

1. Scientific scope of our work

For many years, our group has been investigating the VUV spectroscopy and photochemistry of large molecules of astrophysical and prebiotic interest. We have studied simple molecules like acetic acid [1], acetonitrile [2], acetamide [3], as well as molecules of biological importance (amino acids, nucleic acid bases) [4]. Polyynes and cyano-polyynes have been investigated too [5] since these linear molecules are very important in the ISM. An aerosol source for soft vaporization has been developed since many bigger (bio-) molecules of astrophysical importance are not easily vaporized [6]. We mainly used synchrotron radiation as a light source (BESSY II and Soleil) in connection with different kind of experimental setups.

We consider **gas phase measurements** as particularly necessary since they permit to measure the *intrinsic* photophysical properties of molecules of astrophysical interest. Only the gas phase permits the study of *elementary* photoreactions. On the other hand, the condensed phase has a large and very variable influence on spectroscopic and photochemical data. Being in important subject of its own, the interpretation of matrix studies and the role of "grain photochemistry" needs dedicated experiments and theory.

Absolute photoabsorption cross sections (σ_{abs}), photoionization cross sections (σ_{ion}), dissociative ionization reaction channels and their involved excited states have been studied in the past. **Branching ratios (BR)** of these reactions have been determined. The **quantum yield of ionization** has also been determined for some molecules. **Figure 1** shows a typical example of our earlier measurements (CH_3CN). Two spectral regions have to be considered:

1) The region of non-ionic processes. Here, photodissociation yields neutral fragments which have to be post-ionized in order to be detected by TOF-MS. Pulsed ns lasers are needed to measure BRs. We plan to do pump-probe spectroscopy in collaboration with the University of California Davis (see section 3). As can be seen nicely in Figure 1, also beyond the IE, non-ionic processes including photodissociation reactions yielding neutral fragments, take place since the quantum yield of ionization is well below unity over a wide spectral range (upto 22 eV in the case of CH_3CN). To our knowledge, the study of elementary photoreactions in this domain, which is a particular focus of our collaboration with UC Davis, has never been achieved for molecules with more than 4 atoms.

2) The region of ionic processes. This region can be studied using cw experimental techniques in conjunction with synchrotron radiation. In the past, mass spectrometry and photoelectron spectroscopy has been used to elucidate in detail photophysical processes, including dissociative ionization. Very recently, the SAPHIRS molecular beam multipurpose chamber, a permanent endstation of the DESIRS beamline at Soleil, has been widely used. SAPHIRS has unique capabilities including time-of-flight mass spectrometry and velocity map electron and ion imaging [7]. The e^-/i^+ coincidence technique furthermore permits the analysis of relaxation pathways of excited states. Examples of this work are shown in Figures 2-4.

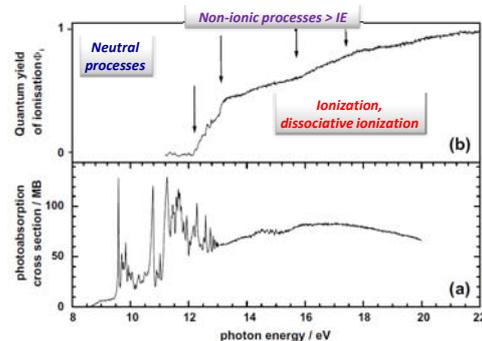


Figure 1: (a) Absolute photoabsorption spectrum of acetonitrile (CH_3CN) from 8 to 20 eV. (b) Quantum yield of ionization of CH_3CN from the IE upto 22 eV. Arrows indicate the first four ionization energies. This figure shows three different photophysical domains to be addressed by studies of photodissociation reactions and their BRs. This spectrum is published in ref. [2b].

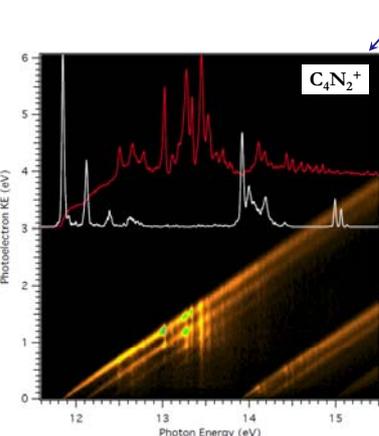


Figure 2. Photoionization of dicyanoacetylene (C_4N_2) studied at the DESIRS beamline [manuscript in preparation]. (a) Red: total ion yield (TIY) spectrum (m/z 76). In the photon energy domain shown in fig. 2, no dissociative ionization occurs. The TIY spectrum is calibrated by a standard (propane) and thus $\sigma_{ion}(\lambda)$ can be extracted. (b) White: Slow photoelectron spectrum (SPES), arb. units. (c) 3D color code: Number of photoelectrons formed with a certain kinetic energy KE at photon energy E. This kind of plots is used to analyze relaxation pathways of autoionizing Rydberg states.

2. Future perspectives

- ❖ Cyanopolynes and polyynes: at lot of UV / VUV data available now (needs to be completed); in the future bigger molecules like for example $\text{H}_3\text{C-CHNH}_2\text{-CN}$, will be studied.
- ❖ Absorption spectra often limited to 11.5 eV because of window material.
 - Development of a **semi-open gas cell** using a "nid d'abeille" as optical path delimiter.
- ❖ The ionization cross section σ_{ion} is difficult to determine for non-gaseous compounds.
- ❖ BRs of **elementary photoreactions involving neutrals** (see section 3)
- ❖ **Fundamental spectroscopy** (addressing for example the identification of ionic states and their vibrational progressions) is important too and will stay an aim of our studies.
- ❖ Ionization and diss. ionization of fragile (bio-) molecules: an **aerosol source for soft vaporization** has been developed @DESIRS [6] (integrated into SAPHIRS), open to users.
- ❖ **Support by quantum chemistry calculations** is necessary for:
 - Analysis and comprehension of fragmentation pathways.
 - Understanding of absorption and photoionization efficiency spectra.
 - Calculate UV spectra (only below IE).

3. Perspective: Study of BRs of photodissociation reactions involving the formation of neutral fragments (collaboration with UC Davis, department of chemistry)

This important class of photodissociation reactions has so far not been addressed by our group. However, **BRs of "neutral" photodissociation reactions are particularly missing in the VUV spectral domain**, especially for bigger molecules. That is why we have started a collaboration with UC Davis (Profs. W.M. Jackson & C.Y. Ng) in order to do pump-probe spectroscopy using ns lasers sources in connection with velocity map ion imaging. The group of Profs. Jackson and Ng is well known for the development of tunable, pulsed VUV laser sources [10a,b]. VUV laser radiation is produced by four wave resonance-enhanced sum or difference frequency mixing (FWRSDFM). Very recently, the group W.M. Jackson has developed a unique set-up where two VUV laser sources are coupled to one ion imaging apparatus (Figure 5). Such a setup is ideal to study photodissociation reactions over a wide photon energy range, from 5 to 16 eV approximately.

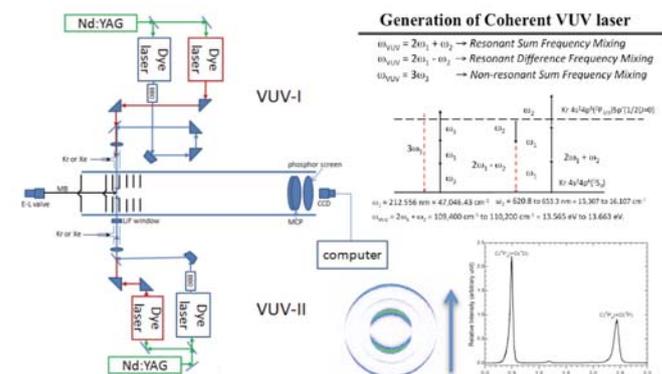


Figure 5. Experimental setup at UC Davis, department of chemistry [10a,b]. Two widely tunable VUV laser sources are used to photodissociate the molecule under study (1st photon) and post-ionize residual parent neutrals and formed fragments (2nd photon). The ions are analyzed using Time-sliced velocity map imaging [10a,b].

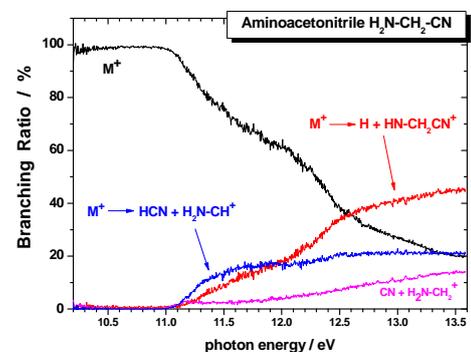


Figure 3. Photoionization of aminoacetonitrile ($\text{H}_2\text{N-CH}_2\text{-CN}$) studied at the DESIRS beamline [8]. The graph shows BRs of dissociative ionization reactions from the IE = (10.07 ± 0.01) eV upto 13.6 eV. The IE of this compound was unknown before. Black: parent ion M^+ (m/z 56) Red: m/z 55 (H loss of M^+), Blue: m/z 29 (HCN loss of M^+), Magenta: m/z 30 (CN loss of M^+).

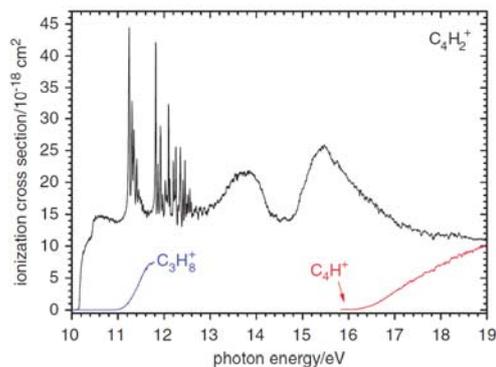


Figure 4. Photoionization of diacetylene (C_4H_2) studied at the DESIRS beamline [9]. Black: parent cation C_4H_2^+ (m/z 50). Blue: parent cation of propane C_3H_8^+ (m/z 44) used as a standard for the determination of the photoionization cross sections of C_4H_2 . Red: C_4H^+ (m/z 49) formed by H loss of the parent cation. Spectral resolution 1 Å (8.5 meV at 10.3 eV). Electrons with $\text{KE}_{\text{max}} = 5.7$ eV are taken into account for e^-/i^+ coincidences (PEPICO).

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