# Photoelectron spectroscopy of methylated benzene

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## Introduction

The recently developed technique of photoelectron spectroscopy was implemented in the Artemis beamline, with the vacuum ultraviolet probe being generated by HHG. The photoelectron spectra of a selection of methylated benzene species in both liquid and gas phases were measured and the first eight molecular orbitals (MOs) were identified. A uniform decrease in the measured binding energy of the liquid MOs of ~0.9 eV was observed compared to the gas phase values.

## Experimental method

The experiment used the photoelectron spectroscopy of liquids method developed at the Artemis facility at a previous beam time (2013) [1]. For the measurements presented here the monochromated 19th harmonic (29.6 eV) was used as the probe with a bandwidth measured as 0.56 eV. This was produced using HHG and the VUV monochromator at Artemis.

The liquid targets of methylated benzene species were produced using a micro liquid jet in vacuum. This technique (explained in detail in [1]) produces a $\sim 20$ $\mu$m diameter liquid jet of laminar flow region of $\sim 1$ mm in length in vacuum. Previously this technique was used by the authors at Artemis to probe the ultrafast binding energy shake-up in water following vibrational excitation. The organic solvents used here were particularly suited for production of liquid jets in vacuum due to their typically low vapour pressure and low freezing point. As a result the injected liquids were cooled below 0 °C. The combination of liquid cooling and low vapour pressure resulted in a background pressure in the experimental chamber of $\sim 3 \cdot 10^{-6}$ mbar.

Photoelectron spectra were measured by initially referencing the VUV focus with a YAG crystal. The liquid jet was aligned to this position (imaged using internally mounted CCDs). At this position photoelectrons were collected in the electron spectrometer however evaporated gas phase surrounds the liquid jet and produces significant counts.

To collect photoelectrons produced from the liquid jet the position of the VUV focus was aligned to maximise the count rate. In this position electrons are collected from both the liquid jet and surrounding gas. Spectra were taken with both s and p polarisations of the VUV field (controlled by a half wave plate inserted in the fundamental 780 nm field). For the gas phase only, the VUV focus was aligned away from the jet towards the electron spectrometer aperture by ~50 $\mu$m and photoelectron spectra with s and p polarisations were collected. In this position there was no contribution from liquid phase molecules.

## Discussion

Photoelectron spectra of 1,3,5-trimethylbenezene produced by p-polarised VUV probe are shown in figure 1.
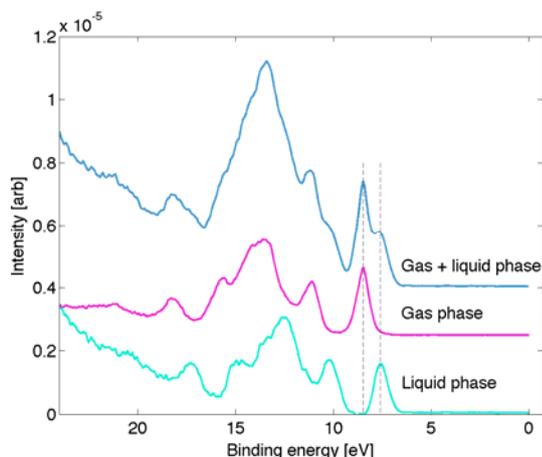


Figure 1: Photoelectron spectra of 1,3,5 trimethylbenezene with horizontally polarised VUV (29.6 eV).

The spectrum labeled 'Gas + liquid phase' was collected at the position of maximum counts and the spectrum labeled 'Gas phase' was collected at a position ~50 μm towards the electron spectrometer.

The HOMO ($1e_{1g}$) of 1,3,5-trimethylbenzene in the gas phase spectrum is a clear single peak with a central binding energy of 8.47 eV, however in the Gas + liquid phase spectrum a secondary peak is clearly visible. Our assumption is that this is the HOMO of liquid phase 1,3,5-trimethylbenzene – offset from the gas phase value. The liquid phase spectrum was produced by subtraction of the gas phase spectrum from the gas + liquid phase with a scaling factor for the gas phase of 1.6 accounting for the lower gas density measured 50 μm from the jet.

The similarity between the gas and liquid spectra is clear. In figure 2 the liquid phase spectrum has been offset by 0.87 eV to align the $1e_{1g}$ HOMO. Interestingly the spectra are almost identical. The source of this uniform difference in binding energy is interesting. Charging effects of the liquid jet can be ruled out as the difference observed was invariant with jet velocity and the space charge from excessive photoelectrons appeared at higher VUV flux.

An almost identical difference in binding energy was previously observed at BESSY for ARPES measurements using a VUV probe by Dudde *et al* [2]. Dudde absorbed a monolayer of benzene onto Ag(111) and observed a 0.8 eV decrease in the binding energy of MOs of the surface layer compared to a gas phase spectrum. Smaller shifts in binding energy have also been observed for multiple layers on benzene absorbed onto Ag(111) with a shift dependent upon the number of layers [3].

The near uniform shift for all measured molecular orbitals is intriguing, especially if we assume the source of the shift is intermolecular bonds forming in the liquid: principally van der Waals forces. It is not immediately clear why the binding energy of π bond associated MOs ($1e_{1g}$ and $1a_{2u}$) and the σ bond associated MOs ($3e_{2g}$, $3e_{1u}$, $1b_{2u}$, $2b_{1u}$, $3a_{1g}$ and $2e_{2g}$) are all decreased by ~0.9 eV in the liquid phase.
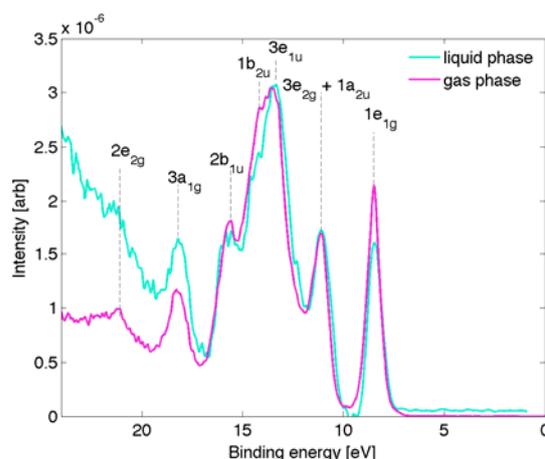


Figure 2: Liquid and gas phase spectra of 1,3,5 trimethylbenezene with assigned molecular orbitals. The liquid spectrum has been offset by 0.87 eV to align with the gas spectrum.

The direction and magnitude of the binding energy shift is consistent with benzene absorption measurements. In the case of [2] where a VUV (37 eV) synchrotron source was used 9 MOs were identified and all (both π and σ) were uniformly shifted by 0.8 eV. Reference [3] used a two-photon photoemission technique where MOs were not identified and an image state was measured. However the direction and magnitude of the shift is in agreement. What is common among all three measurements is that they are surface sensitive. Measurements [2] and [3] use carefully prepared layers (from 1 to 5) of benzene, whereas the liquid measurements presented here use a surface sensitive probe. The non-elastic mean free path of electrons produced by the 29.6 eV probe used at Artemis restricts measurements to electrons produced within the first few monolayers of the liquid jet. The source of the binding energy shift is still under investigation, but one implication is the shift observed in [2] and [3] may be predominately due to benzene layering rather than the presence of Ag(111).

Similar shifts were measured for other methylated benzene species (1,2,3-trimethylbenzene, 1,2,4 trimethylbenzene, o-Xylene and m-Xylene) and are detailed in a forthcoming publication by the authors.

## Conclusions

The PES of liquids technique using the VUV developed at Artemis has allowed the first measurements of the binding energy of MOs in liquid phase methylated benzene to be conducted. While the results are still under analysis, the uniform shift in the binding energy between liquid and gas phase is intriguing and may have implications for previously report results of benzene absorbed onto metal.

The extension of the PES of liquids technique from water to other solvents at Artemis coupled with the application of PES of liquids to time resolved measurements demonstrated last year opens the door to ultrafast

measurements in solvents and solutions fundamental to chemistry.

**Acknowledgements**

**References**

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