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A new broadly tunable (7.4–10.2 eV) laser based VUV light source and its first application to aerosol mass spectrometry

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ABSTRACT

A laser based vacuum ultraviolet (VUV) light source using resonance enhanced four wave difference mixing in xenon gas was developed for near threshold ionization of organics in atmospheric aerosol particles. The source delivers high intensity pulses of VUV light (in the range of 10^{10} to 10^{13} photons/pulse depending on wavelength, 5 ns FWHM) with a continuously tunable wavelength from 122 nm (10.2 eV) to 168 nm (7.4 eV). The setup allows for tight (<1 mm^2) and precise focusing (μrad pointing angle adjustability), attributes required for single particle detection. The generated VUV is separated from the pump wavelengths by a custom monochromator which ensures high spectral purity and minimizes absorptive losses. The performance of the source was characterized using organic molecules in the gas phase and optimal working conditions are reported. In the gas phase measurements, photoionization efficiency (PIE) curves were collected for seven different organic species with ionization energies spanning the full wavelength range of the VUV source. The measured appearance energies are very close to the literature values of the ionization energies for all seven species. The effectiveness of the source for single particle studies was demonstrated by analysis of individual caffeine aerosols vaporized by a pulsed CO_2 laser in an ion trap mass spectrometer. Mass spectra from single particles down to 300 nm in diameter were collected. Excellent signal to noise characteristics for these small particles give a caffeine detection limit of 8×10^5 molecules which is equivalent to a single 75 nm aerosol, or approximately 1.5% of a 300 nm particle. The appearance energy of caffeine originating from the aerosol was also measured and found to be 7.91 ± 0.05 eV, in good agreement with literature values.

1. Introduction

Single photon ionization (SPI) using vacuum ultraviolet (VUV) light is a very effective soft ionization method for analytical mass spectrometry. It has been used in measurements as diverse as diagnostics of automobile exhaust [1,2], analysis of amino acids [3], and monitoring of waste incineration flue gas [4]. Unlike multiphoton ionization, no intermediate molecular resonances are required, making SPI a universal ionization technique [5]. As long as the photon energy is higher than the ionization energy of the molecule of interest, ionization will occur. Many SPI sources operate at a fixed photon energy, but tunable sources have many advantages. They allow the photon energy to be set very close to the ionization threshold minimizing fragmentation. In addition, a tunable source makes it possible to differentiate mixtures by the appearance energies of the components. A tunable source also makes it possible to measure ionization energies (IEs). Having both the IE and the SPI mass spectrum of the molecule is a powerful combination for product identification in analytical applications.

Pulsed lasers are an excellent source of VUV light. Unlike synchrotrons, they are laboratory based instruments, and although considerably more complex than discharge lamps, they can produce high intensity pulses of coherent radiation. The coherent light from a laser source has several advantages. It is highly collimated and can be steered over considerable distances by conventional optics. In addition the bandwidth can be very narrow, the spectral purity can be high, and the polarization can be easily controlled. There is also no higher order VUV radiation which can be an issue with synchrotron undulator sources [6]. Pulsed lasers sources are also well suited for measuring discreet events, such as in pump-probe experiments or single particle mass spectrometry.

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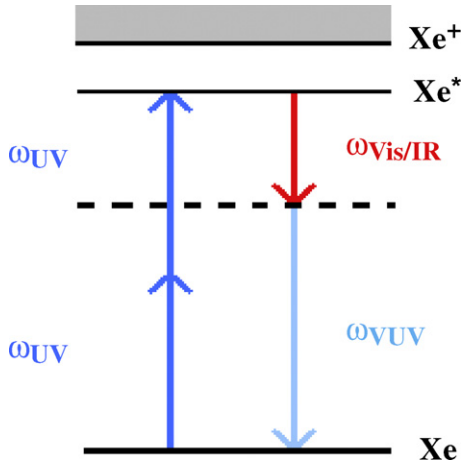

Fig. 1. Schematic of resonance enhanced four wave difference mixing in xenon gas.

Continuously tunable laser based VUV light sources capable of scanning over a wide frequency range are predominantly based on four wave sum or difference mixing in rare gases or metal vapors. Here three applied frequencies of light are used to produce a fourth based on the non-linear response of a gas phase medium [6–8]. Resonance enhanced four wave mixing increases the VUV output by having two of the applied frequencies set to reach a two-photon resonance in the medium. The third applied frequency is tunable and allows tunable VUV to be generated [6,7,9]. This is shown schematically in Fig. 1.

The majority of tunable VUV sources based on four wave mixing use two dye lasers. One of the lasers has its output fixed at the wavelength of the two-photon resonance, and the other is scanned to produce tunable output. In these systems tuning over a wide range of VUV energies requires frequent dye changes, which is time consuming and not suitable for rapid and routine analysis. For example, Hilber et al. used thirteen different dyes to produce VUV light between 127 nm and 147 nm [10]. Some variations on the two dye laser scheme have been employed. Faris et al. used a combination of a dye laser and an ArF excimer laser, although dye changes were still required in order to scan over a broad frequency range [11]. Alternatively, Qi and McIlroy used two OPOs pumped by separate Nd:YAG lasers [12], a system which overcomes the necessity of frequent dye changes.

A serious concern in analytical applications of VUV generated by four wave mixing is spectral purity. The generated light will contain the residual high intensity UV and visible or IR radiation used for the four wave mixing process, which are typically 6–8 orders of magnitude more intense than the generated VUV radiation. This, particularly in the case of the UV, can lead to unwanted multiphoton ionization. To avoid these effects, the VUV must be separated from the pump frequencies. Traditional grating monochromators typically have only about 10% efficiency in the VUV, and are easily damaged by intense UV pulses. Monochromators based on refractive optics such as prisms or lenses have higher efficiencies and damage thresholds. An off-axis lens monochromator has the advantage of focusing the light and allowing optimal discrimination. This technique has been used quite extensively in experiments where 355 nm light is tripled to produce VUV radiation at 118 nm [13–16] and was reported in a tunable monochromator by Vondrasek et al. in 1988 [17]. However, no design to our knowledge has been presented that is capable of giving a precisely positioned VUV focus while scanning over a broad range of frequencies.

In this work we present a new VUV light source based on four wave difference mixing in xenon gas which incorporates both a dye laser and an OPO. The dye laser is used at a fixed frequency to access a two-photon resonance and the OPO provides the tunable wavelength. This has the advantage of allowing wavelength scanning between 122 nm and 168 nm, while requiring only one dye change. Both the dye laser and OPO produce narrow bandwidth light which allows for high resolution VUV scanning (bandwidth on the order of 0.5 cm^{-1}). In addition, a custom monochromator based on a single MgF_2 lens has been incorporated into the design to separate the generated VUV from the pump wavelengths, to ensure high spectral purity, and to minimize absorptive losses. Furthermore, the monochromator was specially designed to maintain a tight and precisely positioned focus even as the VUV wavelength is changed over tens of nanometers. Careful computer control of the pump optics and the monochromator lens allows a precisely positioned and uniformly sized focus to be maintained in the center of the ionization region while scanning. To the best of our knowledge, this is the first demonstration of a laser based VUV source that is capable of routinely scanning over this wide frequency range while maintaining a tight and precise focus and maintaining a high spectral purity.

Although our system has other potential applications, it was designed specifically as an ionization source for single particle aerosol mass spectrometry. Aerosol particles, which range in size from 2 nm to tens of microns [18], are ubiquitous in the earth's atmosphere, and a very significant mass fraction (20–90%) of the submicron aerosol component is composed of, or contains, organic molecules [19]. The composition of these organic aerosols has been shown to be extremely complex and often consists of large, fragile molecules which present a significant challenge to standard analytical techniques [20,21]. In recent years a wide variety of new instrumentation has been developed to study these particles, with one very powerful technique being aerosol mass spectrometry [22–27].

For mass spectrometric analysis of organic aerosols, ionization using traditional 70 eV electron impact leads to extensive fragmentation and complex mass spectra. To reduce this fragmentation, several groups have coupled aerosol mass spectrometers with soft ionization sources, some examples of which include low energy electron impact (PERCI) [28], chemical ionization (CI) [29,30], metal attachment [27], resonance enhanced multiphoton ionization (REMPI) [31–35], and single photon ionization.

Tripling the third harmonic of a Nd:YAG laser to produce 118 nm light has been used quite extensively in aerosol mass spectrometers [36–38]. It is a relatively simple system and gentle in comparison with many other ionization methods, although it has been shown that even 118 nm light is high enough in energy to cause significant fragmentation of organics [39]. Other avenues that have been explored include VUV lamps [40,2,41], use of a synchrotron [42–45], and resonance enhanced four wave difference mixing to give VUV light at 142 nm (8.75 eV) [39]. Recently developed rare-gas excimer lamps have been successfully deployed as photoionization sources for mass spectrometry [46,47] while the Advanced Light Source in Berkeley California has been used very effectively to characterize the products of heterogeneous reactions involving small organic aerosols [42]. However, the new rare-gas excimer lamps are cw, broadband, and not continuously tunable. The synchrotron is also cw, and access to such a facility is limited.

The first objective of this work was to develop a new, continuously tunable, laboratory based VUV light source designed specifically for single particle aerosol mass spectrometry. Our source has a high photon flux, which is a prerequisite for aerosol studies, especially for single particle studies (a 1 μm aerosol has $\sim 10^9$ molecules, ~500 fg of material). It is continuously tunable from 7.4 eV to 10.2 eV (168 nm to 122 nm) so that fragmentation can be minimized and compounds can be separated by ionization energies. A custom monochromator maintains a tight and precisely