Sum-frequency generation with a blue diode laser for mercury spectroscopy at 254 nm

J. Alnis,[a] U. Gustafsson, G. Somesfalean, and S. Svanberg,[b]
Department of Physics, Lund Institute of Technology, P.O. Box 118, S-221 00 Lund, Sweden

Blue diode lasers emitting 5 mW continuous-wave power around 400 nm have recently become available. We report on the use of a blue diode laser together with a 30 mW red diode laser for sum-frequency generation around 254 nm. The ultraviolet power is estimated to be 0.9 nW, and 35 GHz mode-hop-free tuning range is achieved. This is enough to perform high-resolution ultraviolet spectroscopy of mercury isotopes. The possibility to use frequency modulation in the ultraviolet is demonstrated; however, at present the ultraviolet power is too low to give advantages over direct absorption monitoring. Mercury detection at atmospheric pressure is also considered which is of great interest for environmental monitoring. © *2000 American Institute of Physics.*
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Absorption spectroscopy using diode lasers is a fast and sensitive method for detection of many gases in atmospheric monitoring.[1] The technique has been widely employed in the mid-infrared spectral region (2–15 μm), where numerous species of interest have fundamental vibrational absorption bands, and in the near-infrared region (0.6–2 μm), where weaker overtone and combination bands occur. Near-infrared spectroscopy makes extensive use of low-cost and room-temperature operated diode lasers which are readily available in this wavelength region. Atomic trace element detection in, e.g., a graphite furnace,[2,3] using diode-laser based absorption is an attractive possibility. Midinfrared absorption measurements apply cryogenically cooled lead-salt diode lasers or utilize difference-frequency generation in a nonlinear crystal pumped by two near-infrared diode lasers.[4] Many species also have strong electronic transitions in the ultraviolet (UV) spectral region (200–400 nm). These transitions are typically one or two orders of magnitude stronger than the mid-infrared transitions. Additionally, interference from water vapor is less significant in the UV spectral region.

Mercury (Hg) is the only pollutant present as a free atom in the lower atmosphere and has a strong transition at 253.7 nm that allows detection at low concentrations. Typical background concentrations of mercury in air are a few ng/m^3,[5] but much higher mercury concentrations exist around mercury mining areas and chloralcali plants.[6] Zeeman absorption,[7] differential optical absorption spectroscopy (DOAS)[8] or light detection and ranging (Lidar)[6] techniques are used for mercury measurements in air. A diode-laser-based spectrometer in the UV region could be especially interesting for low absorption measurements, since modulation techniques,[9,10] which give several orders higher sensitivity compared to direct absorption, can be easily employed.

The access to the UV spectral region employing diode lasers is usually provided by quadrupling[11–13] or sum-frequency generation.[14] The sum-frequency generation is generally conducted in two successive stages. The first stage is frequency doubling of a near-infrared diode laser output, and the second stage is mixing the second harmonic with another or the same near-infrared diode laser. The nonlinear conversion efficiency can be increased by mode locking an external-cavity laser based on a high-power tapered semiconductor amplifier.[11,12,14] A spectral linewidth of about 100 GHz is usually obtained, and that is typically 100 times larger than the required resolution for spectroscopic measurements. Another method to increase the conversion efficiency is to place the nonlinear crystal in an external buildup resonator.[13] This generates relatively high UV powers ($\sim$2 mW), but suffers from limited continuous tuning range and increased system complexity.

Very recently Nichia Corporation introduced blue diode lasers[15] and we have studied the possibility to use them for potassium and lead spectroscopy.[16,17] At present we report on the generation of UV radiation around 254 nm for mercury spectroscopy based on frequency mixing of a blue diode laser and a red diode laser.

The setup for sum-frequency generation is shown in Fig. 1. The blue diode laser (Nichia NLHV500 with a nominal wavelength of 404 nm at 25 °C and a free-running output power 5 mW) was operated in a Littrow-type cavity that ensured single-mode operation and less sensitivity to back reflections. We used a Thorlabs system based on a diode laser mount (TCLDM9), a piezoelectric mirror mound (KC1-PZ) and a 2400 1/mm grating (Edmund Scientific 43224).
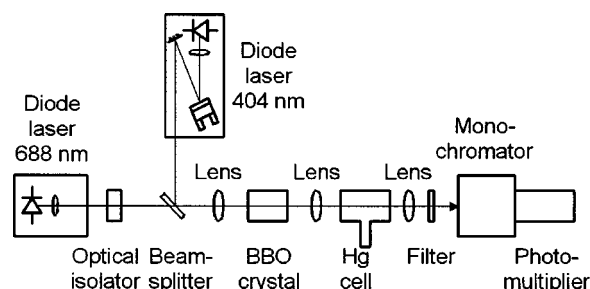

FIG. 1. Experimental setup for sum-frequency generation at 254 nm.

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[a]Also with the Institute of Atomic Physics and Spectroscopy, University of Latvia, Rainis Blvd. 19, LV-1586 Riga, Latvia.
[b]Electronic mail: sune.svanberg@fysik.lth.se

The output power with the laser operated in the external cavity was 1 mW. The single-mode red diode laser (Toshiba TOLD 9150, 688 nm, 30 mW) was free-running and could be scanned continuously over 35 GHz by a current ramp. Moulded glass aspheric lenses with $f = 4.5$ mm were used for collimation (Geltech C230TM). The diode lasers were temperature and current controlled using low-noise diode laser drivers (Melles Griot 06DLD 103). Both lasers were polarized vertically. An optical diode (OFR IO-5-NIR-I) was placed in the red diode laser beam to reduce backscattering from the nonlinear crystal. The blue and red beams were spatially overlapped via a dichroic beamsplitter and focused by a Nikon camera objective with a 50 mm focal length onto a 8-mm-long BBO crystal cut at $\theta = 49°$ and $\varphi = 90°$. Type I phase matching was achieved by tilting the crystal horizontally. A quartz lens of 50 mm focal length was used to collimate the UV light exiting the crystal. The detection side consisted of an $f = 50$ mm quartz lens, a 254 ± 10 nm interference filter, a monochromator (Oriel 77250) tuned to 254 nm, and a photomultiplier (EMI 9558 QA). Without the monochromator a strong background existed from the not converted red and blue laser light. The signal from the photomultiplier was sent to a transimpedance amplifier (Itacho 1212) and a preamplifier (Stanford Research 560) and further to a signal averaging oscilloscope (Tektronix TDS520B).

It was not possible to measure the UV light power directly and we estimated it by photon counting. At optimized setup $n = 5 \times 10^6$ pulses per second were counted. The quantum efficiency of the photomultiplier at $\lambda = 254$ nm is $\eta = 0.2$. That gives the UV power at the detector $P = nhc/(\lambda \eta) \approx 2 \times 10^{-11}$ W. The two quartz lenses, the interference filter, and the monochromator had a transmission of 0.84, 0.28, and 0.09, respectively, thus the UV power after the crystal was about 0.9 nW.

From the theory of sum-frequency mixing of focused Gaussian beams and assuming a lossless crystal, the UV power can be expressed as[18,19]

$$P_3 = \frac{4\omega_1 \omega_2 \omega_3 d_{\text{eff}}^3 P_1 P_2 l h}{\pi \epsilon_0 c^4 n_3^2}, \qquad (1)$$

where ω_i are the angular frequencies ($\omega_1 < \omega_2 < \omega_3$), P_i are the powers, n_i are the refractive indices of the crystal, d_{eff} is the effective nonlinear coefficient, l is the crystal length, and h is a dimensionless focusing parameter. The effective nonlinear coefficient was calculated to $d_{\text{eff}} = 1.59 \times 10^{-12}$ m/V according to the expressions in Ref. 20, and from the plots presented in Ref. 18 for the focusing parameter, we estimated $h = 0.01$. Using the measured input powers (measured after the camera objective lens to $P_1 = 0.76$ mW and $P_2 = 25$ mW) and accounting for the approximately 7% reflection losses at the crystal input and output faces, we calculated a theoretically generated UV power $P_3 = 1.9$ nW. We believe that the approximately 2 times smaller UV power experimentally observed is due to imperfect overlap of the two input beams.

The spectrum of a natural isotopic mixture of mercury contains 5 peaks, that are formed by 10 Doppler-broadened transitions.[21,22] An absorption signal from a low pressure quartz cell containing a natural mixture of mercury is shown in Fig. 2(a). The spectrum was recorded by sweeping the red
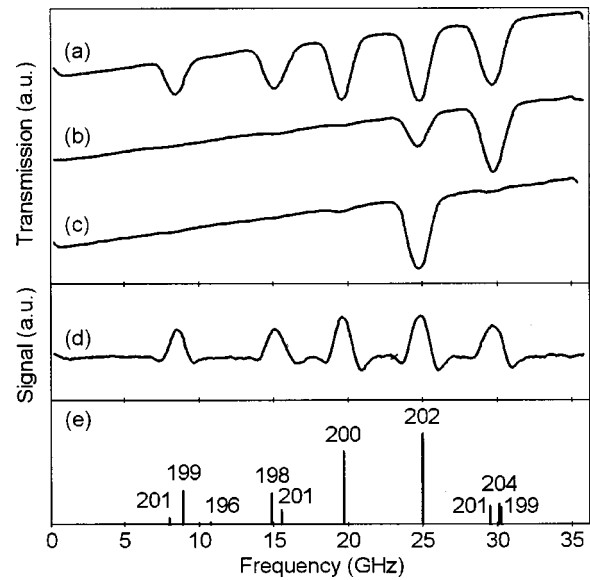

FIG. 2. Recorded UV absorption spectra from low pressure cells at -20 °C containing (a) natural isotope mixture of Hg, (b) enriched with ^{204}Hg, (c) enriched with ^{202}Hg, and (d) wavelength modulation signal from a natural isotope mixture of Hg. (e) Designation and relative strength of the Hg isotope lines according to Ref. 22.

laser 35 GHz, and that resulted in an equally long scan in the UV. The mercury cell had a finger that was cooled by liquid nitrogen, because at room temperatures there was a 100% absorption on all the peaks. Absorption signals from two isotopically enriched low pressure cells with ^{204}Hg and ^{202}Hg are shown in Figs. 2(b) and 2(c), respectively. As a reference the designation and relative line strength of the isotope lines are displayed in Fig. 2(e).

The possibilities to use wavelength modulation in the UV region were also explored. A modulation frequency of 5 MHz was applied to the red diode laser through a bias tee. At the detection side the photomultiplier signal was amplified by a high frequency preamplifier and mixed with a frequency-doubled 5 MHz signal (standard radio-frequency components from Mini Circuits). The output from the mixer was low-pass filtered at 1 kHz, amplified and fed to the oscilloscope. Figure 2(d) shows the recorded second-harmonic ($2f$) signal. We also recorded low-frequency wavelength modulation signals at a few kilohertz frequency by modulating the external cavity grating angle with a piezo. Two-tone frequency-modulation signals with a setup used by our group extensively[17,23–27] were also recorded. Usually frequency modulation techniques have higher sensitivity compared to direct absorption, because the detection bandwidth is moved to higher frequencies, where laser excess ($1/f$) noise is very low, resulting in shot-noise limited measurements. At very low laser power though, as in our case, it is no advantage to use frequency modulation instead of direct detection.

At atmospheric pressures the isotope lines broaden and overlap to form a single absorption feature.[6,7] A scan of about 80 GHz is required to record the absorption at atmospheric pressures. Using our mode-hop-free scanning interval of 35 GHz we have measured the whole mercury absorption feature by recording three separate but overlapping scans. The recorded spectrum is shown in Fig. 3 together with a reference spectrum from a low-pressure cell. It can be
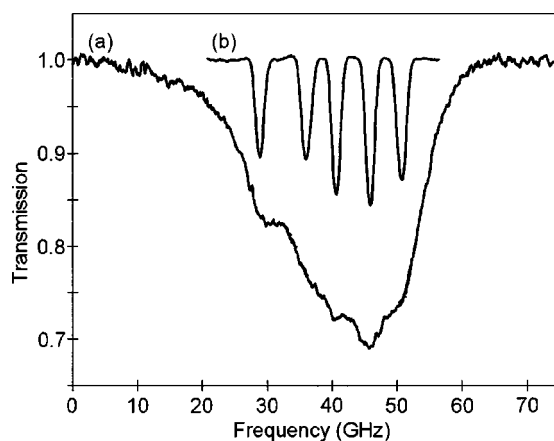
FIG. 3. (a) Hg absorption signal at atmospheric pressure in a 4 mm cell and (b) reference lines from a low pressure cell.

noted that since the isotope shifts are larger than the pressure-broadened linewidth (3.5 GHz obtained in a fit) individual isotope lines are clearly discernable in the recording at atmospheric pressure.

We have demonstrated the applicability of the recently available blue diode lasers for useful sum-frequency generation in the UV spectral region. High resolution absorption spectroscopy signals of mercury at 253.7 nm in a low pressure cell were recorded. Mercury detection at atmospheric pressure was performed, that is of great interest for trace element and environmental monitoring. The possibility to use different modulation techniques in the UV is demonstrated; however, at present the UV power is too low to give advantages over direct absorption monitoring. When higher UV powers become available through the fast development of diode lasers and nonlinear materials, the full power of our scheme combined with modulation techniques can be exploited.

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