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# OH detection by absorption of frequency-doubled diode laser radiation at 308 nm

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## Abstract

Radiation at 308 nm has been obtained by frequency doubling the output of a commercial diode laser cooled to 165 K. A single pass through a crystal of  $\text{LiIO}_3$  converted 1 mW of 616 nm radiation to 50 pW of UV, and this was used to detect the OH radical in absorption in a flow tube. Possible extensions of the method for detection of OH in the atmosphere are discussed. © 2000 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Detection of the OH radical is of crucial importance in both fundamental and applied gas-phase studies. The highly reactive species plays an essential role in both atmospheric [1] and combustion [2] chemistry, and it has become one of the most commonly observed products of quantum state resolved experiments designed to measure detailed reaction dynamics [3]. Observation normally relies on either absorption or laser-induced fluorescence (LIF) on the  $A^2\Sigma^+ - X^2\Pi$  transition in the near UV [4], a region where frequency-doubled tunable dye lasers can be operated efficiently in both pulsed and cw modes. Both types of dye laser have been used near 308 nm in the important and demanding application of atmospheric detection of OH at concentrations of the order of  $10^6 \text{ cm}^{-3}$  in the troposphere [5–11]. Such

lasers however are bulky and expensive, and the lack of a suitable alternative 308 nm source has meant that only a small number of atmospheric OH detection systems operate world wide.

Absorption strategies involving the injection of narrow band radiation into resonant cavities have been shown to yield ultrasensitive detection limits. In 1996 Hall showed that when absorption in a 60 cm long resonant cavity was measured by frequency modulation (FM) techniques, a fractional absorption of 1 part in  $10^{10}$  could be detected in 1 s with unity S/N ratio [12] and this limit has recently been extended by a factor of 50 [13]. Increased effective pathlength within the cavity is the key to the increased sensitivity, in a similar but improved way to that gained by cavity ring-down spectroscopy, already applied with pulsed lasers to OH detection [14–18]. For tropospheric OH the 1 in  $10^{10}$  criterion would translate to measurement of a concentration of  $10^4 \text{ cm}^{-3}$  in a 60 cm path, and thus in principle the technique would offer sufficient sensitivity for it to

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be used in atmospheric observations. A simple and compact cw UV source which could be frequency modulated and injected into a cavity would be an advantage for such applications. Here we describe the production of coherent 308 nm radiation by frequency doubling the output of a cooled semiconductor diode laser, and its use in the detection of OH by single-pass absorption in a flow tube.

## 2. Experimental

The short-wavelength limit of commercial diode lasers operating at room temperature (with the exception of the recently available GaN lasers around 400 nm [19]) is near 635 nm (for an AlGaInP diode structure). Cooling a diode laser leads to an increase in the band gap and thus operation at a shorter wavelength [20]. A 635 nm (Hitachi HL 6314 MG, output 5 mW at room temperature) was removed from its hermetically sealed can and mounted on a brass block equipped with a resistance heater and platinum resistance thermometer. The block was separated from a liquid N<sub>2</sub> filled Dewar by a Delrin spacer, and variation of the power to the heater resulted in a temperature which could be controlled with a precision of  $\pm 1$  mK over the range 290–77 K. The output was frequency doubled by a

single pass through an 8 mm long crystal of LiIO<sub>3</sub>, separated from the fundamental by reflection from dichroic mirrors, and passed into a flow cell of length 1 m. The radiation was chopped at 2 kHz, and the signals before and after the flow tube measured with photomultipliers and processed with lock-in detection. OH radicals were produced from either the reaction of H atoms (from a microwave discharge in H<sub>2</sub>/Ar) with NO<sub>2</sub>, or from a discharge in a He/H<sub>2</sub>O mixture, both at total pressures between 2 and 10 Torr. Fig. 1 shows the experimental arrangement. At a given temperature, ramping the diode laser current allowed its fundamental output wavelength to be varied by typically 0.04 nm before the laser hopped to a different longitudinal mode, causing a jump in wavelength. The output was monitored with both a spectrum analyser (TecOptics V4523) and a wavemeter (Burleigh WA1000) to ensure mode hops were absent and to determine the relationship between laser current and wavelength.

## 3. Results

Fig. 2 shows the variation of diode laser's output wavelength with temperature. The expected decrease of wavelength with temperature is observed, with mode hops clearly apparent, and it can be seen that

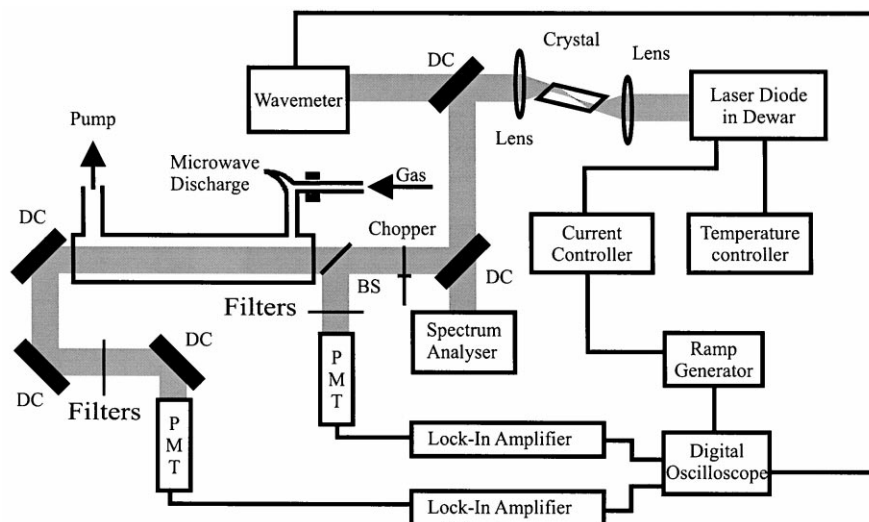


Fig. 1. Experimental arrangement for production of 308 nm radiation and detection of OH in a flow system. PMT = photomultiplier tube; DC = dichroic reflector, BS = beamsplitter.

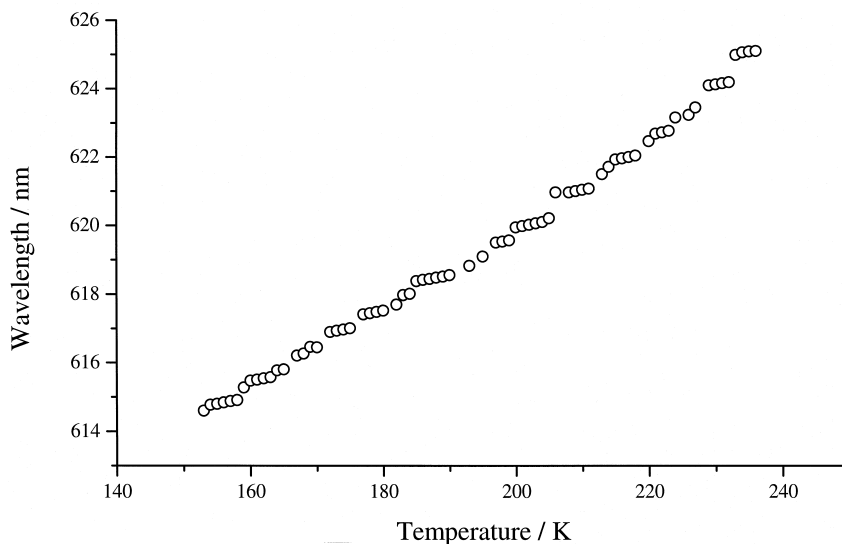


Fig. 2. Temperature tuning curve of the diode laser. The current was varied in this experiment from 55 mA at 290 K to 12 mA at the lowest temperature studied, 153 K. Mode hops can be seen as jumps in the wavelength at specific temperatures, and these restricted the tuning range of the laser as explained in the text.

the required wavelength of 616 nm is reached at a temperature of 165 K. The laser current threshold showed a monotonic decrease with decreasing temperature, attributable to a reduction in the leakage of thermally excited electrons out of the heterojunction region as the temperature is lowered [21,22]. Values ranged from 20 mA at 290 K to 9.5 mA at 153 K. At 616 nm the laser slope efficiency ( $dP_{\text{out}}/dP_{\text{in}}$ , where  $P_{\text{out}}$  is the laser output and  $P_{\text{in}}$  the electrical power applied) was linear over the output range 0–1 mW at a value of 0.24. A maximum output value of 2.5 mW was achieved. Although a continuous wavelength tuning range near 616 nm could not be obtained because of mode hops (the laser was operated without grating feedback control), the available range was sufficient for the observation of isolated OH features following frequency doubling.

Several materials have been evaluated for frequency-doubling diode laser radiation near 635 nm, and although  $\text{LiIO}_3$  appears to have the highest second-harmonic conversion efficiency [23], its use in this wavelength region has been questioned because of its UV absorption between 300 and 350 nm caused by colour centre impurities [23,24]. In the present experiments an output power of 1 mW at 616 nm yielded  $\sim 50$  pW of doubled radiation at 308

nm, a conversion efficiency about an order of magnitude lower than that calculated for an optimally focused Gaussian beam in the crystal. Our UV reflection loss at the crystal output face was estimated to be 30%, and the remaining difference between measured and optimal second-harmonic generation efficiencies may be caused by a combination of absorption losses and poor beam quality. Signal levels however were ample for OH detection. The radical was identified spectroscopically by absorption on the  $P_{11}(1)$ ,  $Q_{11}(3)$  and  $P_{21}(3)$  lines of the  $A^2\Sigma^+ - X^2\Pi(0,0)$  band. Here the spectroscopic notation is  $\Delta J_{F(u)F(l)}(N(l))$ , where  $F(u)$  and  $F(l)$  give the relation between the angular momentum quantum numbers  $J$  and  $N$  ( $F_1$  for  $J = N + 1/2$ ,  $F_2$  for  $J = N - 1/2$ ) for upper ( $u$ ) and lower ( $l$ ) levels. Fig. 3a shows the photomultiplier signals before and after absorption with a single scan of the diode laser output between 308.153 and 308.164 nm, produced by a 2.3 mA linear increase in current applied to the diode laser over a period of 20 s, with the output passed through the doubling crystal but without simultaneous angle tuning. Marked on the figure are the positions expected for absorption at line centre of the  $Q_{11}(3)$  transition and its  $P_{21}(3)$  satellite, and, when the data were corrected for background varia-

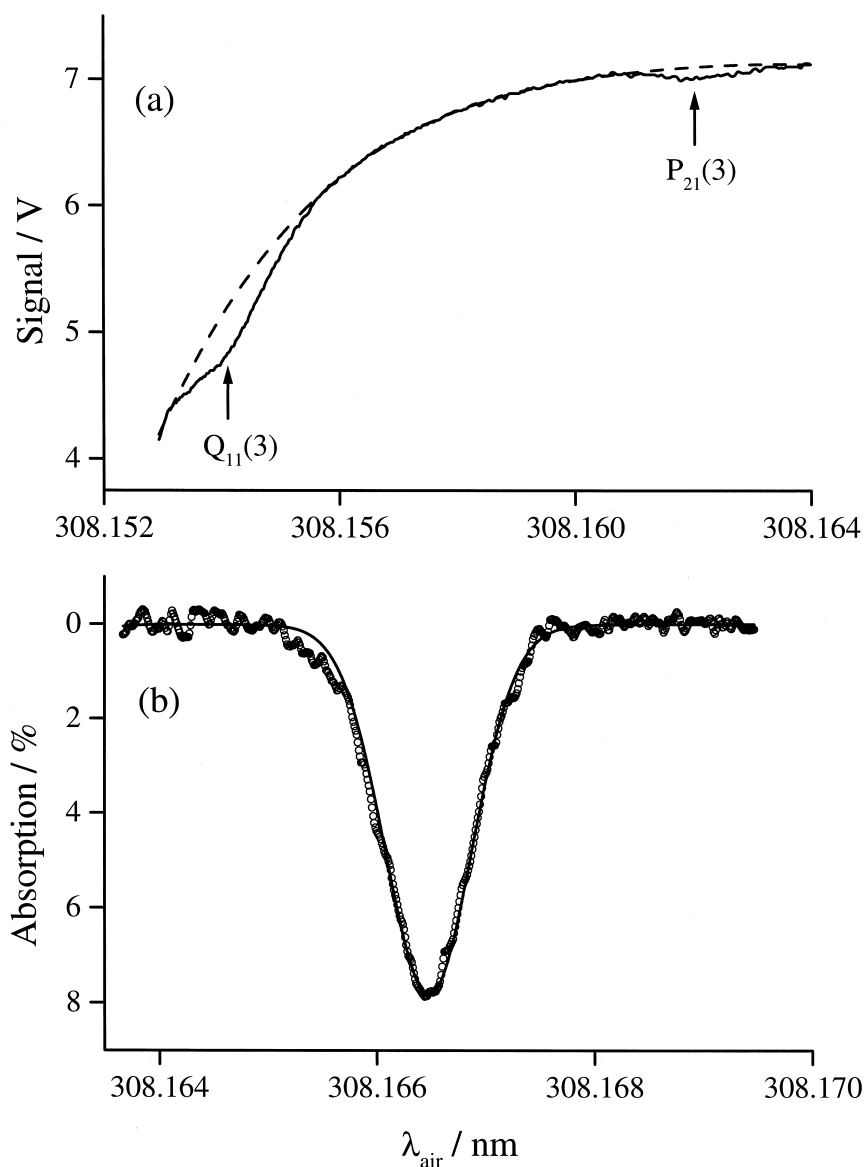


Fig. 3. Absorption spectrum of the OH radical near 308.16 nm. The upper trace, (a), shows a single scan of the diode laser producing frequency doubled output between 308.153 and 308.164 nm. Traces before (dashed line) and after (solid line) passing through the flow tube show absorption features identified as the  $Q_{11}(3)$  and  $P_{21}(3)$  transitions in OH. The lower trace, (b), shows the background corrected absorption on the  $P_{11}(1)$  feature of OH at 308.1665 nm, with the solid line a simulation for absorption by a room temperature sample at 10 Torr total pressure.

tion the peak heights were in the ratio expected from the relative line strengths of the two transitions from the  $F_1$   $N=3$  lower level. Fig. 3b shows an average of four scans at a slightly higher wavelength indicating absorption on the  $P_{11}(1)$  transition at 308.1665

nm, with the solid line showing a simulation of the Voigt lineshape expected for a 300 K sample at a total pressure of 10 Torr He [25]. From the absorption cross-section data [25] the product of total OH concentration and path length is calculated to be

$2 \times 10^{14} \text{ cm}^{-2}$ , from which we estimate an OH concentration averaged along the flow tube of  $2 \times 10^{12} \text{ cm}^{-3}$ . The major source of noise on the data shown in Fig. 3 originates from the microwave discharge. Scattered photons were two orders of magnitude higher in intensity than the 308 nm radiation formed from the laser, and electrical noise contributed to the varying baseline.

#### 4. Discussion

Although diode lasers have been used in the past to produce 308 nm radiation (by mixing the 835 nm output of a diode laser with 488 nm  $\text{Ar}^+$  radiation in a crystal of BBO [26]), we are not aware of previous reports of formation of this wavelength by straightforward frequency doubling. For operation as a sensitive detection scheme in absorption we note that an output larger than the present 50 pW level is needed, but this will be able to be attained in a resonant doubling cavity such as has been extensively used with  $\text{LiIO}_3$  as the non-linear medium at longer wavelengths [27–30]. Doubling efficiencies depend upon both wavelength and input powers, and we give examples of generation of 44 mW at 410 nm from 600 mW of Ti:sapphire radiation [27] and 18  $\mu\text{W}$  at 370 nm from 10 mW of diode laser radiation [28]. Although we have used a commercial diode laser in these experiments, we are aware of research devices which operate at or close to room temperature at the required wavelength [22,31,32], albeit with relatively high threshold currents. Furthermore, with the recent availability of diode lasers near 400 nm [19], generation of 308 nm radiation by mixing the outputs of two diode lasers in a non-linear crystal becomes a possibility. For FM detection within a resonant cavity we shall need to produce modulation in the UV. FM of the diode laser fundamental output can be carried out directly by current modulation, and this can be efficiently extended into the frequency-doubled region by modulation such that both the carrier and sidebands are resonant with the doubling cavity: we have demonstrated this by modulating a 680 nm diode laser at 1.3 GHz, the free spectral range of the doubling cavity containing the  $\text{LiIO}_3$  crystal. We note that although the sensitivity of resonant cavity

absorption at 308 nm should be adequate for the observation of tropospheric OH, there are major problems of overlapping absorptions (from  $\text{SO}_2$ ,  $\text{H}_2\text{CO}$  and naphthalene) near the OH transitions [8]. Furthermore, the enhanced 308 nm radiation levels in a resonant cavity can lead to OH formation through reactions of  $\text{O}(^1\text{D})$  produced from the photolysis of ozone [8]. If these problems can be overcome, the use of this relatively straightforward way of generating 308 nm radiation from a compact laser system should lead to the development of a light, portable easily electrically controlled OH monitor for atmospheric applications. Absorption methods have already been used in measurements of the nascent lineshapes of products formed by photodissociation [33] and chemical reactions [34], and we anticipate that a 308 nm source will aid in the extension of these studies to the OH radical.

#### 5. Conclusions

Radiation at 308 nm has been produced from frequency doubling the output of a commercial diode laser cooled to 165 K, and has been used to detect the OH radical in absorption. The method of generating coherent light at this wavelength from a simple and compact device may find use in a detection method for the radical in the atmosphere.

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