Report on the outcomes of a Short-Term Scientific Mission[1]

Action number: CA20129 MultIChem

Grantee name: João Ameixa

Details of the STSM

Title: Electronic excited states characterization of ethanolamine and 2-methoxyethanol: astrophysical relevance

Start and end date: 13/03/2023 to 18/03/2023

Description of the work carried out during the STSM

Through the present STSM at AU-UV beam line at the synchrotron ASTRID2 at ISA, Aarhus University, Denmark, absolute cross-sections for VUV photoabsorption by molecules with relevance for astrochemistry and cancer radiation therapy have been measured as summarized in Table 1. In addition to the molecules initially proposed to be studied, we carried out successfully measurements with 5-bromo-2-chloropyrimidine. Herein, the experimental procedure employed for the determination of absolute cross-sections for VUV photoabsorption by a given molecule has been previously described in references [1] and [2] related to the present STSM. In brief, the set-up consists of a gas cell mounted on the output of the light monochromator separated from the ultra-high vacuum of the beam line by a MgF_2 window. A photomultiplier tube (PMT) measures the light intensity transmitted through the gas sample. The absolute pressure of the effusive molecular gas is measured with a capacitance manometer. In order to avoid any absorption of O_2 from the air in measurements below 200 nm (energies above 6.20 eV), the small gap between the PMT and the MgF_2 gas cell exit window is evacuated using a scroll pump. For higher wavelength measurements, air is admitted into the gap at atmospheric pressure to allow O_2 to absorb any higher orders of light produced by the monochromator. Absolute photoabsorption cross sections (σ) were obtained at room temperature (~25 °C) by using the Beer−Lambert attenuation law (1),

$$I_t = I_0 exp(-N\sigma l) \quad (1)$$

where I_t and I_0 are the light intensity transmitted through the gas sample and the evacuated cell, respectively, N is the molecular density, and l is the absorption path length (15.5 cm). The VUV spectra were acquired in shorter sections (about 10 nm) to allow for optimizing the pressure according to the observed cross sections. The samples were introduced as received and degassed prior to the experiments through several freeze-pump-thaw cycles.

[1] This report is submitted by the grantee to the Action MC for approval and for claiming payment of the awarded grant. The Grant Awarding Coordinator coordinates the evaluation of this report on behalf of the Action MC and instructs the GH for payment of the Grant.

Due to intrinsic characteristics of ethanolamine, 1-methoxy-2-propanol and 2-methoxyethanol, including reasonable vapor pressure and the absence of fine structure features in the wavelength range of 215-114 nm, we managed to finalize the proposed work plan early than expected, i.e., on Wednesday 15.03. Thus, we selected the molecule 2-aminobenzonitrile for measurements for it is structurally like the benzonitrile molecule detected in the ISM [3]. However, the strong water contamination made the measurements unfeasible. Then, we measured absolute cross sections for VUV photoabsorption by 5-bromo-2-chloropyrimidine mainly because this molecule fits in a set of previous studies, such as reference [1], which are not only related with the present STSM, but also relevant for the COST Action MultIChem.

Table I. List of investigated molecules during the STSM to the AU-UV beamline at the ASTRID2 synchrotron.

Investigated molecules	**Period (Initial day – Final day)**
Ethanolamine	Monday 13.03 – Tuesday 14.03
1-methoxy-2-propanol	Tuesday 14.03 - Wednesday 15.03
2-methoxyethanol	Wednesday 15.03
2-aminobenzonitrile	Thursday 16.03
5-bromo-2-chloropyrimidine	Thursday 16.03 - Friday 17.03

[1] Mendes, M. *et al.* Int J Mol Sci, 22, 6460 (2021)

[2] Pereira da Silva, J. *et al.* PCCP, 23, 2141 (2021)

[3] McGuire, B. A. *et al.* Science, *359*(6372), 202–205 (2018)

Description of the STSM main achievements and planned follow-up activities

The goal of the present STSM is to measure VUV photoabsorption spectra of ethanolamine, 1-methoxy-2-propanol and 2-methoxyethanol in the photon energy range from 3 to 11 eV using the AU-UV beamline at the ASTRID2 synchrotron, which are shown in figures 1 to 3. In addition to the successful measurement of the proposed molecules, Figures 4 shows the acquired VUV photoabsorption spectra of 5-bromo-2-chloropyrimidine. Please note that these results are yet preliminary as a closer inspection of the data is ongoing. For all figures, individual wavelength ranges are highlighted in different colours, since the VUV spectra were acquired in shorter sections (about 10 nm) as previously mentioned. Through an agreed collaboration, colleagues with expertise in quantum chemistry will perform a set of calculations aiming to support the assignment of electronic excited states (valence and Rydberg) and respective oscillator strengths, fine structure and spin-orbit coupling effects due to the presence of a heavy atom like Br. Therefore, our joint experimental and theoretical study will reveal what are the electronic states accessible by VUV photons of energies between 3 and 11 eV, as well as to reveal and quantify the effect of the CH_3-functionalization of 2-methoxyethanol on the absorption of VUV photons. The expect outcome of this STSM is thus a publication of interest for a broad of applied and fundamental sciences, ranging from astronomy to atomic and molecular physics, physical chemistry, and chemical physics. Therefore, this completed STSM will help the MultIChem COST Action to achieve its planned objects as well as its deliverables.

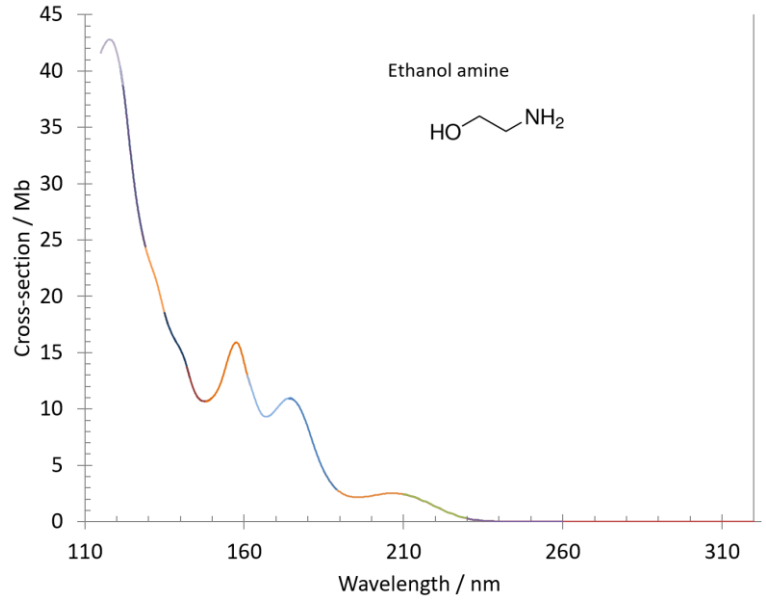

Figure 1. VUV photoabsorption spectrum of ethanol amine (320-115 nm) and its respective molecular structure. The individual wavelength ranges are colour highlighted.

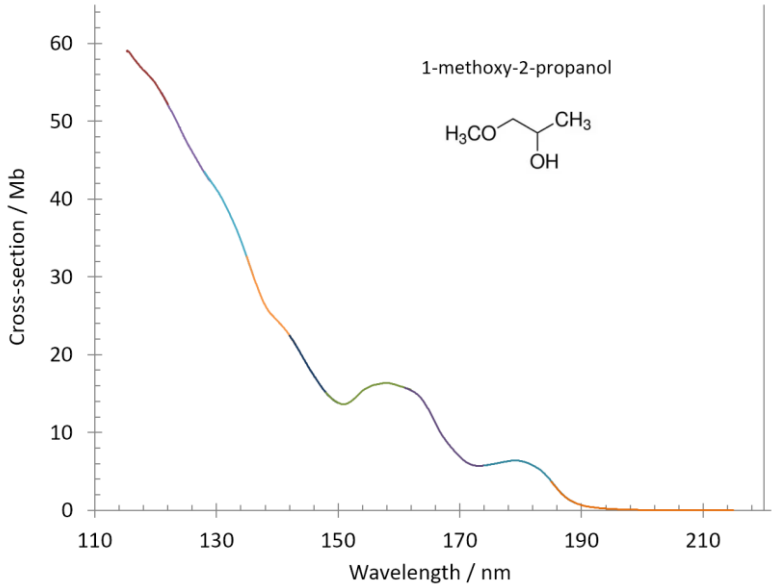

Figure 2. VUV photoabsorption spectrum of 1-methoxy-2-propanol (220-115 nm) and its respective molecular structure. The individual wavelength ranges are colour highlighted.

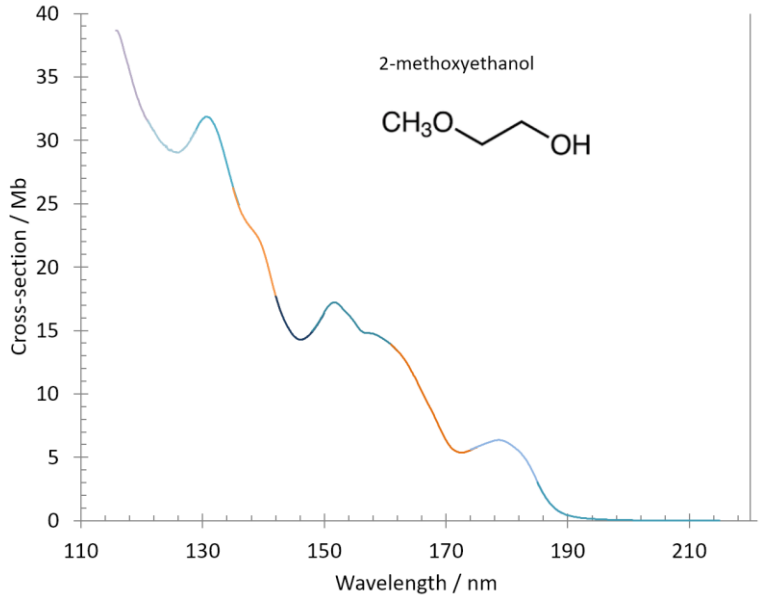

Figure 3. VUV photoabsorption spectrum of 2-methoxyethanol (220-115 nm) and its respective molecular structure. The individual wavelength ranges are colour highlighted.

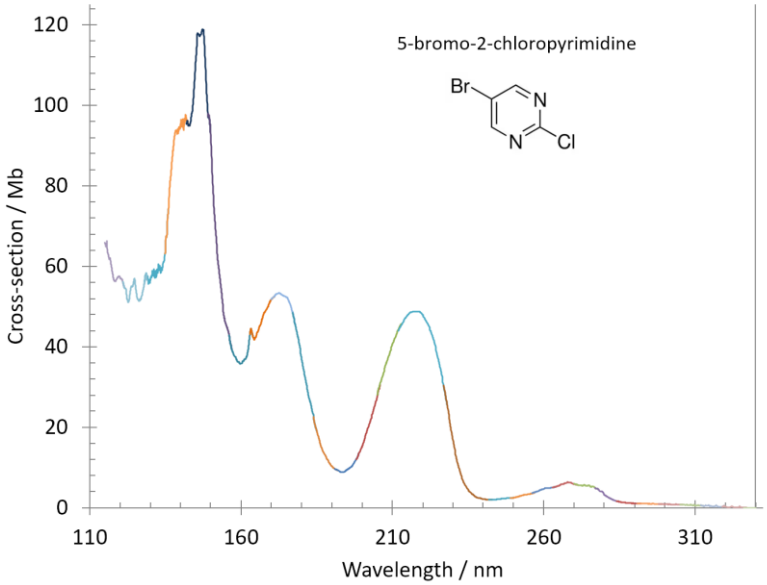

Figure 4. VUV photoabsorption spectrum of 5-bromo-2-chloropyrimidine (320-115 nm) and its respective molecular structure. The individual wavelength ranges are colour highlighted.