Spectrochimica Acta Rev. Vol. 15. No 5. pp. 291–299. 1993.

0958-319X/93 $24.00

The diode laser as a spectroscopic tool

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Abstract—The properties of diode lasers that make them attractive as spectroscopic sources are discussed, along with the use of extended cavities to enhance their tuning range and reduce their linewidths. Semiconductors can now provide efficient, tunable, narrow linewidth laser light over much of the red and near-i.r. region of the spectrum. The progress in using nonlinear optics to extend the useful wavelength range of diodes lasers is also considered. Our recent analytical work with diode laser spectroscopy provides examples of their application.

1. Introduction and Basic Properties

Inherent low noise, low cost, tunability, and simplicity make diode lasers unique spectroscopic sources, and their use in this respect has been reviewed several times [1–5]. Here we will focus briefly on general characteristics and then explore some of the new technologies and applications, with particular interest in spectroscopy and ultrasensitive detection.

There are two main types of laser diodes available. The type we will deal with here are the visible and near-infrared lasers fabricated from the group III–V semiconductor compounds (for example: AlGaInP, AlGaAs, InGaAs and InGaAsP). The approximate distribution of wavelength and power for commercial lasers of this type are shown in Fig. 1. The other basic type of diode lasers are commonly known as lead-salt lasers which operate at wavelengths between 3 and 30 μm. These lasers are distinct in that they are only operated at cryogenic temperatures, and are not considered here [6].

Although red cw diodes with nominal wavelengths as short as 635 nm are commercially available, there have been diode lasers developed at shorter wavelengths [7, 8]. However, coincidences between strong atomic or molecular lines and wavelength ranges of available diodes remain the exception rather than the rule. The visible and near-i.r. diodes can be tuned roughly 3–4 nm from the nominal wavelength with a 20°C temperature change. The tuning is in a step-wise fashion; for instance, smooth

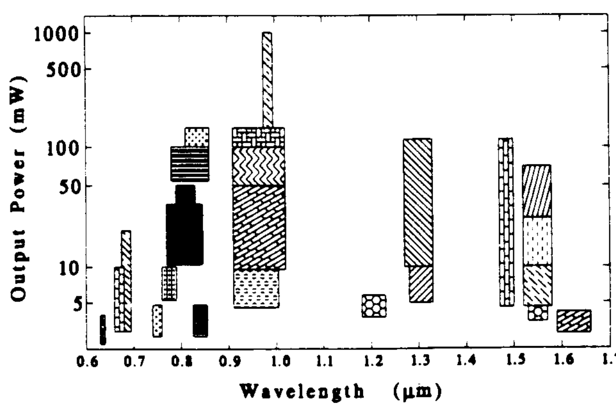

Fig. 1. Commercially available cw laser diodes in the 600–1600 nm wavelength range. The data bars represent families of laser products as advertised by a number of different manufacturers.

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tuning for typically one fourth of a nanometer, followed by a transition (mode-hop) in wavelength to another mode. Tuning with injection current (~0.01 nm/mA) exhibits similar behavior, and hysteresis is often observed at the mode hops in either case. Thus it is difficult to ensure that a given diode will reliably reach all wavelengths near the nominal. This problem is usually overcome by either having a sample of several diodes to choose from or by using optical feedback to control the lasing frequency. A common example of the latter method is the use of a diffraction grating in an extended cavity laser, as discussed in the next section. A second example is the use of a small mirror placed close to one of the laser facets, effectively forming an etalon which forces the laser to operate in a specific longitudinal mode [9]. The mode may then be wavelength tuned with current or temperature; success in achieving complete wavelength coverage near the nominal has been reported [10,11] with this technique.

These comments on tuning apply mainly to single-mode Fabry–Perot type diodes as opposed to distributed-feedback (DFB) lasers. DFB lasers have superior tuning characteristics (but restricted wavelength range), typically tuning ~10–12 nm with temperature before encountering a mode-hop. Unfortunately, they are as yet widely available only in the 1.3 and 1.55 μm telecommunications band wavelengths and are relatively expensive.

Many of the diode lasers available now are designed to operate in a single longitudinal mode. This is of course preferable for absorption measurements, since power in side modes (off the absorption feature) does not contribute to the signal but does add shot noise and mode competition noise to the detected photocurrent. A laser running with significant power in more than one mode may exhibit greatly increased amplitude noise (AM) due to mode competition [12]. Lasers with a few modes running usually have the highest level of mode-partition-noise whereas those with either a large number of modes or one mode have low AM noise. In fact the detected photo-current of a typical near-i.r., single-mode laser driven with a good low noise current source will show amplitude fluctuations that are within a factor of 10 of the shot noise limit in the frequency range above 100 kHz. These low intrinsic noise levels are just one of the reasons that diode lasers are attractive as spectroscopic sources.

Many groups have reported impressive sensitivities in detecting atoms and molecules by exploiting modulation techniques to take advantage of the low amplitude noise exhibited in the higher frequency range [13–15]. Several studies have compared detection sensitivities obtained at different modulation frequencies [16–18]. A separate approach is to work closer to the base-band frequency range but use negative electronic feedback to suppress the amplitude fluctuations inherent at the lower frequencies [19, 20]. With these methods it is possible to approach the shot noise limit and greatly enhance the signal-to-noise ratio in absorption detection. It is important to realize that the low intrinsic noise does not, however, mean that diode lasers are free from systematic amplitude changes as their frequency is swept or modulated. The linear power vs. current curve exhibited by diodes leads to a sloping baseline if direct detection is used. A more serious problem that limits detection sensitivities is the residual AM that accompanies frequency modulation.

The spectral linewidth of even a typical solitary diode laser is quite narrow with respect to Doppler or atmospheric pressure-broadened lines. AlGaAs, near-i.r. lasers operating well above threshold have linewidths in the 10–40 MHz range. Some high-power long-cavity solitary lasers have reported linewidths of a few megahertz. The visible AlGaInP lasers exhibit broader linewidths, typically 150 MHz. For high resolution work a number of methods have been developed to achieve greatly reduced linewidths. The most common method is to employ an extended cavity (see Section 2), but resonant optical feedback from a confocal cavity has also been successfully used in a number of experiments [21, 22]. Techniques to achieve substantially narrower linewidths than the hundreds of kilohertz afforded by standard extended cavities are discussed in a number of articles [23–25].

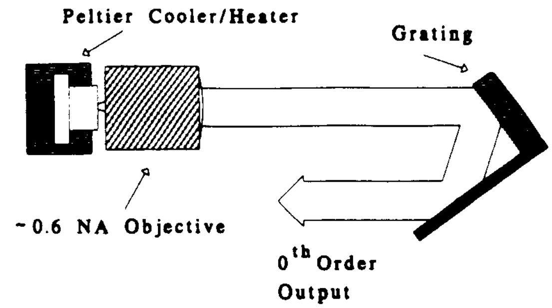

Fig. 2. Basic form of an extended cavity diode laser system. In this example an optical grating in a Littrow configuration is used as a wavelength selective tuning element. A piezoelectric element (not shown) on the grating assembly provides for fine wavelength sweeping. Angular sweep of the output beam with tuning is eliminated with a mirror attached at 90° to the grating as shown.

2. Methods for Broad Tuning

At NIST most of our work with diode lasers has concentrated on high resolution spectroscopy of narrow atomic resonances, but there is a much wider spectrum of applications that will require broadly tunable sources without stringent linewidth requirements. For most of these applications it is also necessary to reach a specific wavelength of interest. This may require some form of wavelength-selective optical feedback in order to extend and even fill in a laser's tuning range [26]. The most common method is to use an optical grating for selective feedback in an extended-cavity-diode-laser (ECDL) configuration. An example ECDL system is shown in Fig. 2. Extended cavity lasers are relatively simple, and up to now many groups have been building these systems for their own use. The number of users and applications can be expected to increase as more advanced commercial diode laser sources become available.

Many variations on the basic ECDL scheme are possible, and a variety of different tuning elements have been used, although gratings seem to be the most common. Grating tuning of ± 20 nm from the nominal diode wavelength is possible with near-i.r. AlGaAs lasers without changing the diode temperature. However, this represents rather optimum results, dependent upon the device and laser anti-reflection (AR) coating. A tuning range of ± 10 nm is more common.

Other important characteristics of a diode used in an extended cavity include a moderate loss of power and a much narrower linewidth as compared to the solitary diode. The usable single-frequency, tunable output power can be as low as 30% of the rated single-mode diode power. This is due in part to a change in the output coupling, but is also often due to lower injection currents required to stay in a stable operating regime. The observed linewidth will depend upon the cavity length as well as the lasers' environment. Although the fundamental linewidth decreases as the square of the cavity length, low frequency ($\leq$ 100 kHz) environmental and $1/f$ noise soon become the dominant frequency noise contributions. This leads to observed linewidths that range from tens to hundreds of kilohertz depending mostly on construction and external perturbations. We also note, that with this sort of frequency fluctuations, the "linewidth" that one measures depends on the observation time of the measurement, and is thus somewhat ill-defined [25].

With simple grating feedback and average anti-reflection coatings an ECDL will not usually tune single-frequency with no mode hops over the laser's entire gain bandwidth. This is due to a number of factors, paramount of which is the residual output facet reflectance of the laser chip (as discussed below). For single-frequency scanning without mode-hops it is necessary to synchronously scan the extended cavity length with the pass-band of the wavelength selective element(s) (such as a grating and/or etalon). Several techniques that accurately change the cavity length together with the grating angle have accomplished single-mode tuning over 1000 GHz [27, 28]. Again these are exceptional results rather than typical, which might show scanning from 10 to 100 GHz depending on a number of factors.

Special regimes of ECDL operation called "autostabilization" also exist [29] where single-mode tuning ranges of more than 20 GHz are possible with just cavity length changes and no change of the grating angle. This broad tuning is the result of semiconductor device non-linearities that help to maintain single-mode operation. We note that this is typical for ~5–20 cm long ECDLs, and is in fact single mode scanning of about ten free spectral ranges of the extended cavity with no mode hops.

ECDLs generally operate in a straight-forward, single-mode manner but it is also easy to reach unacceptable operating conditions (multimode or chaotic) that depend on parameters both internal and external to the laser. Spectroscopic applications are particularly sensitive to outside factors that affect the laser's frequency, such as stray optical feedback, temperature and current fluctuations, and even vibrations for ECDLs. A more fundamental cause of instabilities in ECDLs is the fact that the laser is a coupled-cavity system with potentially incommensurate boundary conditions [30–32]. In applying these lasers we have to find ways to avoid regions of instability. Three techniques are useful to increase the stable operating regions of grating tuned lasers: (1) operate at slightly lower powers, (2) use short extended cavities [33,34] and (3) improve the AR coatings on the output facet so that the system is dominated by the grating feedback. All of these techniques are helpful in achieving broad tuning and stable operation even though they have the inherent disadvantages of low output power, broader linewidths, and complications of additional processing respectively. A compelling reason to strive for very low output facet reflectance ($R < 10^{-3}$), is that with such AR coatings it is possible to obtain complete spectral coverage over the laser's gain profile without having to change the laser's temperature [35].

Fortunately, many of the higher power lasers that are commercially available already have some AR coating on their output facet. These lasers will work as supplied in ECDL systems, but they can also be improved. For our extended-cavity systems we generally add additional coatings to the output facet in order to reduce the reflectance. After some experience we routinely achieve facet reflectances of 10^{-3} on ordinary commercial lasers. Lower reflectance is possible but is difficult to achieve because of a number of factors; not the least of which is the fact that we lack detailed knowledge of the structures and materials of specific commercial lasers. In addition, most of the lasers come from the manufacturers with coatings already on the facets. We typically find single layer $\lambda/4$ coatings with reflectance of ~5% for high power lasers and $\lambda/2$ with 30% reflectance for low power devices. These coatings are for passivation as well as tailored reflectance and generally make it more difficult to reach very low reflectance with additional coatings. Quite a lot of information on coating lasers is available in the literature [36–39], particularly with regard to making optical amplifiers. Our coatings at NIST achieve good reliable results with common optical coating materials (HfO_2, Al_2O_3 and SiO) and techniques (thermal, e-beam and RF-sputtering) [40].

3. Higher Power and Access to Other Spectral Regions

The main problem in using diode lasers for spectroscopic applications is the limited number of wavelengths that are accessible. Using only semiconductors based on various derivatives of GaAs and InP, the wavelength coverage could be nearly complete over the spectral region from 630 nm to 1.7 μm. In practice this is not the case (see Fig. 1) because the manufacturers concentrate production at certain wavelengths. Other wavelength regions may be accessible with different semiconductor materials; for example blue–green diode lasers based on ZnSe have been reported recently [7]. Also some research laboratories have produced i.r. lasers in the 2.0–2.3 μm region based on GaInAsSb [41, 42]. These spectral regions will see important spectroscopic applications if development is successful and if there is sufficient commercial demand to support production.

An alternative to direct semiconductor sources for other spectral regions is to use diode lasers in conjunction with nonlinear optical techniques to generate new wavelengths. This requires high intensity beams and materials with large nonlinear coefficients. Until recently we have been limited to a few tens of milliwatts of single-mode power from diode lasers in the best cases. Consequently, resonant cavities are useful to increase the intensity and thus generate nonlinear products more efficiently. The future promises to make this much easier with new higher power lasers and better nonlinear materials.

Two basic techniques have demonstrated high-power single-mode single-frequency operation of semiconductor diode lasers. These are (1) injection-locking of high-power broad-area lasers with a single-mode laser [43–45] and (2) single-mode master-oscillator-power-amplifier systems (MOPAs) [46]. The distinction between these two methods is just whether the power device operates above or below threshold without the master laser's input. Injection locking can be done with low power single-mode master lasers to lock the frequency of the higher power (hundreds of milliwatts) semiconductor laser sources. MOPA systems have been reported with pulsed outputs of 27 W and cw outputs of up to 2 W. At present many of these high power systems are relatively expensive which we expect to change with time. The question remains of how broad a wavelength coverage will be available with these very high power systems.

There are already a few nonlinear optical techniques that work particularly well with diode lasers. One of these is the fortuitous match of the wavelength of the high-power AlGaAs lasers and 90° phase-matching in potassium niobate ($KNbO_3$). High efficiency second-harmonic generation (SHG) at fundamental wavelengths from about 840 to 930 nm can be achieved in this material with temperature tuning of the crystal from about −40 to 180°C [47]. As much as 40 mW of blue light has been generated with a diode laser and $KNbO_3$ [48]. Using less infrared power, others [49, 50] have reported conversion efficiencies from diode power to blue light in the range of 1–10%. These results are consistent with our experience in using a ring buildup cavity that generates 30 mW of blue light at 423 nm for 150 mW of diode laser power. The main limitation in our system is the spatial mode of the diode laser that limits the coupling efficiency of the laser into the ring. Improvements in the mode matching and laser power should increase the overall conversion efficiency since $KNbO_3$ is capable of producing much higher blue light powers [51].

A promising technique that has demonstrated excellent results for SHG and sum-frequency mixing is the fabrication of periodic domains in the crystal structure [52–54]. This involves reversing properties of the crystal on a periodic basis, which allows the fundamental and harmonic waves to retain a constructive phase relationship over much longer distances than would otherwise be the case. Yet another approach to tunable blue light from semiconductor sources is to phase-match for sum-frequency mixing of a diode laser output with the second harmonic of a diode pumped Nd–Yag laser. Output powers of 4 mW at 459 nm have been demonstrated [55] in this manner, using a monolithic KTP resonator and approximately 30 mW of input power from each laser.

Nonlinear mixing to longer wavelengths has also been recently demonstrated using diode lasers. Using difference frequency mixing SIMON [56] and collaborators have generated tunable mid-i.r. light from diode lasers. The i.r. output powers are low at present (~3 nW), but the principle of difference frequency generation from diode laser sources has been proven. In this case the non-linear materials that seem the most appropriate are $AgGaS_2$ and $AgGaSe_2$, which can potentially cover the wavelength range from 4 to 18 μm.

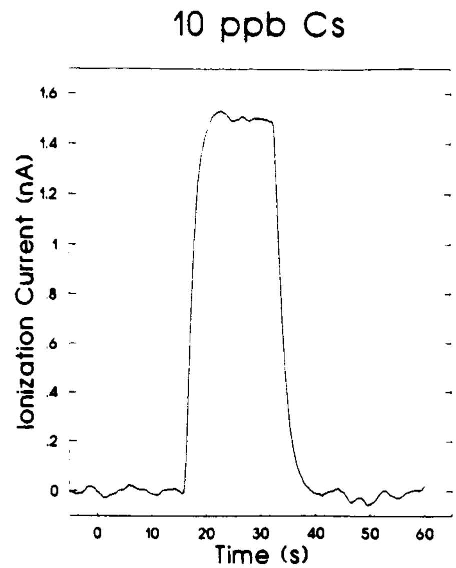

Fig. 3. Diode laser-enhanced ionization (LEI) signal obtained with 10 ppb of Cs in water. The laser was tuned to the strong peak of the Cs D_2 line. The limiting background noise was contamination by easily ionized elements in the burner equipment, which led to an increased flame background current.

4. Applications

4.1. *Atomic spectroscopy*

The use of diode lasers as spectroscopic sources in the setting of analytical chemistry for trace detection of atoms has been reported by several groups. Absorption, fluorescence and ionization-based methods have all been demonstrated, using a variety of atom sources including flames [57], a graphite furnace [58, 59], a thermionic diode [60], a glow discharge [61], and a thermal filament [62].

Along these lines we have used diode lasers for the detection of trace levels of Rb and Cs in solutions using laser-enhanced ionization spectroscopy (LEI) in a flame. Our very elementary set-up consisted of a water-cooled cathode in a premixed air–hydrogen flame with a pneumatic nebulizer for liquid sample introduction [63, 64]. The cathode was held at a potential of about -100 V with respect to the burner, and the laser beam chopped and directed through the flame. Resonant absorption on the $S_{1/2}$ to $P_{3/2}$ transition in the alkalis changes the charge density in the flame since there is a differential ionization potential between the S and P states. This causes a change in the current flowing between the burner and the cathode, which is phase sensitively detected at the laser chopping frequency.

Figure 3 shows the signal obtained with a water solution of Cs at a concentration of 10 ppb (an atomic density of approximately 10^8 cm^{-3} in the flame). The baseline is obtained by aspirating deionized water into the flame. An extended-cavity grating tuned laser was used, which produce 1.9 mW of output power with a 2 mm diameter beam that was passed through the flame twice. In this example the use of a relatively narrow linewidth (~100 kHz) extended-cavity laser as opposed to a solitary diode laser is not significant (other than for ease of tuning) since the absorption is homogeneously broadened by atmospheric pressure. The laser beam was positioned for maximum signal, approximately one beam diameter below the flame electrode.

Limits of detection for Cs and Rb were calculated by extrapolating the signals obtained for 10 ppb solutions down to the concentration that would give a signal equal to three times the r.m.s. noise level of the deionized water baseline. A 1 s time constant on the lock-in amplifier was used for these measurements. For Cs at 852 nm a limit of detection of 0.25 ppb was achieved. For Rb at 780 nm the limit of detection was 0.3 ppb. The limiting source of noise at the detection limit was contamination by easily ionized elements in the burner equipment, which led to an increased flame background current. For both Cs and Rb, the sensitivity was diminished by the high fraction of normal flame ionization of these low ionization potential elements, which reduces the atomic fraction available for LEI. In the case of Cs, approximately 90% of the population is thermally ionized before laser excitation.

Our limit of detection for Rb compares well with that reported by HAVRILLA [65], using LEI in the air–hydrogen flame with a dye laser pumped by a cw krypton ion laser. They reported a limit of detection of 0.09 ppb, with a laser power approximately two orders of magnitude higher. The laser system used in that work was considerably more complex and expensive, requiring 30 kW of power and cooling water at 50 l min^{-1}. No comparable LEI measurement of Cs has been reported. Future development of LEI using diode lasers depends on expansion of wavelength availability. Several attempts were made to make LEI measurements of other elements using transitions beginning from excited states with near-i.r. wavelengths where diode lasers were available. The very low Boltzmann population of the lower levels of these transitions in the flame prevented our observation of LEI.

4.2. *Molecular spectroscopy*

The detection of molecular species instead of constituent atom concentrations is often of interest. Although in general the molecular absorption bands in the near-i.r. are weak compared to the vibrational bands at longer wavelengths, the room temperature operation of the near-i.r. lasers makes them very attractive nevertheless. Many groups have applied the 1.3 and 1.5 μm lasers to probing various molecular resonances, including CH_4 [66, 67], C_2H_2 [68], CO_2 and CO [69], NH_3 and H_2O [70], HCN [71], HDO [72] and HCl [73]. Particularly important due to its role in atmospheric pollution is NO_2, which has been investigated by several groups [14, 15, 74, 75].

In some on going work at NIST in collaboration with NOAA [76], red diode lasers are being used to detect NO_3 radicals. This molecule plays an important role in atmospheric photochemistry. In the stratosphere its photochemistry affects ozone depletion, and it acts as a strong oxidizer in the troposphere. NO_3 has a strong electronic absorption band at 662 nm that can be reached with commercial red diode lasers. In these experiments a solitary diode laser is used to detect the time-dependent concentration of NO_3 in an excimer-laser photodissociation experiment. Good detection sensitivities are achieved with simple direct absorption measurements (noise-limited absorption sensitivity $\sim 10^{-4}$ at DC with a 200 kHz detection bandwidth). This corresponds to about 5×10^{10} NO_3 molecules/cm^3 and a 1 m single-pass absorption path length. The detection sensitivity could be improved with: subtraction of residual low-frequency AM noise, or high frequency modulation, or multi-passing the absorption cell. This experiment illustrates the potential for using very simple diode laser systems to detect reactive molecular species that play an important role both in the laboratory and in the earth's atmosphere.

5. SUMMARY AND PROJECTIONS

The rapid growth in the field of diode laser spectroscopy is the direct result of the simplicity and good performance that can be achieved with inexpensive commercial semiconductor lasers. These lasers are becoming more readily available, and in addition we now have a better understanding of how to control them and apply them to a variety of scientific and technical problems. With some acknowledged limitations we can now have low cost, portable, tunable, low noise, narrow linewidth laser sources at a number of wavelengths. Very high power devices are becoming available which will extend the opportunities with diode lasers in part by accessing other wavelength regions. Important spectroscopic and analytic roles are recognized for both simple solitary laser systems as well as broadly tunable extended cavity laser systems. Areas of precision optical physics such as atomic clocks, frequency and length standards.

and laser cooling of atoms are also being strongly affected by diode lasers. The capabilities of these systems continues to increase as does the number of applications. The time is not far in the future that we will consider diode laser systems as standard research tools.

Acknowledgements—We acknowledge the important contributions to this work by N. Mackie, T. Zibrova, A. S. Zibrov, J. H. Marquardt, J. S. Wells and the NOAA group [76]. Our thanks to U. Simon for information about difference frequency generation. This work has been supported in part by the NASA upper atmospheric research program, and the Air Force office of scientific research.

References

[1] J. C. Comparo, *Contemp. Phys.* **26**, 443 (1985).
[2] J. Lawrenz and K. Niemax, *Spectrochim. Acta.* **44B**, 155 (1989).
[3] C. Wieman and L. Hollberg, *Rev. Sci. Instrum.* **62**, 1 (1991).
[4] D. E. Cooper and R. U. Martinelli, *Laser Focus World* **Nov.**, 133 (1992).
[5] M. Ohtsu and K. Nakagawa, *Spectroscopy by Semiconductor Lasers*, In *Coherence, Amplification, and Quantum Effects in Semiconductor Lasers*, Ed. Y. Yamamoto, Chap. 5. John Wiley, New York (1991).
[6] *Tunable Diode Laser Applications*, Eds. A. I. Nadezhdinskii, A. M. Prokhorov, *Proc. SPIE* **1724** (1992); and C. B. Carlisle, D. E. Cooper and H. Preier, *Appl. Opt.* **28**, 2567 (1989).
[7] M. A. Haase, J. Qiu, J. M. DePuydt and H. Cheng, *Appl. Phys. Lett.* **59**, 1272 (1991).
[8] H. Jeon, J. Ding, W. Patterson, A. V. Nurmikko, W. Xie, D. C. Grillo, M. Kobayashi and R. L. Gunshor, *Appl. Phys. Lett.* **59**, 3619 (1991).
[9] A. P. Bogatov, P. G. Eliseev, L. P. Ivanov, A. S. Logginov, M. A. Manko and K. Y. Senatorov, *IEEE J. Quant. Elect.* **QE-9**, 392 (1973).
[10] L. J. Bonnell and D. T. Cassidy, *Appl. Opt.* **28**, 4622 (1989).
[11] D. T. Cassidy, D. M. Bruce and B. F. Ventrudo, *Rev. Sci. Instrum.* **62**, 2385 (1991).
[12] K. Ogawa, *IEEE J. Quant. Elect.* **QE-18**, 849 (1982).
[13] W. Lenth, *Opt. Lett.* **8**, 575 (1983).
[14] W. Lenth and M. Gehrtz, *Appl. Phys. Lett.* **47**, 1263 (1985).
[15] G. R. Janik, C. B. Carlisle and T. F. Gallagher, *J. Opt. Soc. Am.* **B3**, 1070 (1986).
[16] L. Wang, H. Riris, C. B. Carlisle and T. F. Gallagher, *Appl. Opt.* **27**, 2071 (1988).
[17] D. B. Bomse, A. C. Stanton and J. A. Silver, *Appl. Opt.* **31**, 718 (1992).
[18] F. S. Pavone and M. Inguscio, *Appl. Phys. B* **56**, 118 (1993).
[19] G. Björk, *Phys. Rev. A* **45**, 8259 (1992).
[20] L. Hollberg, R. Fox, N. Mackie, A. S. Zibrov, V. L. Velichansky, R. Ellingsen and H. G. Robinson, In *Tenth International Conference on Laser Spectroscopy*, Eds. M. Ducloy, E. Giacobino and G. Camy, World Scientific, Singapore, New Jersey, London, Hong Kong (1992).
[21] B. Dahmani, L. Hollberg and R. Drullinger, *Opt. Lett.* **12**, 876 (1987).
[22] A. Hemmerich, D. H. McIntyre, D. Schropp, Jr, D. Meschede and T. W. Hänsch, *Opt. Commun.* **75**, 118 (1990).
[23] H. R. Telle, *Appl. Phys.* **B49**, 217 (1989).
[24] M. Ohtsu, *Highly Coherent Semiconductor Lasers*, Artech House, Boston (1992).
[25] R. W. Fox, H. G. Robinson, A. S. Zibrov, N. Mackie, J. Marquardt, J. Magyar and L. Hollberg, *Proc. SPIE*, Vol. **1837**, 360–365 (1993).
[26] E. M. Belenov, V. L. Velichansky, A. S. Zibrov, V. V. Nikitin, V. A. Sautenkov and A. V. Uskov, *Sov. J. Quant. Elect.* **13**, 792 (1983).
[27] F. Favre, D. Le Guen, J. C. Simon and B. Landousies, *Elect. Lett.* **22**, 795 (1986).
[28] A. T. Schremer and C. L. Tang, *IEEE Phot. Tech. Lett.* **2**, 3 (1990).
[29] A. M. Akul'shin, V. Y. Bazhenov, V. L. Velichanski, M. V. Zverkov, A. S. Zibrov, V. V. Nikitin, O. G. Okhotnikov, V. A. Sautenkov, N. V. Senkov and E. K. Yurkin, *Sov. J. Quant. Elect.* **16**, 912 (1986).
[30] H. Olesen, J. H. Osmundsen and B. Tromborg, *IEEE J. Quant. Elect.* **QE-22**, 762 (1986).
[31] R. W. Tkach and A. R. Chraplyvy, *J. Lightwave Tech.* **LT-4**, 1655 (1986).
[32] D. R. Hjelme, A. R. Mickelson and R. G. Beausoleil, *IEEE J. Quant. Elect.* **27**, 352 (1991).
[33] N. Schunk and K. Petermann, *IEEE Photon. Tech. Lett.* **1**, 49 (1989).
[34] Y. A. Bykovski, V. L. Velichanski, I. G. Goncharov, A. P. Grachev, A. S. Zibrov, S. I. Koval and G. T. Pak, *Sov. J. Quant. Elect.* **19**, 730 (1989).
[35] P. Zorabedian, W. R. Trutna, Jr and L. S. Cutler, *IEEE J. Quant. Elect.* **QE-23**, 1855 (1987).
[36] D. R. Kaplan and P. P. Deimel, *AT&T Bell Lab. Tech. J.* **63**, 857 (1984).
[37] T. Saitoh, T. Mukai and O. Mikami, *J. Lightwave Tech.* **3**, 288 (1985).
[38] G. Eisenstein, G. Raybon and L. W. Stulz, *J. Lightwave Tech.* **6**, 12 (1988).
[39] V. M. Baev, J. Eschner, E. Paeth, R. Schüler and P. E. Toschek, *Appl. Phys.* **B55**, 463 (1992).
[40] R. Fox, G. Turk, N. Mackie, T. Zibrova, S. Waltman, M. P. Sassi, J. Marquardt, A. S. Zibrov, C. Weimer and L. Hollberg, *Solid State Lasers: New Developments and Applications*, Proc. Nato Advanced Study Institute, Elba Italy, Plenum (1993).

[41] A. N. Baranov, A. N. Imenkov, M. P. Mikhailova, A. A. Rogachev and Y. P. Yakovlev, *Proc. SPIE* **1408**, 188 (1989).
[42] S. J. Eglash and H. K. Choi, *Appl. Phys. Lett.* **57**, 1292 (1990).
[43] K. Soichi and K. Tatsuya, *IEEE J. Quant. Elect.* **QE-17**, 681 (1981).
[44] P. Isabelle, G. Philippe, D. Guy and C. Claude, *IEEE J. Quant. Elect.* **QE-24**, 148 (1988).
[45] L. Goldberg and M. K. Chun, *Appl. Phys. Lett.* **53**, 1900 (1988).
[46] R. Parke, D. F. Welch, A. Hardy, R. Lang, D. Mehuys, S. O'Brien, K. Dzurko and D. Scifres, *IEEE Phot. Tech. Lett.* **5**, 297 (1993).
[47] J. C. Baumert, P. Günter and H. Melchior, *Opt. Commun.* **48**, 215 (1983).
[48] W. J. Kozlovsky, W. Lenth, E. E. Latta, A. Moser and G. L. Bona, *Appl. Phys. Lett.* **56**, 2291 (1990).
[49] G. J. Dixon, C. E. Tanner and C. E. Wieman, *Opt. Lett.* **14**, 731 (1989).
[50] A. Hemmerich, D. H. McIntyre, C. Zimmermann and T. W. Hänsch, *Opt. Lett.* **15**, 372 (1990).
[51] E. S. Polzik and H. J. Kimble, *Opt. Lett.* **16**, 1400 (1991).
[52] J. Webjörn, F. Laurell and G. Arvidsson, *IEEE Phot. Tech. Lett.* **1**, 316 (1989).
[53] F. Laurell, J. B. Brown and J. D. Bierlein, *Appl. Phys. Lett.* **60**, 1064 (1992).
[54] E. J. Lim, M. M. Fejer, R. L. Byer and W. J. Kozlovsky, *Elect. Lett.* **25**, 731 (1989).
[55] W. P. Risk and W. J. Kozlovsky, *Opt. Lett.* **17**, 707 (1992).
[56] U. Simon, C. E. Miller, C. C. Bradley, R. G. Hulet, R. F. Curl and F. K. Tittel, *Opt. Lett.* **18**, 1062 (1993).
[57] P. E. Walters, T. E. Barber, M. W. Wensing and J. D. Winefordner, *Spectrochim. Acta* **46B**, 1015 (1991).
[58] A. Zybin, C. Schnürer-Patshan and K. Niemax, *Spectrochim. Acta* **47B**, 1519 (1992).
[59] P. A. Johnson, J. A. Vera, B. W. Smith and J. D. Winefordner, *Spectrosc. Lett.* **21**, 607 (1988).
[60] J. Lawrenz, A. Obrebski and K. Niemax, *Anal. Chem.* **59**, 1232 (1987).
[61] J. Lawrenz and K. Niemax, *Spectrochim. Acta* **44B**, 155 (1988).
[62] R. W. Shaw, J. P. Young and D. H. Smith, *Anal. Chem.* **61**, 695 (1989).
[63] G. C. Turk, *Anal. Chem.* **53**, 1187 (1981).
[64] J. C. Travis, G. C. Turk, J. R. DeVoe, P. K. Schenck and C. A. Van Dijk, *Prog. Anal. At. Spectrosc.* **7**, 199 (1984).
[65] G. J. Havrilla, S. J. Weeks and J. C. Travis, *Anal. Chem.* **54**, 2566 (1982).
[66] Y. Shimose, T. Okamoto, A. Maruyama, M. Aizawa and H. Nagai, *IEEE Phot. Tech. Lett.* **3**, 86 (1991).
[67] K. Uehara and H. Tai, *Appl. Opt.* **31**, 809 (1992).
[68] S. Sudo, Y. Sakai, H. Yasaka and T. Ikegami, *IEEE Phot. Tech. Lett.* **1**, 281 (1989).
[69] D. T. Cassidy and L. L. Bonnell, *Appl. Opt.* **27**, 2688 (1988).
[70] M. Ohtsu, H. Kotani and H. Tagawa, *Jap. J. Appl. Phys.* **22**, 1553 (1983).
[71] H. Sasada and K. Yamada, *Appl. Opt.* **29**, 3535 (1990).
[72] T. Ohshima and H. Sasada, *J. Mole. Spec.* **136**, 250 (1989).
[73] A. C. Stanton and J. A. Silver, *Appl. Opt.* **27**, 5009 (1988).
[74] M. Gehrtz, G. C. Bjorklund and E. A. Whittaker, *J. Opt. Soc. Am.* **B2**, 1510 (1985).
[75] J. Reid, M. El-Sherbiny, B. K. Garside and E. A. Ballik, *Appl. Opt.* **19**, 3349 (1980).
[76] R. J. Yokelson, J. B. Burkholder, A. R. Ravishankara and C. J. Howard, National Oceanic and Atmospheric Administration Aeronomy Laboratory, Boulder, Colorado.