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J. Franzke, R.W. Fox, L. Hollberg

Institute of Physics, University of Hohenheim, Gerbenstrasse 30, D-70599 Stuttgart Germany
National Institute of Standards and Technology, Boulder, Colorado USA
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J. Franzke\textsuperscript{a,*}, R.W. Fox\textsuperscript{b}, L. Hollberg\textsuperscript{b}

\textsuperscript{a}Institute of Physics, University of Hohenheim, Gärbenstrasse 30, D-70599 Stuttgart Germany
\textsuperscript{b}National Institute of Standards and Technology, Boulder, Colorado USA

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Abstract

High resolution atomic absorption measurements of lead at 283 nm in a vapor cell were performed by frequency doubling an 850 nm laser diode to obtain 425 nm light, followed by sum frequency generation of the harmonic radiation with a second 850 nm laser diode. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Laser diode; Second harmonic generation; Sum frequency generation; Lead

1. Introduction

The sensitive detection of lead (Pb) is of continuing interest because of the element’s toxic effects in biological systems. Methods such as atomic absorption spectroscopy in a graphite furnace, or a flame are most often used for the analytical detection of Pb. Typically, hollow cathode lamps (HCL) are used as light sources. As a result of the much higher spectral brightness and the ability to modulate the wavelength, a laser source offers an improved signal-to-noise ratio and subsequent lower detection limits in comparison to HCL. However, these attributes are still offset by the cost and size of typical tunable ultraviolet (UV) laser sources, which in most cases are frequency doubled dye lasers, pumped by expensive gas lasers. Therefore, an alternative tunable UV light source based on semiconductor lasers is of interest obviously [1].

In addition to lower detection limits, absorption spectroscopy with lasers also offers isotope selective measurements, allowing the possibility of tracing samples, as well as determining the origin or age of the samples in some instances. For the detection of Pb using the strong resonance absorption line at 283 nm, a laser tuning range of ~ 30 GHz covers the isotope splitting. Isotope selective analysis can also be performed by graphite furnace atomic absorption spectroscopy with HCL, however, publications on the determination of Pb have reported numerous interferences which were dependent on the volatility of Pb [2]. It was demonstrated that isotope dilution in isotope-selective diode laser spectrometry may be used not only for calibration, but also as a useful method to cancel severe matrix effects in optical spectrometry [3].

As presently available diode lasers radiate in the
range of red and IR, the use of non-linear optics is required to observe lines in the blue and the UV. The low powers that are typical of diode lasers are not well suited for non-linear frequency generation (although the commercially available power is now steadily increasing). In Pb, the 405 nm line (6p₂⁻3P₂⁻7s 3P₁; 405.897 nm) and the 283 nm line (6p₂⁻3P₀⁻7s 3P₇; 283.389 nm) are both transitions with strong oscillator strengths at wavelengths that can be obtained with suitable combinations of commercially available diode lasers and non-linear crystals. As the initial state of the 405 nm line is a metastable state, the use of a non-thermal excitation graphite furnace would be required to populate efficiently the metastable level [4]. In this work, we probed the 283 nm line, which was a strong transition originating from the ground state, and the isotope splitting was well resolved even in a Doppler-broadened gas. We chose to perform Pb spectroscopy in a thermal vapor cell as a first step towards a graphite furnace-based system, which was ideal for the detection of Pb in aqueous samples, but was more complex.

In the literature, a number of methods were used to generate radiation tunable in the range 243–310 nm from diode lasers, including:

- sum-frequency mixing of diode laser radiation with Ar⁺-laser radiation [5],
- single-pass frequency doubling by two successive stages [6],
- resonant cascaded doubling [7], and
- frequency tripling of the same laser (Third Harmonic Generation) [8].

In this article we describe another solution, second harmonic generation (SHG) followed by sum frequency generation (SFG) with two diode lasers and two crystals to generate a tunable 283 nm radiation. The second harmonic of the 850 nm fundamental radiation was generated in a KNbO₃ crystal, followed by sum frequency mixing of the second harmonic with a second 850 nm fundamental radiation in a BBO crystal. The second 850 nm diode laser is a smoothly tunable distributed-Bragg-reflector (DBR) laser. The wavelength of the first diode is fixed in order to facilitate second harmonic generation in an optical cavity. Although one high-power 850 nm laser would be sufficient to reach 283 nm, the two laser approach...
has the advantage that the resonant KNbO₃ cavity does not need to be scanned to scan the UV wavelength. This greatly simplifies the operation of the system, particularly when broad scans are required.

2. Experiment and results

The experimental arrangement is shown in Fig. 1, which is divided into three sections. In the first section, 425 nm light is produced by coupling the beam of an 850 nm laser into a monolithic KNbO₃ build-up cavity [9]. In the second section, the 425 nm beam is sum frequency mixed in BBO with a separate 850 nm DBR diode laser beam. The third section shows the experimental arrangement for the detection of Pb in a vapor cell.

2.1. SHG of 850 nm in KNbO₃

The wavelength of a commercial laser diode (nominal power = 50 mW, wavelength at room temperature = 850 nm) was tuned by temperature to 849.85 nm. This radiation was frequency doubled in a small monolithic KNbO₃ cavity with a 13 GHz free-spectral-range. The laser was locked by electronic feedback to the injection current using a Pound-Drever-Hall configuration [10]. The cavity was 5 mm long with 7 mm radius of curvature ends. The input surface coating reflectance is 95% in the IR, and the output surface coating reflectance is 99.3% in the IR, and transmits > 95% in the blue. The cavity resonance is much larger than the laser line-width, so no line-width narrowing technique such as an extended cavity diode laser was necessary. In the monolithic cavity, Type-I non-critical phase matching at 850 nm is achieved near 0°C. The KNbO₃ crystal was temperature stabilized to better than 50 mK, and was housed in a box which had dry N₂ gas to avoid condensation on the crystal faces.

The mode waist in the middle of the crystal was calculated to be 16 μm. Two simple lenses (one of positive and the other of negative focal length) were used to couple the ~ 3 mm diameter laser beam to the cavity mode. The separation between the lenses and the distance to the crystal were adjustable with translation stages to optimize the input coupling. The fundamental spatial mode contained 72% of the total transmitted IR power. This was limited by the non-circularity of the laser beam and could be improved with an adjustable set of anamorphic prisms.

The efficiency with which the fundamental was coupled in the ring cavity was measured by observing the cavity reflection. This signal is the interference between the forward cavity mode transmitted through the input coupler, and the reflection of the input beam off the coupler. This interference term will be zero in the case of perfect spatial and impedance mode-matching. Our cavity reflection dip was about 50% on resonance relative to the off-resonance reflection. To mode-match the impedance properly, the cavity losses (linear and non-linear) should equal the transmittance of the input coupler. Based on measurements of the cavity finesse made by scanning the laser wavelength and measuring the resonance widths and the free spectral range, the total round-trip cavity linear loss, δ, was determined to be within measurement uncertainty equal to the known surface losses of approximately 5.7%. We conclude that the total linear losses apart from the input coupler transmission are < 1%, and are dominated by the 0.7% loss of the output mirror.

The laser’s output power was kept at 45 mW to avoid operating at or above the maximum power output of 50 mW. The power incident on the doubling cavity was about 80% of this value, i.e. 36 mW. Considering the measured spatial mode coupling efficiency of 72%, the power coupled into the fundamental mode is 25.9 mW. The circulating IR power was about 900 mW (the build-up in the cavity is approximately 28⁻¹ ~ 35). At this input power, and at the optimum crystal temperature, there was 2.8 mW of blue power emitted from the crystal. This corresponds to a non-linear efficiency of 0.7%, which is a factor 2–3 lower than that expected for KNbO₃. This was likely because of a damaged (partially de-poled) crystal. We also tried a larger bow-tie cavity (crystal in an external ring resonator) but we were still limited in blue power as a result of crystal problems.

2.2. SFG of 425 and 850 nm in BBO

In order to reach the wavelength of the 283.39 nm Pb transition, the sum-frequency was generated by combining the frequency doubled light with the radiation from a 100 mW DBR laser diode. SFG was carried out in an 11 mm long Brewster-cut BBO
Fig. 2. Rapid scan of the 283.3 nm line measured in a Pb vapor cell and the positions of the isotope components of Pb.

crystal (cut for type 1 SFG at 850 nm and 425 nm, θ = 40.6°). The crystal was characterized by a theoretically effective non-linear coefficient d_{eff} = 1.72 pm/V, a walk-off angle of ρ = 75.4 mrad and an internal acceptance angle of 0.20 mrad/cm⁻¹ [11].

The SFG efficiency can be predicted by the Boyd-Kleinman [12] expression with focused Gaussian beams, with a sum frequency power of

\[ P_3 = \left(8\omega_0 k_0 d_{eff}/\pi n_1 n_2 n_3 c^3\right)h(B, ξ)(1 - γ^2)P_1P_2 \]

where n₁, n₂, and n₃ are the refractive indices 1.660, 1.688, 1.679 at wavelengths 850.3 nm, 424.9 nm and 283.3 nm, respectively. The mean input beam frequency is \( ω_0 = (ω_2 + ω_1)/2 \), the mean wave vector \( k_0 = (k_1 + k_2)/2 \). The factor \( (1 - γ^2) \) describes the deviation from the SHG efficiency, where the same frequencies are mixed. In our case, \( γ = (1 - ω_1/ω_0) = -1/3 \). The focusing parameter, \( h \), is a function of \( ξ = Lb_0 \), and the walk-off parameter

\[ B = \rho\sqrt{Lk_0}/2. \]

With a walk-off angle, ρ, of 75.4 mrad, a crystal length, \( L \), of 11 mm, and a mean input wave vector \( k_0 \) of 18.6 × 10⁷ cm⁻¹, the walk-off parameter is 17. This indicates that \( ξ \) should be 1.39 to maximize \( h(B, ξ) \) [12]. This yields an optimum equivalent beam waist radius, given by \( ω_0 = 20 \mu m \). Using these values we estimate that \( h = 0.05 \), and predict a sum frequency power of 6.7 × 10⁻⁴\( P_1P_2 \) (W/W²) [12].

With 72 mW of 850 nm power and 1.8 mW of blue power incident on the BBO crystal, 37 nW of UV light was measured. This is somewhat less than half of the UV power predicted by theory, although it is still a usable power level for spectroscopic applications. The difference between theory and experiment is likely because of less than ideal spatial mode-matching in the BBO crystal.

2.3. Detection of Pb at 283 nm

In this initial experiment, the beam of the DBR laser was modulated by a mechanical chopper, and the generated UV light was passed through a Pb vapor cell. The UV beam transmitted through the cell was detected by a solar blind phototube. The photo-current was measured with a trans-impedance amplifier using a 1 GΩ resistor, followed by a lock-in amplifier. The modulation frequency of 1 kHz was a compromise between high levels of amplitude noise on the blue beam at lower frequencies and the rapid signal fall-off as a result of the limited detector bandwidth.

3. Discussion

A scan of the DBR laser current gives an absorption spectrum of the 283 nm Pb line as shown in Fig. 2. Since the ultimate goal is to use this UV source with a conventional graphite tube atomizer, the time of the measurement is designed to be as short as the atomization phase (0.5–2 s). The intensities and line positions shown in the lower part of Fig. 2 represent the ratios of the natural abundances of lead isotopes as given by Kirchhof [13]. These positions and intensities correlate with the intensities shown in the measured spectrum. The shifts in optical frequency of \( ^{207}\text{Pb}(1/2\rightarrow1/2) \rightarrow ^{206}\text{Pb}, ^{208}\text{Pb} \rightarrow ^{206}\text{Pb}, ^{209}\text{Pb} \rightarrow ^{208}\text{Pb} \) and \( ^{207}\text{Pb} \rightarrow ^{207}\text{Pb}(1/2\rightarrow3/2) \) are 5.636, 2.188, 2.488 and 2.878 GHz, respectively. Note that the
The $^{207}\text{Pb}-^{208}\text{Pb}$ isotope shift refers to the center of gravity of the hyperfine structure of the $^{207}\text{Pb}$ line. The $^{207}\text{Pb}$ isotope has a nuclear spin $I = \frac{1}{2}$, and the transition is a $J = 0 \rightarrow J' = \frac{1}{2}$. The relative intensities of the $F = 1/2 \rightarrow F' = 1/2$ and the $F = 1/2 \rightarrow F' = 3/2$ hyperfine components are 50 and 100, respectively. Both hyperfine structure components of $^{207}\text{Pb}$ are clearly resolved in the data, along with the $^{206}\text{Pb}$ and the $^{208}\text{Pb}$ lines. The $^{204}\text{Pb}$ line vanishes in a background which is primarily because of intensity noise, although some etalon effects were observed.

Utilizing wavelength modulation spectroscopy [14] to shift the detection bandwidth to a higher frequency would result in lower noise. This was not possible in our experiment because of the photo-tube capacitance and the 1 GΩ trans-impedance, which severely limited the detector bandwidth (to ≤ 1 kHz). More UV power would allow a smaller resistor, facilitating the use of higher modulation frequencies. Using the same sum-frequency efficiency obtained here in BBO, a UV power level of 5 µW should be possible with 60 mW of blue light and 300 mW of IR incident on the crystal. These power levels are feasible with newly available diode lasers.

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References

[9] The Fabry-Perot laser was a SDL 5400 series laser, while the DBR laser was a SDL 5710. These products are identified solely for purposes of comparison.
For a full and complete Guide for Authors please refer to Spectrochimica Acta, Part B, Vol. 52B, No. 1, pp. i-VII. The instructions can also be found on the World Wide Web: access under http://www.elsevier.nl or http://www.elsevier.com.

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