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Tunable Vacuum-UltraViolet Laser Photoionization Studies of Aromatic Molecules in Molecular Beams.

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[Introduction] Multiphoton ionization methods have been employed effectively and extensively in the study of gas phase molecules and clusters, particularly in molecular beams. Typically, photons from available laser sources are not of sufficient energy to directly photoionize most molecules and so ions can only be generated by two sequential processes – initial photoexcitation to an excited state of the molecule (typically S_1) followed by absorption of a second photon capable of ionising the excited molecule. The drawback to this approach is that absorption of the second photon competes with the range of alternate photophysical and photochemical pathways available to the excited state molecule and is thus ineffective in some cases, for example if the excited state molecule undergoes rapid intersystem crossing. This problem is circumvented if the molecule can be excited directly from the ground state (S_0) to the photoionized state (D_0). For most molecules this requires photons in the vacuum ultraviolet (VUV) region of the spectrum. To this end we have constructed a tunable VUV laser system capable of directly photoionizing the majority of molecules directly with a single photon. Here we present details of the instrument and its application to the study of a range of chlorinated aromatic molecules in a supersonic jet cooled gas expansion. The instrument has applications both in fundamental spectroscopic studies of molecules and clusters and in a range of analytical techniques including atmospheric monitoring.

[Instrumentation] An ideal VUV laser source will be sufficiently powerful to observe gas phase molecules seeded in molecular beams of rare gases and will be tunable over a wide range of wavelengths to allow threshold spectra and thus ionisation energies to be determined for molecules of interest.

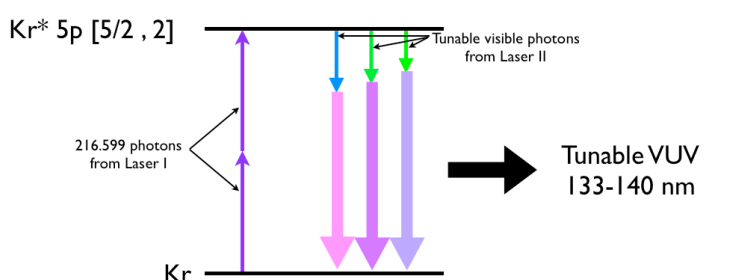
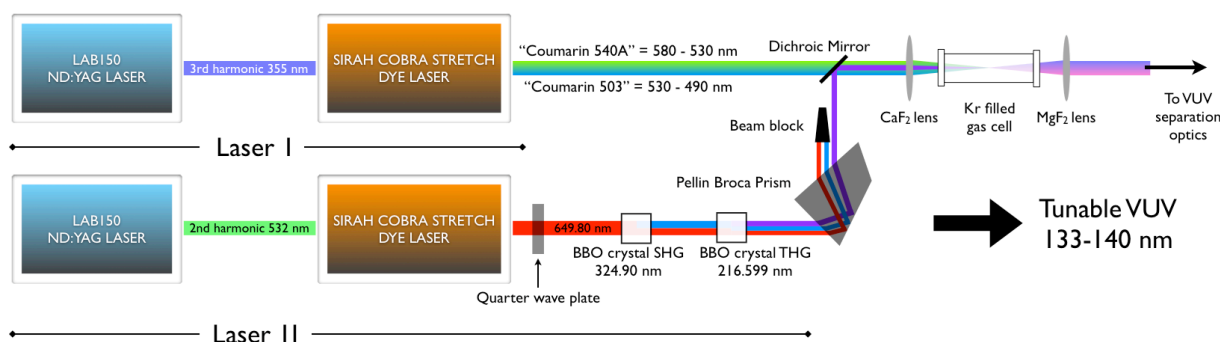


Figure 1. Four wave mixing scheme and experimental arrangement for generation of tunable VUV radiation



In addition, the beam must be free from UV or visible photons, which may give rise to other photoprocesses. This is an important requirement when generating high-energy photons from the combination of lower energy photons. Our VUV laser system employs a four-wave mixing process in a rare gas to generate VUV light tunable from 124 nm to 148 nm and 133 nm to 188 nm using krypton and xenon respectively. For the range of chlorinated aromatics studied here, VUV generation took place in krypton gas using two UV photons of 216.599 nm to access the 5p [5/2,2] excited state of krypton. Figure 1 shows the four wave mixing process involved, along with the experimental layout of the laser system. A custom-built wavelength separator isolates the VUV photons from the remaining UV and visible light before they enter the vacuum chamber and impinge on the molecular beam. The ions produced by photoionization are detected using a linear time-of-flight mass spectrometer. This allows simple distinction between direct photoionization and photofragmentation processes and in conjunction with the tunable VUV source offers a powerful tool for examining the ground and ionic states of molecules.

[Experimental] We present data from a range of chlorine-substituted benzenes, using both mass spectral data and VUV photoionization threshold measurements to examine, in detail, the photoionization processes in these molecules. As an example, figure 2a shows the mass spectrum obtained from direct VUV photoionization of a mixture of chlorobenzene and chloroethylbenzene. These two molecules have very similar ionisation thresholds, but their photoionization can be studied independently and simultaneously due to the mass separation of their photo-ions. Figure 2b shows the photoionization threshold spectra obtained simultaneously for these two molecules by monitoring independently the two distinct mass peaks present in the mass spectrum, which correspond to the chlorobenzene and chloroethylbenzene cations. It is also worth noting that direct VUV photoionization provides a phenomenally fragment free method of ion generation, allowing unequivocal assignment of mass channels and showing enormous promise as a technique for analysis of complex mixtures, particularly in conjunction with photoionization threshold selectivity.

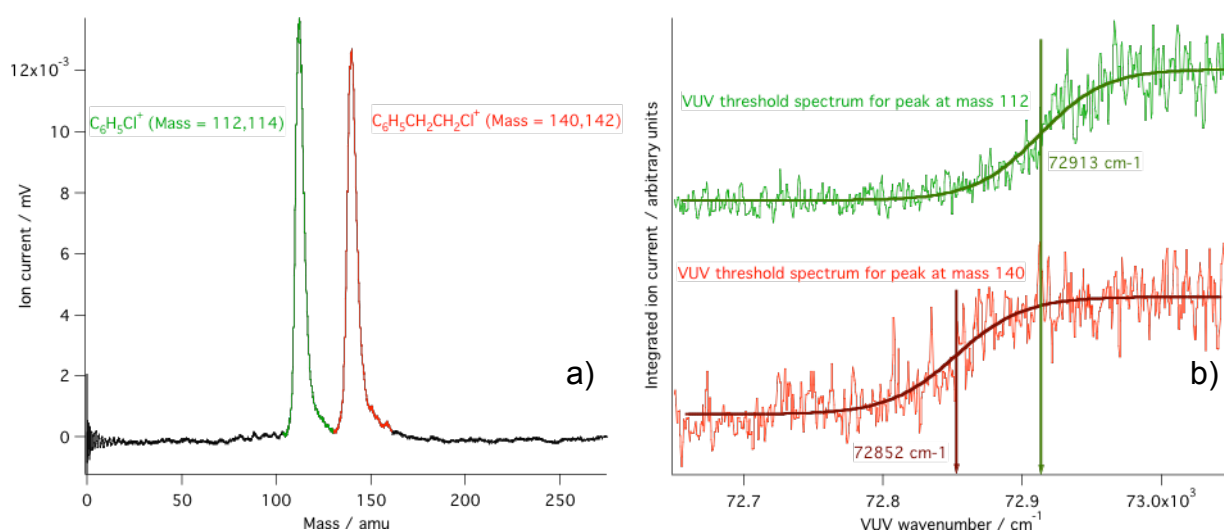


Figure 2. a) Mass spectrum obtained from 73400 cm⁻¹ photoionization of a molecular beam containing chlorobenzene and chloroethylbenzene. b) VUV Threshold photoionization spectra corresponding to the two mass peaks in a).