VUV spectroscopy and photophysics of interstellar and prebiotic molecules: *Case of acetyl cyanide*

Ayad Bellili, Y. Bénilan, M.-C. Gazeau, N. Fray, J.-C. Guillemin, L. Poisson, M. Hochlaf, M. Schwell

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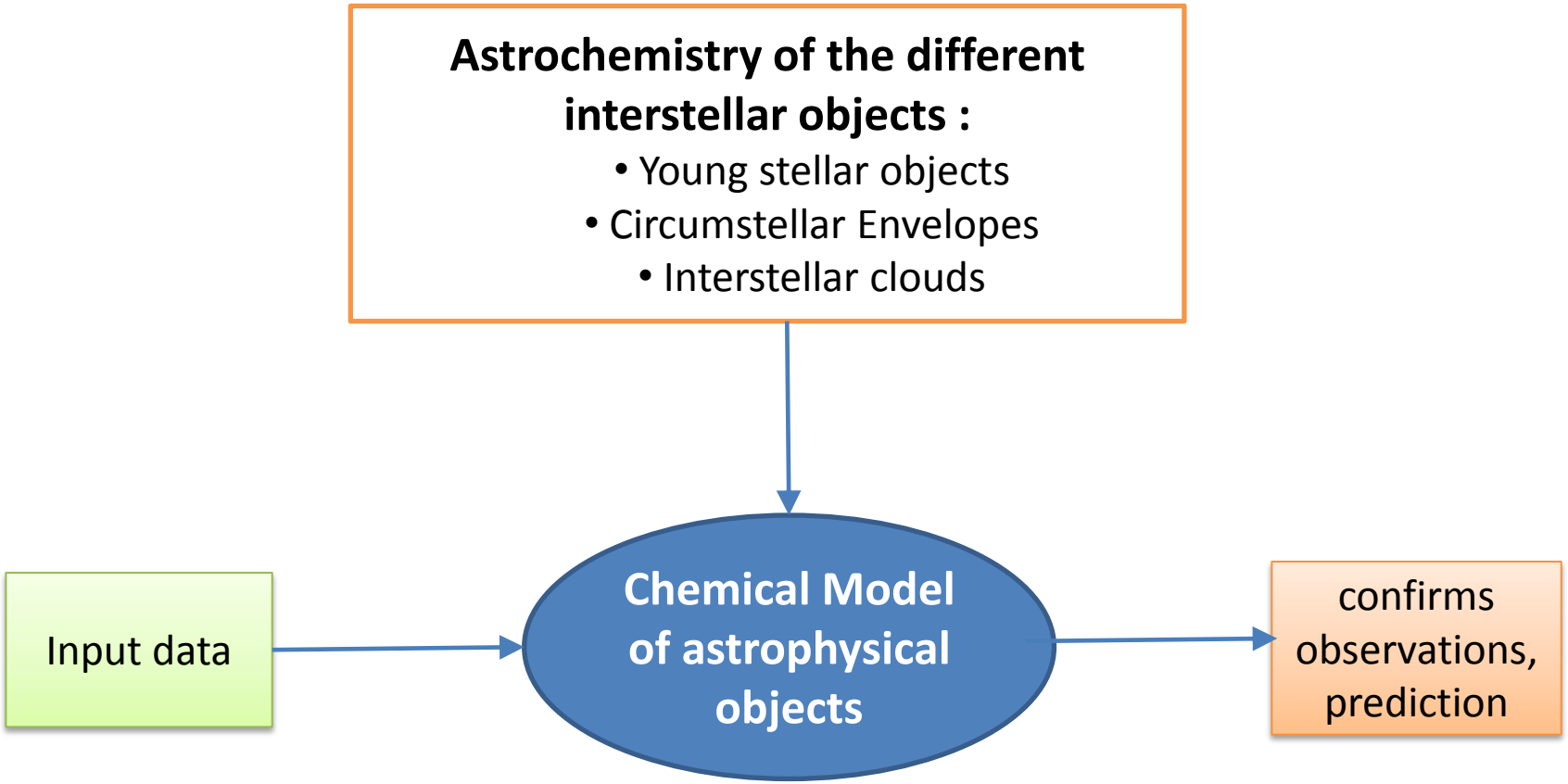
MSME
Laboratoire Modélisation et Simulation Multi Echelle

Sciences Chimiques de Rennes
UMR CNRS 6226

lisa | Laboratoire Inter-universitaire des Systèmes Atmosphériques

General context



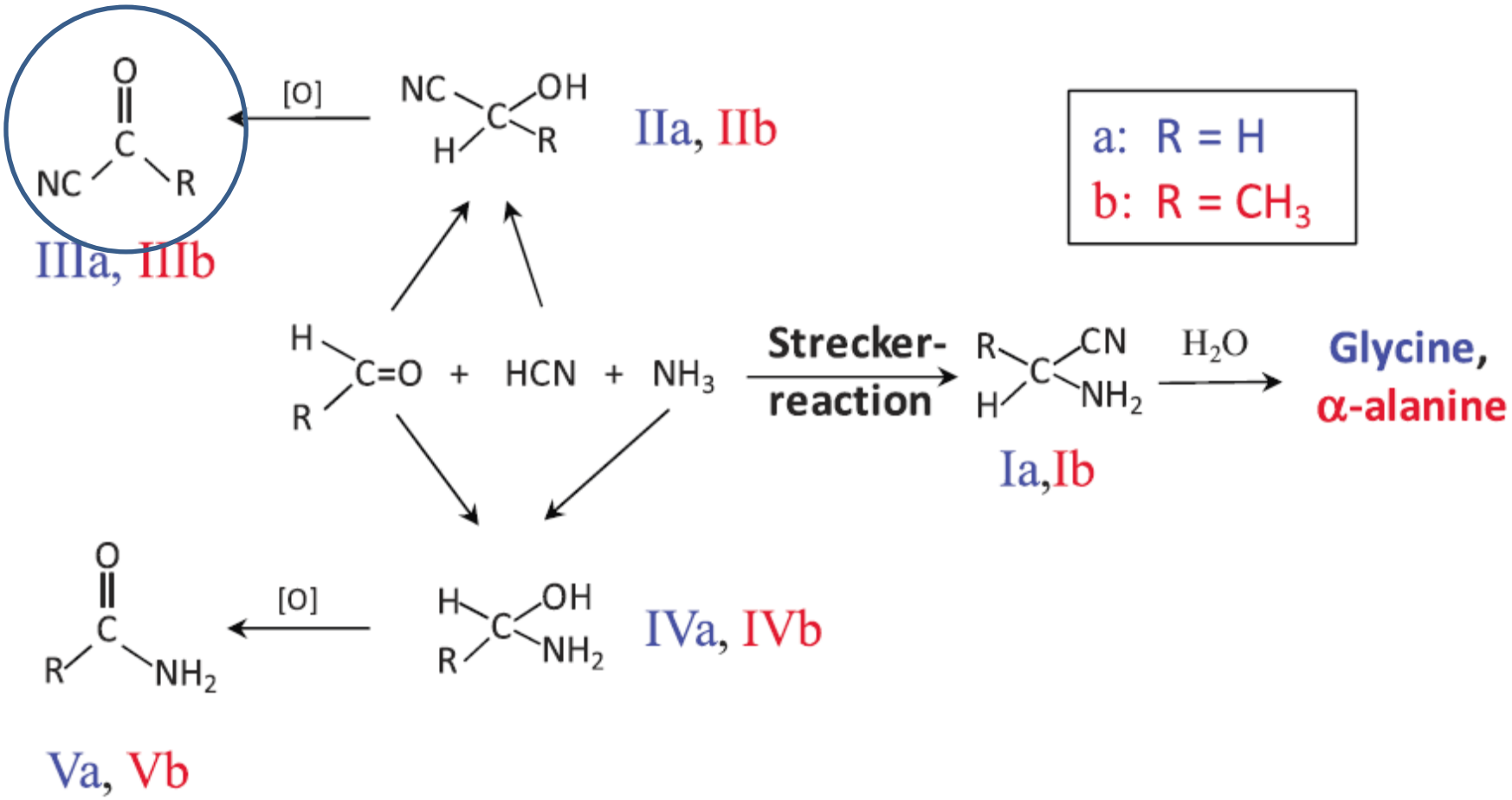
VUV photophysics of interstellar and prebiotic molecules

- Useful properties determined in the frame of our project:
  - Absorption cross sections
  - Ionization cross sections
  - Branching ratios of fragmentation reactions

- Fundamental analysis of spectra, photophysical processes and fragmentation pathways
  - Spectroscopic measurements
  - Associated quantum chemical calculations

- Molecules studied in 2013/14:
  - Photoion/photoelectron spectroscopy @ DESIRS: aminoacetonitrile, acetyl cyanide
  - Quantitative photo absoption spectra @ BESSY: aminoacetonitrile, acetyl cyanide, methyl isocyanide, propynal

Prebiotic molecules formed by the Strecker reaction



UV spectroscopy of acetyl cyanide (species IIIb, "AC") : state of literature

The photophysics of **neutral AC** has been studied extensively in the **mid-UV** using laser experiments.

- A study of AC photofragmentation was performed using Laser induced fluorescence (LIF) spectroscopy at λ = 193 nm [1]
- Ultrafast (fs) spectroscopy in connection with mass spectrometry was used to study the fragmentation of AC at the same wavelength of λ = 193 nm [2].

[1] Horwitz RJ, Francisco JS, Guest JA (1997) Photofragmentation of Acetyl Cyanide. *J Phys Chem A* 101:1231-1237.

[2]. Owrutsky JC, Baronavski AP (1999) Ultrafast photodissociation studies of acetyl cyanide and acetic acid and unimolecular decomposition rates of the acetyl radical products. *J Chem Phys*111:7329.

UV spectroscopy of acetyl cyanide (species IIIb, "AC") : state of literature

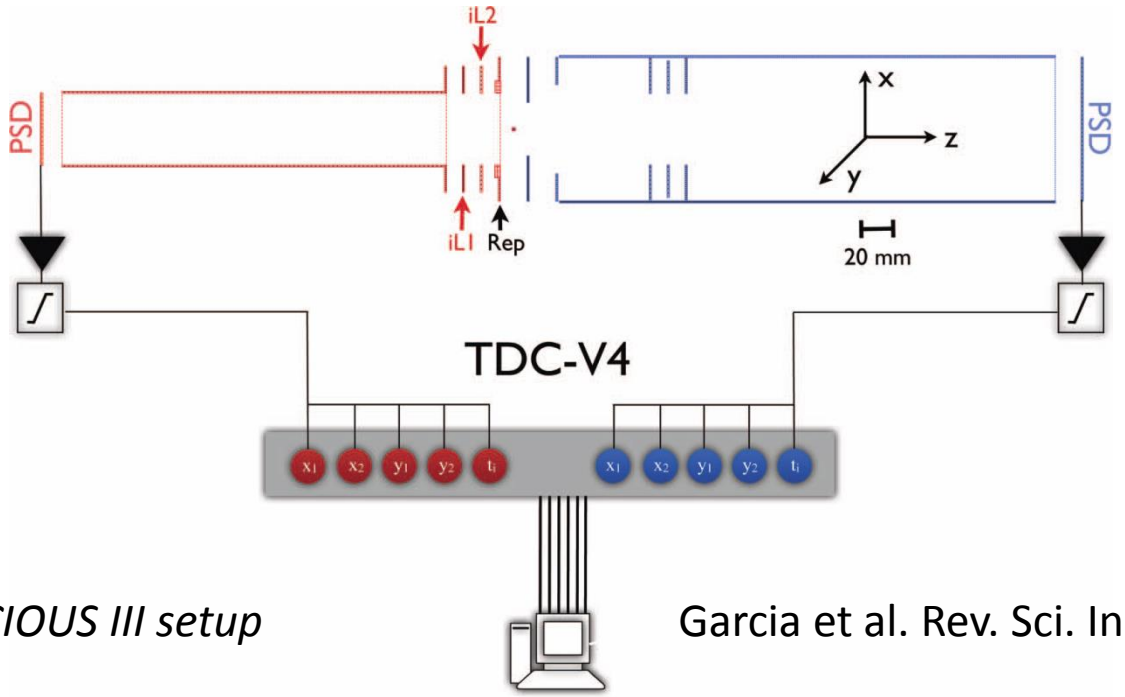
- **AC^+ cation**: an overview of the structure of the ground state and the five lowest electronic states was detailed in the experimental work of Katsumata et al [3] in 2000.

- Their HeI photoelectron spectrum extends up to 19 eV and consists of broad bands that have been assigned using MP2 / 6-31G (d) and G3 calculations.

- To our knowledge, there is
  - no photoionization mass spectrometry study of AC,
  - no information about the unimolecular decomposition processes of the AC^+ cation formed by photoionization of the AC neutral.

[3] Katsumata S, Tabayashi K, Sugihara T, Kimura K (2000). HeI photoelectron and ab initio study of acetyl cyanide and its cation. *J Electron Spectrosc Rel Phen* 113:49–55.

Exptl. VUV spectroscopy of acetyl cyanide studied with DELICIOUS III at DESIRS



DELICIOUS III setup

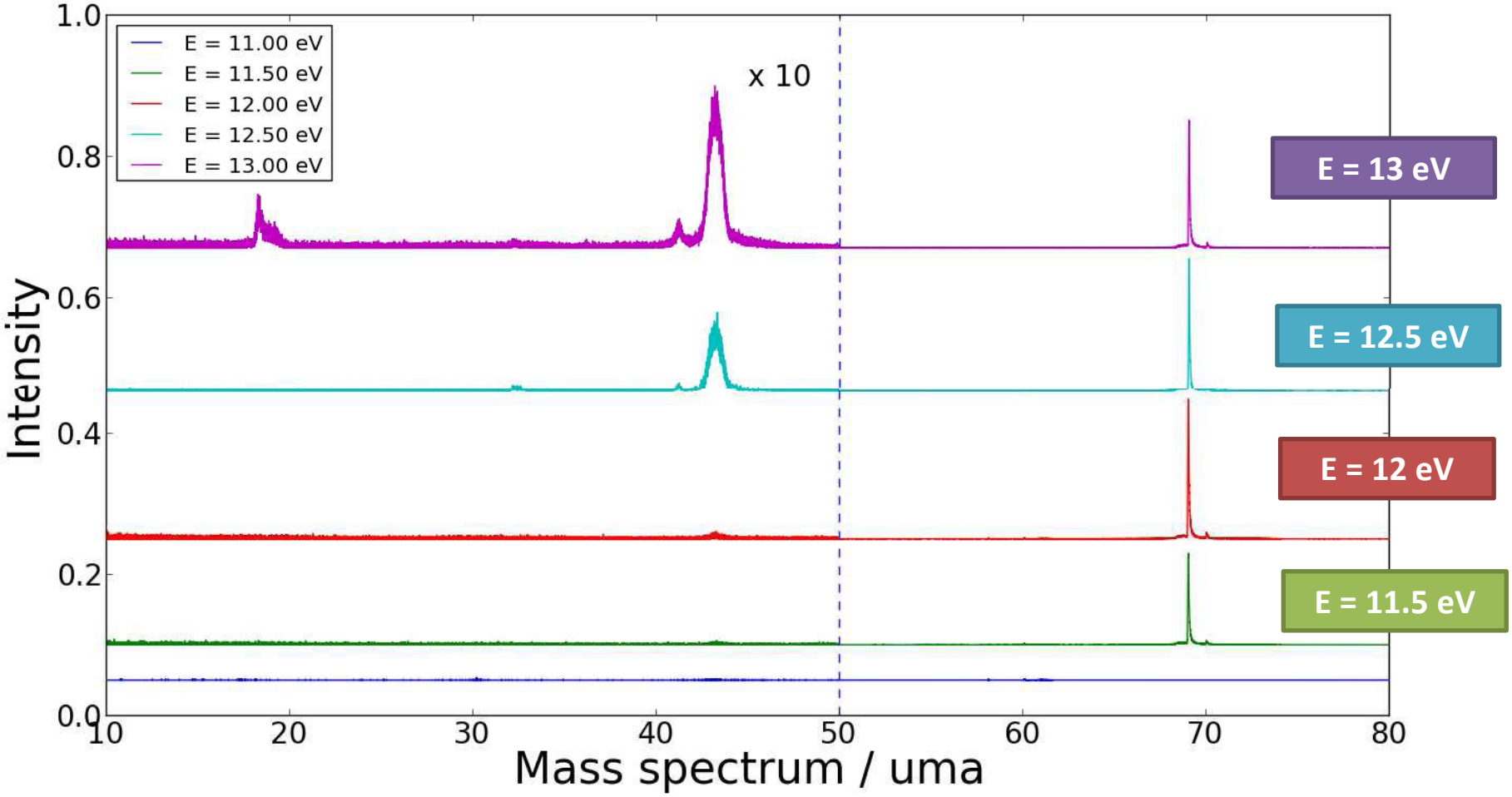
Garcia et al. Rev. Sci. Instrum. **84, 053112 (2013)**

- Detection of electrons and ions in coincidence
- High resolution photoelectron spetroscopy

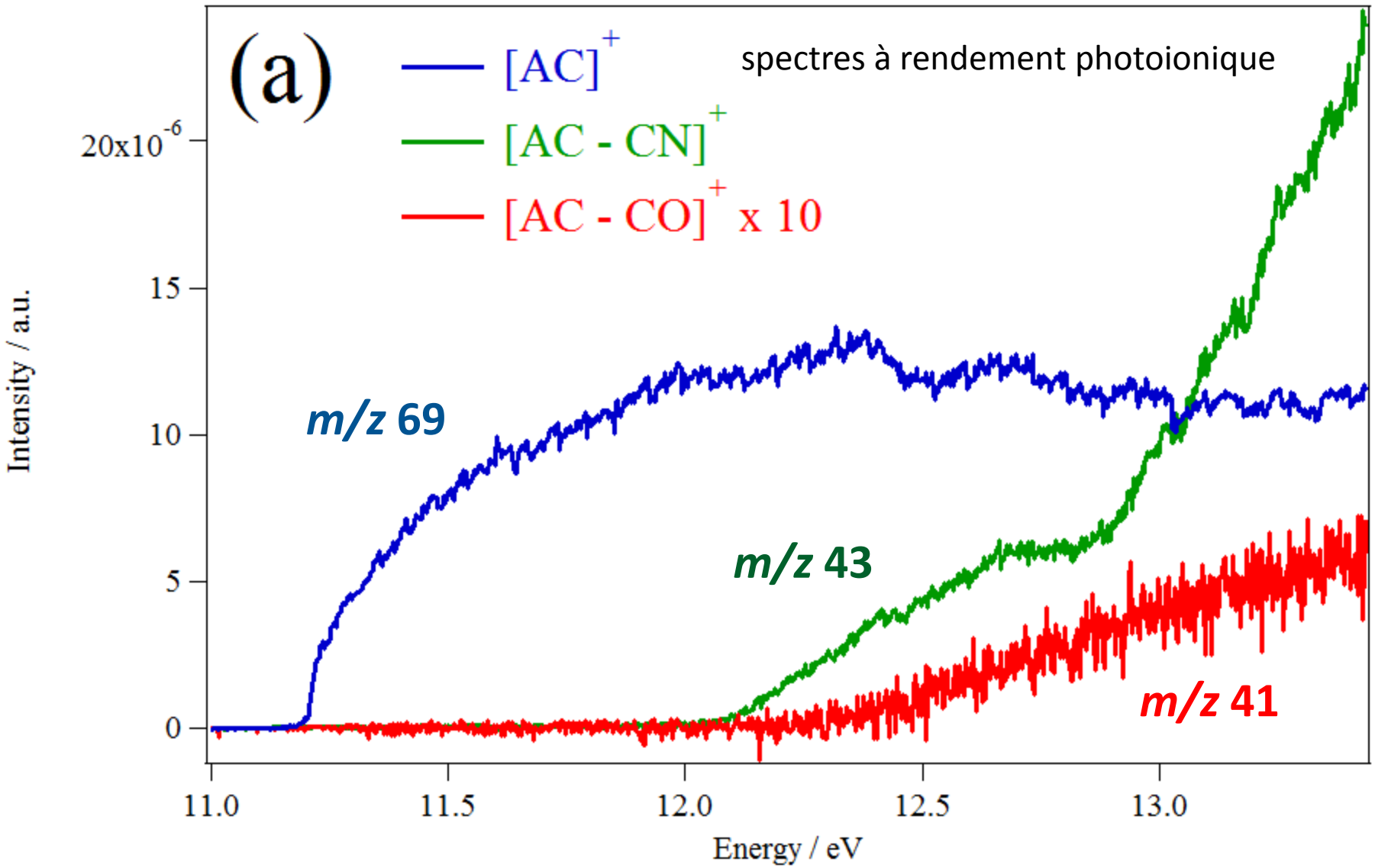
This study:

$AC + h\nu$ (11 à 13.6 eV) $\rightarrow$ $AC^+ + e^- \rightarrow F_i^+ + N_j$

Time-of-flight mass spectra of acetyl cyanide at different photon energies

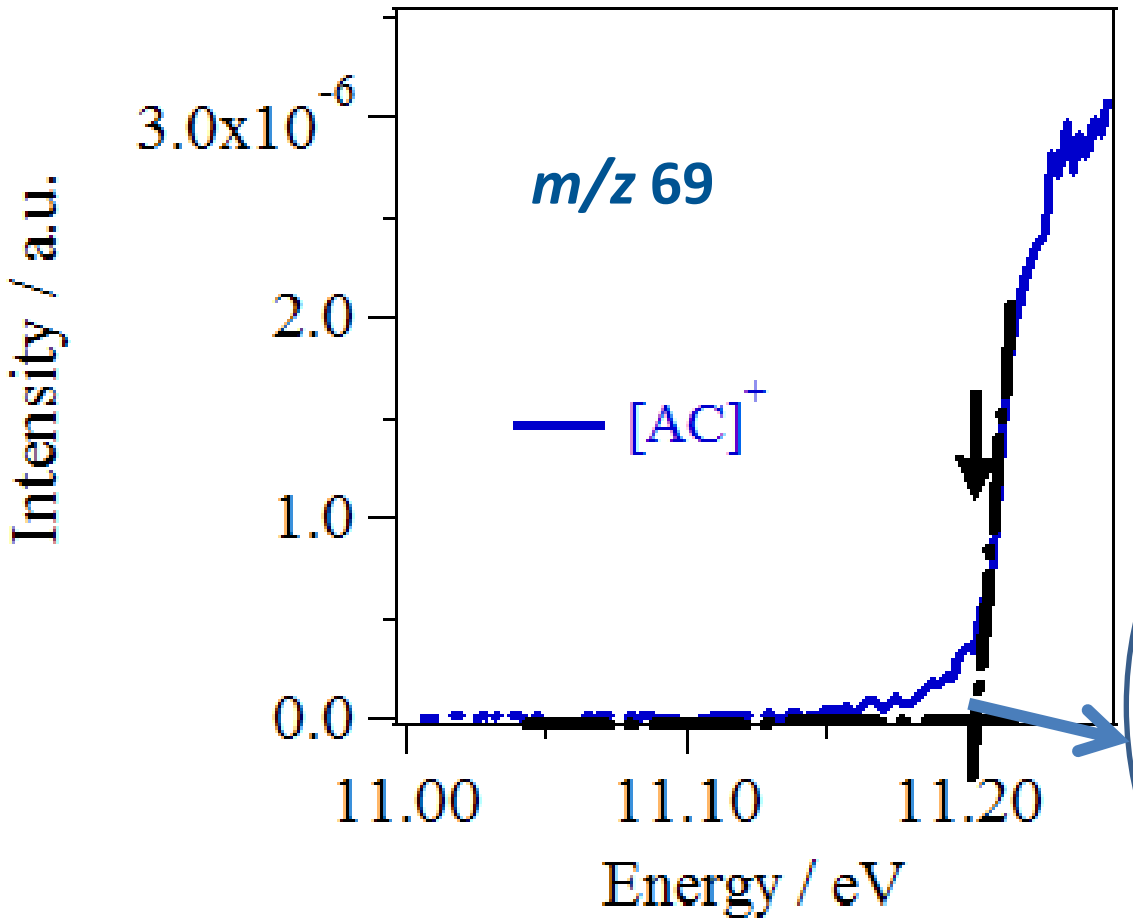


PEPICO spectra of acetyl cyanide

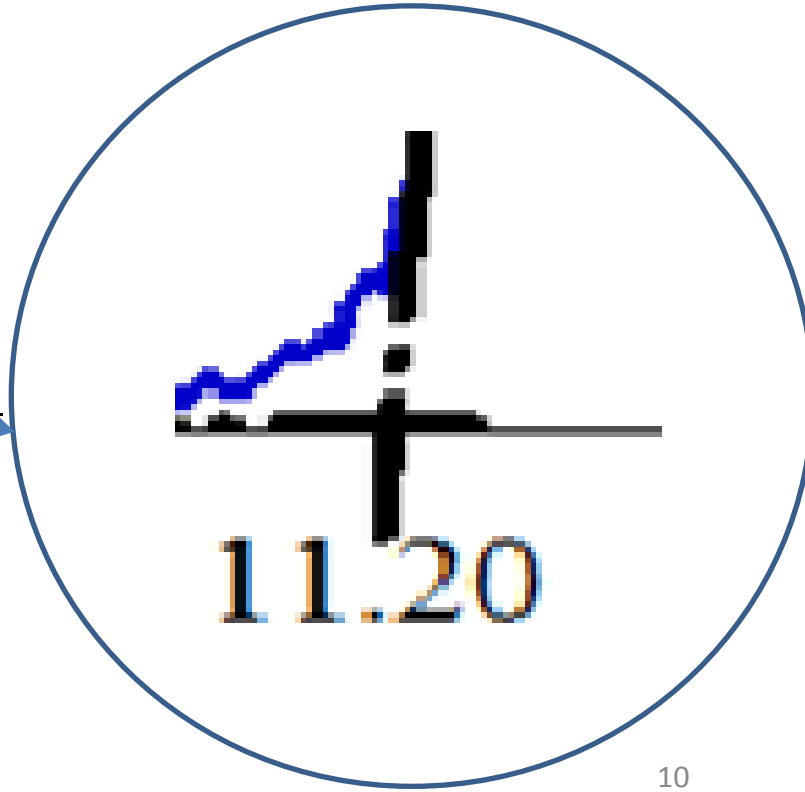


PEPICO spectra as a function of the photon energy in the 11-13.5 eV range for AC+

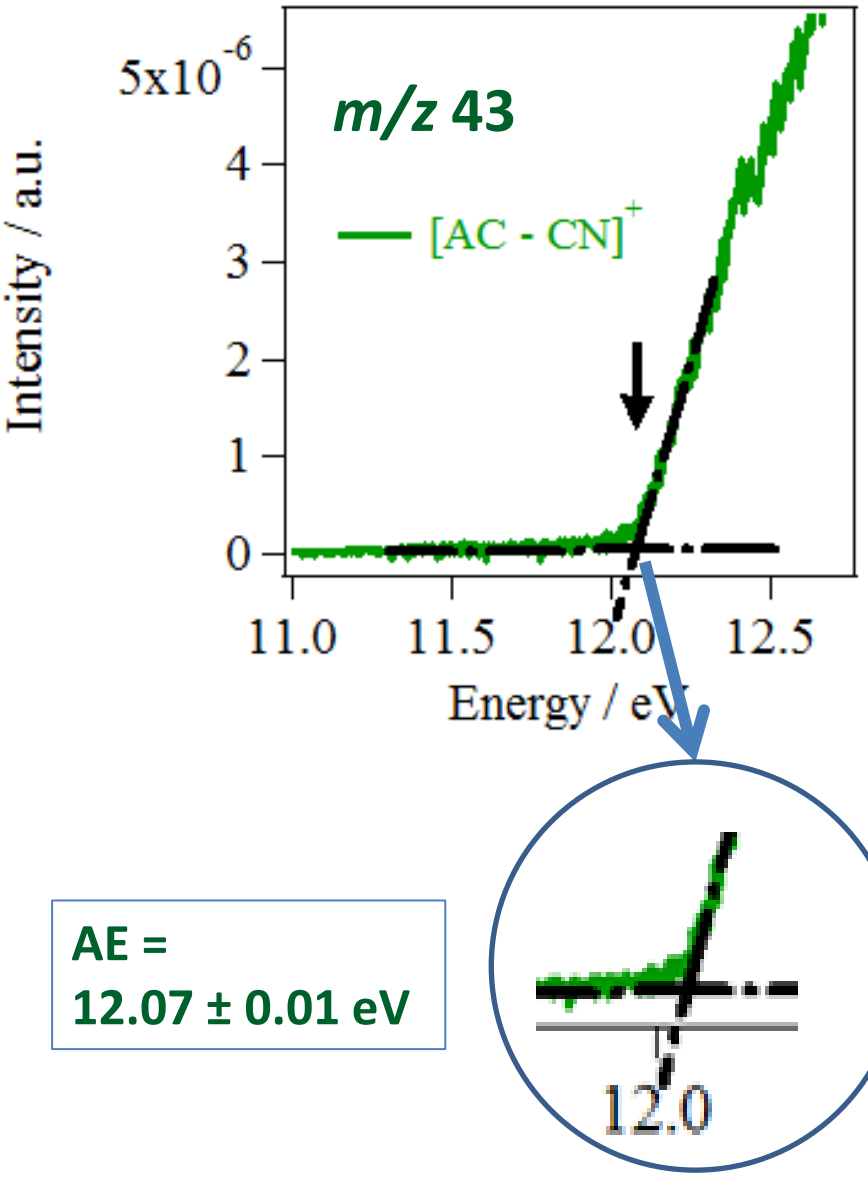
Acetyl cyanide : experimental determination of its adiabatic ionization energy (AIE)



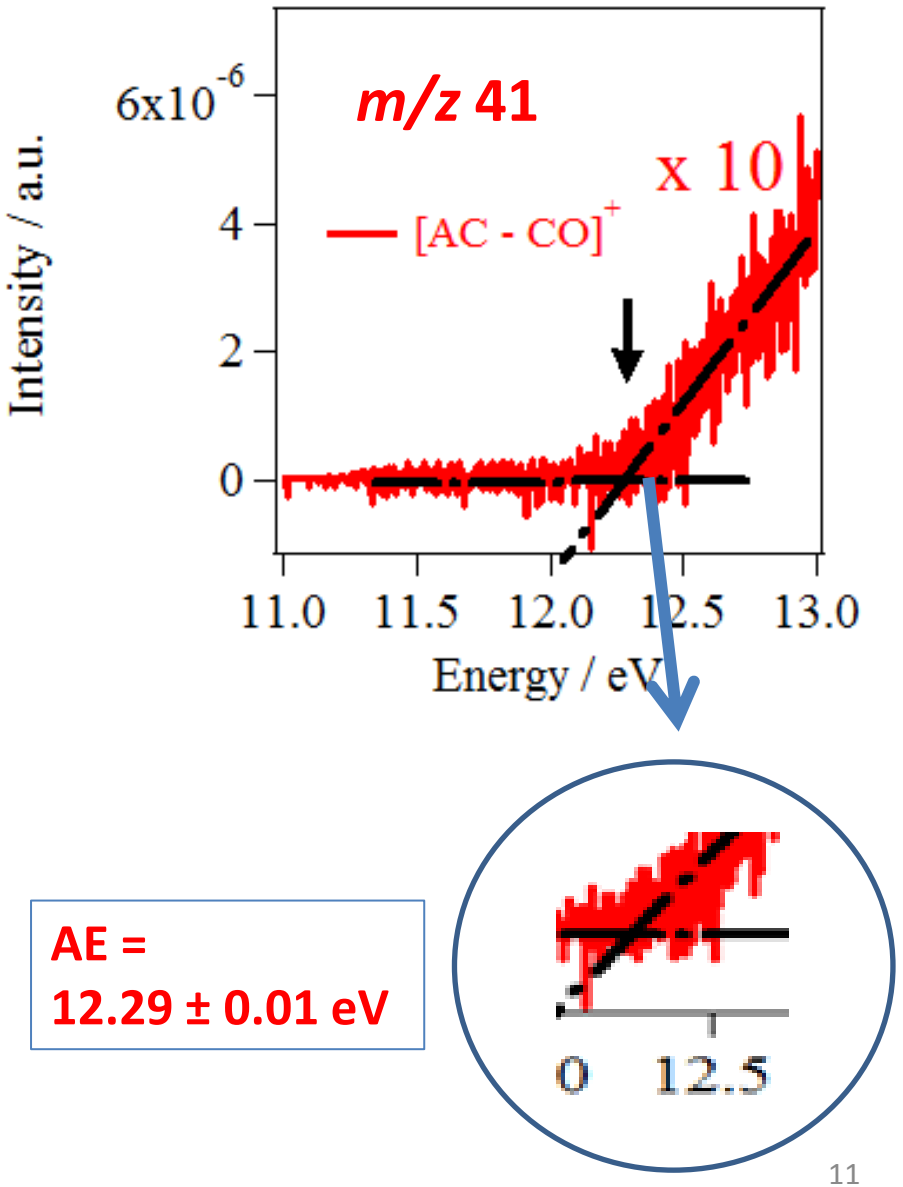
AIE(AC) = 11.20 ± 0.01 eV.



Acetyl cyanide : expl. determination of fragment appearance energies AE



AE =
12.07 ± 0.01 eV



AE =
12.29 ± 0.01 eV

Calculation methods

- MP2/AVTZ (Opt)
- CCSD(t)/AVTZ (SP)
- CCSD(t)/AVQZ (SP)
- CCSD(t)-F12/AVDZ (Opt)
- CCSD(t)-F12/AVTZ (SP)

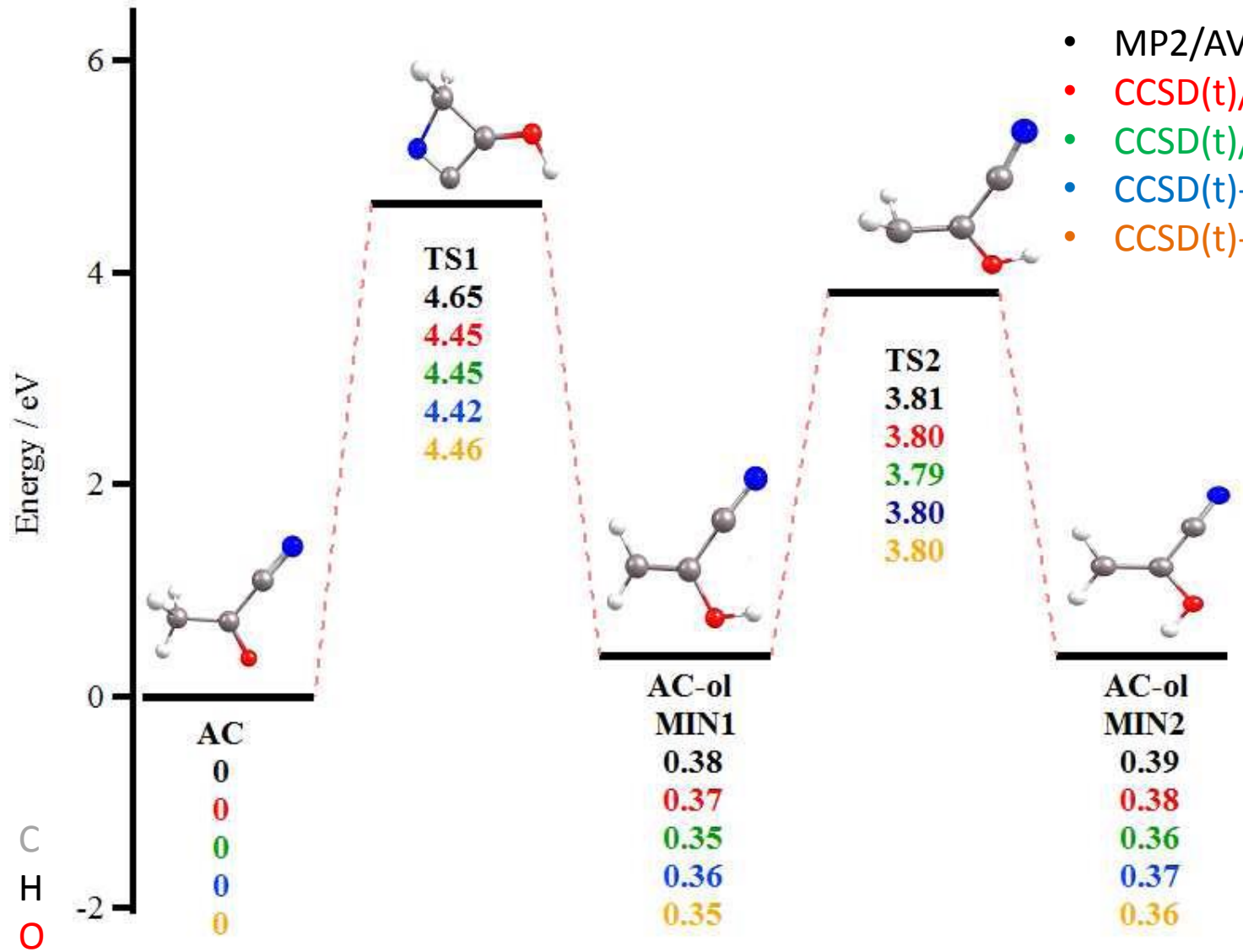
Characterization of neutral and ionic species as well as transition states with all these methods

Molden
http://www.cmbi.ru.nl/molden

Gaussian (09)
http://www.gaussian.com

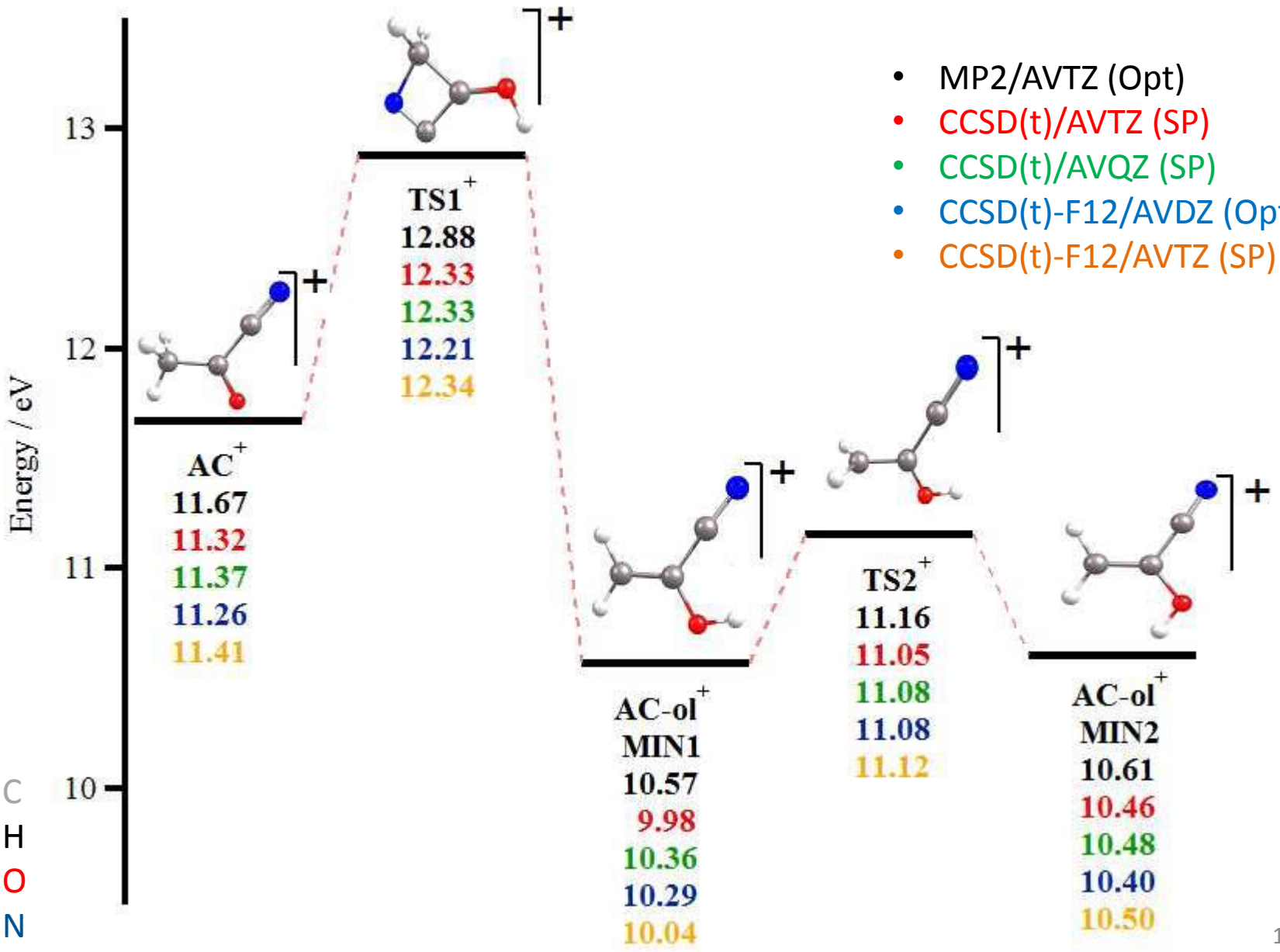
Molpro
http://www.molpro.net

Results of q-c calculations: Neutral AC and its tautomes & TS for tautomerism

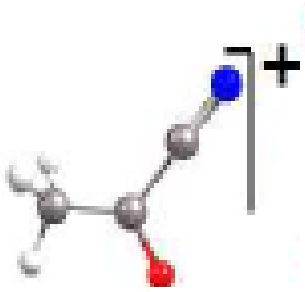


Bellili et al J. Chem. Phys. 141, 134311 (2014)

Results of q-c calculations: AC^+ cation and its tautomers & TS for tautomerism



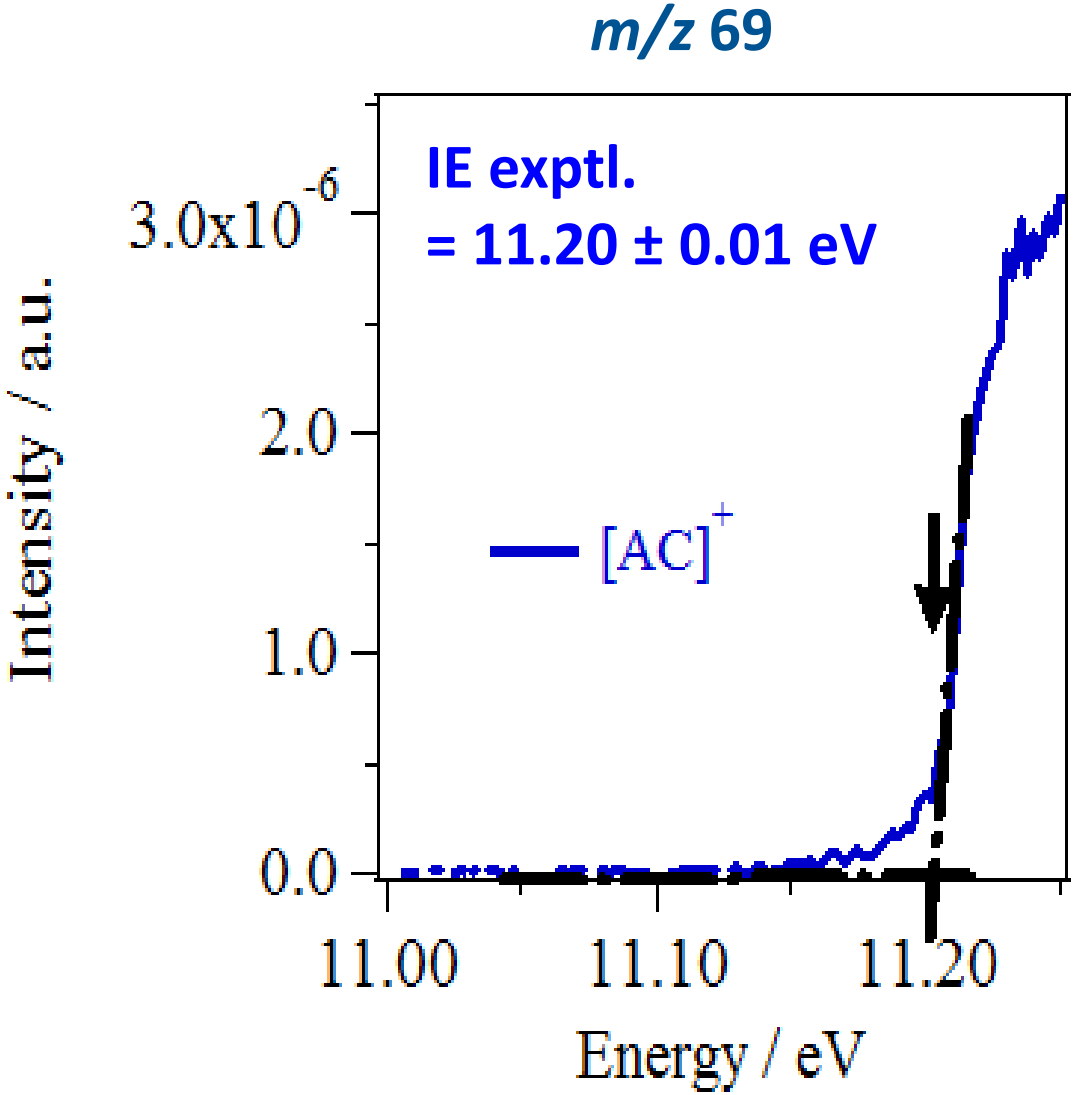
Ionization energy of AC, exptl. vs theo



IE theo

AC^+
11.67
11.32
11.37
11.26
11.41

- MP2/AVTZ (Opt)
- CCSD(t)/AVTZ (SP)
- CCSD(t)/AVQZ (SP)
- CCSD(t)-F12/AVDZ (Opt)
- CCSD(t)-F12/AVTZ (SP)



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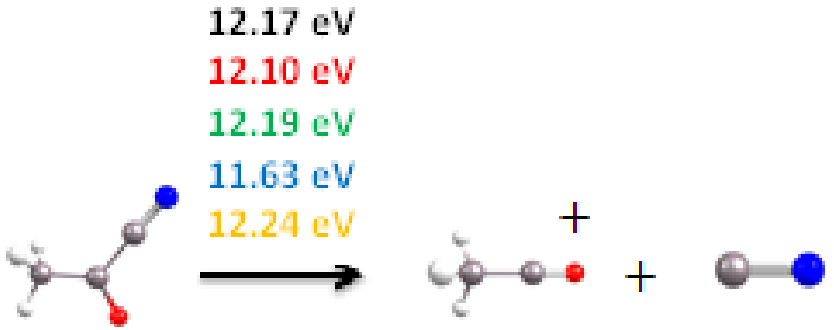
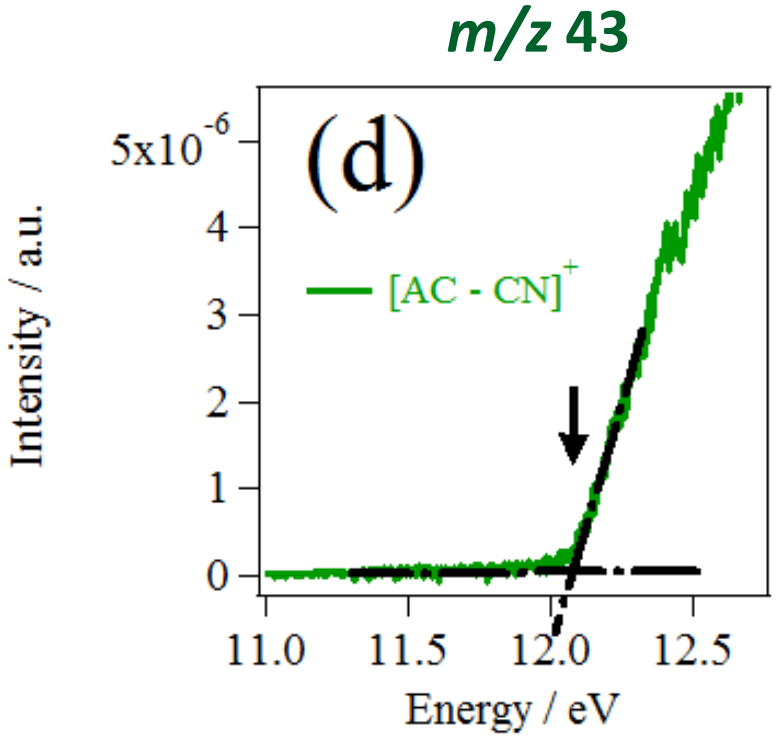
Dissociative ionization: exptl vs theo

CN loss reaction:

Exptl AE ($[AC\text{-}CN]^+$) = 12.07 ± 0,01 eV (formation of *m/z* 43)





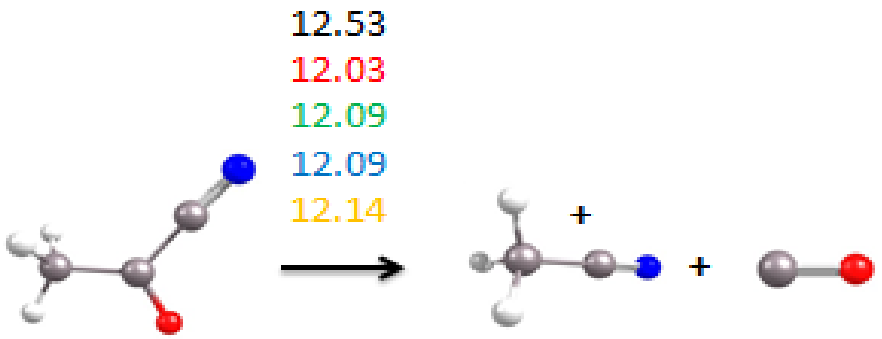
- MP2/AVTZ (Opt)
- CCSD(t)/AVTZ (SP)
- CCSD(t)/AVQZ (SP)
- CCSD(t)-F12/AVDZ (Opt)
- CCSD(t)-F12/AVTZ (SP)

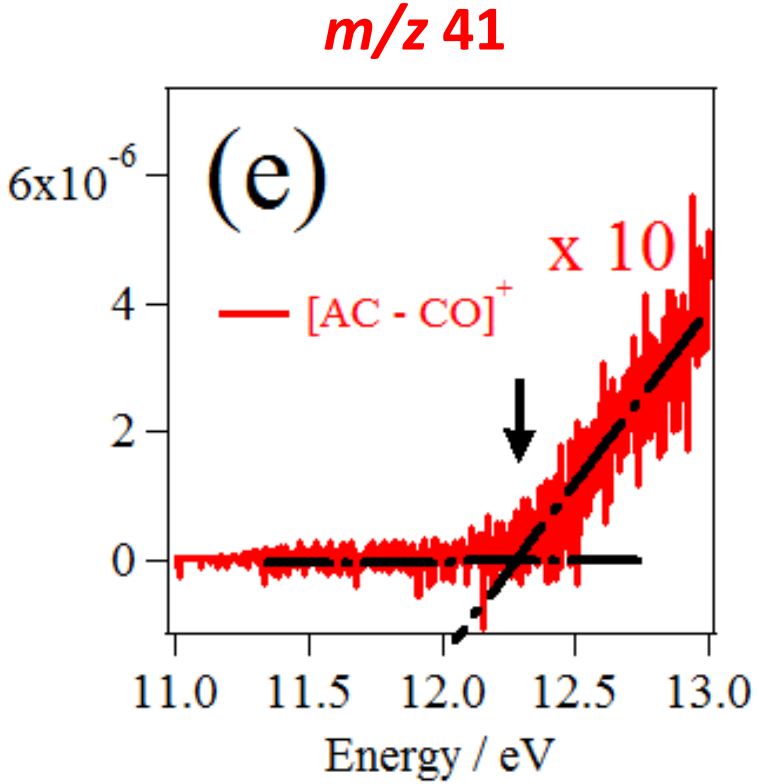
Bellili et al J. Chem. Phys. 141, 134311 (2014)

Dissociative ionization: exptl vs theo

CO loss reaction:

Exptl AE ($[AC\text{-}CO]^+$) = 12.29 ± 0,01 eV (formation of *m/z* 41)





- MP2/AVTZ (Opt)
- CCSD(t)/AVTZ (SP)
- CCSD(t)/AVQZ (SP)
- CCSD(t)-F12/AVDZ (Opt)
- CCSD(t)-F12/AVTZ (SP)

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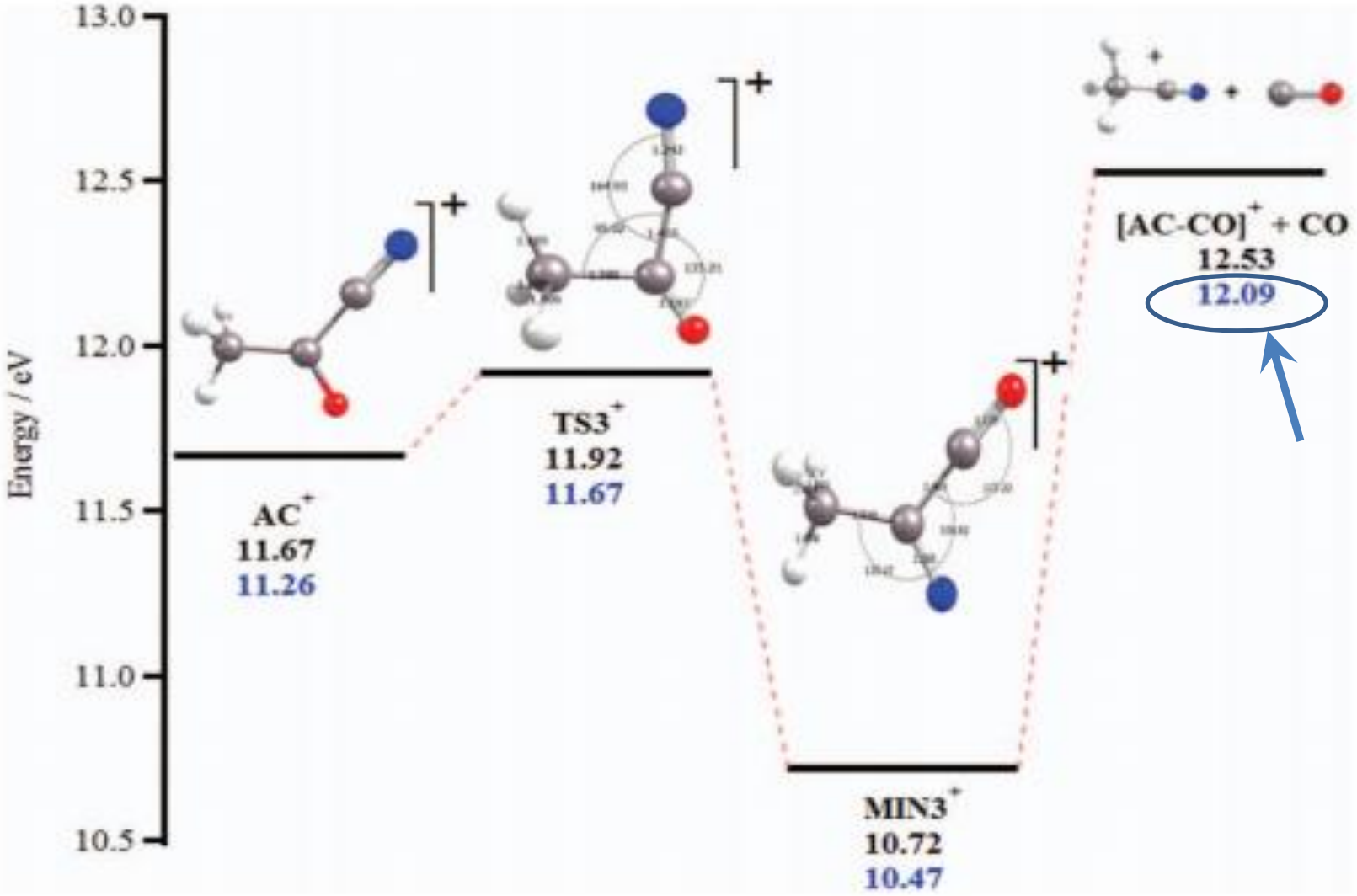
Energy profile of the decarbonylation reaction

Exptl AE ($[AC\text{-}CO]^+$) = 12.29 ± 0,01 eV



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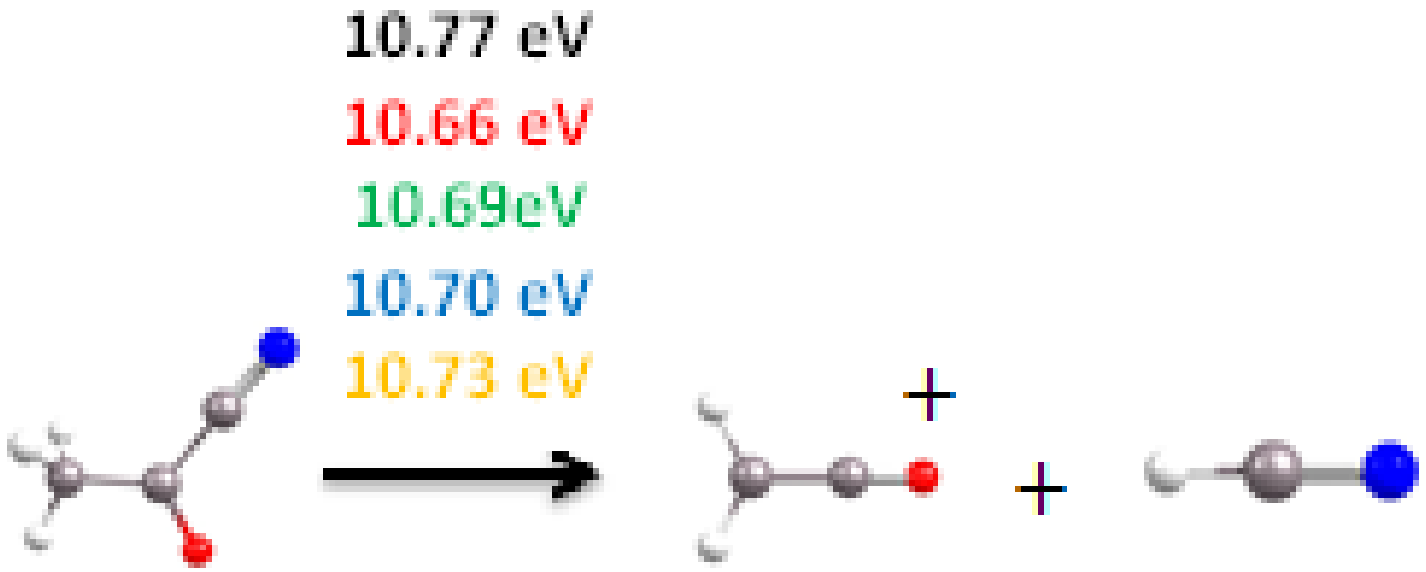
Other experimentally not observed fragmentation pathways

HCN loss reaction (formation of $O{=}C{-}CH_2^+$):



- MP2/AVTZ (Opt)
- CCSD(t)/AVTZ (SP)
- CCSD(t)/AVQZ (SP)
- CCSD(t)-F12/AVDZ (Opt)
- CCSD(t)-F12/AVTZ (SP)

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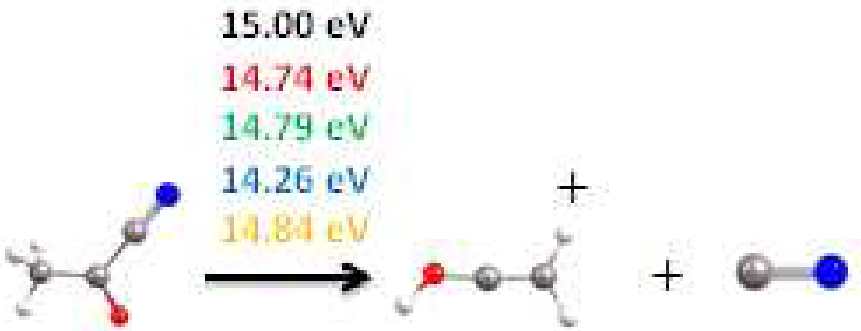
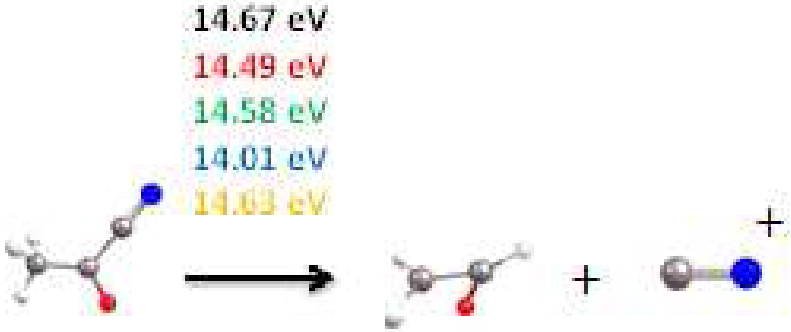
Other experimentally not observed fragmentation pathways

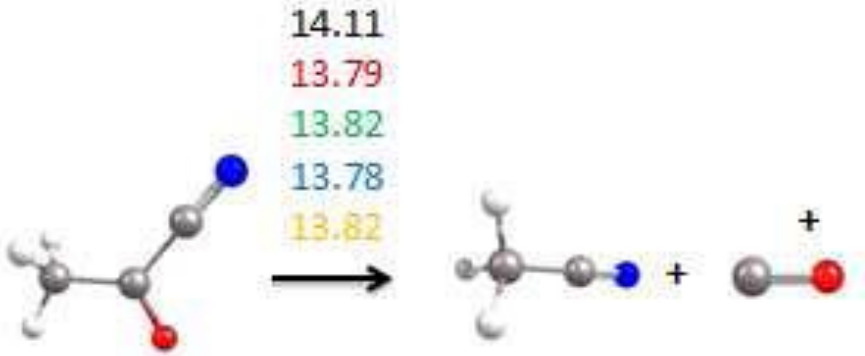
Loss of CN and formation of a different $C_2H_3O^+$ isomer



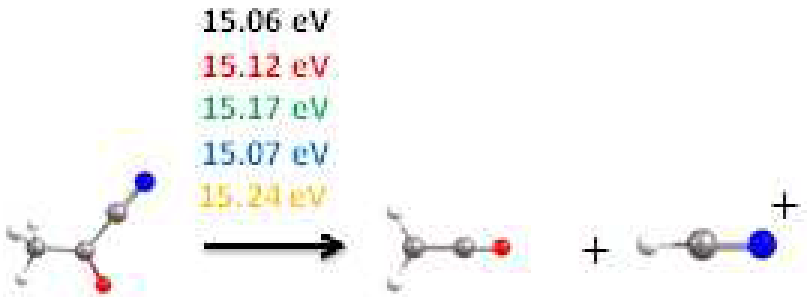
Formation of CN^+ (*m/z* 26)



Formation of CO^+ (*m/z* 28)



Formation of HCN^+ (*m/z* 27)



Conclusion ionization of acetyl cyanide

- The photoionization of acetyl cyanide has been studied in depth both **experimentally and theoretically** using state-of-the-art methods
- The ionization and appearance energies of various fragment ions have been calculate using **5 different methods** in order to determine **the best method adapted for this type of molecules**.
- **Different fragment isomers** have bee considered in the calculations.
- Slightly different chemistry is observed when **comparing mid-UV and VUV** photodissociation
  - Below its IE, AC produces CH_3 + COCN (minor channel however) and CN + CH_3CO (main diss. channel) (Horwitz et al. 1997, and other studies).
  - Above the IE, the CO loss reaction is observed in addition in our study . This chemical signature occurring upon ionization is new. However the CN loss reaction is still the main fragmentation pathway of the dissociative ionization of AC^+.

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