Continuous-wave infrared laser spectrometer based on difference frequency generation in AgGaS$_2$ for high-resolution spectroscopy

P. Canarelli, Z. Benko, R. Curl, and F. K. Tittel

Department of Electrical and Computer Engineering, Rice Quantum Institute, Rice University, P.O. Box 1892, Houston, Texas 77251

A high-resolution cw spectrometer based on difference frequency generation (DFG) in a 20-mm-long AgGaS$_2$ crystal pumped by two stabilized single-frequency cw dye–Ti:sapphire lasers is described. Experiments performed with a Rhodamine 6G and DCM dye laser combination pumped by a 20-W argon laser are reported. Infrared radiation is generated from 7 to 9 μm with an ultranarrow linewidth (<0.5 MHz) and an output power of 1 μW by making use of 90° type I phase matching. The performance of the DFG laser spectrometer is evaluated by using a portion of the ν_2 band of NH$_3$ near 1177 cm^{-1}.

INTRODUCTION

High-resolution laser spectroscopy in the infrared region requires a tunable coherent cw radiation that is capable of precise wavelength resolution, high spectral brightness, and good frequency and amplitude stability. A wavelength resolution of better than 1 MHz and a power greater than 1 μW are desirable for high sensitivity and time-resolved absorption spectroscopy. For wavelengths beyond ~2 μm the only practical tunable laser sources are color-center lasers, ternary salt diode lasers, and sources based on difference frequency generation (DFG). The color-center lasers operate extremely well with single-frequency power levels up to 100 mW but only in a limited spectral range from 1.1 to 3.5 μm and at liquid-nitrogen temperatures. Diode lasers, on the other hand, can cover a wide wavelength range (from 2 to 30 μm) based on the semiconductor composition, but the tuning range of any single diode is very small (~100 cm^{-1}). Moreover, commercially available diode lasers that are currently available do not cover their nominal wavelength ranges continuously and also require low temperatures (<100 K). In addition, power and coverage tend to degrade on temperature cycling. Tunable infrared sources based on DFG require suitable nonlinear-optical materials and tunable pump sources of the appropriate wavelengths, such as dye or solid-state lasers.

Generation of tunable infrared radiation by DFG is reported by many groups,[1-3] but cw sources are reported less frequently. A cw pump source offers significantly smaller spectral linewidths than a pulsed source, better frequency stability, and continuous scan possibilities at the expense, however, of a lower conversion efficiency. Pine[4] described cw DFG for a spectrometer based on LiNbO$_3$, covering the region from 2.2 to 4.2 μm at a power level of 0.5 μW with a resolution of 5 × 10^{-4} cm^{-1} and a scan precision of 2 × 10^{-3} cm^{-1}. Recently two groups[5,6] reported improved performance of such a laser spectrometer in terms of output power (~10 μW) and

linewidth (<10^{-4} cm^{-1}). Using LiIO$_3$, Wellegehausen *et al.*[7] obtained coherent infrared radiation from 2.3 to 4.6 μm at ~0.5 μW. A combination of both crystals was used by Bawendi *et al.*[8] for high-resolution spectroscopy between 1.9 and 5.3 μm.

The optical and physical properties of the nonlinear-optical material is critical to generation of cw infrared radiation by difference frequency mixing. The nonlinear crystal must be transparent in the infrared and visible at all three mixing frequencies. For achieving the highest possible output by avoiding walk-off effects, collinear 90° phase matching over the entire wavelength region used is desirable. Other important desidered characteristics are a high nonlinear coefficient, a large damage threshold, good chemical stability, and commercial availability.

Silver thiogallate (AgGaS$_2$) meets these requirements. It exhibits low optical absorption from 0.5 to 12 μm (typically ~0.04 cm^{-1}, except near the ends of this wavelength range) and is 90° phase matchable from 2 to 10 μm.[9] The nonlinear polarizability of AgGaS$_2$ was first investigated by Chemla *et al.*[10] and Boyd *et al.*[11]; its nonlinear coefficient was found to be four times larger than that of LiNbO$_3$. However, to date the only mixing experiments using that crystal have been carried out with pulsed dye lasers employing non-90° phase matching. For instance, Hanna *et al.*[12] generated infrared radiation from 4.6 to 12 μm, and Seymour *et al.*[13] extended the spectrum to 18.3 μm. Elsaesser *et al.*[14] and more recently Yodh *et al.*[15] achieved tuning ranges from 3.9 to 9.4 μm and from 3.4 to 7 μm, respectively. Pulsed operation of an optical parametric oscillator based on AgGaS$_2$ was also reported.[16]

The current availability of AgGaS$_2$ crystals of high optical quality in large dimensions (>45 mm), along with stabilized cw tunable dye–Ti:sapphire sources, now makes it possible to design an infrared coherent radiation source, suitable for high-resolution spectroscopy, that is tunable from 3 to 9 μm at the 10-μW power level.

Results of a 90° phase-matching calculation carried out for AgGaS$_2$ with the refractive-index data given in Ref. 16
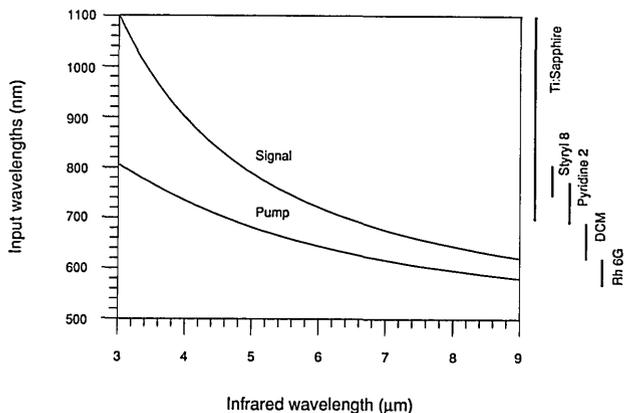
Fig. 1. 90° phase-matching curves of AgGaS$_2$ based on the refractive-index data given in Ref. 15.
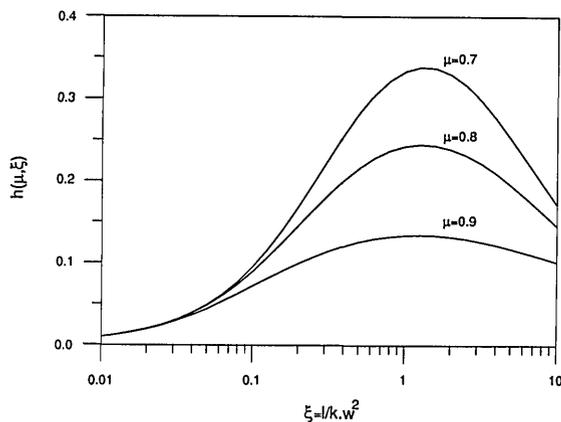
Fig. 2. Plot of the focusing function $h(\mu, \xi)$ versus the $\xi = l/b$ parameter for μ equal to 0.7, 0.8, and 0.9 ($\mu = \mathbf{k}_s/\mathbf{k}_p$).

are shown in Fig. 1. It can be seen that infrared radiation can be generated from 3 to 9 μm provided that the input beams are tuned from 580 to 800 nm (pump) and from 620 to 1100 nm (signal). This tuning can be achieved by using two dyes, Rhodamine 6G and DCM plus a Ti:sapphire laser for the pump and the signal beams.

An analysis was performed in order to estimate the cw infrared DFG output power based on Refs. 17 and 18 with Gaussian input beams and a lossless crystal assumed. In this case the DFG power can be expressed as

$$P_i = \frac{4\omega_i^2 \mathbf{k}_s d_{eff}^2 l}{\epsilon_0 \pi c^3 n_p n_s n_i (1 + \mu)} P_s P_p h(\mu, \xi), \tag{1}$$

where the subscripts p, s, and i refer to the pump, signal, and infrared beams, respectively, $\mathbf{k}$ is the wave vector, d_{eff} the effective nonlinear coefficient, l the crystal length, and n the refractive index; μ is the ratio of the input wave vectors ($\mu = \mathbf{k}_s/\mathbf{k}_p$) and, ξ is the ratio of the crystal length to the confocal parameter (assumed to be equal for both input beams). The dependence of the focusing function $h(\mu, \xi)$ on ξ is depicted in Fig. 2 for three different values of μ. The maximum dependence corresponds to optimum focusing.

For the case of a 2-cm-long AgGaS$_2$ crystal pumped by two equal-power beams of 1 W total power and focused optimally, an infrared power larger than 50 μW over most of the spectral range (Fig. 3) is predicted. It is worth noting that the output power is proportional to the crystal length,

and higher power levels can be achieved by increasing this dimension. Increasing the crystal length also increases the diameter of the beam waist of the pump lens proportionally, permitting the use of higher pump powers without crystal damage.

SPECTROMETER DESCRIPTION

A schematic of the DFG spectrometer system is shown in Fig. 4. A 20-W argon-ion laser is used to pump both a computer-controlled, frequency-stabilized, tunable Coherent 899-29 ring dye–Ti:sapphire laser and a Coherent 699-21 dye laser. A beam splitter is employed to separate the all-lines Ar$^+$ pump beam into two beams of equal power. In order to prevent degradation of the pump beam quality because of interference effects of the beam splitter, the beam splitter is wedged. The range of wavelengths covered by the two tunable lasers extends from 580 to 1100 nm and from 580 to 900 nm, respectively, with a single-frequency output power higher than 0.5 W when they are pumped with a 6-W all-lines argon laser beam. Even higher pump powers can be used effectively if the dye flow is cooled below room temperature. Each ring laser operates stably in a single mode selected by a three-plate birefringent filter and two intracavity étalons. The output frequency of each laser is actively stabilized to 0.5 MHz by feedback locking to an external reference cavity. The 899-29 ring laser also possesses a built-in
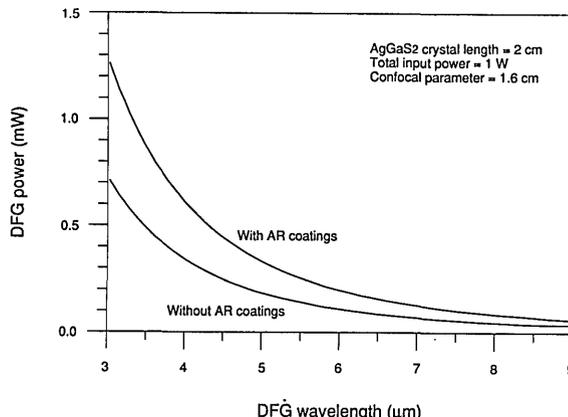
Fig. 3. Calculated DFG output power as a function of the wavelength. The case of focused Gaussian beams in AgGaS$_2$ is considered in the calculation. A value of 31 pm/V (Ref. 19) is used for d_{36}.
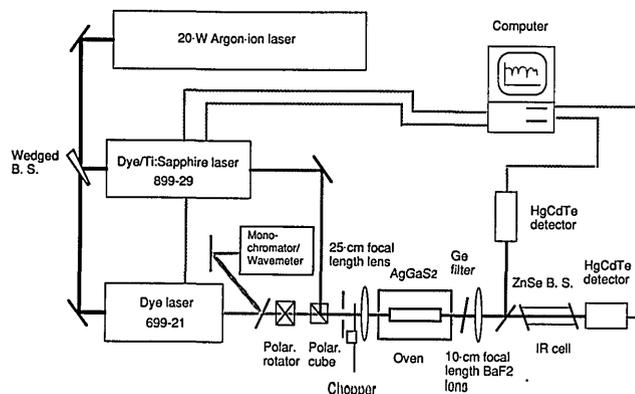
Fig. 4. Schematic diagram of the cw DFG infrared laser spectrometer system. B. S.'s, beam splitters; Polar., polarization.
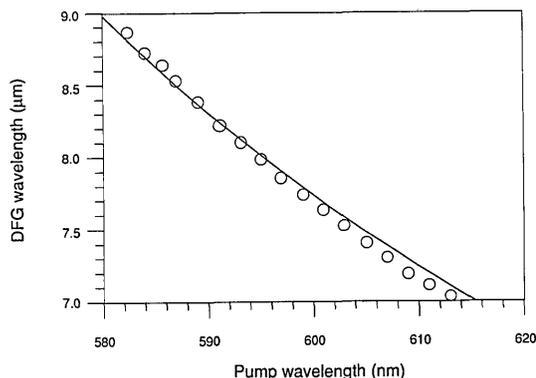
Fig. 5. Experimental 90° phase-matching curve of AgGaS$_2$. The solid curve corresponds to the calculated curve.

wavelength meter whose accuracy is 200 MHz. In scans the I$_2$ absorption spectrum is simultaneously acquired, providing accurate frequency calibration. The 699-21 wavelength determination is currently performed by means of a monochromator in conjunction with optogalvanic observation of atomic reference lines, a system that is to be replaced by a Michelson wavemeter with an accuracy of ~500 MHz (Ref. 19) and with an exact frequency setting to be determined by short scans over the I$_2$ absorption spectrum. The two tunable laser beams both emerge from their laser heads vertically polarized but must be perpendicularly polarized, so one beam is polarization rotated to the horizontal, and then the two laser beams are recombined by an antireflection- (AR) coated prism. Good spatial overlap of the two dye laser beams was accomplished by rotation of the prism mount. Collinearity was verified at various locations on the beam path with a high-resolution CCD camera. For spectroscopic scans near 8 μm the merged beams are chopped and focused by a 25-cm-focal-length lens into a 2-cm-long 90°-cut AgGaS$_2$ crystal. The crystal was placed in an oven (Chromatix Model 400) capable of temperatures up to 450°C with a short-term drift of ±0.03°C and a stability of ±0.1°C/day.

The nonlinear-optical response of the crystal generates a polarization, and thus an electromagnetic field, oscillating at a frequency that is the difference between the two input frequencies. The infrared output power is maximized by phase matching the wave vectors of the three beams throughout the length of the crystal by means of type I 90° phase matching (the shortest wavelength is the extraordinary wave, whereas the other two wavelengths are ordinary waves). The beams leaving the crystal pass through a germanium filter (AR coated for the 7–9-μm range in the initial experiments), which transmits the infrared beam while blocking the visible beams. In order to avoid burning the output coating of the crystal with the reflected visible radiation, the germanium filter is slightly tilted. The divergent infrared beam is then recollimated or focused by means of a 10-cm-focal-length BaF$_2$ lens. The absorption spectrum is recorded with two balanced HgCdTe detectors, one of which provides a reference.

The 4 mm × 4 mm × 20 mm AgGaS$_2$ crystal was AR coated for the 600–900-nm range on its input side and for the 3.8–9.1-μm range on its output side. Its optical absorption was investigated by a calorimetric method, and an absorption coefficient of ~4% cm^{-1} at 600 and 650 nm

was measured. From transmission measurements performed with a Fourier transform infrared spectrophotometer, an absorption coefficient of <4% cm^{-1} was deduced in the infrared region between 4 and 8.5 μm.

EXPERIMENTAL RESULTS

Initial experiments were performed using the dyes Rhodamine 6G for the 899-29 laser (580–610 nm) and DCM for the 699-21 laser (620–680 nm), generating cw infrared radiation from 7 to 9 μm. In Fig. 5 the resulting experimental phase-matching points at room temperature are compared with the theoretical 90° phase-matching curves based on the refractive-index data of Fan *et al.*[16] for the high-frequency pump laser. The difference seen between experiment and theory is explained in part by the limited accuracy of the wavelength calibration of the 699-21 dye laser, which at present depends on a monochromator (±0.15 nm). Slight variations in the refractive index from crystal to crystal may also play a role in causing these differences.

The measured DFG power is shown in Fig. 6 as a function of the generated wavelength, along with the visible-to-infrared conversion efficiency relative to the theoretically calculated value. The infrared output power was deduced from the sensitivity of two different HgCdTe detectors and compared with a calibrated power meter. The observed power of ~1 μW seems low in comparison with the powers of Fig. 3. However, the dye laser powers used here are much lower than those employed in the calculations of Fig. 3 because of laser damage to the output coating. The output side of the nonlinear crystal was AR coated for maximum transmission in the infrared spectrum. The damage threshold of this infrared coating was determined to be ~3 kW/cm^2 at ~600 nm, requiring that the total input pump power be set at <300-mW power. This setting reduces the expected power by slightly more than an order of magnitude compared with Fig. 3 [but the observed power is still only ~1/8 of that expected from Eq. (1)].

With an uncoated crystal this coating-damage limitation can be avoided. For a crystal without the output coating and a total input power of 1 W, the extrapolated DFG power that would be generated is at the 10-μW level, even with 1/8 the expected conversion efficiency, despite a
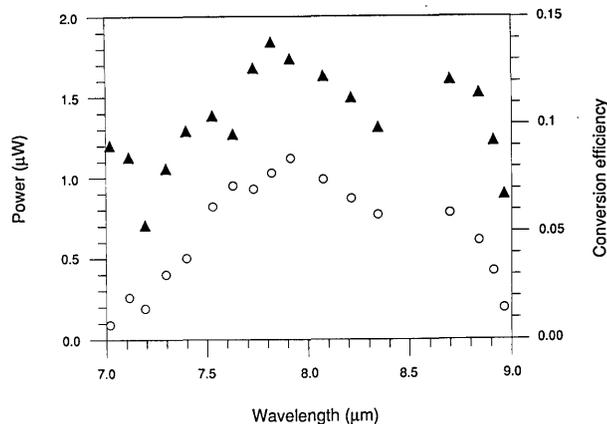
Fig. 6. Dependence of infrared DFG power and conversion efficiency on the infrared wavelength for AgGaS$_2$. The filled triangles and circles denote the IR power and the percentage of the theoretically determined efficiency, respectively.
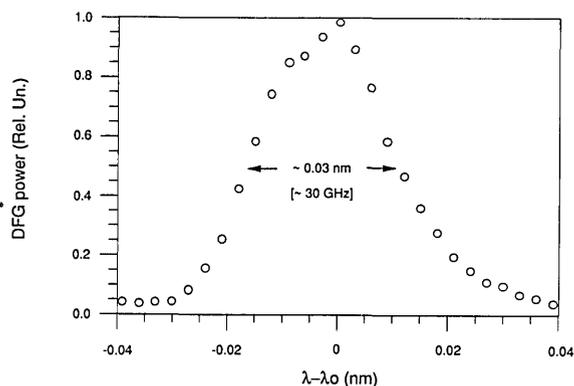
Fig. 7.   Dependence of the output power on the pump wavelength tuned close to its phase-matching value at 598.28 nm. The signal wavelength is fixed at 634.0 nm.

17% reflection loss of infrared radiation at the output surface. Such high powers are likely to damage the input AR coating, and it now seems best to use a totally uncoated crystal and accept the reflection losses at each surface in order to use all the dye laser power available.

The actual conversion efficiency is ~12% of the theoretical, as may be seen from Fig. 6. An explanation of part of the discrepancy is that the spectral beam modes differ slightly from an ideal TEM_{00} mode. Optical absorption by the $AgGaS_2$ crystal is not taken into account in the power calculation, but this effect should account for less than 15% of the discrepancy. A wide range of d_{36} nonlinear coefficients from 9 to 57 pm/V from measurements at various wavelengths have been reported.[20] If Miller's δ_{36} parameter is used to remove the wavelength dependence, a discrepancy between the $\delta_{36}(AgGaS_2)$ values found by groups using different measurement techniques appears. Groups employing second-harmonic generation report a $\delta_{36}(AgGaS_2)$ of ~0.22 pm/V, while DFG experiments yield a value of ~0.1 pm/V.[20] For the calculations we chose $\delta_{36}(AgGaS_2) = 0.23$ pm/V, obtained from our spontaneous parametric emission measurements.[20] However, if a value of $\delta_{36}(AgGaS_2) = 0.08$ pm/V, obtained recently by Yodh *et al.*,[15] is chosen, there is good agreement between the predicted and the observed infrared DFG power.

The $AgGaS_2$ crystal phase-matching bandwidth was also investigated. With the wavelength of the 699-21 dye laser fixed at 634.0 nm, the wavelength of the other pump source was tuned in steps of 0.003 nm (~3 GHz) around a central value of 589.20 nm. The phase-matching bandwidth was measured to be 0.03 nm (~1 cm^{-1} or ~30 GHz) from the plot shown in Fig. 7. Thus continuous frequency scans of 1 cm^{-1} (~30 GHz) can be achieved by tuning only one input wavelength without enormous loss of infrared power. Furthermore, it has been demonstrated that the effect of temperature on phase-matching characteristics in $AgGaS_2$ is small but significant.[20] From these data it is estimated than an increase of 1 cm^{-1} of the DFG frequency is obtained by decreasing the temperature by ~2.5°C while keeping the signal frequency constant. Thus the use of controlled-temperature phase matching leads to a significant increase in the wavelength scan range capability of up to several tens of inverse centimeters with reasonable crystal temperatures (<150°C).

No direct measurements of the spectral characteristics of the infrared DFG beam have been made. However, the linewidth, the jitter, and the drift will be of the same order of magnitude as those of the two visible pump sources, which are 0.5 MHz, 0.5 MHz, and 50 MHz/h, respectively, for each of the dye laser systems.

SYSTEM PERFORMANCE

In order to test the performance of the above-described infrared DFG spectrometer, the spectrum of the ammonia molecule was probed spectroscopically. A portion of the ν_2 band of NH_3 near 1177 cm^{-1} was chosen for a study of the performance characteristics of the DFG laser spectrometer. The Coherent Autoscan computer system and software of the 899-29 laser makes it possible to scan continuously over a range of 30 GHz (~1 cm^{-1}) in steps as small as 0.5 MHz. Data-acquisition software permits monitoring of the signal and reference infrared detectors simultaneously as the laser frequency is scanned. With this capability the 899-29 dye laser wavelength can be finely tuned over a maximum range of 30 GHz with the 699-21 dye laser frequency and a fixed crystal temperature, producing a high-resolution molecular absorption spectrum with relative convenience and speed.

A 30-cm-long absorption cell with two BaF_2 windows was filled with 1 Torr of NH_3. Figure 8 shows a portion of the ν_2 band of the NH_3 spectrum obtained with the 899-29 laser centered at 590.34 nm, the 699-21 laser fixed at 634.0 nm, and the oven temperature set at 63.5°C. The absorption peak positions obtained previously for NH_3 by Fourier transform spectroscopy[21] are used to set the single parameter of absolute infrared frequency location, because the absolute frequency of the longer-wavelength dye laser is not known with the same accuracy. The Fourier transform infrared NH_3 lines are shown as filled triangles across the bottom of the graph. The linewidth is ~110 MHz (~3.6 × 10^{-3} cm^{-1}), as can be seen in the inset for Fig. 8. The theoretical Doppler profile,
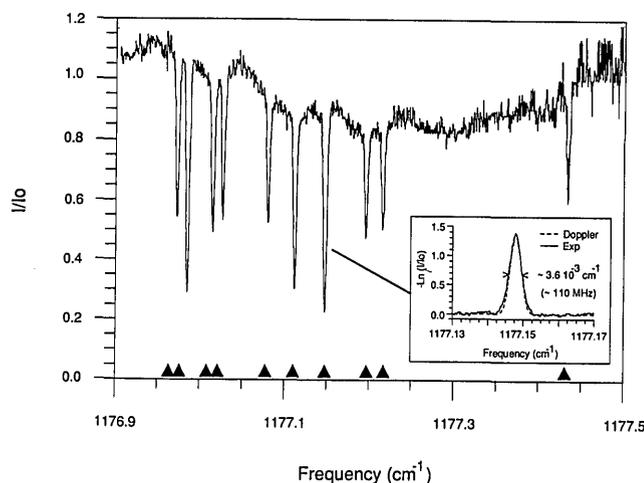
Fig. 8.   High-resolution spectrum of the ν_2 absorption band of NH_3 near 1177 cm^{-1}. The NH_3 pressure is 1 Torr, and the absorption path length is 30 cm. The inset shows the shape of the line near 1177.145 cm^{-1} compared with that predicted from the Doppler width corrected by a pressure-broadening contribution of 20 MHz. $\Delta\nu_{Tot} = [(\Delta\nu_{Dopp})^2 + (\Delta\nu_{press})^2]^{1/2}$.
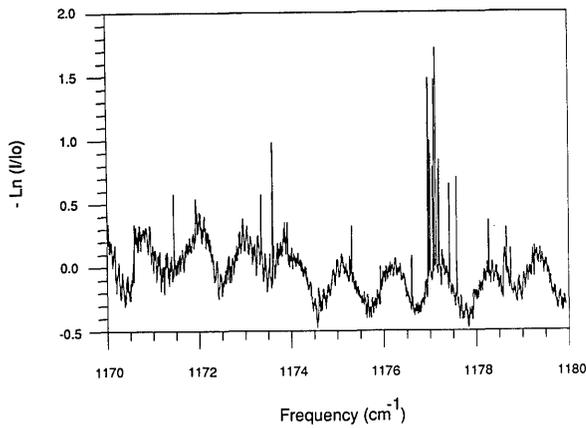
Fig. 9. Survey absorption spectrum of the ν_2 band of NH_3 between 1170 and 1180 cm^{-1}. The NH_3 pressure is 2 Torr, and the absorption path length is 30 cm.

corrected for an approximate pressure broadening of ~20 MHz/Torr, is also shown for comparison.[22]

As is described above, temperature phase matching can be used to increase the range of the wavelength scan. From an initial temperature of 80°C, the crystal temperature was decreased by ~1.6°C at the end of each 20-GHz scan, which allowed synchronous tracking of the phase-matching conditions for the next 20-GHz scan. Figure 9 shows such a long frequency scan of the absorption spectrum of NH_3 between 1170 and 1180 cm^{-1}. The periodic undulation of the absorption signals in Figs. 8 and 9 is due to an étalon effect resulting from parallel faces of the $AgGaS_2$ crystal. This effect can be eliminated by using a wedged (say, ~1°) crystal output face.

CONCLUSION

We describe a cw infrared spectrometer that is continuously tunable from 3 to 9 μm, which is suitable for high-resolution spectroscopy based on difference frequency mixing of two frequency-stabilized dye lasers and a computer-controlled dye–Ti:sapphire ring laser to generate difference frequency radiation in an $AgGaS_2$ crystal. Initial experiments have demonstrated a tuning range from 7 to 9 μm with power higher than 1 μW. Based on spectral characteristics of the input sources, the infrared radiation linewidth is of the order of 0.5 MHz or less, with low jitter and drift. Continuous scans of 1 cm^{-1} have been achieved over absorption lines of NH_3. The system shows considerable promise as a computer-controlled infrared spectrometer with good sensitivity, wavelength tunability, and resolution.

Potential improvements lie in increasing the generated infrared power and in the measurement and control of the wavelength-calibration accuracy. More intense pumping of the $AgGaS_2$ crystal, up to 1 W of total power, combined with a longer crystal should result in DFG power well in excess of 10 μW. The convenience of setting the fixed laser is limited by the use of a low-resolution mono-chromator for this operation. A wavelength meter (currently being built) will make the setting procedure much simpler by providing a frequency rapidly with an accuracy within 500 MHz.

APPENDIX A: EQUATIONS FOR DIFFERENCE FREQUENCY GENERATION WITH GAUSSIAN BEAMS AND 90° PHASE MATCHING

The power generated for DFG with Gaussian beams and 90° phase matching was given by Chu and Broyer[18] as

$$P_i = \frac{(16\pi\omega_i d_{\text{eff}})^2}{n_p n_s n_i c^3} \frac{h(\mu,\xi)}{(k_s^{-1} + k_p^{-1})} l P_s P_p, \tag{A1}$$

where the subscripts are i, idler or infrared; p, pump or highest frequency; and s, signal or intermediate frequency. $h(\mu,\xi)$ is the focusing function, and the k's are the propagation constants. The focusing function is the integral

$$h(\mu,\xi) = \frac{1}{2\xi}\int_0^\xi d\tau'' \int_{-\xi}^\xi d\tau' \frac{1 + \tau'\tau''}{(1 + \tau'\tau'')^2 + \frac{1}{4}[(1-\mu)/(1+\mu)] + [(1+\mu)/(1-\mu)]^2(\tau' - \tau'')^2}. \tag{A2}$$

The units in Eq. (A1) are cgs, and ϵ_0 was not factored out of d. In the mks notation of Byer and Herbst[17] this equation becomes

$$P_i = \frac{(2\omega_i d_{\text{eff}})^2}{n_p n_s n_i c^3 \pi \epsilon_0} \frac{h(\mu,\xi)}{(k_s^{-1} + k_p^{-1})} l P_s P_p, \tag{A1'}$$

where ϵ_0 has been factored out of the susceptibility. In the near-field approximation $\xi(=l/b) \to 0$, $h(\mu,\xi) \to \xi$, giving for Eq. (A1), when $b = k_s w_s^2 = k_p w_p^2$ (here the w's are the beam waist parameters) is introduced, the equations

$$P_i = \frac{(16\pi\omega_i d_{\text{eff}})^2}{n_p n_s n_i c^3} \frac{l^2}{w_s^2 + w_p^2} P_s P_p \quad \text{(cgs)}, \tag{A3}$$

$$P_i = \frac{(2\omega_i d_{\text{eff}})^2}{n_p n_s n_i c^3 \pi \epsilon_0} \frac{l^2}{w_s^2 + w_p^2} P_s P_p \quad \text{(mks)}. \tag{A3'}$$

Equation (A3) is the formula used by Pine[4] to estimate the expected difference frequency power for $LiNbO_3$.

ACKNOWLEDGMENTS

REFERENCES

1. K. Kato, "High-power difference frequency generation at 5–11 μm in $AgGaS_2$," IEEE J. Quantum Electron. **QE-20**, 698 (1984).
2. D. S. Bethune and A. C. Luntz, "A laser infrared source of nanosecond pulses tunable from 1.4 to 22 μm," Appl. Phys. B **40**, 107 (1986).

3. P. Mutin and J. P. Boquillon, "Very narrow-bandwidth tunable infrared difference frequency generation with injection-locked dye lasers," Appl. Phys. B **48**, 411 (1989).

4. A. S. Pine, "Doppler-limited molecular spectroscopy by difference frequency mixing," J. Opt. Soc. Am. **64**, 1683 (1974); "High-resolution methane ν_3-band spectra using a stabilized tunable difference-frequency laser system," J. Opt. Soc. Am. **66**, 97 (1976).

5. D. Bermejo, J. L. Domenech, P. Cancio, J. Santos, and R. Escribano, "Infrared difference frequency laser amd SRS spectrometers. *Q*-branch of CD_3H ν_1 band," *Laser Spectroscopy IX*, M. S. Feld, J. S. Thomas, and A. Mooradian, eds. (Academic, New York, 1989), p. 126.

6. C. M. Lovejoy, D. J. Nesbitt, P. O. Ogilby, and C. D. Moore, "Infrared flash kinetic spectroscopy. The ν_1 and ν_3 spectra of singlet methylene," J. Chem. Phys. **86**, 3151 (1987).

7. B. Wellegehausen, D. Friede, H. Vogt, and S. Shaldin, "Generation of tunable cw infrared radiation by difference frequency mixing," Appl. Phys. **11**, 363 (1976).

8. M. G. Bawendi, B. D. Rehfuss, and T. Oka, "Laboratory observation of hot bands of H_3^+," J. Chem. Phys. **93**, 6200 (1990).

9. R. S. Feigelson and R. K. Route, "Recent developments in growth of chalcopyrite crystals for nonlinear infrared applications," Opt. Eng. **26**, 113 (1987).

10. D. S. Chemla, P. J. Kupecek, D. S. Robertson, and R. C. Smith, "Silver thiogallate, a new material with potential for infrared devices," Opt. Commun. **3**, 29 (1971).

11. G. D. Boyd, H. Kasper, and J. H. McFee, "Linear and nonlinear optical properties of $AgGaS_2$, $CuGaS_2$ and $CuInS_2$, and theory of the wedge technique for the measurement of nonlinear coefficients," IEEE J. Quantum Electron. **QE-7**, 563 (1971).

12. D. C. Hanna, V. V. Rampal, and R. C. Smith, "Tunable infrared down-conversion in silver thiogallate," Opt. Commun. **8**, 151 (1973).

13. R. J. Seymour and F. Zernike, "Infrared radiation tunable from 5.5 to 18.3 μm generated by mixing in $AgGaS_2$," Appl. Phys. Lett. **29**, 705 (1976).

14. T. Elsaesser, H. Lobentanzer, and A. Seilmeier, "Generation of tunable picosecond pulses in the medium infrared by down-conversion in $AgGaS_2$," Opt. Commun. **52**, 355 (1985).

15. A. G. Yodh, H. W. K. Tom, G. D. Aumiller, and R. S. Miranda, "Generation of tunable mid-infrared picosecond pulses at 76 MHz," J. Opt. Soc. Am. B **8**, 1663 (1991).

16. Y.-X. Fan, R. C. Eckardt, R. L. Byer, R. K. Route, and R. S. Feigelson, "$AgGaS_2$ infrared parametric oscillator," Appl. Phys. Lett. **45**, 313 (1984).

17. R. L. Byer and R. L. Herbst, "Parametric oscillation and mixing," in *Nonlinear Infrared Generation*, V. R. Shen, ed. (Springer-Verlag, New York, 1977), p. 81.

18. T.-B. Chu and M. Broyer, "Intracavity cw difference frequency generation by mixing three photons and using Gaussian laser beams," J. Phys. (Paris) **46**, 523 (1985).

19. J. L. Hall and S. A. Lee, "Interferometric real-time display of cw dye laser wavelength with sub-Doppler accuracy," Appl. Phys. Lett. **29**, 367 (1976).

20. P. Canarelli, Z. Benko, A. Hielscher, R. Curl, and F. K. Tittel, "Measurement of nonlinear coefficient and phase matching characteristics of $AgGaS_2$," IEEE J. Quantum Electron. **28**, 1 (1992).

21. G. Guelachvili and R. K. Narahari, *Handbook of Infrared Standards* (Academic, New York, 1986).

22. C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (McGraw-Hill, Orlando, Fla., 1955), Table 13-3, p. 362.