Experimental conditions for vacuum ultraviolet laser spectroscopy

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An efficient wavelength-tunable vacuum ultraviolet (VUV) laser source has been developed at our institute in recent years. This laser source works on the principle of sum-frequency mixing of dye laser pulses in a magnesium vapour medium, which is prepared in a crossed heat pipe system. The laser source is coupled to a pulsed supersonic expansion and is in use for spectroscopic measurements. In this paper, we present a complete characterization of the experimental setup. The source yielded 25-ns-long pulses of VUV radiation with peak power of approximately 1 mW. The wavelength is currently tunable over the range 142.7–146.7 nm with a spectral bandwidth of 0.25 ± 0.05 cm^{-1}. Suggested refinements of the experimental technique include an increase in the repetition rate of the measurements and shorter gas pulses.

Introduction

The vacuum ultraviolet (VUV) is the region of the spectrum between 105 and 200 nm. Because of the lack of tunable laser sources in this spectral range, there are several interesting applications of laser spectroscopy in the VUV which have not yet been investigated thoroughly.

The tunable VUV laser source constructed in our laboratory[1] works on the principle of two-photon resonant four-wave sum-frequency mixing[2] of pulsed dye laser beams in a magnesium vapour medium. This is a third-order nonlinear optical process that generates vacuum ultraviolet light at the sum-frequency $\omega_{sum} = \omega_1 + \omega_1 + \omega_2$, where ω_1 and ω_2 are the frequencies of the two dye lasers. The conversion efficiency is enhanced, first, by tuning ω_1 to a two-photon resonance of atomic magnesium. The frequency ω_2 provides the tunability of the resulting sum-frequency. Second, for efficient sum-frequency generation, the refractive index of the medium must be the same for the visible and VUV light, a condition called phase matching. This requires the addition of krypton gas to the magnesium vapour, the ability to fine-tune the magnesium–krypton pressure ratio and a high degree of homogeneity and stability of the mixture, which is achieved in a crossed heat pipe system.[3]

This source is currently used in conjunction with a pulsed supersonic noble gas jet to achieve high-resolution, laser-induced fluorescence (LIF) excitation spectroscopy of CO molecules seeded into the jet. The undispersed fluorescence originating from the irradiated volume in the supersonic jet is detected as a function of the VUV excitation wavelength as the wavelength is tuned.

In this paper, we describe the experimental setup, including the VUV source and the supersonic jet as sample.

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Experimental setup

This is shown schematically in Fig. 1. A XeCl excimer laser (Lambda Physik EMG 302 MSC) was used to pump two dye lasers (both Lambda Physik FL3001X with Coumarin 440 dye) simultaneously. These dye laser beams, in the visible wavelength range, were polarized circularly in opposite directions and combined collinearly. The combined beams were focused into the magnesium vapour–krypton gas medium inside the heat pipe system, where the conversion to VUV took place.

The crossed heat pipe system consisted of a vertical heat pipe heated by a thermal element and containing a sodium vapour column at constant temperature. The temperature of this vapour column could be set to temperatures in the range of about 650–900°C, by adjusting the external buffer gas pressure. The typical operating temperature in this experiment was 750°C. The vertical heat pipe functioned as an isothermal oven for the inner horizontal heat pipe, containing the magnesium vapour and krypton gas mixture. Phase matching was done by adjusting the krypton gas pressure by varying the volume of the connected krypton gas reservoir.

The supersonic jet was formed by allowing a gas mixture containing up to 25% of CO in argon or neon as carrier gas to expand from a stagnation pressure of 3–4 bar through the nozzle (0.8 mm cross section) of a pulsed valve (General Valves series 9) into a low-pressure chamber. The chamber was maintained at $\sim 5 \times 10^{-5}$ mbar by a turbo molecular pump (Pfeiffer TPH200).

The beam of coherent VUV light crossed the supersonic jet

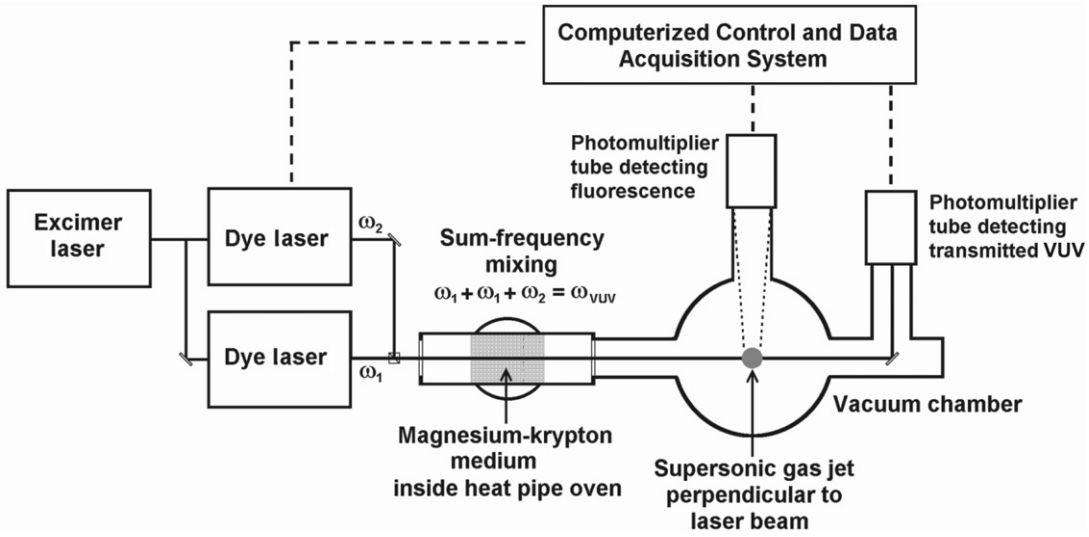

Fig. 1. Schematic illustration of the experimental setup.

about 25 nozzle diameters below the nozzle. The gas and laser pulses were synchronized by a delay generator (Stanford Research Systems DG535). The VUV fluorescence from the irradiated volume of the jet was detected by a solarblind photomultiplier (EMR Electronic 542G-08-18-03900) positioned perpendicular to the laser beam. A second photomultiplier (Hamamatsu R973) was used to measure the transmitted radiation. This photomultiplier was also used in conjunction with a vacuum monochrometer (McPherson Model 218) for additional measurements of the VUV radiation (in order to separate the sum-frequency and third harmonic wavelengths). Scattered light was limited by using baffles in front of both photomultipliers and having the surfaces inside the chamber painted matt black. A personal computer running a custom HP VEE (version 3.12) program was used to control the setup and acquire the data from two boxcar integrators (Stanford Research Systems SR250).

Results and discussion

The experimental setup was demonstrated as a reliable source of narrow-bandwidth tunable vacuum ultraviolet radiation suitable for spectroscopy. Once the heat pipe was at operating temperature (after about 1.5 hours), the conditions of the medium inside the heat pipe was found to remain stable for prolonged use (it was tested for up to 12 hours). The critical experimental parameters in the VUV source were the correct resonance frequency ω_1 for resonance enhancement, the correct magnesium–krypton pressure ratio in the medium for phase matching, and good spatial overlap of the two dye laser beams. We used the $3s^2$-$3s3d$ two-photon resonance of magnesium at 430.88 nm. Phase matching was typically achieved at a krypton–magnesium medium pressure of 24 kPa, as illustrated in Fig. 2. Other parameters influencing the VUV output were the dye laser intensities and the wavelength-dependent attenuation of the VUV generated in the medium. Figure 3 shows a typical tuning curve of the radiation over a part of the available tuning range.

The characteristics of the generated radiation were closely related to those of the incident laser beams that provided moderate pulse energies of approximately 2 mJ and pulse duration of 20 nm. The VUV had an estimated peak power in the order of 1 mW, corresponding to a typical conversion efficiency of 10^{-7}. The spectral bandwidth in the VUV was about 0.25 ± 0.05 cm^{-1}. With the laser dyes currently used, tuning in the range 142.7–146.7 nm was possible.

The spectroscopic results obtained with this equipment include

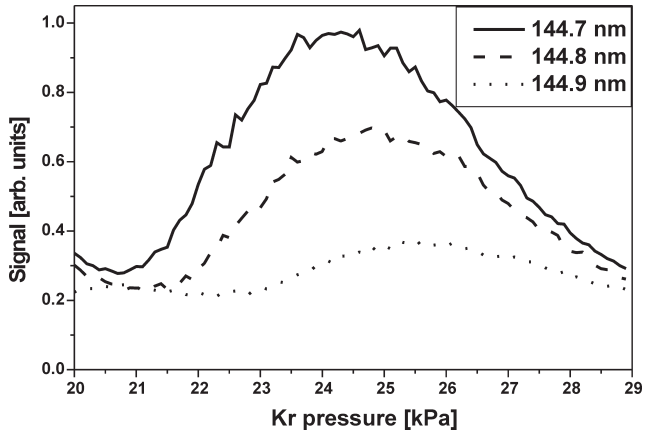

Fig. 2. Typical phase matching curves: the sum-frequency peak power as a function of the krypton–magnesium medium pressure for dye laser wavelengths at 441 nm, 442 nm and 443 nm.

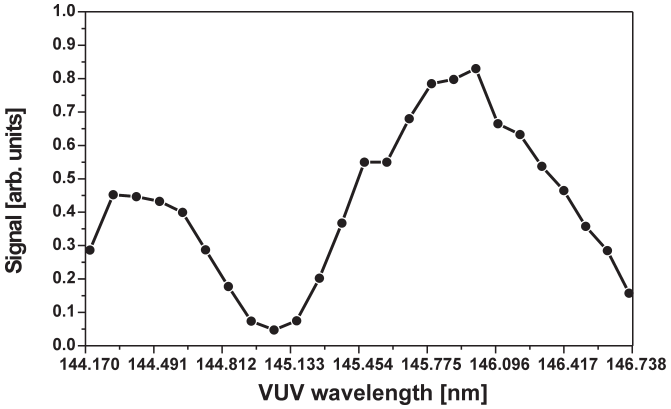

Fig. 3. The sum-frequency peak power as a function of wavelength over a large part of the available tuning range, with the current dye used.

rotationally resolved, laser-induced fluorescence excitation spectra of the $A^1\Pi(v' = 3) - X^1\Sigma^+(v'' = 0)$ rovibronic band of CO isotopomers.[4, 5] These results demonstrated the functionality of the experimental setup for high-resolution spectroscopy in the VUV. The concentration limit for the detection of CO molecules by the laser-induced fluorescence method was found to be as low as 3 parts per million. This sensitivity facilitated the detection of the naturally rare $^{12}C^{17}O$ and $^{12}C^{18}O$ isotopomers. The spectral resolution, determined by the laser bandwidth, was sufficient to resolve rotational lines of different isotopomers with wavenumber spacing as small as 0.2 cm^{-1}. The noise due to scattered VUV light was less than the detection limit and it was electronic noise and drift of the signal that limited the smallest spectral features that could be observed.

The rotational temperature of the CO molecules in the jet was determined from the measured spectra. The stagnation pressure, percentage CO in the gas mixture and the noble gas species used as carrier gas were the most important conditions influencing the temperature. Rotational temperatures as low as 2 ± 1 K could be achieved by optimization of the parameters. The low temperature had definite advantages for spectroscopy. The low rotational temperature not only simplified the spectrum of each CO isotopomer, but it also increased the intensity of the fluorescence associated with transitions between low rotational states, facilitating spectroscopic detection of trace species.

Refinement of the experimental technique is required for further investigations. An increase in the repetition rate will

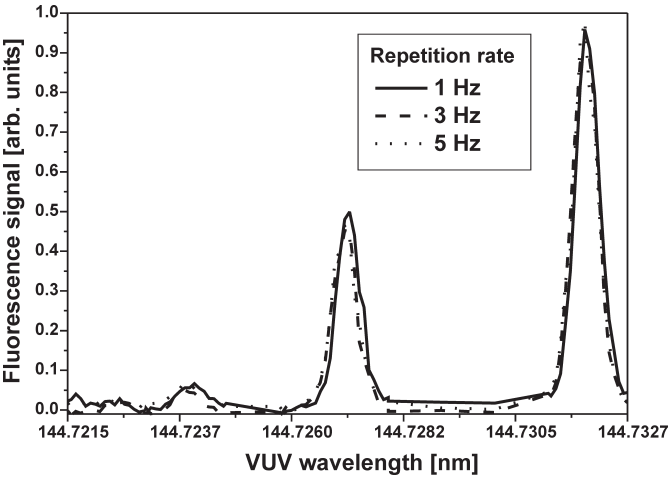

Fig. 4. A typical laser-induced fluorescence excitation spectrum of CO (four rotational lines) in the VUV, showing good correspondence between measurements up to 5 Hz.

allow faster measurements, which minimizes the effect of temporal variations. The effect of repetition rate was investigated experimentally and the results are presented in Fig. 4, which shows a typical laser-induced fluorescence excitation spectrum. Within the range 1–5 Hz, the repetition rate did not have a significant influence on the spectroscopic results. Above 5 Hz, the background pressure in the vacuum chamber became too high (about 10^{-2} mbar). This affected the supersonic expansion and enhanced the risk of damage to the photomultiplier tube. Another possible refinement is the use of shorter gas pulses, facilitating the creation of even lower temperature conditions in the jet while allowing higher repetition rates.

Conclusions

The experimental setup developed in our laboratory was thoroughly characterized and demonstrated to be suitable for high-resolution spectroscopy of CO as an example of a fluorescing molecular species with an electronic excitation spectrum in the VUV. The critical factors for the generation of the tunable narrow-band vacuum ultraviolet radiation were the two-photon resonance, the krypton–magnesium pressure ratio for phase matching, and optimal spatial overlap of the incident laser beams. The tunable VUV radiation was used to obtain rotationally resolved spectra of CO molecules and to detect trace amounts of the rare $^{12}C^{17}O$ and $^{12}C^{18}O$ isotopomers. The extent of cooling the sample molecules in the supersonic noble gas jet was most strongly influenced by the stagnation pressure, the percentage of sample molecules in the gas mixture and carrier gas species. The low temperature simplified the analysis of overlapping spectra and contributed to lowering the detection limit for trace species. Refinements of the methods that are suggested after experimental testing are the use of higher repetition rates and shorter gas pulses, allowing higher repetition rates.

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