Diode-laser-based sum-frequency generation of tunable wavelength-modulated UV light for OH radical detection

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Greater than 1.5 μW of tunable wavelength-modulated 308-nm radiation was generated by sum-frequency mixing of 90 mW of 835-nm diode-laser output and 1.5 W of 488-nm Ar^+ -laser output in a beta-barium metaborate crystal. Hydroxyl radicals formed in a discharge-flow reactor were detected by use of the generated UV beam by direct absorption, wavelength-modulation absorption spectroscopy, and laser-induced fluorescence. Wavelength modulation with second-harmonic detection yielded an estimated minimum detectable absorbance of 8.5×10^{-6} at a 1-Hz bandwidth. This absorbance level corresponds to an OH detection sensitivity of 11.7 parts per trillion for a 1-m path length at 1 atm and 298 K.

Quantitative high-sensitivity detection of trace species by use of high-frequency wavelength-modulation spectroscopy (WMS) with tunable diode lasers has been amply demonstrated.^{1,2} By the superimposition of high-frequency modulation onto the bias current of the diode laser, high-frequency WMS detection was demonstrated with minimum detectable absorbances of 10^{-6} or lower by use of visible,³ near-IR,^{4,5} and mid-IR² diode lasers.

This study stems from our interest in developing tunable wavelength-modulated UV sources for spectroscopic applications, whereby we can have access to strong electric-dipole transitions of small radicals and molecules. Most of the near-infrared diode-laser-based blue-green light generation schemes^{6,7} use resonant cavity designs to increase the circulating pump power, resulting in high doubling efficiency. The wavelength of the second-harmonic output, which is limited to longer than ~ 410 nm owing to the available near-IR diode lasers, cannot be readily tuned.

Sugiyama *et al.*⁸ reported 1 μW of sum-frequency output at 369 nm by mixing 21 mW of 1.31- μm distributed-feedback laser output and 1.3 W of 515-nm Ar^+ -laser output in a beta-barium metaborate (β -BBO) crystal employing single-pass transmission of the pump beams. Although the mixing efficiency may be low in single-pass transmission, one can readily tune and wavelength modulate a sum-frequency-generated UV beam by varying and modulating the diode-laser current. To our knowledge, however, diode-laser-based tunable UV radiation has not been used for high-frequency WMS. The hydroxyl (OH) radical was chosen as a target species for detection based on UV WMS because of its important role in atmospheric chemistry⁹ and combustion chemistry.¹⁰

Figure 1 shows the experimental arrangement used for UV generation from sum-frequency mixing. The 150-mW single-mode output from an 835-nm diode laser (Spectra Diode Laboratories) was collimated into an ~ 2 mm $\times$ 6 mm rectangular beam, passed through an optical isolator (Electro-Optics), corrected

for astigmatism, and circularized before being focused to a beam waist of ~ 33 μm ($1/e$ power diameter) with an $f = 20$ cm lens. Approximately 90 mW of 835-nm diode-laser power was available after the focusing lens.

An 8-W Ar^+ laser (Lexel 3500-8) was operated in a single-frequency mode with 1.5 W of 488-nm output by use of a temperature-stabilized intracavity étalon. A half-wave plate installed at the output end matched the output beam polarization to that of the diode-laser beam. We combined the Ar^+ beam with the diode-laser beam, using a dichroic mirror, and focused it to a beam waist ($1/e$ power diameter) of ~ 22 μm with an $f = 10$ cm lens. A 5- μm pinhole mounted on an XYZ translation stage was used to characterize the beam waists and to optimize overlap of the pump beams. The Ar^+ -laser power after the focusing lens was 95% to 98% of the initial output power.

A 4 mm $\times$ 4 mm $\times$ 7 mm β -BBO crystal (Cleveland Crystals), cut at $\Phi = 90^\circ$ and $\theta = 37.5^\circ$ for type I phase matching, was mounted upon a temperature-stabilized ($50.0 \pm 0.1^\circ\text{C}$) copper block to prevent any water condensation. The copper-block/thermoelectric cooler assembly was mounted onto a rotation stage for fine angular positioning.

Fig. 1. Experimental arrangement for sum-frequency mixing the 835-nm diode-laser beam with the 488-nm Ar^+ beam in a β -BBO crystal.

The output beams from the β -BBO crystal were first collimated with an $f = 5$ cm lens and then passed through a UV calcite polarizer (Karl Lambrecht) to separate the pump beams from the generated UV beam. Small residual amounts of the pump beams were attenuated further with a UV interference filter centered at 313 nm ($\sim 10\%$ transmission at 308 nm). A UV-sensitive Si photodiode (0.17 A/W sensitivity at 308 nm) was used in the photovoltaic mode with a lock-in amplifier to monitor the UV power level while the diode-laser beam was chopped mechanically.

Figure 2 shows the measured UV output power level as a function of the 488-nm Ar^+ -laser power while 90 mW of 835-nm diode-laser power at the β -BBO crystal was maintained. Accounting for the 10% transmission of the interference filter at 308 nm, coupled with the 0.17 A/W detector responsivity, we estimate that $1.5 \mu\text{W}$ of UV power was generated when the Ar^+ -laser power was 1.5 W. This estimate does not account for any losses of the UV beam within the β -BBO crystal, collimating lens, or calcite polarizer. If a total UV power loss of $\sim 40\%$ is estimated ($\sim 4\%$ loss per surface for ten surfaces), we may have generated as much as $2.5 \mu\text{W}$ of UV power when mixing 1.5 W of 488-nm and 90 mW of 835-nm beams.

The theory of sum-frequency mixing of focused Gaussian beams was developed by Boyd and Kleinman.¹¹ Sugiyama *et al.*⁸ showed that the UV output power (P_3) may be expressed as

$$P_3 = 4\omega_1\omega_2\omega_3 d_{\text{eff}}^2 \exp(-\alpha^* l) P_1 P_2 l h / (\pi \epsilon_0 c^4 n_3^2), \quad (1)$$

where ω_i is the angular frequency for which $\omega_1 < \omega_2 < \omega_3$, d_{eff} is the effective nonlinear susceptibility, $\alpha^* = (\alpha_1 + \alpha_2 - \alpha_3)/2$ is a effective absorbance,⁸ l is the crystal length, h is the dimensionless focusing function, and n_3 is the index of refraction of the crystal at the UV wavelength. Using the expression given by Nikogosyan,¹² we calculated d_{eff} at the phase-matching angle to be 1.9 pm/V. A value of 0.03 was estimated for the focusing function h based on plots presented by Boyd and Kleinman,¹¹ and, using these values in Eq. (1), we calculated a generated UV beam power P_3 of $12 \mu\text{W}$.

This calculation assumes the most favorable mode-matching condition, and it does not include any losses of the UV power. If the estimated cumulative reflection loss of 40% is applied, then $\sim 7.2 \mu\text{W}$ of UV power is expected at the detector. The experimentally observed UV power is approximately five times smaller, presumably as a result of less-than-optimum focusing of the diode-laser beam and imperfect overlap of the pump beams in the β -BBO crystal.

We generated the OH radical by reacting F atoms with excess H_2O in a low-pressure discharge-flow reactor. This flow reactor was used previously to measure room-temperature line strengths of the HCO radical and was described in detail elsewhere.³ For OH radical detection using the UV beam in the flow reactor, we used a single optical pass transverse to the flow direction. The reactor side arms were fitted with wedged windows to provide optical access for the UV beam. Ar purge flows in the side arms

confined the gas mixture to form a well-defined probe volume with minimum radical residence time. We estimated the confined flow diameter to be 5 cm by measuring an H_2O absorption feature with an In-GaAsP distributed-feedback laser diode near $1.51 \mu\text{m}$ with and without the Ar purge.

The diode-laser wavelength was current tuned for access to the $Q_1(1) + Q_{21}(1)$ line pair in the (0,0) band of the OH $A^2\Sigma^+ \leftarrow X^2\Pi$ transition. Figure 3 shows the resulting spectra of OH obtained by direct absorption, wavelength modulation ($2f$), and laser-induced fluorescence (LIF) emission detection. For direct-absorption measurements the detector photocurrent was low-pass filtered and amplified with a low-noise preamplifier. For wavelength-modulation detection the diode laser was sine-wave modulated at 40 kHz, and $2f$ detection was performed with a digital lock-in amplifier (Stanford Research Systems 8360). The OH LIF signal was collected with a three-element $f/1.5$ lens and imaged into a photomultiplier tube (Hamamatsu H5783-03). The photocurrent from the photomultiplier tube was monitored as the voltage drop across a 100-k Ω load resistor, which was low-pass filtered and amplified.

Fig. 2. Observed UV power from sum-frequency mixing as a function of Ar^+ pump power (835-nm diode-laser power fixed at 90 mW).

Fig. 3. Spectra of the $Q_1(1)$ and $Q_{21}(1)$ line pair of the (0,0) band of the OH $A^2\Sigma^+ \leftarrow X^2\Pi$ transition recorded with direct absorption, $2f$ WMS, and LIF emission detection.

A computer-controlled waveform generator (Qua-Tech) provided sawtooth current ramps for repetitive sweeps of the diode-laser wavelength, and a fast analog-to-digital board (Analog Devices RTI-860) digitized and averaged the spectra before storing them in a computer. Each wavelength sweep consists of 512 data points, acquired with a dwell time of 50 μ s per point. The spectra shown in Fig. 3 resulted from coadding 200 such scans, resulting in an effective detection bandwidth per bin of 100 Hz. The direct-absorption spectrum and the LIF spectrum in Fig. 3 were taken simultaneously, followed by the $2f$ WMS spectrum.

The absorption at line center of the $Q_1(1)$ line was measured to be 6.3%. We estimated the signal-to-noise ratio (SNR) at the 100-Hz detection bandwidth used in these experiments for both direct-absorption detection and $2f$ WMS detection by noting the ratio of the signal level at the center of the $Q_1(1)$ absorption line to the baseline noise. For direct-absorption detection we observe a SNR of 42, whereas the result for $2f$ WMS is a SNR of 740. The corresponding minimum detectable absorbances (SNR of 1) at the 100-Hz bandwidth are 1.5×10^{-3} (direct absorption) and 8.5×10^{-5} ($2f$). Assuming that the SNR improves with the square root of averaging time, the estimated minimum detectable absorbance at a 1-Hz bandwidth for $2f$ detection is 8.5×10^{-6} . For comparison, the observed SNR of the OH LIF spectrum at the 100-Hz bandwidth was 1.7×10^4 .

With 0.65 μ W of 308-nm radiation at the Si photodiode the detector shot noise is estimated to be equivalent to 1.7×10^{-6} absorbance and the thermal noise to be equivalent to 1.4×10^{-8} absorbance at the 1-Hz detector bandwidth. Detection sensitivity may be improved by use of a photomultiplier tube to measure the absorbance. We can realize further improvement in the $2f$ WMS detection sensitivity by increasing the modulation frequency to 500 kHz or higher, where the $1/f$ source noise was observed to level off.

The concentration of OH radicals giving rise to 6.3% peak absorbance at the $Q_1(1)$ line can be calculated by use of Beer's law. A value of $\sigma = 5.08 \times 10^{-16}$ cm² per molecule for the line-center absorption cross section was obtained from the Einstein A coefficient (4.108×10^5 s⁻¹) for the $Q_1(1)$ line¹³ with an assumed Doppler-limited line shape at 298 K and 2 Torr.¹⁴ For an absorption path length of 5 cm we obtain $N = 2.5 \times 10^{13}$ molecules/cm³ for the OH radical concentration in the confined flow. With 8.5×10^{-6} at the 1-Hz detection bandwidth as the minimum detectable absorbance, an OH detection sensitivity of 3.3×10^9 molecules/cm³ is inferred for the 5-cm path length. At 1 atm and 298 K, for which a value for the $Q_1(1)$ line-center absorption cross section of 3×10^{-16} cm² per molecule is estimated, we arrive at an OH detection sensitivity of 11.7 parts per trillion for a 1-m path length.

Daytime concentrations of OH in the clean troposphere are generally believed to be in the low 10^6 cm⁻³ range. Recent long-path absorption detection of tropospheric OH by Mount¹⁴ showed daytime values as high as 8×10^6 cm⁻³. With an absorption path length of 150 m or more, we believe that quantitative measurement of tropospheric OH concentrations will be possible by use of this UV light source with high-frequency WMS.

In conclusion, we have demonstrated the feasibility of implementing high-frequency WMS in the UV wavelength region by generating a tunable wavelength-modulated UV beam by means of sum-frequency mixing Ar⁺-laser and diode-laser outputs. High detection sensitivity by use of high-frequency WMS is demonstrated by the measurement of OH radicals formed in a low-pressure discharge-flow reactor. Given an optical path length of 150 m or more, quantitative measurement of tropospheric OH seems possible.

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