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Sum frequency generation at 309 nm using a violet and a near-IR DFB diode laser for detection of OH

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ABSTRACT We have used a violet diode laser at 404 nm and a distributed feedback diode laser at 1320 nm to produce 0.8 nW of radiation at 309 nm by sum frequency generation in beta-barium borate. The UV radiation was tuned mode-hop-free over 30 GHz and used to detect OH radicals produced in a microwave discharge. By chopping the UV light at 500 Hz, we observed a concentration of 2×10^{12} cm^{-3} with a signal to noise ratio of 30 : 1.

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1 Introduction

The hydroxyl (OH) radical is one of the most important species in atmospheric chemistry [1], as its high reactivity dominates the daytime oxidation of many trace species in the troposphere. Knowledge of the concentration of OH in the atmosphere is thus extremely important for a quantitative understanding of tropospheric chemistry, but its measurement presents a technical challenge, as its reactive nature means it is present in the atmosphere at a very low concentration, of the order of 10^6 cm^{-3}. Observation of the radical is generally based either on direct-absorption or laser-induced-fluorescence techniques using frequency-doubled dye lasers to probe the strong electronic transition of OH near 308 nm [2–5], but these systems are bulky, heavy and expensive. Thus there is interest in finding a source of radiation at 308 nm utilising cheaper and lighter diode lasers. The output of a near-infrared (NIR) diode laser has been mixed with that of an argon-ion laser to produce 1.5 μW of radiation at 308 nm [6], but this still requires the relatively expensive and bulky Ar^+ laser. Previously, our group has demonstrated the first all-diode-laser-based source of tunable 308-nm light by frequency-doubling a cooled red laser [7], but this has the disadvantage of low output power and the necessity of cooling the diode to 165 K. In this paper we report an alternative approach, namely mixing the output of a violet diode laser at 404 nm and a distributed feedback (DFB) laser operating at 1320 nm in a crystal of beta-barium borate (BBO) to produce light at 309 nm. Recently available violet diodes have been successfully used in frequency-mixing experiments to produce UV light at 254 nm for mercury spectroscopy [8], thus demonstrating their utility in extending the range of wavelengths available by sum frequency generation (SFG) of diode lasers into the UV. DFB lasers have the advantage of tuning continuously with current or temperature, thus obviating the need to construct an external cavity, as with normal diode lasers, in order to achieve mode-hop-free scanning. In this paper we describe the generation of 309-nm radiation by mixing these two lasers in a crystal of BBO, and its use in the detection of OH by single-pass direct absorption in a flow cell.

2 Experimental

The experimental set-up used for SFG and subsequent OH detection is shown in Fig. 1. The violet diode laser (Nichia NLHV500C) was used in a home-made Littrow-geometry arrangement based on the design of Arnold et al. [9]. A collimation tube and lens antireflection-coated for the violet (Thorlabs LT110P5-A) were used, held in an adapted Newport Ultima U100-P mirror mount. A 3600 l/mm holographic grating (Edmund Scientific) was glued to a piezo-disc and mounted in a Littrow configuration with the laser diode. We did not observe a clear decrease in the lasing threshold for the violet diode (which remained at ∼ 33 mA), but the efficiency of the grating was only 30% into the first order. In

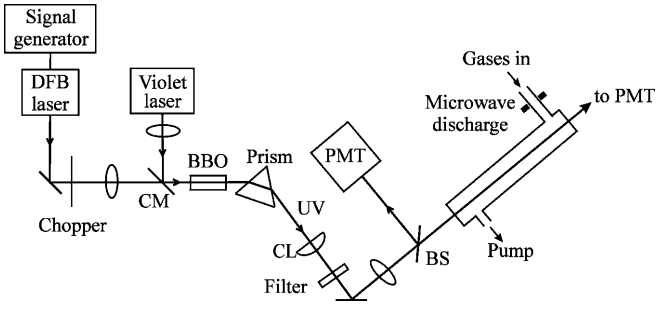

FIGURE 1 Schematic diagram of the apparatus. DFB = distributed feedback laser, CM = cold mirror, BBO = beta barium borate mixing crystal, CL = cylindrical lens, BS = beam splitter, PMT = photomultiplier tube

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a similar experiment with a violet laser diode in a Littrow geometry, Conroy et al. [10] observed no decrease in lasing threshold with a 30% efficient grating, and a reduction from 27 to 26.4 mA for a 55% efficient grating. It therefore seems likely that there is not enough feedback from our grating to reduce the threshold measurably (the smallest increment of our current controller being 0.1 mA). The laser was driven at 35.6 mA, producing 0.56 mW in the output beam off the grating, reduced to 0.47 mW just in front of the mixing crystal. It was operated just above threshold, even though the power produced was small compared with the maximum quoted output of 5 mW, because we found that at higher currents the laser tended to become unstable, jumping between modes despite being held at constant temperature and current. Run at 35.6 mA, the laser produced a single stable mode at 403.5 nm, as verified using a wavemeter (Burleigh WA5500). It was mounted on a brass block for thermal stability and driven by home-made current and temperature controllers.

The 1320-nm DFB diode laser (Marconi, quoted bandwidth < 2 MHz) was also mounted on a brass block, thermally stabilised and collimated using a standard lens. It operated free-running in a single-frequency mode with a threshold current of 29 mA, and could be tuned mode-hop-free over nearly 3 nm by current and temperature tuning as shown in Fig. 2. Both lasers were polarised vertically such that they were ordinary beams in the BBO crystal for type I phase matching.

The two beams were combined through a cold mirror and focused into a $7 \times 4 \times 4\,\mathrm{mm}^3$ crystal of BBO, which was cut for type I phase matching at $\theta = 32.7°$, $\varphi = 90°$. There was no optical isolation in either beam path but, although the beams were incident normally on the crystal, we did not observe any instability that might have been caused by feedback into the lasers. The violet laser beam, which had an elliptical beam shape of $\sim 2.3 \times 1.5\,\mathrm{mm}^2$, was focused into the crystal using a 10-cm focal length lens a distance 10.3 cm from the crystal. The DFB laser, which had an elliptical beam shape of $\sim 1 \times 4\,\mathrm{mm}^2$, was focused using a second 10-cm focal length lens, which was mounted on a translation stage and adjusted to optimise the UV output by improving the overlap between the focused regions of the beams along the crystal axis. Maximum UV output was found with the lens 10.7 cm from the crystal.

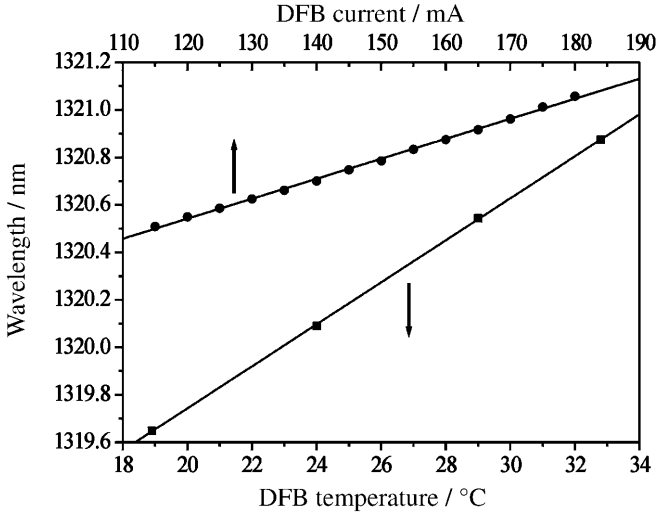

FIGURE 2 Variation of the wavelength output of the DFB laser with current (*filled circles, upper horizontal scale*) at a temperature of 32.8 °C, and with temperature (*filled squares, lower horizontal scale*) at a current of 160 mA. Mode-hop-free operation is seen over these ranges

We measured an output of 0.4 nW in the UV which, allowing for losses through the interference filter and at the surfaces of the optical components, means 0.8 nW was generated inside the crystal. From the theory of SFG using optimised focused Gaussian beams [11, 12] for a lossless crystal, the UV power may be expressed as

$$P_3 = \frac{4\omega_1\omega_2\omega_3 {d_{\mathrm{eff}}}^2 P_1 P_2 l h}{\pi\varepsilon_0 c^4 {n_3}^2} \tag{1}$$

where ω_i ($\omega_1 < \omega_2 < \omega_3$) are the angular frequencies, P_i are the powers, $n_3 = 1.59$ is the refractive index of the crystal at 309 nm, d_{eff} is the effective non-linear coefficient, l is the crystal length and h is a dimensionless focusing parameter. Using input powers measured before the crystal of $P_1 = 35$ mW and $P_2 = 0.47$ mW, $d_{\mathrm{eff}} = 2.0$ pm/V [13] and a value of $h = 0.05$ estimated from [11], we find a theoretical UV output of 6.6 nW. We attribute the difference between the theoretically predicted and observed intensities to be due to imperfect beam overlap in the crystal and non-optimal spatial beam properties of the lasers. It was not possible to measure the bandwidth of the UV output directly, but we conclude that it will be dominated by that of the violet laser. GaN lasers in similar configurations have been measured recently to have bandwidths of 5 MHz [10] and 8.3 MHz [14], larger than the quoted bandwidth of the DFB laser (< 2 MHz), and thus we estimate an upper limit of ~ 10 MHz for the 309-nm radiation. This is some three hundred times smaller than the line width expected for the OH radical, as discussed in Sect. 3.

The three beams exiting the crystal were separated using a quartz prism, and scattered violet light removed from the beam path using an interference filter. The UV beam was found to be elliptical, and was focused in the vertical plane using a 9-cm focal length cylindrical lens before passing through a 50-cm focal length quartz lens into a 1.5-m flow tube. Prior to entering the flow cell, 1% of the generated UV radiation was reflected onto a reference photomultiplier tube (PMT) (EMI9813QB) to allow monitoring of the incident power. OH radicals were produced using a 2.45-GHz microwave discharge in a He/H_2O mixture at total pressures of between 3 and 10 Torr. Light exiting the flow cell passed through three irises and a filter, which reduced the noise observed from the discharge, and was focused onto another PMT (EMI9125Q).

Direct-absorption measurements were taken by applying a ±10-mA triangular-wave ramp to the injection current of the DFB laser at 12 Hz. This scanned the DFB frequency over 30 GHz, observed using a spectrum analyser (Melles Griot, 10 GHz), corresponding to 30 GHz in the UV. The PMT signal was then averaged over 50 scans using a digital oscilloscope (LeCroy 9304, quad 175 MHz). The background was then fitted assuming a fourth-order polynomial variation in the incident light, and removed from the traces. Without averaging the direct-absorption scans, fluctuations in the background disguised the peaks.

In order to increase the sensitivity of our measurements, the IR beam was mechanically chopped at 500 Hz, resulting in modulation of the UV at the same frequency. In these experiments the DFB laser was scanned at 12.5 mHz, over 30 GHz as before, and the signals from the PMTs demodulated using lock-in detection (Perkin Elmer 7265) with a time constant of 1 s. Once again, the background was fitted and removed. In both the direct and the modulated cases, the resulting absorption profiles were fitted using Gaussians.

3 Results

The OH radical was detected by absorption on the $Q_{22}(2)$ and $Q_{22}(3)$ lines of the $A^2\Sigma^+ - X^2\Pi(0,0)$ band. This notation gives $\Delta J_{F(u)F(l)}(N(l))$, where u, l correspond to the upper and lower levels, and F gives the relationship between the two angular-momentum quantum numbers, N and J, in those levels [F_1 for $J = N - 1/2$, F_2 for $J = N + 1/2$]. These Q_{22} transitions correspond to $\Delta J = 0$, $J = N - 1/2$ in both the upper and lower levels, and $N = 2$ or $N = 3$ respectively. As they lie close together at 309.075 nm and 309.076 nm, they give a distinctive partially overlapping line shape. These lines were those with the highest cross sections in the region of the spectrum accessible using the two diodes. The highest cross section for a room-temperature sample of OH is for the $Q_{11}(2)$ line at 308 nm, a wavelength which would be possible to produce with diodes emitting at slightly different wavelengths from those available here. This project is being pursued currently in our laboratory.

A typical absorption profile obtained using the 500-Hz modulation and lock-in amplifier is shown in Fig. 3. A linear increase in frequency with current, and hence time, was verified using the spectrum analyser, enabling conversion of the x-axis scale to frequency by assuming the central frequencies of the transitions [15]. The solid lines show a fit of a Gaussian profile to each of the absorption peaks, and a fit to the entire data. Pressure broadening under the conditions of Fig. 3 (8.2 Torr Ar) contributes only 2.5% of the total line width, and was thus neglected in the data fitting. The widths of the two profiles in the figure are found to be the same within experimental error, giving a Doppler width of 3 GHz as expected at room temperature. The ratio of the width to their separation is 0.55, which gives good agreement with the known separation in frequency of the lines and their Doppler width.

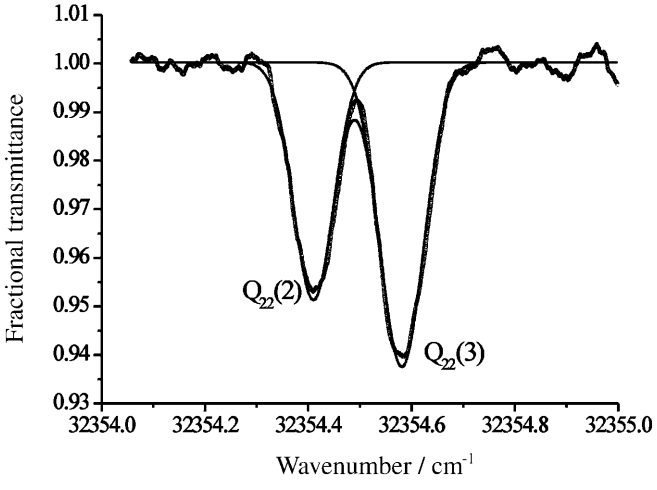

FIGURE 3 Fractional transmittance of the UV radiation through a sample containing OH produced in a microwave discharge of a He/H_2O mixture at a total pressure of 8.2 Torr. The two features observed are the $Q_{22}(2)$ and $Q_{22}(3)$ lines of the $A^2\Sigma^+ - X^2\Pi(0,0)$ band, and the fit is to a room-temperature sample of the radical at thermal equilibrium

A 50-scan-average direct-absorption measurement with no chopping showed a 7.2% $Q_{22}(3)$ absorption and a signal to noise (S/N) ratio of 25 : 1 (peak signal to rms baseline noise), whilst with a slightly lower OH concentration a single-scan chopped signal gave only a 4.9% $Q_{22}(3)$ absorption but an improved S/N ratio of 30 : 1, thus demonstrating a minimum detectable absorption in the modulated case of 0.18%.

Using the approach of Dorn et al. [16], spectral line parameters from Goldman and Gillis [15] and a 300-K Boltzmann distribution for the populations of the energy levels of OH, the absorption cross sections of the $Q_{22}(3)$ and $Q_{22}(2)$ lines were calculated to be 2.25×10^{-16} cm^2 and 2.07×10^{-16} cm^2 respectively at their line centres and under Doppler-broadened conditions. The natural logarithms of the fractional transmittance at the frequencies of these two lines are found to be in the ratio of their cross sections, as expected. Assuming a path length of 1.5 m gives OH concentrations within the flow tube of $2–3 \times 10^{12}$ cm^{-3}. The modulated detection method gives a detectivity of 9×10^{10} cm^{-3} for a S/N ratio of 1 : 1 in 80 s. Our relatively high noise level in the experiment appears to be caused by fast amplitude fluctuations in the violet-laser output.

4 Conclusions

Radiation at 309.1 nm has been produced from sum frequency mixing the output of two diode lasers, and has been used to detect the OH radical by absorption spectroscopy. A detectivity of 9×10^{10} cm^{-3} for a S/N ratio of 1 : 1 has been achieved, which is five orders of magnitude less sensitive than required for atmospheric detection. We note however that we have used a very simple modulation technique: we would expect a marked increase in sensitivity by frequency- or wavelength-modulation spectroscopy and this is being pursued currently. In addition the detectivity may be increased by the use of higher-power violet diodes, the construction of an external cavity around the crystal to enhance the UV production and the use of a longer detection path, e.g. by placing mirrors around the flow cell.

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