



VACUUM ULTRAVIOLET BEAMLINE: NEW PERSPECTIVES FOR GAS-PHASE CHEMISTRY AND PHYSICS IN EASTERN EUROPE

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Research of the chemical behavior of ions in the gas phase continuously brings important information for the basic chemical knowledge [1]. Direct applications are indeed found in atmospheric and interstellar chemistry, because the experimental conditions mimic these media. However, many other fields profit from the ideas and concepts, which are based on the fundamental knowledge obtained from studies of isolated molecules. For example, investigations of reactivities of small metal clusters in the gas phase can lead to the elucidations of the underlying reaction mechanisms and thereby help in optimizing the properties of metal catalysts in a large, industrial scale [2]. Another important field, which benefits from the gas-phase studies, comprises biochemistry and bioinorganic chemistry. Determinations of proton affinities, bond energies, or ionization energies for simple models of, for example, active centers of enzymes provide important insight into the intrinsic properties of these systems [3]. Investigation of fragmentations of biomolecules, on the other hand, can shed light on possible mechanisms of degradation in artificial and natural environments [4]. Last but not least, gas-phase experiments using synchrotron radiation provide powerful tools for analytical chemistry in that the unimolecular chemistry of an ionized molecule is unique and can thus be used for trace analysis of specific molecules in complex matrices [5, 6].

The most common experimental approach for the investigation of ions in the gas phase is mass spectrometry. It provides a tool to separate ions according to their mass-to-charge ratio and subsequently study their structures, stabilities, and energetics. A dedicated experimental design enables the investigation of reactivities of mass-selected ions and conclusions about reaction mechanisms. Contributions of synchrotron radiation to these particular studies can be twofold. (i) VUV photons can be used for the generation of ions thereby providing accurate ionization energies of molecules and also enabling studies of unimolecular or bimolecular reactivities of the ions in dependence of their internal energies [7, 8]. Such an approach can, for example, lead to the unprecedented determinations of barrier heights for the chemical reactions [9]. (ii) A novel application of synchrotron radiation for studying ions can be introduced, if the VUV light is used in a reaction chamber for the ionization of trapped, mass-selected ions [10]. Such an approach would provide a possibility to study, for example, second ionization energy of metal complexes (e.g. oxidation of Cu^I to Cu^{II}) and thereby obtain important information about their energetics. The change of the oxidation state of a metal center could also lead to an induction of chemical reactions in the complex. Such a unique experimental arrangement is likely to produce very valuable data for research of metal catalysts and also for investigation of biomimetic reactions [11].

The proposed parameters of the VUV beamline is based on the design of the VUV beamline DESIRS of the new synchrotron SOLEIL near Paris [12]. It should provide photons within the energy range of about 5 to 40 eV, the resolution should be in the range of 10^{-1} Å, the photon flux should reach 10^{10} to 10^{12} ph/sec and the light should be polarized [13, 14]. The design of the proposed end station results from a compromise between the demands of the various users on one hand, and the flexibility and the price on the other hand. As a solution, a versatile instrument based on the triple quadrupole configuration is suggested with the possibility of replacing this default end station by special user's devices is envisaged.

The proposed apparatus (Figure 1) could be used for mass-spectrometric- and gas-phase studies. It will include two ion sources connected to the first mass analyzer by a deflector. The first ion source will involve photoionization by VUV photons and should be constructed in order to also enable PEPICO (photo-electron photo-ion coincidence) experiments. This ion source would allow internal-energy resolved studies of atoms and molecules. Thus, ions generated by photoionization would be mass-selected by means of the first quadrupole (Q1) and either (i) directly detected in order to determine the ionization or fragmentation thresholds or (ii) deflected to the multipole (O, presumably octopole) collision cell. Various collision- and reaction gases could be introduced into the collision cell and thereby the reactivity of the internal-energy resolved ions could be studied. The products of the reactions would be deflected to the second quadrupole (Q2) in order to mass-analyze and detect them.

The second ion source would employ electrospray ionization and thereby allow to study biomolecules and metal complexes [15]. The ions generated would be mass-selected by means of Q1 and deflected to the multipole cell. In this type of experiment, the synchrotron radiation would be used in axis with the multipole, which would also function as a linear ion trap in order to increase the cross section of interaction with light. Thus, ions would be ionized by tunable photons and the resulting dications would be detected by means of Q2. This arrangement would allow to determine second ionization threshold and fragmentation thresholds. We note that this conception of the end-station inherently requires that the position of the instrument would have to be altered for both experiments.

An additional advantage of this arrangement could stem from the flange for user-designed instruments at the deflector between Q1 and O. For example, the investigation of the interactions of internal-energy resolved and mass-selected ions prepared by means of the PI source and Q1 with various surfaces would be possible [16]. Such studies may allow to disentangle the complex interplay of internal and kinetic energy in collisions of ions with sur-

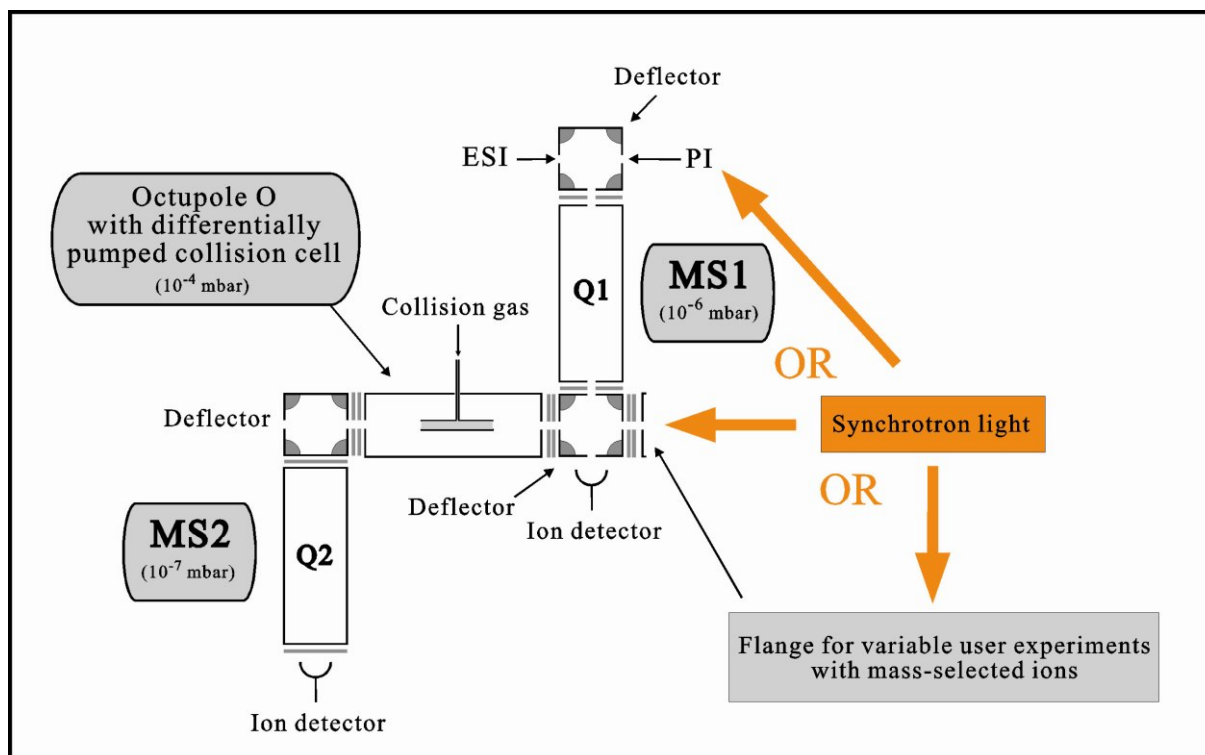


Figure 1. Scheme of the proposed end station for the VUV beamline

faces and might lead to a breakthrough in the understanding of these phenomena.

The properties of the VUV beamline, namely the resolution, would allow also a whole array of other experiments as fluorescent spectroscopy, investigation of radical reactivity, or surface experiments. The VUV beamline would therefore offer a large array of experiments for scientist from Czech Republic and other countries from European Union.

- Sablier M, Fujii T (2002) Mass Spectrometry of free radicals. *Chem. Rev* **102**: 2855 – 2924.
- Woodruff DP (ed) (2007) The Chemical Physics of Solid Surfaces. Atomic Clusters: From Gas Phase to Deposited, vol. 12, Elsevier, Amsterdam.
- Ervin KM (2001) Experimental techniques in gas-phase ion thermochemistry. *Chem. Rev.* **101**: 391 – 444.
- Pilling S, Lago AF, Coutinho LH, de Castilho RB, de Souza GGB, Naves de Brito A (2007) Dissociative photoionization of adenine following valence excitation. *Rapid Commun. Mass Spectrom.* **21**: 3646 – 3652.
- Kempson I. M., Kirkbride K. P., Skinner WM, Coumbaros J (2005) Applications of synchrotron radiation in forensic trace evidence analysis. *Talanta* **67**: 286 – 303.
- Wang J, Yang B, Li YY, Tian ZY, Zhang TC, Qi F, Nakajima, K. (2007) The tunable VUV single-photon ionization mass spectrometry for the analysis of individual components in gasoline. *Int. J. Mass Spectrom.* **263**: 30.
- Roithová J, Schröder D, Loos J, Schwarz H, Jankowiak H-Ch, Berger R, Thissen R, Dutuit O (2005) Revision of the second ionization energy of toluene. *J. Chem. Phys.* **122**: 094306.
- Roithová J, Žabka J, Ascenzi D, Franceschi P, Ricketts CL, Schröder D (2006) Energetics of fragmentations of indene dication from photoionization experiments. *Chem. Phys. Lett.* **423**: 254.
- Schröder D, Loos J, Schwarz H, Thissen R, Dutuit O, Mourgues P, Audier HE (2002) Barrier height titration by tunable photoionization combined with chemical monitoring: Unimolecular keto/enol tautomerization of the acetamide cation radical. *Angew. Chem. Int. Ed.* **41**: 2748 – 2751.
- Hall RI, Avaldi L, Dawber G, McConkey AG, McDonald MA, King GC (1994) Double Photoionization of CO₂, OCS, C₂H₂, CF₄, and C₆H₆ Studied by Threshold Photoelectrons Coincidence (TPESCO) Spectroscopy. *Chem. Phys.* **187**: 125 – 135.
- Gray HB, Malmstrom BG, Williams RJP (2000) Copper coordination in blue proteins. *J. Biol. Inorg. Chem.* **5**: 551.
- <http://www.synchrotron-soleil.fr/portal/page/portal/Recherche/LignesLumiere/DESIRS>.
- Agre MY (2006) Theory of spin polarization phenomena in atomic and molecular photoeffects. *Optics Spectrosc.* **101**: 356.
- Nahon L, Garcia GA, Harding CJ, Mikajlo E, Powis I (2006) Determination of chiral asymmetries in the valence photoionization of camphor enantiomers by photoelectron imaging using tunable circularly polarized light. *J. Chem. Phys.* **125**: 114309.
- Fenn JB (2003) Electrospray wings for molecular elephants (Nobel lecture). *Angew. Chem. Int. Ed.* **42**: 3871 – 3894.
- Herman Z (2003) Collisions of slow polyatomic ions with surfaces: The scattering method and results. *J. Am. Soc. Mass Spectrom.* **14**: 1360.