UV-pump-VUV-probe photoelectron spectroscopy experiments at ARTEMIS: unravelling the ultrafast relaxation dynamics of aniline

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Introduction

Aniline ($C_6H_5NH_2$) is a structural motif found in the purine nucleotides, adenine and guanine, and in the pyramidine nucleotide, cytosine. The UV absorption spectrum of aniline is dominated by two bands centered around 282 nm and 230 nm corresponding to $\pi^* \leftarrow \pi$ transitions to the first two $^1\pi\pi^*$ states, labelled $1^1\pi\pi^*$ and $2^1\pi\pi^*$. The first dissociative $^1\pi\sigma^*$ state, $1^1\pi\sigma^*$, lies between the $1^1\pi\pi^*$ and $2^1\pi\pi^*$ states; it has $\pi3s$ character in the Franck-Condon region but becomes dissociative along the N–H stretch coordinate and forms conical intersections with the $1^1\pi\pi^*$ state and the ground electronic state at modest N–H bond lengths.

There have been a number of recent experimental studies of the photochemistry of isolated aniline molecules *in vacuo* using H-atom (Rydberg) photofragment translational spectroscopy,[1] femtosecond pump-probe photoionisation spectroscopy,[2] femtosecond pump-probe velocity map imaging,[3] and time resolved photoelectron imaging.[4-9] There have also been a number of recent theoretical investigations of the potential energy landscape and relaxation pathways following excitation to the first few singlet excited states.[10,11] However, there has not yet been a direct measurement to support our recent proposal that non-radiative decay from the $2^1\pi\pi^*$ state involves a barrierless pathway from the Franck-Condon region to a conical intersection between the $2^1\pi\pi^*$ state and the ground-state, that passes through a 3-state conical intersection involving the $2^1\pi\pi^*$, $1^1\pi\sigma^*$ and $1^1\pi\pi^*$ states.[11] This question provides our motivation for revisiting the non-radiative relaxation dynamics of aniline using a UV-pump-VUV-probe photoelectron spectroscopy experiment, to extend the observation window and to track repopulation of the ground-state and formation of any photodissociation products.

Results

Before acquiring pump-probe signal we recorded a single-photon photoelectron spectrum using XUV light (21.7 eV) and a two-photon resonance-enhanced photoelectron spectrum using UV light (250 nm, 5.0 eV) of aniline seeded in Helium in a pulsed and skimmed molecular beam. The photoelectron spectra were of high quality and the 21.7 eV photoelectron spectrum is presented in Figure 1. Comparison with He(I) and Penning ionisation spectra allowed calibration and assignment of all the peaks.[12,13] The molecular beam was then replaced with an effusive beam of neat aniline closer to the source region of the photoelectron spectrometer in order to increase the number density of gas-phase aniline pump-probe spectra.
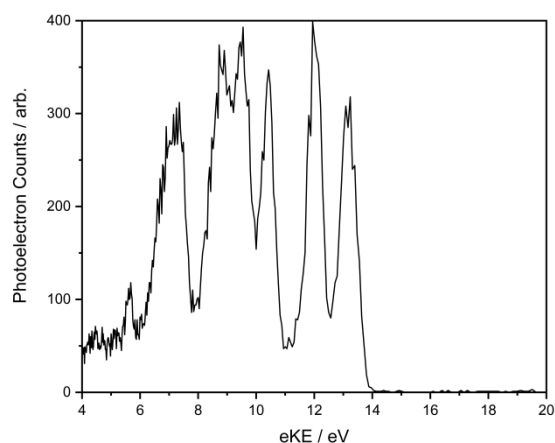

Figure 1: 21.7 eV photoelectron spectrum of aniline. The relative intensities and peak positions agree well with spectra recorded using other methods.[12,13]

We employed three photon resonance ionization of Xe at 249.5 nm to align the UV-pump laser light with the aniline. From this, we were then able to find good spatial overlap between the UV-pump and XUV-probe, and acquire a UV-pump-XUV-probe photoelectron spectrum.

Error! Reference source not found. 2 shows a plot of photoelectron signal as a function of pump-probe delay and photoelectron kinetic energy (eKE), with the signal at a large pump-probe delay subtracted (i.e. the UV-only and XUV-only spectra are subtracted). In this spectrum there is a clear region which shows an increase in counts at around 17.5 eV. This is the energy region where signal is to be expected for UV-excitation followed by VUV ionization.
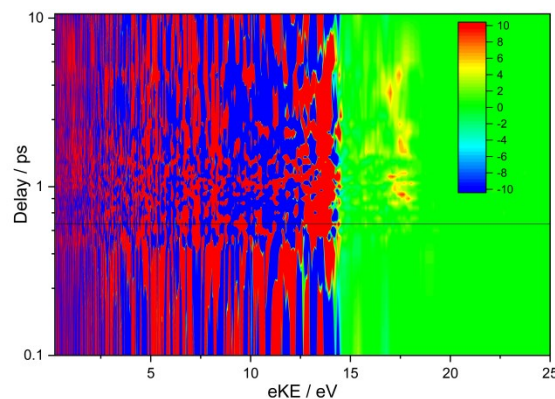

Figure 2: Difference plot of the photoelectron spectra recorded using a 250 nm pump and 21.7 eV probe as a function of time.

Note the increase in signal around 17.5 eV. This is the region where pump-probe photoionisation is observed.

Figure 3 shows the integrated photoelectron signal taken from two regions of the photoelectron spectrum as a function of pump-probe delay. The black line is the integrated signal taken around 17.5 eV eKE and shows the expected rise from a zero background. Though the data has low time resolution, the picosecond timescale is consistent with the previously observed lifetime of the $1^1\pi\pi^*$ populated from the $1^1\pi\sigma^*$ state.[3,4] The blue line shows the integrated signal from around 1 eV in the photoelectron spectrum. This is likely to be due to 1+1 UV ionization. This curve shows a depletion and then rise in signal at the same point of the rise in the 1 eV signal. This could be due to the XUV photons depleting the ground state population of aniline and so, lowering the number of aniline molecules available to absorb the UV photons. This confirms our observation of a pump-probe signal in aniline.
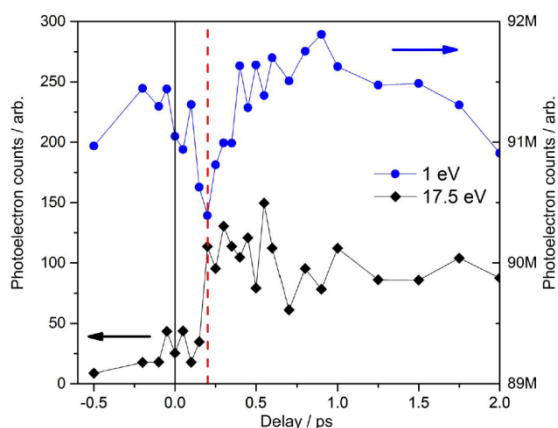

Figure 3: Integrated photoelectron signal as a function of pump-probe delay. Top (blue) curve is in the region of the UV-pump + UV-pump signal, and the bottom (black) curve is in the region of the UV-pump + XUV-probe signal.

We are optimistic that we will be able to record UV-pump XUV-probe spectra for aniline and other organic molecules in the future, provided we have enough molecular beam density and laser power in the interaction region, and good temporal and spatial overlap of the UV and XUV pulses.

Conclusions

Using a UV-pump-XUV-probe methodology we have recorded preliminary time-resolved photoelectron spectra of aniline. Using XUV light as a universal probe of gas-phase dynamics of large molecules at ARTEMIS would pave the way for numerous new experiments aimed at unravelling the complete electronic relaxation pathway of large molecules relevant to biology and nanomaterials following UV photoexcitation.

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