Mass spectrometry of toluene clusters using a laser produced plasma for tunable single photon ionization

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Abstract. Here we report the first operation of a new apparatus of time of flight mass spectrometry using the tunable Vacuum-UV radiation emitted by a laser produced plasma as ionising source. Toluene cluster mass spectra acquired at different ionising wavelength are presented. Due to massive fragmentation the mass spectra change significantly by increasing the photon energy above the toluene ionisation potential. We found that the more reliable information on the cluster distribution can be gained by tuning the photon energy at value slightly higher than the toluene ionisation energy. The results demonstrate that the developed tunable vacuum-UV source can be successfully used as a soft ionisation method in the study of weakly bound complexes as well as of real complex gaseous mixture.

1. Introduction
The chemical analysis of gaseous mixtures of complex composition with high selectivity and sensitivity is a topic of relevance in many branches of science and technology. The impact of the combustion by-products emitted from vehicles, industries and incinerators, on the human health and environment, both on local and global scale, is beyond any doubt. There is therefore a clear need for developing high-throughput methods for comprehensive analysis of a large number of compounds, including the case of low concentrations. The key-concern here is the simultaneous multi-species detection of compounds in complex mixtures with both high sensitivity and selectivity to give a comprehensive picture of the mixture composition.

The requirements of sensitive, selective and simultaneous detection of species in complex mixtures can be achieved by combining the features of the Time of Flight (TOF) Mass Spectrometry with those of the Vacuum-UV (VUV) photoionization. Compared to other ionization methods used in combination with TOF spectrometry [1], the VUV photoinization is not dissociative, giving less congested mass spectra and enabling more affordable analysis. Moreover, the use of VUV photons continuously tunable across and above the ionization threshold adds a spectroscopic tool to the mass analysis and gives access to the details of the molecular structures, particularly if supported by quantum-mechanical modelling. The method has been demonstrated in many experiments using tunable VUV synchrotron light sources at large-scale facilities [2], which are obviously unfit to be integrated in compact instruments for widespread use.

Recently, we have carried out characterization studies on Laser-Produced Plasmas (LPPs) [3] and have proposed an LPP-based VUV light source, suitable for application of tunable Single-Photon Ionization (SPI) to TOF mass spectrometry [4]. LPP-based VUV light sources provide at once:
single-photon ionization, as they emit in the useful spectral range 6-12 eV, ii) spectral tunability, as their emission spectrum is almost continuum in that band, iii) photon fluxes much higher than those achievable with glow-discharge lamps.

Here we report preliminary results using a set-up based on TOF mass spectrometry coupled with a LPP as VUV photoionization source. As a test case, we chose to study the toluene clustering in a supersonic jet. The toluene clusters are van der Waals (vdW) aggregates with bonds far weaker than the chemical bond. The dynamics of the vdw cluster formation in the supersonic jet has been extensively studied [5] by means of mass spectrometry coupled with laser ionisation. The fragmentation induced by the multiphoton ionization was the main drawback of the laser ionization. Great efforts have been devoted to infer reliable information on the neutral cluster distribution (i.e. the real distribution of the clusters formed in the adiabatic expansion of the gas jet) from the analysis of the ion distribution. More information can be gained by using soft and tunable ionisation sources.

The analysis of the toluene clusters formed in a supersonic jet constitutes a severe test for photoionization experiments devoted to detect molecular compounds without fragmentation, aiming eventually towards a comprehensive chemical analysis of complex gaseous mixtures.

2. Experimental apparatus

The SPI-TOF apparatus is housed in two vacuum chambers, separated by a skimmer and evacuated by two 1000 L/s turbomolecular pumps (see figure 1).

![Figure 1. The SPI-TOF set-up. I = gas sample inlet, S = skimmer, E = extraction and focusing electrodes, F = 900 mm free flight region, C = channeltron, G = grating.](image)

A first chamber includes the VUV source based on a Laser Produced Plasma on a Xe supersonic jet. A detailed description of the LPP source set-up has been given in ref [3] and [4] therefore here is only mentioned. Briefly, a Nd-Yag laser beam (1064 nm, 10 ns, 200 mJ) is focused on the axis of a supersonic Xe jet generated by a solenoid pulsed valve (0.8 mm nozzle) at about 1 mm away from the nozzle. The stagnation pressure is 10 bar and the valve aperture time is 400 μs. The radiation emitted by the laser spark is collected, spectrally dispersed and focused by a concave flat field grating (70 mm diameter, 210 mm focal length, 8 nm/mm dispersion) in a line shape volume at the centre of the vacuum chamber. The emission spectrum of the xenon plasma is mostly continuum in the 100-200 nm wavelength range and VUV photon fluxes exceeding $10^{12}$/cm².nm.pulse (with 2% BW @150 nm) have been measured on the grating focus in the first 20 ns from the laser onset. More details on the spectroscopic characterization of the LPP source have been reported elsewhere [3,4]. In the same chamber, a second pulsed valve is used for the gas sample intake. We used a gaseous mixture of 2 bar...
of He and vapour of liquid toluene (Aldrich HPLC 99.9%) at 25°C. A supersonic jet is formed in the expansion of the gas and a molecular beam is selected by a 0.4 mm conical skimmer, coaxially to the TOF tube and crossing the VUV optical axis at 90°. The skimmer is held directly on the wall of an inner chamber (i.d. 60 mm) housing the extraction fields of the TOF, so that the distance between the valve nozzle and the ionization region is minimized to 60 mm. The inner chamber, connected to the flight tube, is provided with 10x30 mm$^2$ MgF$_2$ windows which allow the VUV photons to reach the molecular beam while preventing most of the valve-injected gases from reaching the ionization and flight zone. The mass spectrometer is housed in a second vacuum chamber. It is a home-made linear TOF in a Wiley Mc-Laren geometry, equipped with the extraction/acceleration electrodes, seven cascaded focusing electrodes and a 90cm-long free flight region. The ion detector is a channeltron. With a 200 V/cm continuum extraction field, the resulting mass resolution is m/Δm = 200 @92 a.m.u.

A stepping motor is used for the wavelength scanning and each mass spectrum is acquired by accumulating 300 shots by means of a home made LabVIEW$^\text{®}$ program driving a DAQ card (National Instrument PCI-5152).

3. Results and discussion

Mass spectra of toluene clusters have been acquired by scanning the photon energy from 8 eV to 12.5 eV with a step 0.3 eV. Figure 2 shows the mass spectra of the toluene clusters at three photon energies (8.8, 10.4, 11.5 eV).

![Figure 2. Cluster distribution at three photon energies. The leftmost peak correspond to the toluene monomer, the following peaks to clusters of 2, 3, … molecules.](image)

The cluster ion distributions reported in figure 2A-C show different shapes at increasing photon energy, since the ionization efficiency depends, besides instrumental response, on the neutral cluster concentration as well as on the photoionization cross-section of each cluster, the latter being a function of the photon energy. We measured values of the ionisation potentials of the toluene clusters falling in the range 8.7-8.5 eV, down-shifted with respect to that of monomer (8.8 eV). By using up 9.3 eV photon energy the mass spectra appear like that reported in figure 2A in which the dimer’s peak is higher than the monomer’s. By increasing the photon energy (up to 10.7 eV), the monomer’s peak increases and the mass distribution show clusters with up to 13 molecules (figure 2B). At even higher
energy the cluster ion distribution changes significantly (see the case of 11.5 eV, figure 3C), and heavier clusters disappear from the mass spectra as a result of a massive fragmentation.

We conclude that reliable information on the toluene clustering in the supersonic jet can be gained at near-threshold photoionization (≤ 9 eV). Furthermore, scanning across the ionization threshold can provide additional information about the size distribution of the neutral cluster. Finer details are achievable by increasing the spectral resolution of the ionizing photons.

The results reported above on toluene clusters demonstrate that the developed tunable VUV ionizing source, based on LPP, can be successfully applied to the study of complex gaseous mixture as well as of weakly bound complexes.

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