

VUV spectroscopic study of HC_3N and C_4N_2 cations

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Motivations

1. Determination of spectroscopic properties of ionized molecules relevant for astrobiology/astrochemistry
2. Study of photophysical parameters of prebiotic molecules as function of photons energy in VUV.
3. Provide data necessary for chemical models treating planetary atmospheres, cometary atmospheres, interstellar medium.
4. Dissociative Ionization study and determination of branching ratios of different fragmentation pathways

Studied molecules

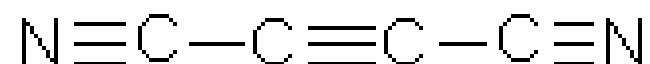
✓ Cyanoacetylene :

- Detected in ISM and in Titan's atmosphere
- Involved in the photochemistry starting by N₂ and CH₄ dissociation and leading to the formation of aerosols in Titan's atmosphere.
- key molecule for chemical models.
- Considered to be of prebiotic molecule

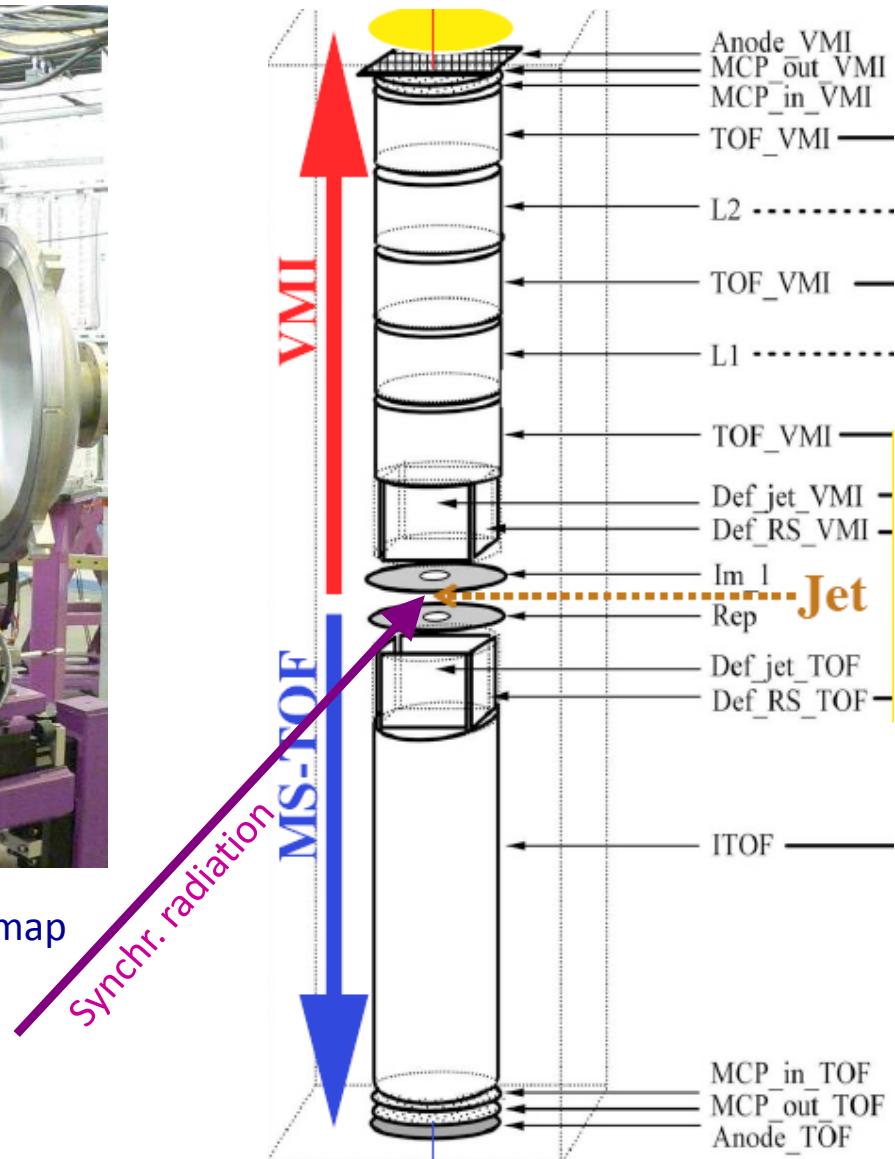
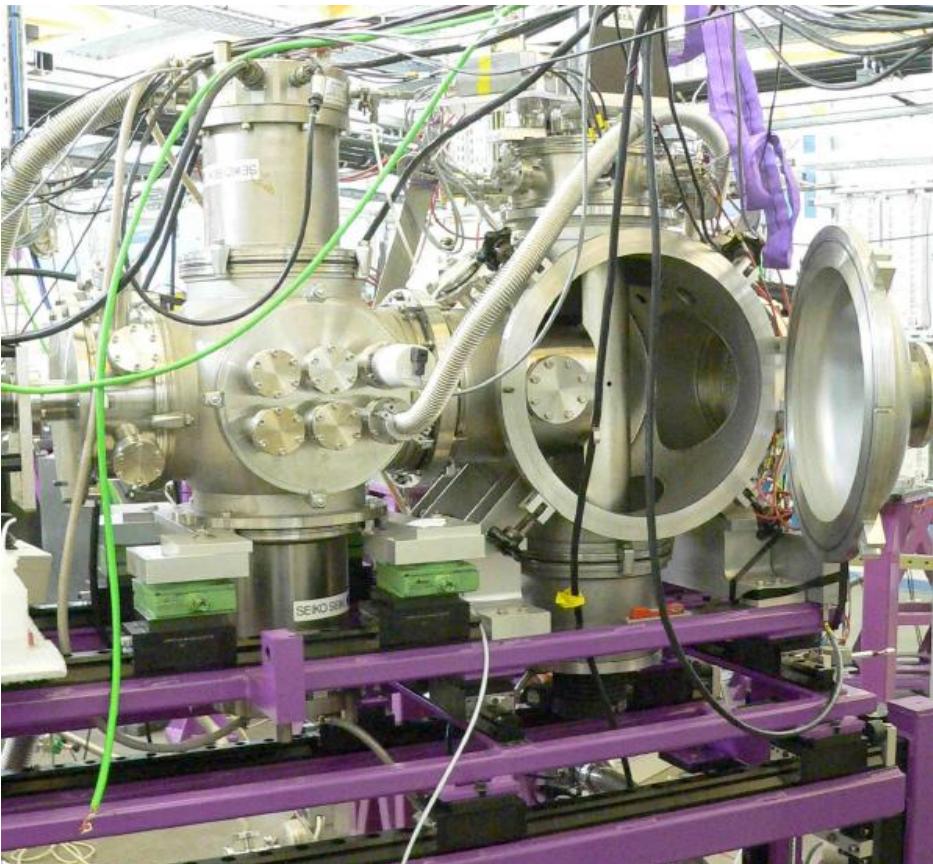


✓ Discyanoacetylene :

- Detected in Titan's atmosphere
- Expected presence in the ISM
- Involved in the photochemistry starting from N₂ and CH₄ and leading to the formation of aerosols in Titan's atmosphere.

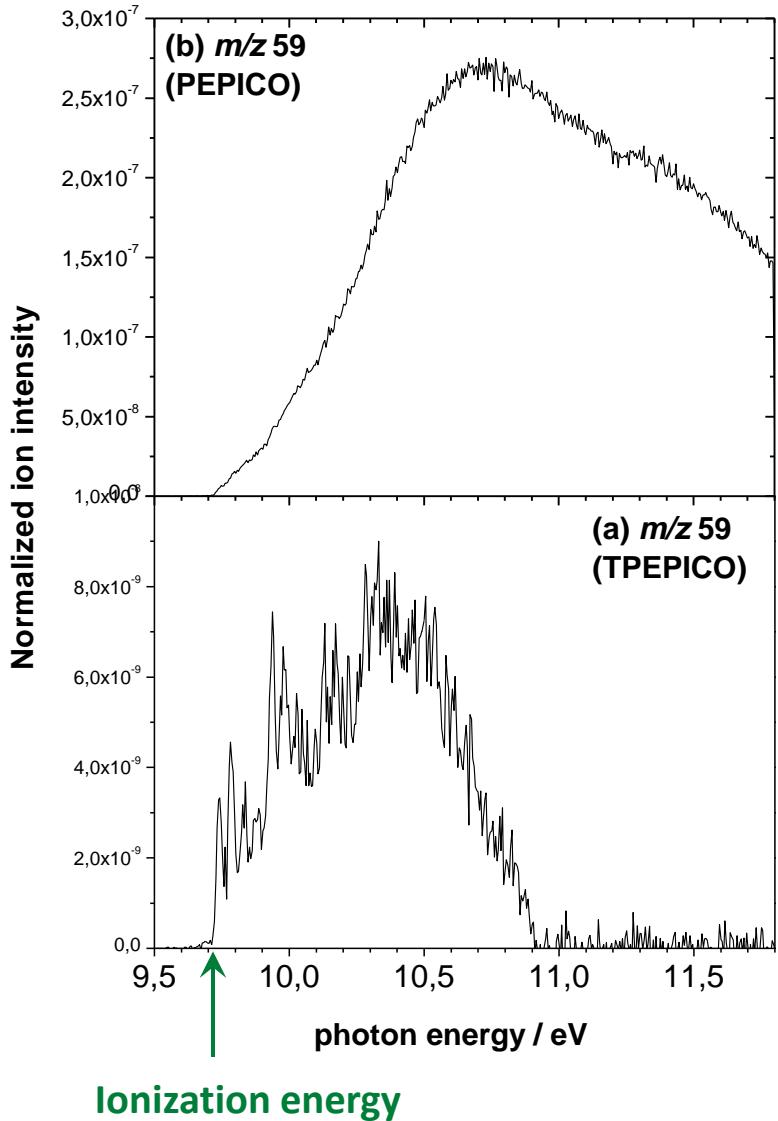


DELICIOUS II spectrometer (DESIRS/Soleil)



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

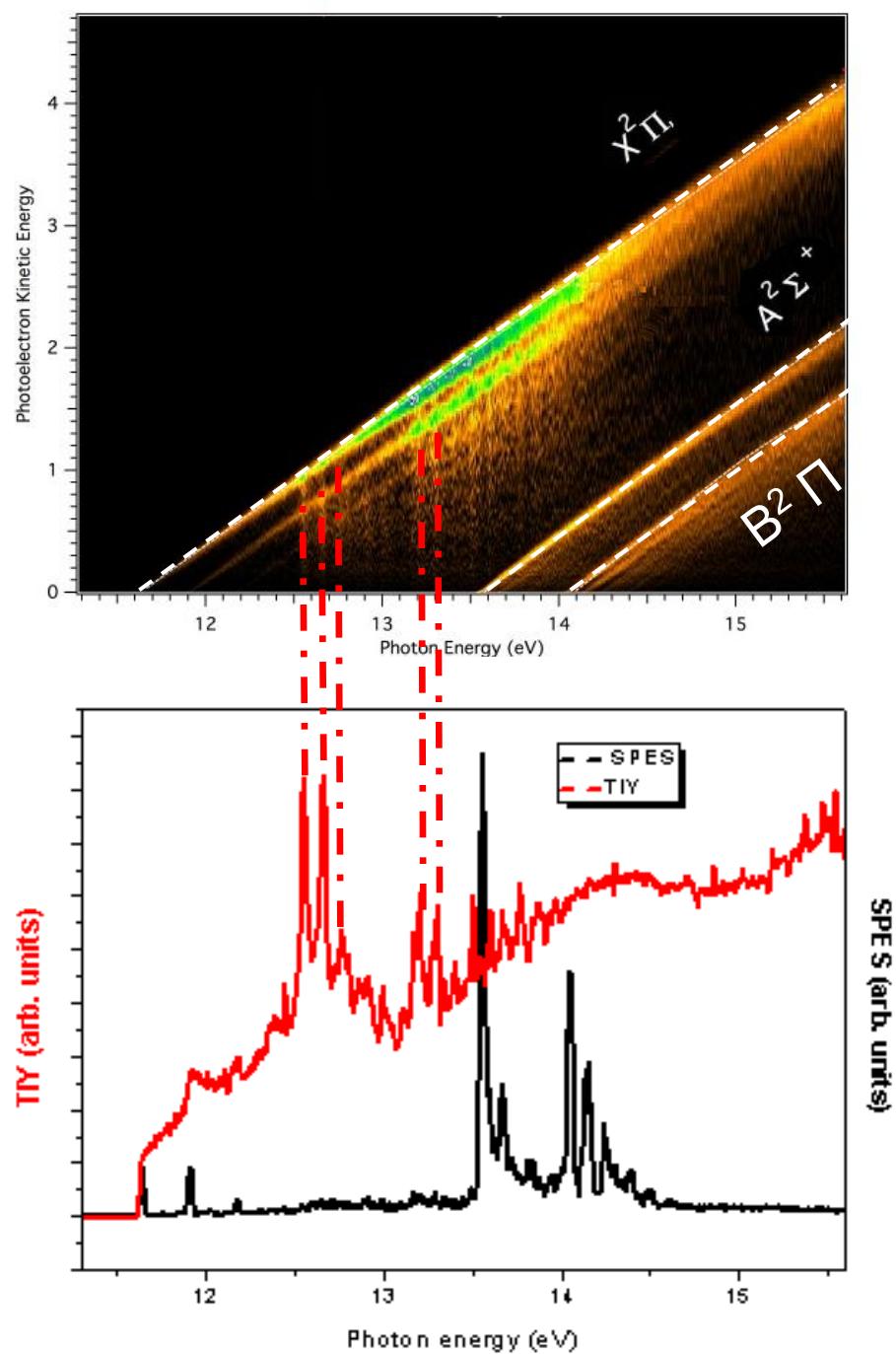
PEPICO vs TPEPICO (example acetamide)



- a) Integration of **all** photoelectron e^- / i^+ coincidence measurements whatever its kinetic energies.
- Total ion yield \propto ionization cross section
 - PEPICO
- b) Integration of **only** threshold electrons ($E_{kin}(e^-) = 0$) for e^- / i^+ coincidence measurements
- Analyse ion structure from vibrational progressions observed, spectroscopy
 - TPEPICO

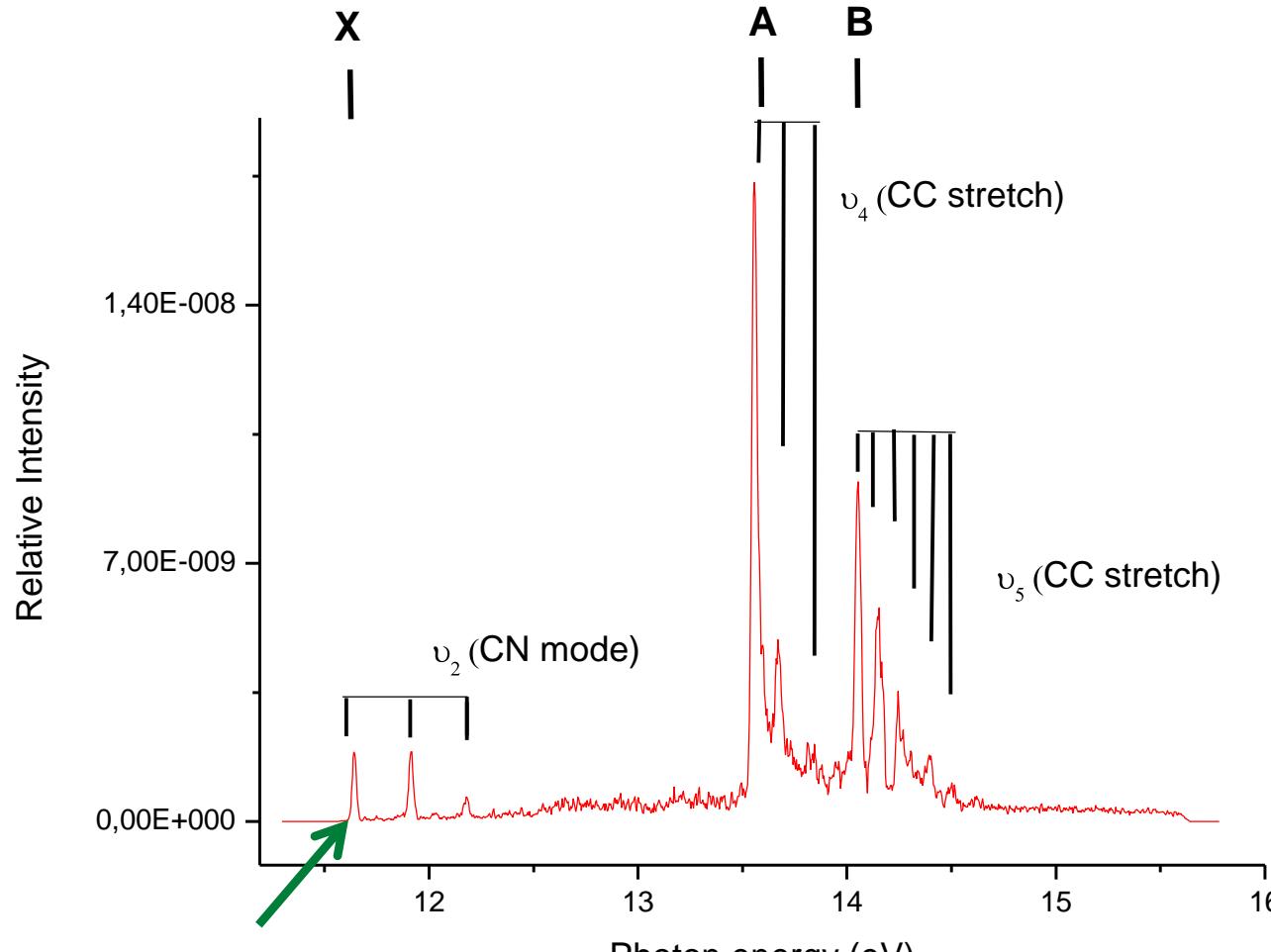
Photoionization of Cyanoacetylene

Photoelectron intensity matrix



SPES (Slow photoelectron
Spectroscopy)
TIY spectrum

Slow photo-electron spectrum analysis

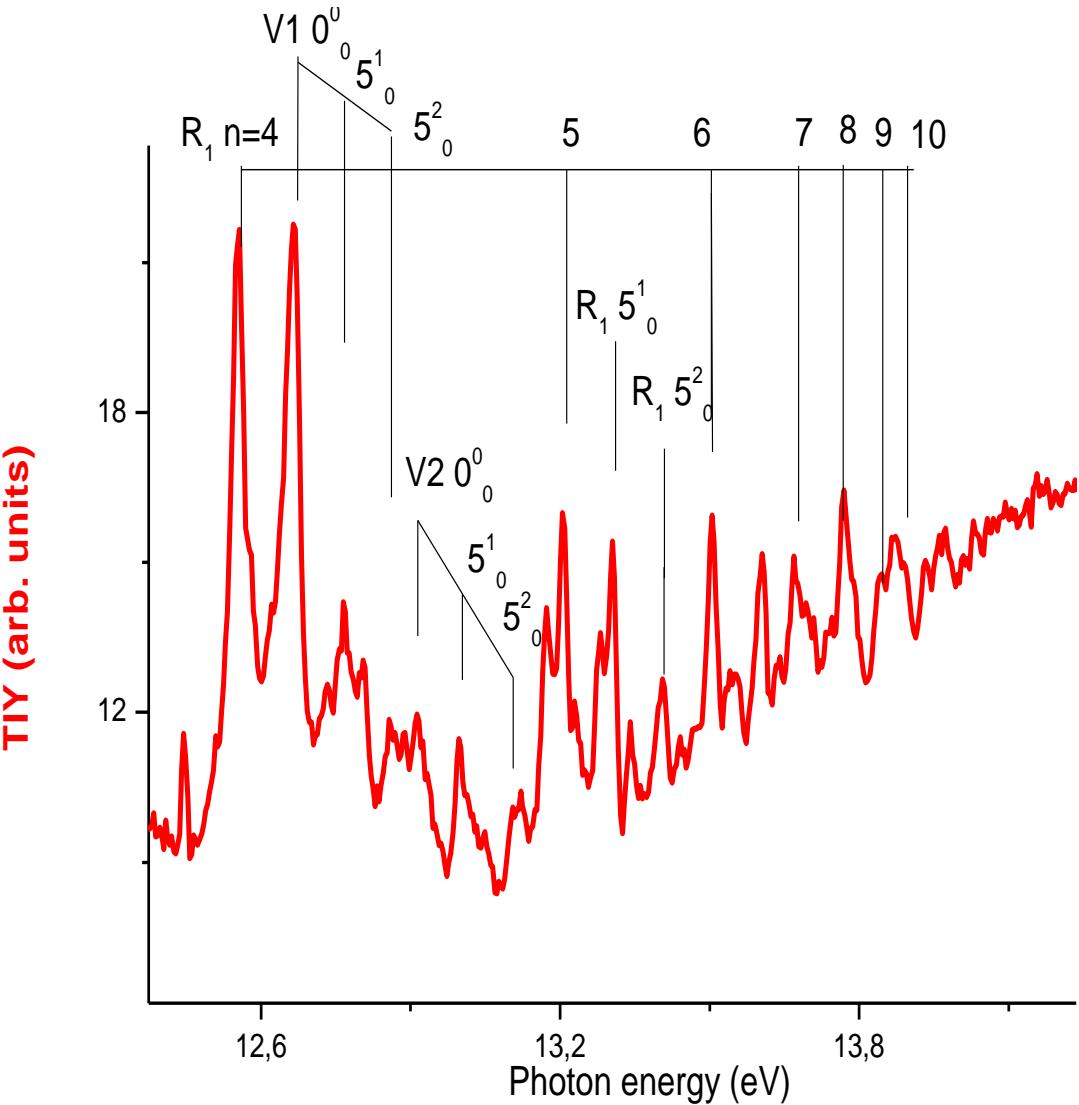


$$IE_{adb} = 11,61 \text{ eV}$$

- Analysis of SPES spectrum with the help of calculations:
- CASSCF for electronic structure and DFT for vibrational modes.
- Good agreement between calculations and experiment

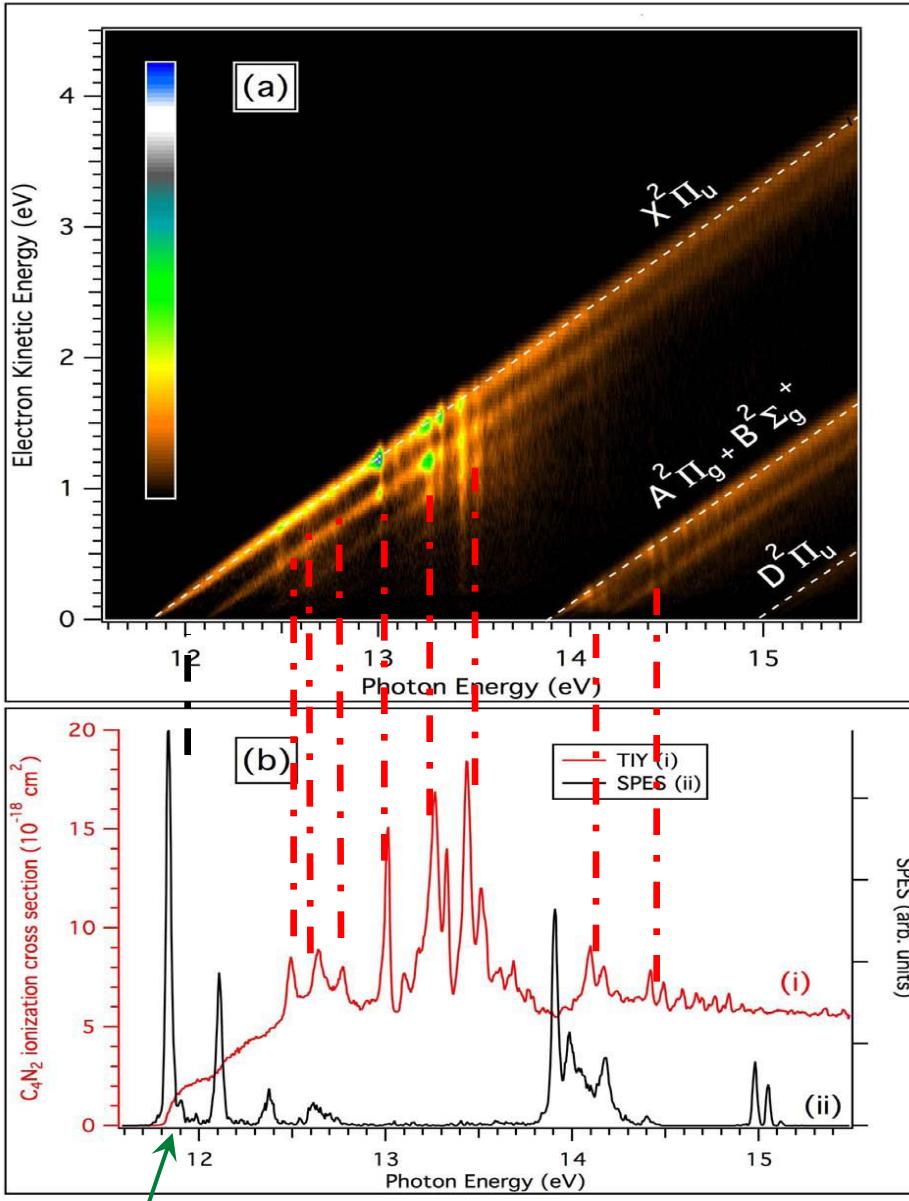
TIY spectrum analysis

- ✓ Identification of 2 valence-shell transition V1 and V2, with vibrational progressions involving v_5
- ✓ V1: Good agreement with calculations by Connors et al. 1984
- ✓ Identification of a Rydberg serie with n up to 10, converging to the B electronic state with IE = 14.057 eV (Quantum defect = 1.0)
- ✓ More detailed assignments are in progress.



Mahjoub et al., manuscript in preparation

Photoionization of Dicyanoacetylene



Ionization energy = $11.81 \pm 0.03 \text{ eV}$

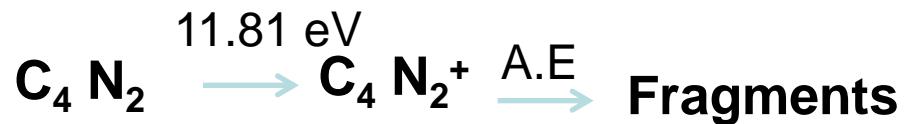
Photoelectron intensity matrix

SPES spectrum
TIY spectrum

Leach et al., submitted to JCP

Dissociative ionization of dicyanoacetylene, C_4N_2

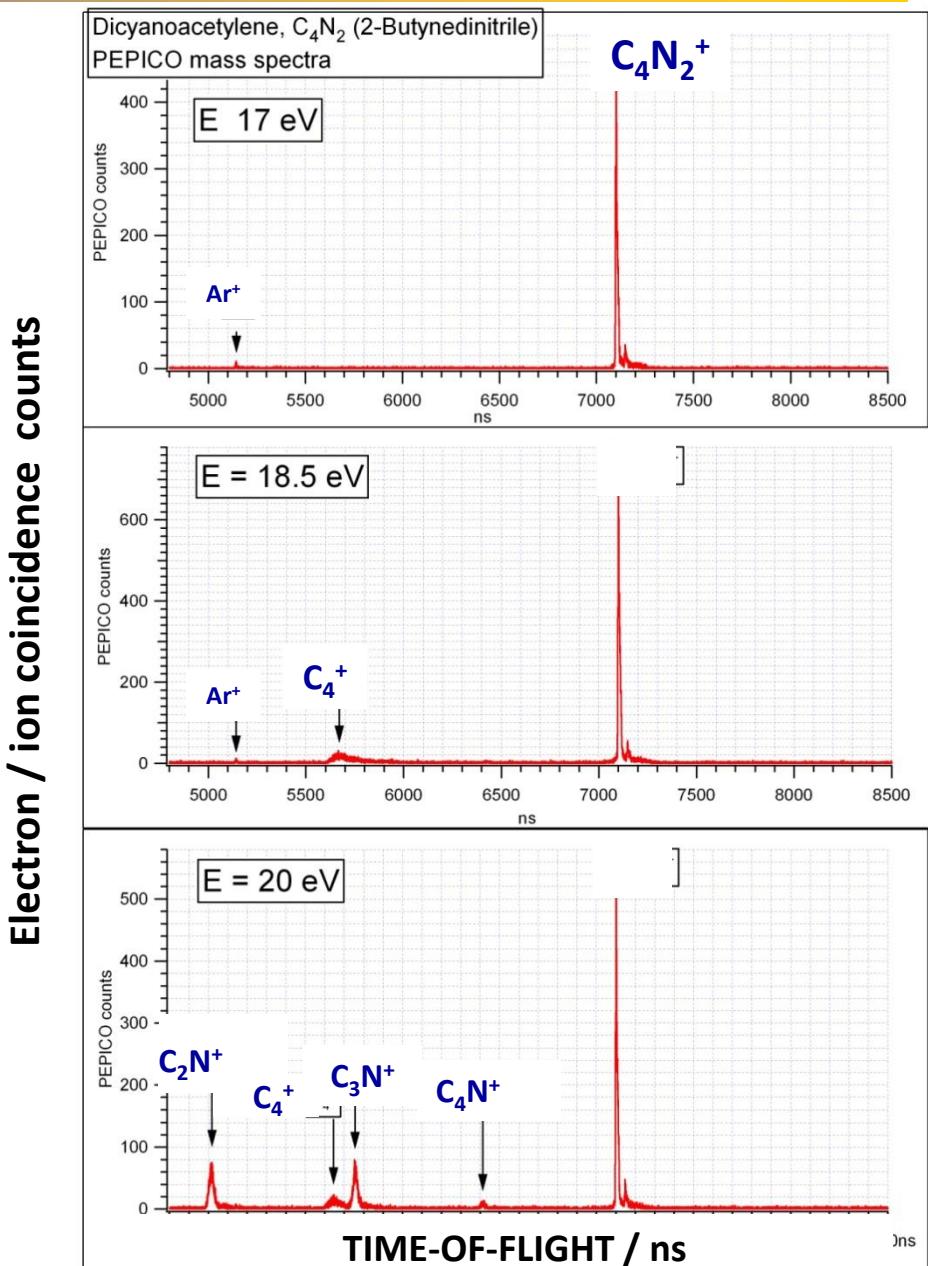
- IE = (11.81 ± 0.03) eV (unknown before)
- Very stable molecular ion (11.81 ± 18 eV)



A.E. : apparition energy

Determination of A.E. for all observed fragmentation pathways

Leach et al., submitted to JCP



Conclusions

- **VUV photophysics & spectroscopy of molecules of astrophysical interest** studied by synchrotron radiation @ SOLEIL .
- In this study we determined for HC₃N and C₄N₂:
 - IE, electronic states, vibrational frequencies.
 - Auto-ionizing neutral states are observed in the TIY spectra:
 - Valence shell transitions
 - New Rydberg series
 - Formation of fragments by dissociative ionization at higher energies
 - Ionization cross sections for astrophysical modelling
- **Perspective: quantitative study:**
 - Development of a **semi-open new cell** coupled to DESIRS beamline @ Soleil for **simultaneous measurement of absorption and ion formation**
 - Study of large molecules (> 5 atoms)