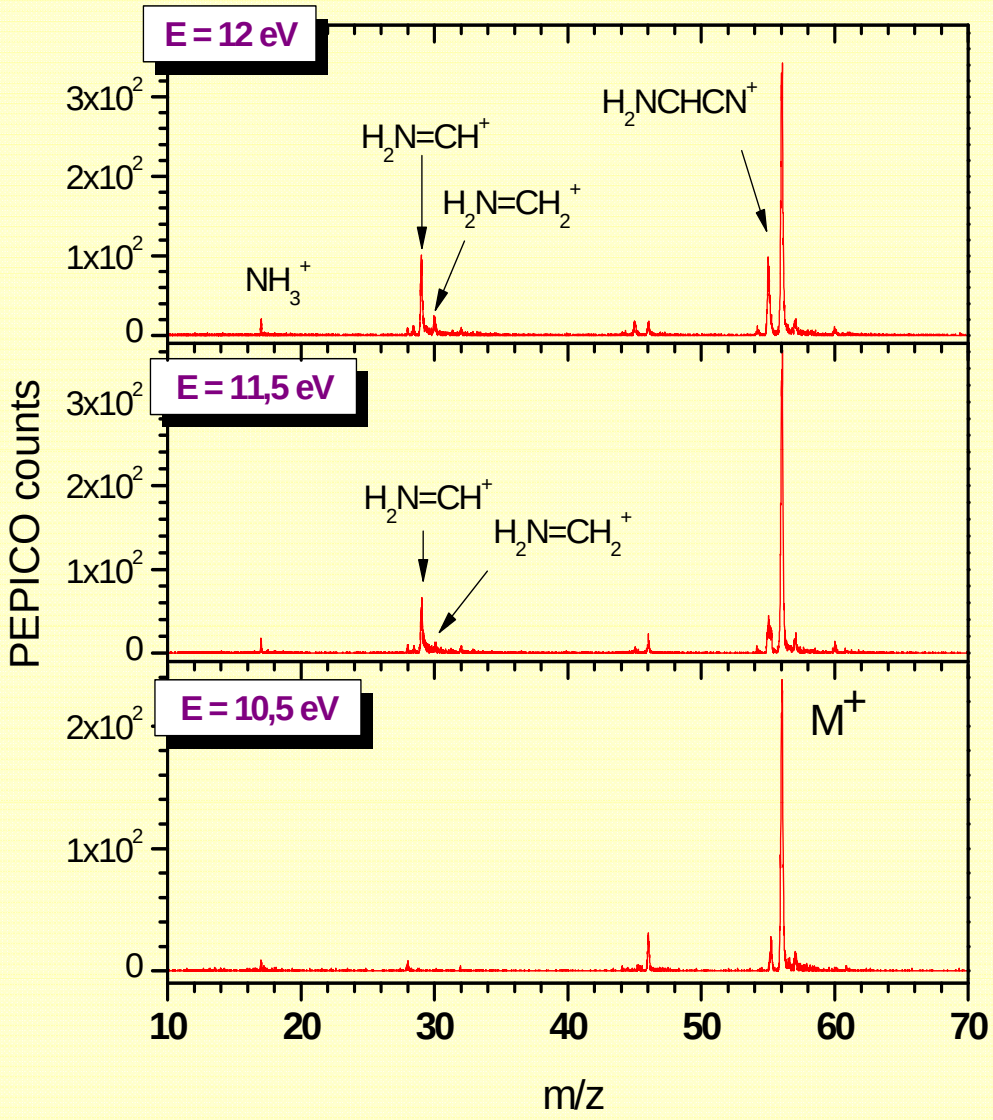
Schwell et al., Chem. Phys. Vol. 393, p. 107 (2012).

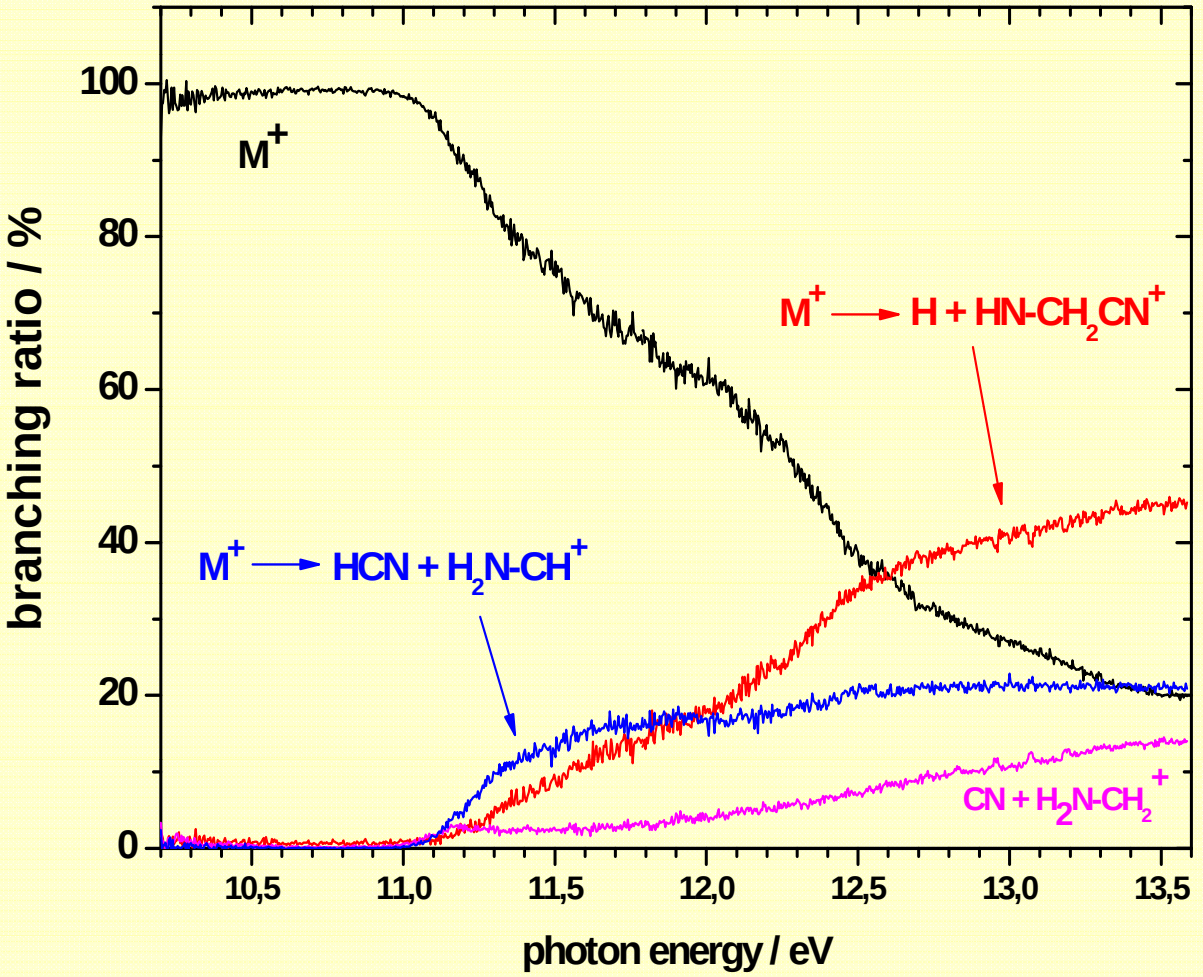
Recent results : Aminoacetonitrile

- 2008: Detection in Sagittarius B2 (N) by Belloche et al., *A&A*, 482, 179-196.
- Very probably a precursor of glycine, formed by Strecker synthesis or other pathways :
  - Elsila et al., *ApJ*, 660, 911-918 (**2007**)
  - Koch et al., *J. Phys. Chem. C,* 112, 2972-2980 (**2008**)



Dissociative photoionization of aminoacetonitrile, $H_2N\text{-}CH_2\text{-}CN$





Adiabatic ionization energy, IE_{ad} = (10.05 ± 0.03) eV (unknown before)

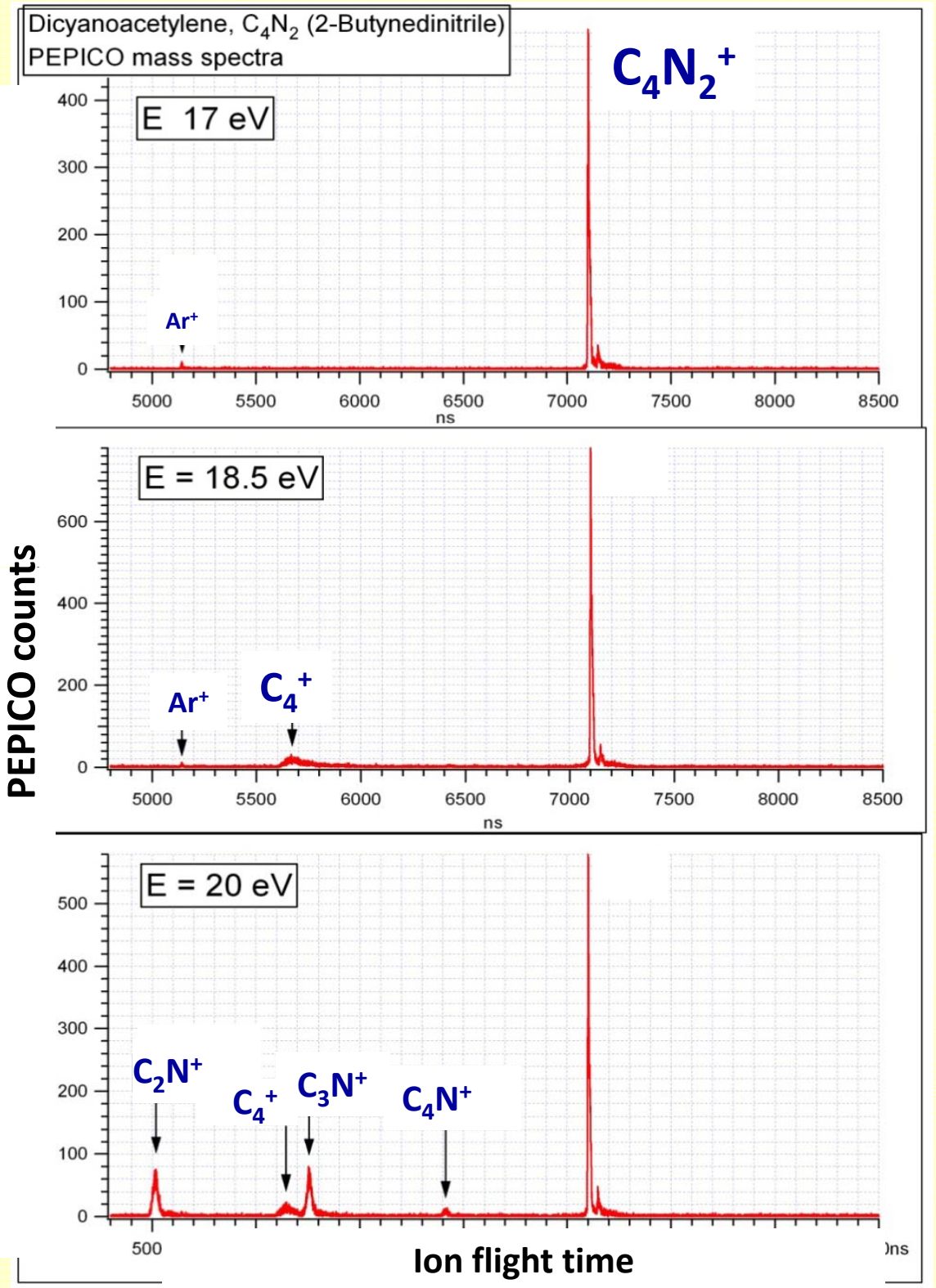
Schwell et al., manuscript in preparation

C_4N_2 remarkable stability

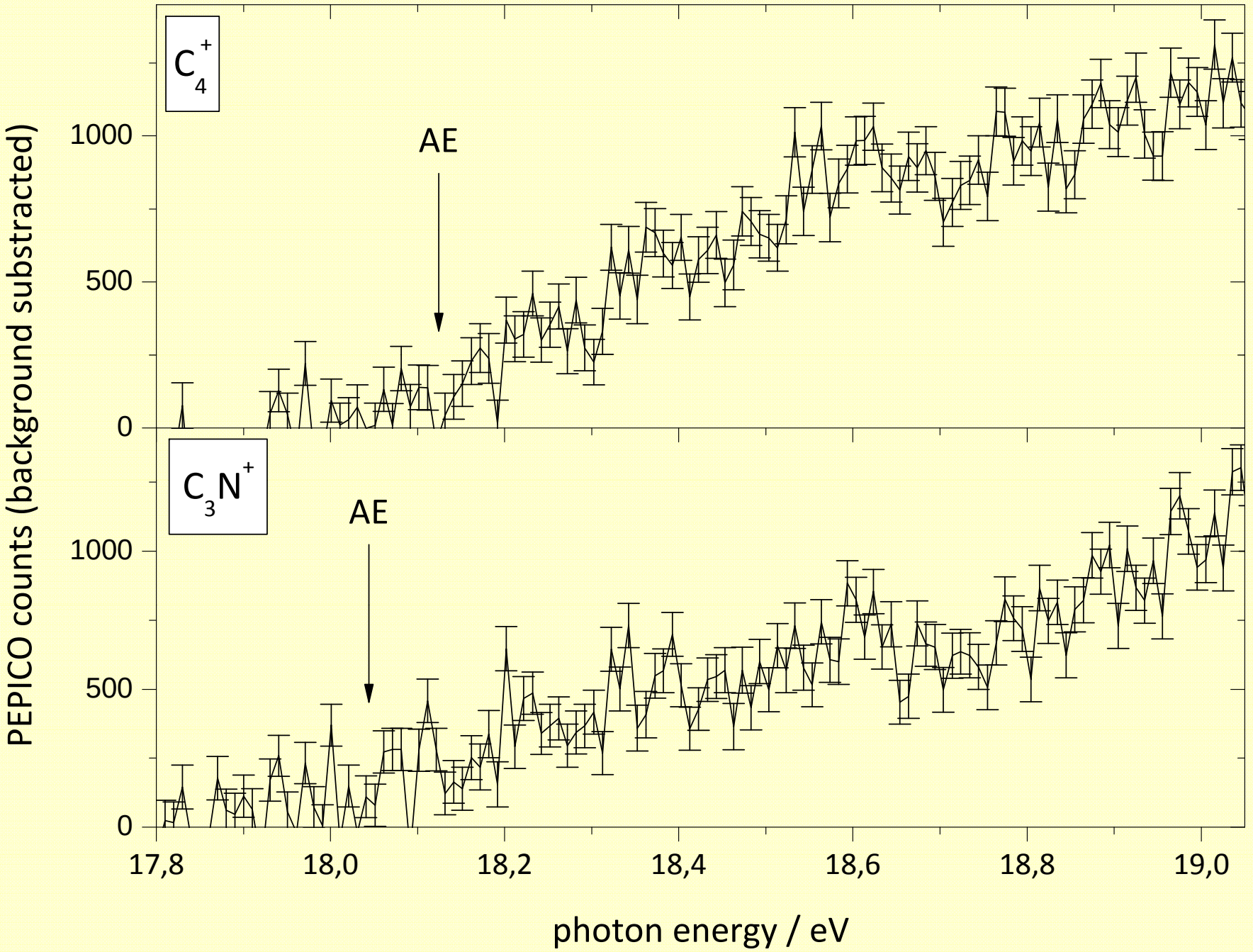
Dissociative ionization of dicyanoacetylene, C_4N_2 (2-Butynedinitrile)

- IE = (11.77 ± 0.03) eV (unknown before)
- Very stable molecular ion (11.77 to 18 eV)

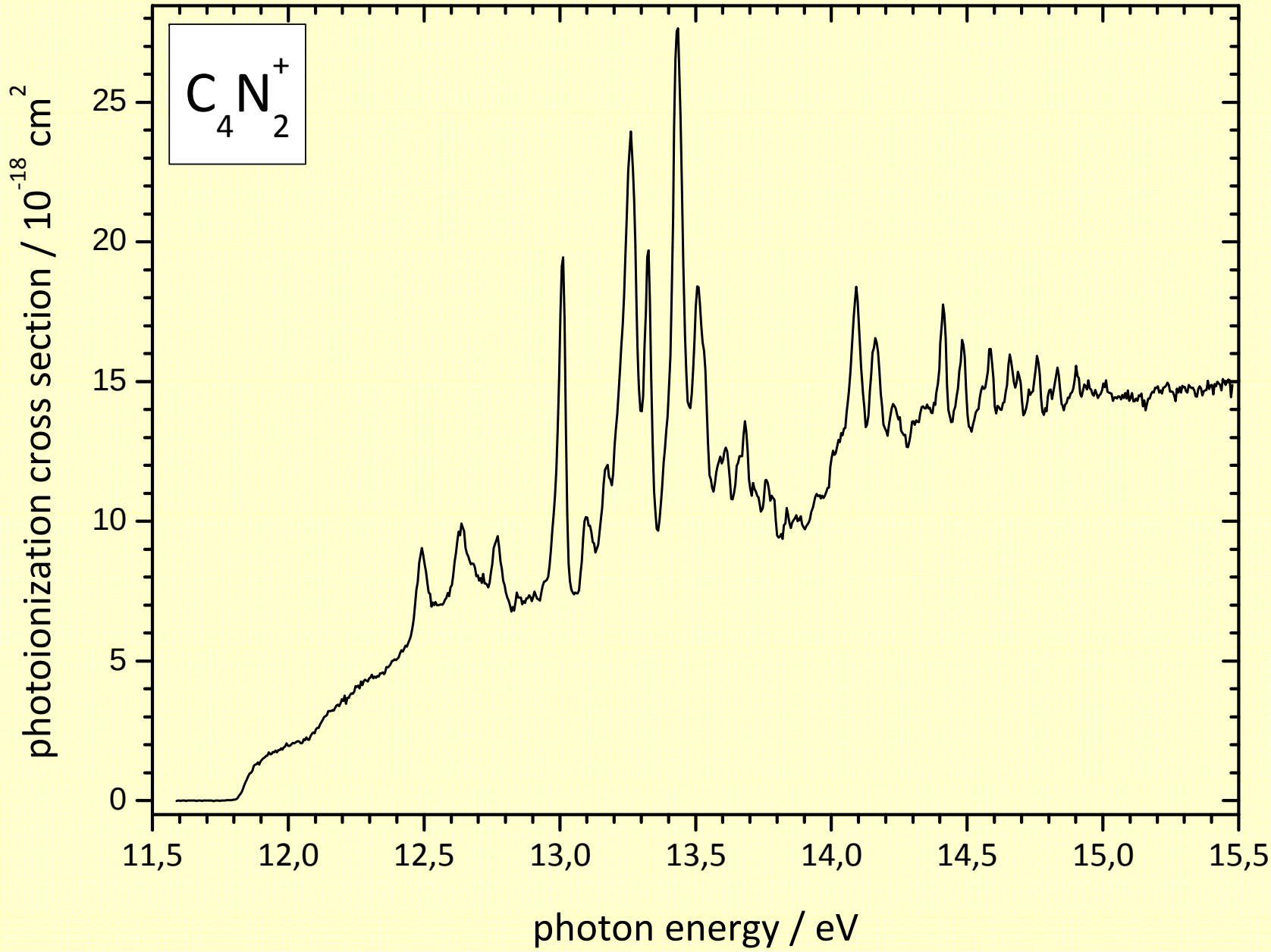
Schwell et al., *manuscript in preparation*



C_4N_2 dissociative photoionization

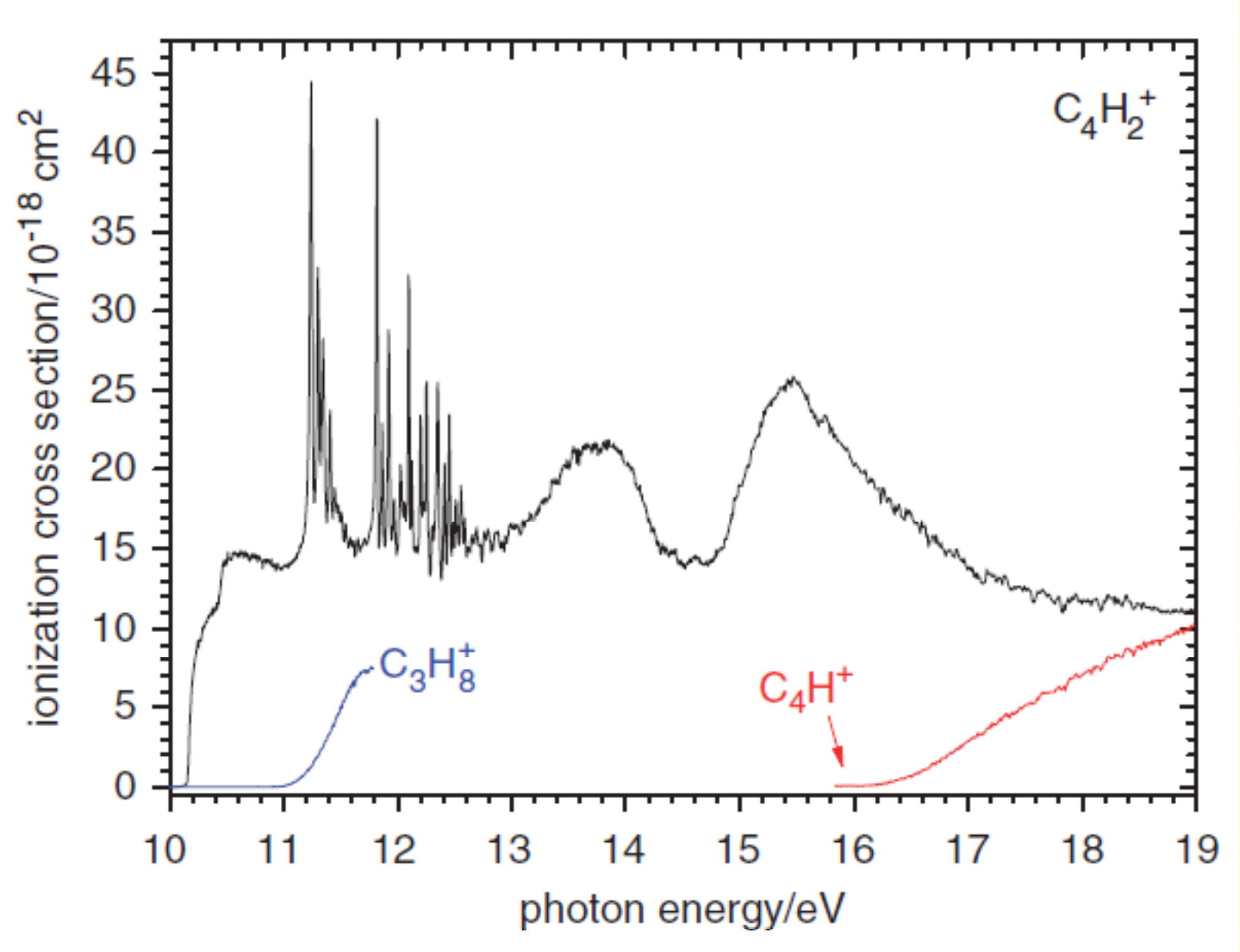


PEPICO - PIE spectrum
Spectral resolution 1 A (13 meV @ 13 eV)



Under analysis, *manuscript in preparation*

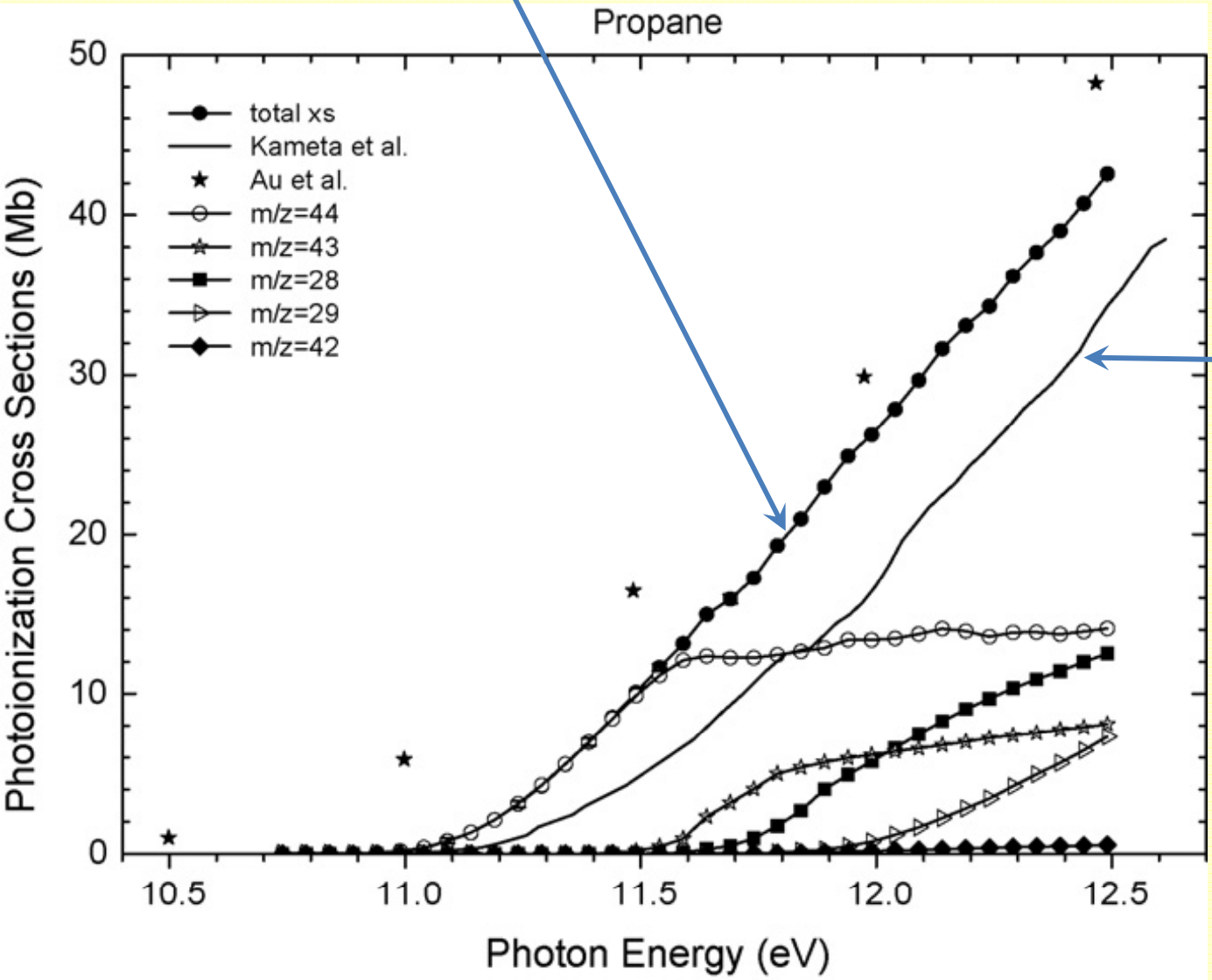
C_4H_2 photoionization



Schwell et al. , Mol. Phys., in press, available online.

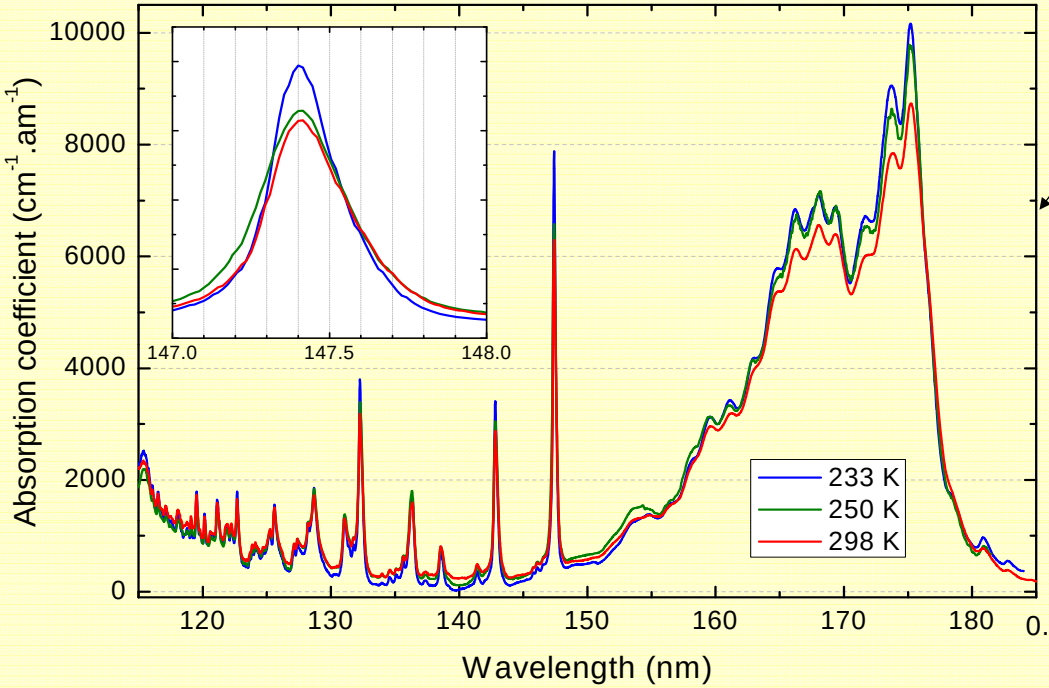
Propane as a standard for photoionization cross section: *there is a problem…..*

J. Wang, B. Yang, T.A. Cool, N. Hansen, T. Kasper,
IJMS 269 (2008), 210-220



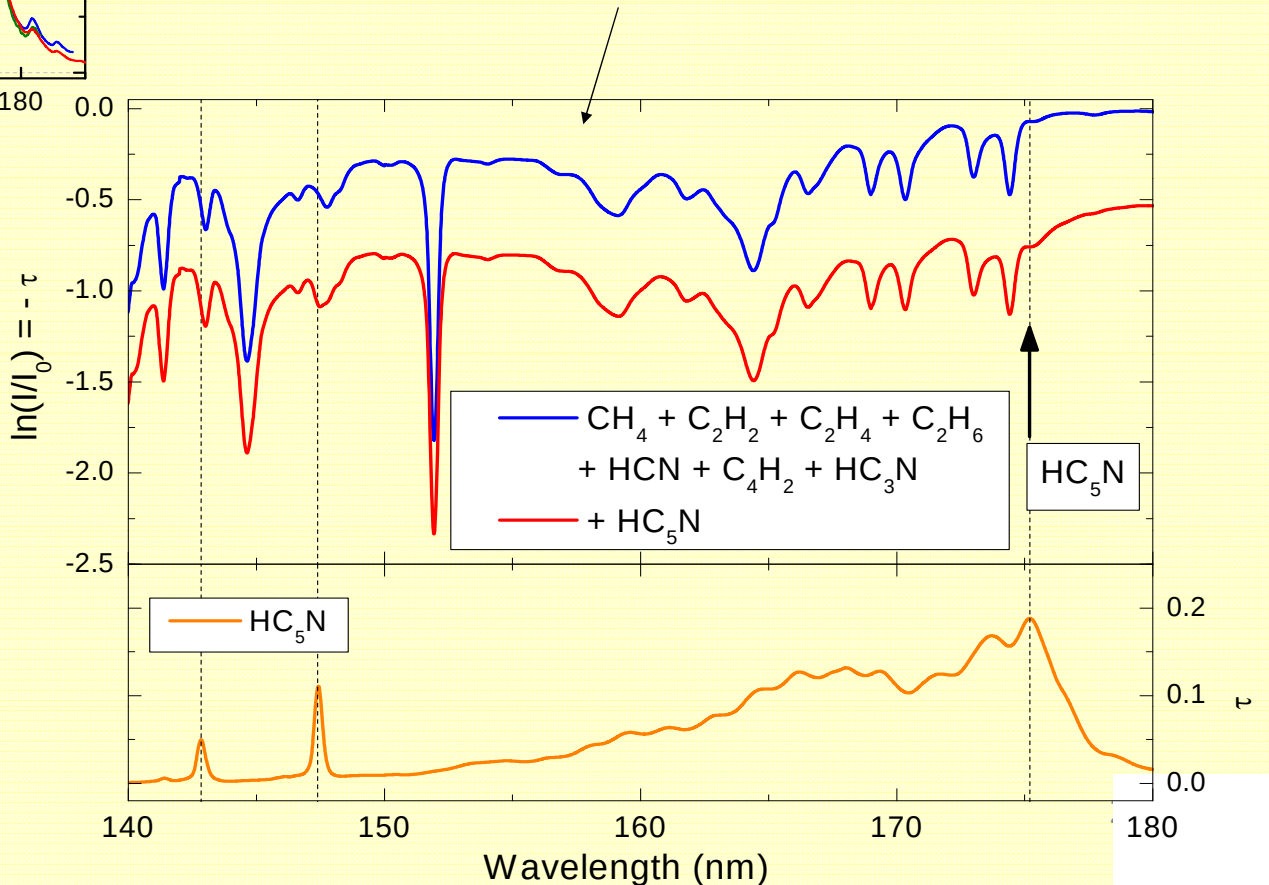
K. Kameta, S. Machida,
M. Kitajima, M. Ukai,
N. Kouchi, Y. Hatano, K. Ito,
J. Electron Spectrosc. Relat.
Phenom. 79 (1996) 391.

HC_5N laboratory spectra : *interpretation of CASSINI UVIS spectra*



First ever measured VUV Absorption spectra

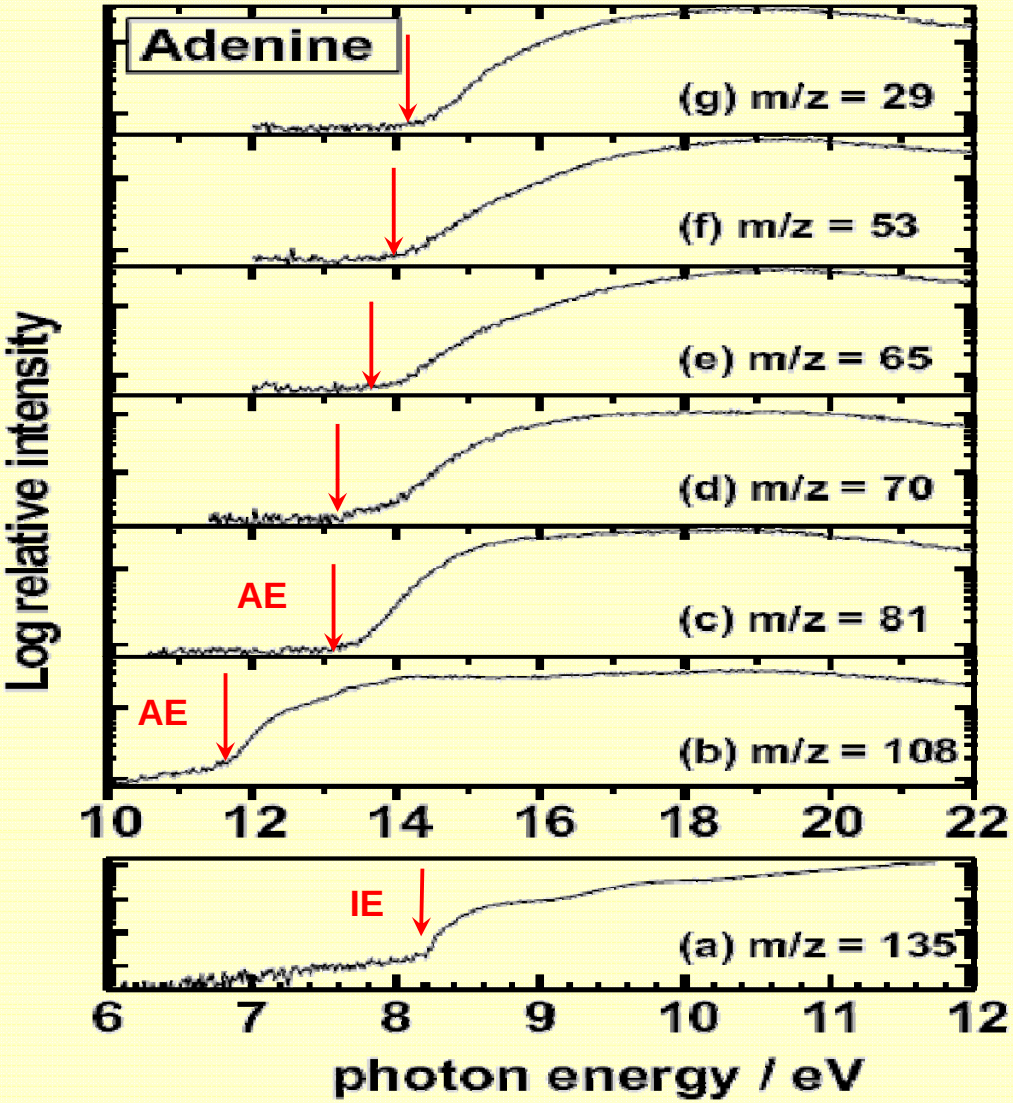
Simulated transmission spectra that should be seen by UVIS



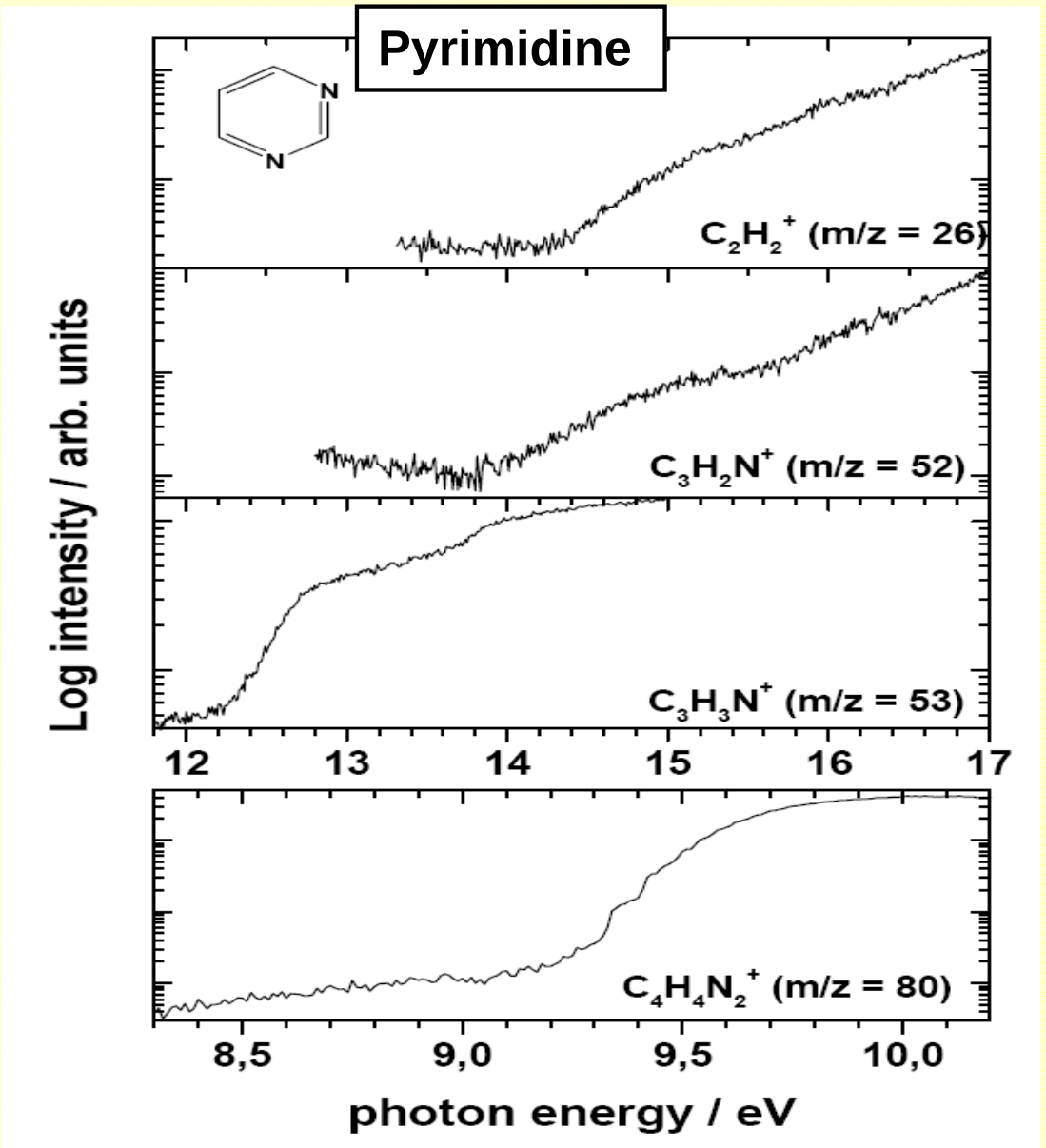
> HC_5N upper limit column density:
> 5×10^{14} cm^{-2}

N. Fray et al.,
J. Geophys. Res. Planets 115 (2010), E06010

Biomolecules: Photoionization mass spectrometry (QMS), heating of macroscopic samples

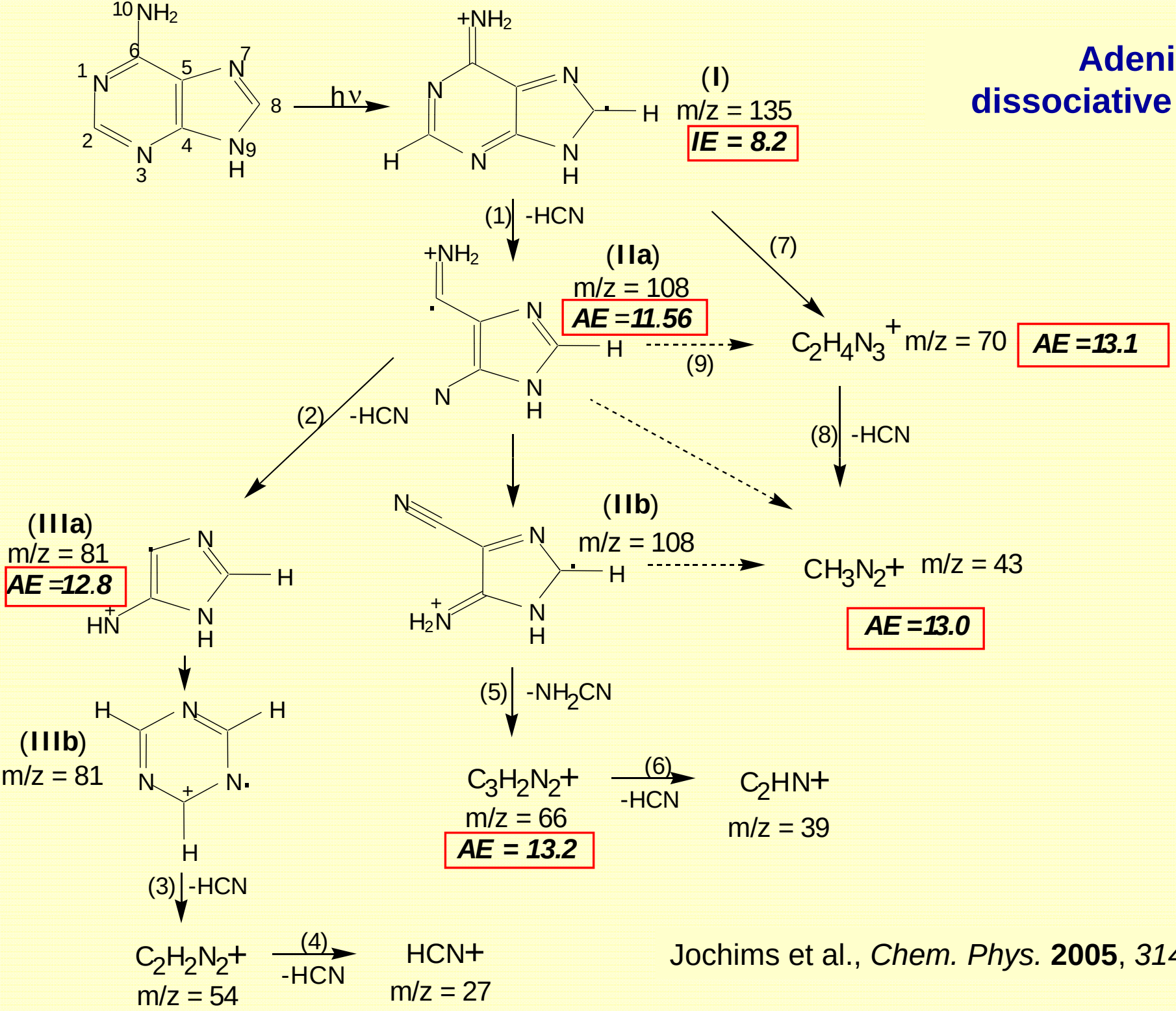


Jochims et al., *Chem. Phys.* **2005**, *314*, 263.



Schwell et al., *Chem Phys*., 353 (**2008**), 145.

Adenine - dissociative ionization



Jochims et al., *Chem. Phys.* **2005**, *314*, 263.

Studying low volatile and/or chemically fragile species using aerosols

- How to bring fragile and non-volatile molecules to the gas phase ?

- Laser desorption (MALDI, MALD) ⟶ Ions or neutrals in the gas phase, pulsed
- Electrospray ionization (ESI) ⟶ Ions (mult. Charged) in the gas phase, cw
- Aerosol Mass Spectrometry (AMS) ⟶ Neutrals in the gas phase, cw

SAPHIRS set-up @ DESIRS beamline: *integration of an aerosol beam*

Fragile or low volatile molecule in solution (H_2O, EtOH, MeOH)

Constant output Nebulizer

Gaseous N_2

Diffusion Dryer

Micro-droplets

Nanoparticles consisting of a pure substance / gaseous N_2

SAPHIRS Chamber

Lens inlet

Aerodynamic Lens

Photomultiplier

Cw laser (532nm)

Position sensitive detector

START

MCPs

L2

μ-metal shield

deflectors

extractor

L1

y

z

x

Heater

repeller

deflectors

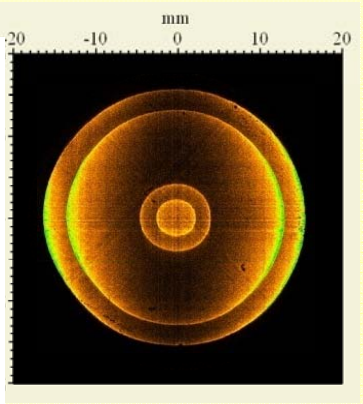
SR

WM-TOF

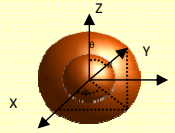
MCPs

STOP

VM Imaging of PEs

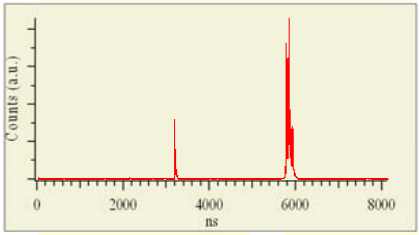


Expanding electrons distribution



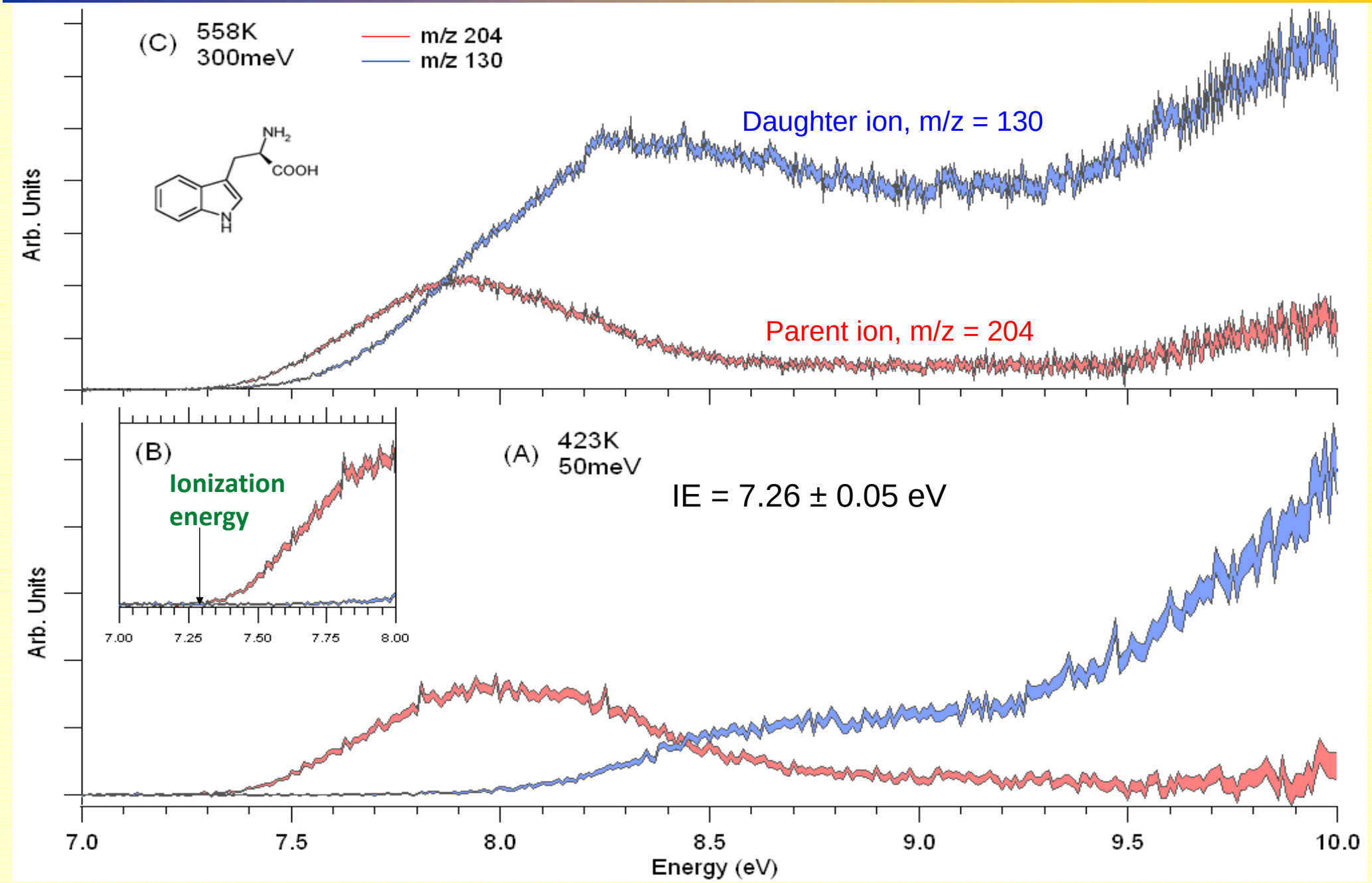
2D projection of the sphere of electrons

TOF-MS



Gaie-Levrel et al., *Phys. Chem. Chem. Phys.* **13**, 7024-7036 (2011)

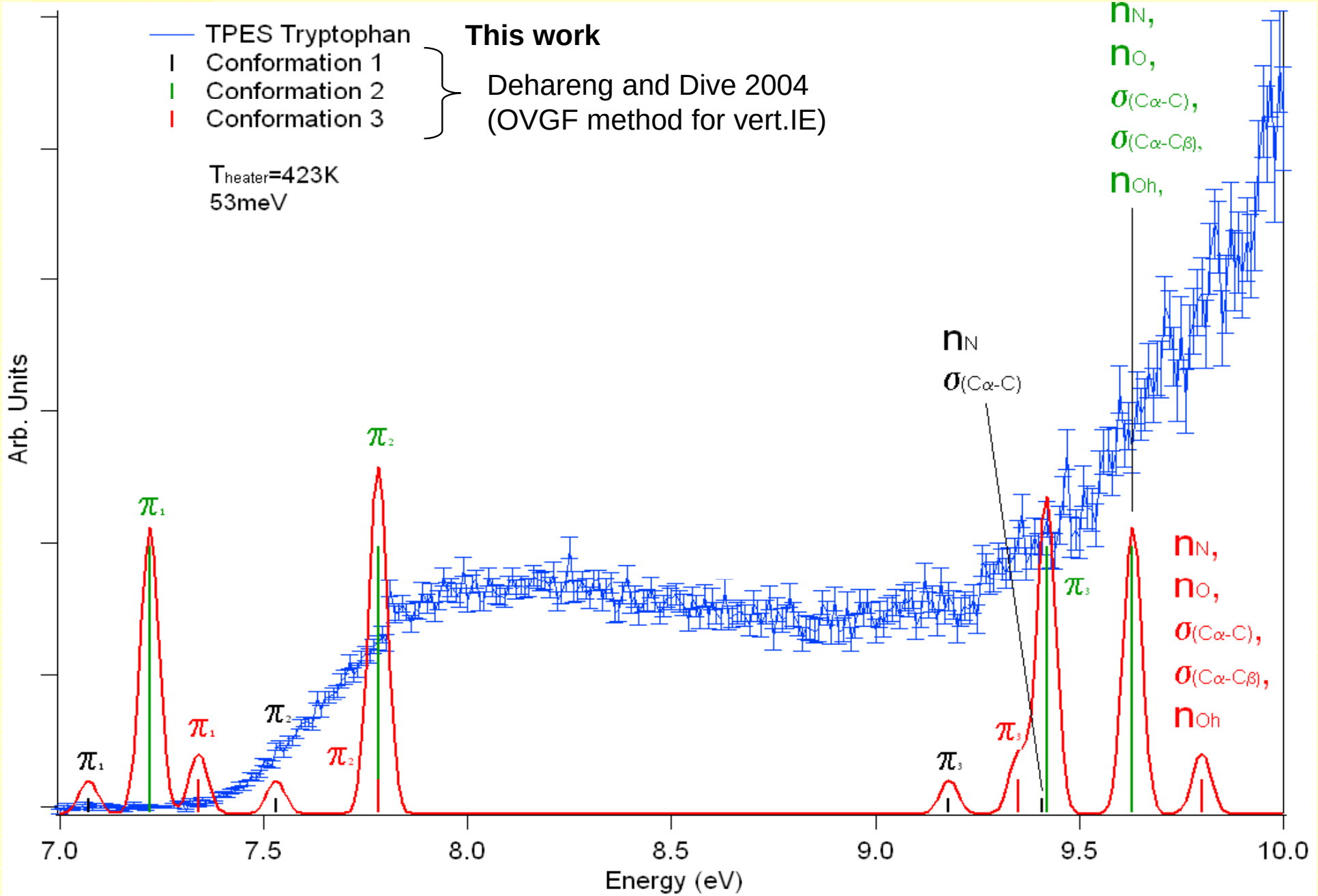
Aerosol mass spectrometry: Tryptophane (T)PEPICO-PIE > Slow PEPICO-PIE



Gaie-Levrel et al., *Phys. Chem. Chem. Phys.* **13**, 7024-7036 (2011)

Tryptophane threshold photoelectron spectrum (TPES),

- comparsion to ab-initio calculation of vert. IEs of different MOs and conformers

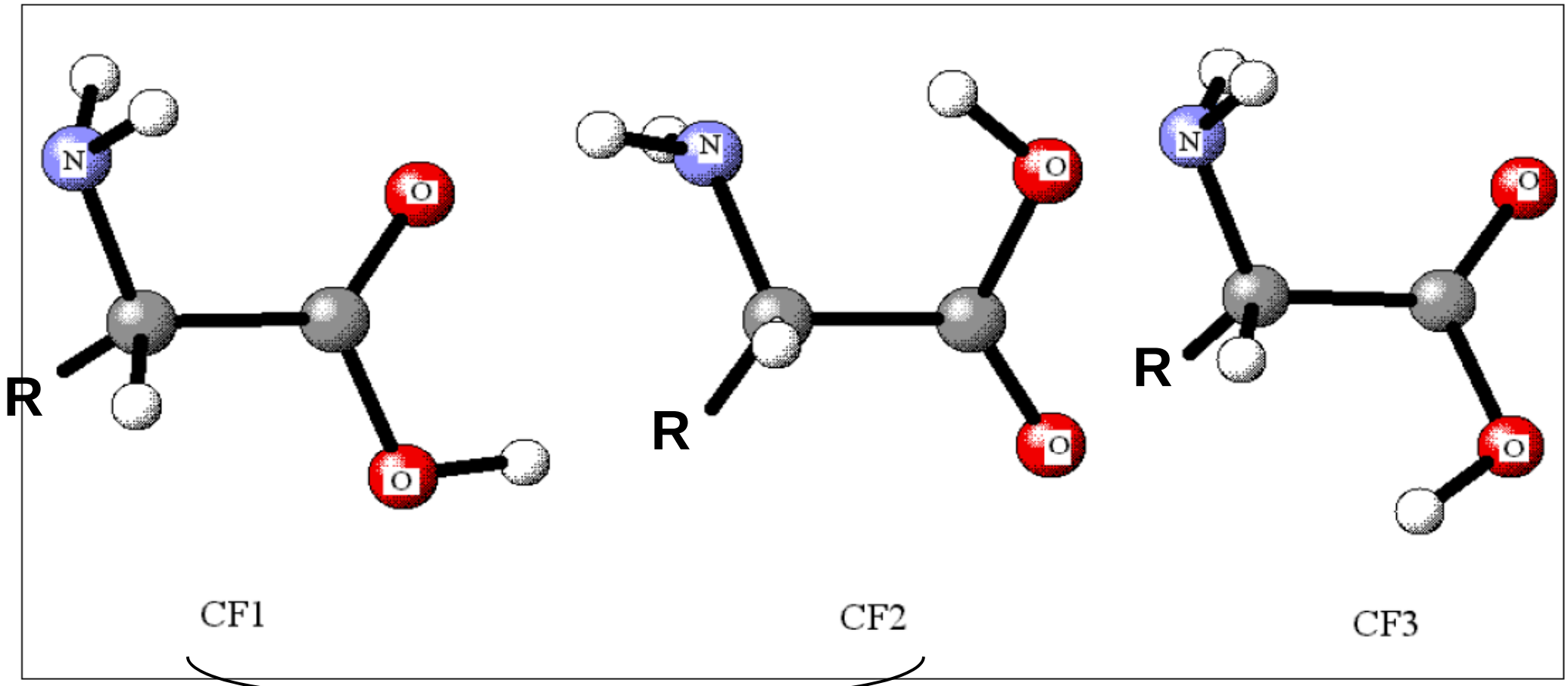


Gaie-Levrel et al., Phys. Chem. Chem. Phys **13**, 7024-7036 (2011)

Vertical Ionization Energies of α-L-Amino Acids as a Function of Their Conformation: *Ab Initio Study*

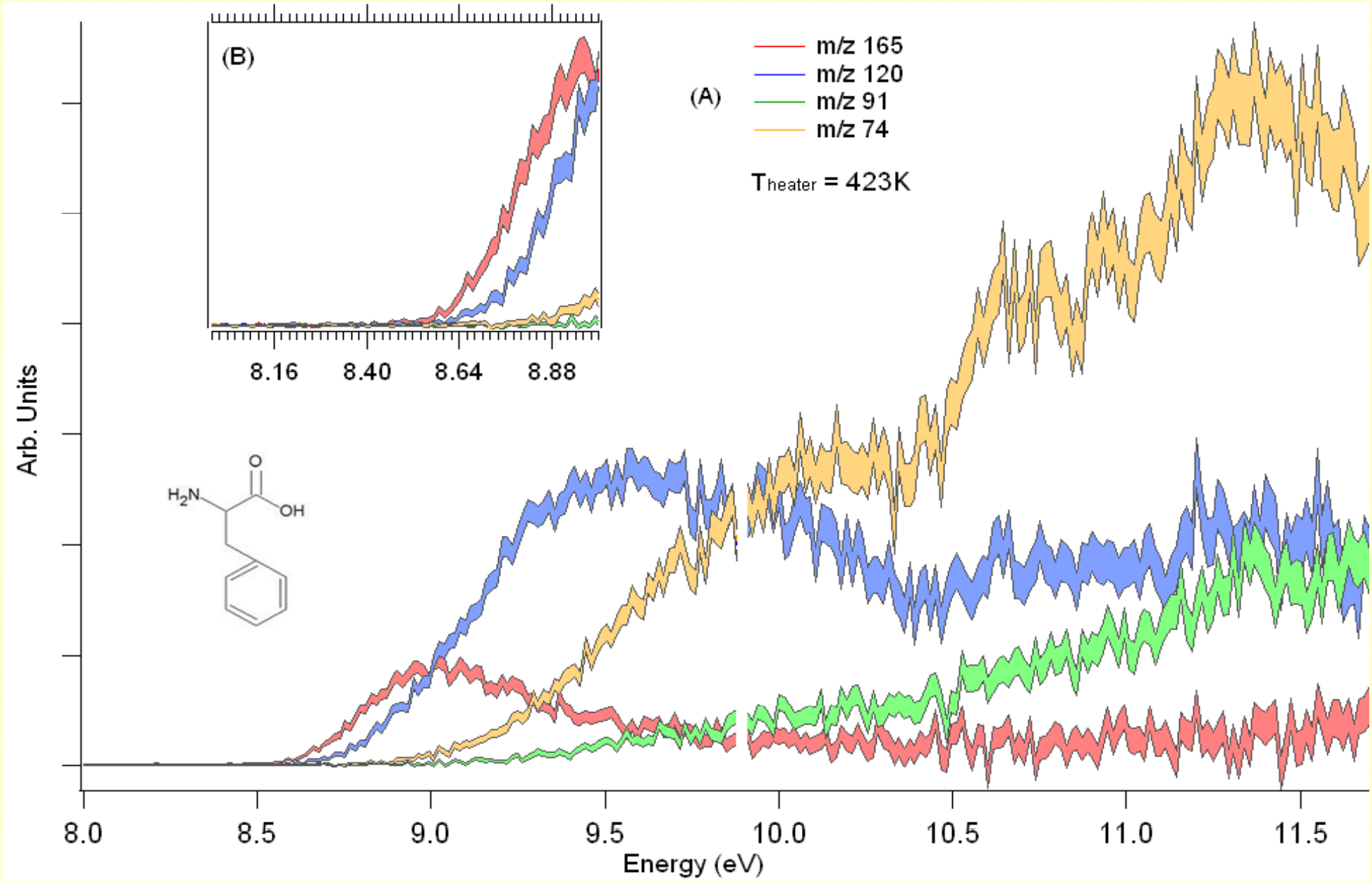
Dehareng and Dive, Int. J. Mol. Sci. 2004 (Université de Liège, Belgium)

Scheme 1. The three backbone conformations studied



Lowest in energy

Phenylalanine: (T)PEPICO-PIE spectra



Gaie-Levrel et al., Phys. Chem. Chem. Phys **13**, 7024-7036 (2011)

Conclusion

The cw-VUV spectroscopy of many molecules of interstellar and planetary interest have been studied in the past decade by our group. They include:

- $HCOOH$, CH_3CN, CH_3COOH, $HCOOCH_3$, $HOCH_2C(O)H$, $CH_3C(O)NH_2$, H_2NCH_2CN
- Linear C,N chain molecules : HCN, HC_3N, HC_5N, C_4H_2, C_4N_2, C_2N_2
- Nucleic acid bases : adenine, thymine, uracil, pyrimidine, imidazole, benzimidazole, cytosine
- Amino-acids : Glycine, α and β-alanine, tryptophane, phenylalanine, α –aminoisobutyric acid (AIB), α-valine

- Measurements include:
  - Absolute photoabsorption spectra upto 20 eV and in some cases T –dependant downto 180K
  - Photoionization cross sections (PEPICO), TPEPICO, TPES spectra in some cases
  - Quantum yield of ion formation
- Aerosols can help to bring fragile and/or low-volatile molecules in the gas phase

Perspectives for collaboration with UC Davis

• Astrophysical application:

$$J(\lambda) = \int_{\lambda_1}^{\lambda_2} \Phi(\lambda) \times \sigma(\lambda) \times S(\lambda) \times d\lambda$$

• For most of the important IS molecules, data on **Φ (λ)** are missing.

• A few studies have been made at A. Suite group at Wayne state University,

on **C_4H_2** and **HC_3N**, but only at 4 fixed wavelengths : 212, 193, 157, 121.6 and 2x212 nm.

These studies can be used as a test case for the 2x VUV tunable laser setup.

• Interesting molecules: **acetamide, aminoacetonitrile, glycolaldehyde, C_4N_2….**

• Dissociative ionization thresholds and absorption spectra (determined with SR) are useful to know for planning experiments with 2x VUV

• Quantum chemical calculations (Majdi Hochlaf's group in Paris) should be made on :

- The identification of the weakest bonds (prior to measurement)
- On high-lying electronic states in the VUV and transition moments to attain them.

(*For solid or liquid molecules (298 K) it is difficult to measure absorption spectra*).

- Ionization and dissociative ionization: calculations on ionic states (ro-) vibrational progressions.