Final Technical Report
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The purpose of this grant was to purchase the equipment necessary to construct a unique infrared laser source based on difference frequency generation in AgGaS₂. This continuous wave, single frequency, tunable infrared source has been assembled and is presently being used for the purpose proposed, i.e. infrared kinetic spectroscopy investigations of small free radicals of importance in combustion.

In this source the output of a scanning, frequency-stabilized dye/Ti-sapphire ring laser is mixed in the non-linear crystal AgGaS₂ with the output of a stabilized ring dye laser to produce single-frequency infrared output. To date, a variety of infrared frequencies in the region 1100 to 2200 cm⁻¹ have been produced, although in principle the source can be tuned from about 1000 to 3100 cm⁻¹ by proper choice of the wavelengths of the two lasers that are mixed. To date, powers of up to 30 μW have been generated (near 1850 cm⁻¹) and there is almost an order of magnitude more pump power available than was used in this experiment giving extrapolated infrared powers of about 200 μW. However, 30 μW is quite adequate for the experiments underway so that the system has not yet been pushed to its limits. This system represents a significant advance in tunable single frequency infrared spectroscopic sources.

Figure 1 depicts the experimental apparatus as it is now being used for infrared kinetic spectroscopy studies of free radicals. In operation, the ~ 20 W multiline output of an argon ion laser (Coherent Inova 200) pumps both a DCM dye (Coherent 699-21) and a Ti-Sapphire ring laser (Coherent 899-29). The output beams of the DCM dye and the Ti-Sapphire ring lasers are then mixed in the AgGaS₂ non-linear crystal. To satisfy the 90° type I phase matching conditions, the two input laser beams must be perpendicularly polarized. This is achieved by inserting a polarization rotator in the DCM beam and combining Ti:Sapphire and DCM radiation in a polarization cube as shown in Fig. 1. After the cube both beams travel colinearly and are focused with a 10 cm focal length lens so that the beam waists are located at the center of the mixing crystal. This focal length was selected to maximize the IR output power produced by the DFG nonlinear optical process. Infrared radiation at the frequency corresponding to the difference between the two input laser beams is generated in the AgGaS₂ crystal. The IR radiation is separated from the visible laser radiation by inserting the 1 mm thick Ge-filter with an anti-reflective IR coating immediately after the crystal as depicted. The infrared source is split into two beams one of which is introduced into the multiple reflection cell and thence to the signal detector, the other beam is sent to a reference detector. The outputs of the signal and reference detectors are combined in a difference amplifier. This results in cancellation of noise caused by amplitude fluctuations of the pump laser. The output of the difference amplifier is then read by a transient digitizer.

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In operation, reactive free radicals are generated by flash photolysis of a suitable precursor by the excimer laser. When the IR frequency is tuned to an absorption of the free radical of interest, the signal from detector monitoring the multipass cell is altered as a result of infrared absorption by the free radical. The transient digitizer acquires this transient infrared absorption signal as a function of time for a 20 to 1000 μsec time window around the time of the excimer flash. The transient digitizer is read by the computer controlling the operation of the lasers, and the data is partially analyzed and the results stored.

Operation of the Laser System

Figure 2 shows a series of operating points tested in the IR range from about 1600 to 1900 cm^{-1} with the actual wavelengths of the pump lasers found to give a particular IR wavenumber plotted as points. For these observations the two lasers are operated as a Ti:sapphire laser and a DCM laser. The single frequency cw DCM dye laser is tunable from 620 to 670 nm with an average output power of ~ 500 mW while the Ti-Sapphire generates about 1 W radiation from 700-760 nm. Single frequency operation in each ring laser is achieved through the intracavity use of a three plate birefringent filter (BRF) and two etalons. Furthermore, both ring lasers are actively frequency stabilized by feedback locking to an external cavity, so that a linewidth of 0.5 MHz is obtained. The Ti:Sapphire laser is equipped with a commercial wavemeter that has an absolute accuracy of better than 200 MHz. The DCM laser frequency is measured by means of a second Michelson type interferometer wavemeter built in this laboratory. The accuracy of this wavemeter was determined to be about 200 MHz based on careful wavelength calibrations against Ne and Fe atomic transitions in optogalvanic cell and the I_2 molecular spectrum.

The dye/Ti:Sapphire ring laser can be tuned to any desired wavelength within its lasing range under computer control using Coherent's Autoscan II software. Additional software was written to permit convenient computer control of the DCM laser. A comparison of the measured and desired wavelengths determines the relative positions of the BRF, thin and thick etalons and a 2 mm Brewster plate. This is accomplished as follows: First a computer driven stepping motor rotates the BRF, which results in frequency mode jumps of 225 GHz, corresponding to the free spectral range of the thin etalon. The BRF is then moved to the mode closest to the desired wavelength. The thin etalon, mounted on a galvanometer drive is then automatically tilted for a wavelength setting within 30 GHz. Subsequently use is made of the standard laser control electronics available for the Coherent 699-21 laser. Computer control determines the position of a galvo driven 2 mm thick Brewster plate, a piezo driven thick etalon with variable spacing and the fine tuning of the thin etalon. In this way a final laser spectrometer wavelength setting is obtained within the wavemeter accuracy of 200 MHz. For external computer controlled wavelength scans of the DCM laser over ~ 30 GHz, a voltage ramp is applied by a D/A output of the computer to the above mentioned standard laser control electronics.

An uncoated 4 x 4 x 45 mm AgGaS₂ crystal (Cleveland Crystals, Inc.) with absorption coefficients of 0.05 cm⁻¹ at 633 nm and 0.01 cm⁻¹ at 1.064 μm (measured by calorimetry) was used for the DFG spectrometer. 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 in order to provide stable phasematching conditions at ~ 20°C. To avoid etalon effects the output face the crystal is wedged at 1 degree from the input face.

Performance as a spectrometer source

Figure 3 depicts the Q-branch of a combination band (11¹1) of N₂O obtained in simple absorption using this difference frequency source. The spectrum shown in Fig. 3 represents a composite of several 30 GHz scans which have been individually corrected for IR power variations. In taking this spectrum the DFG IR beam one meter behind the AgGaS₂ crystal was focused by means of two spherical concave gold mirrors (R = 120 cm) into a multipass absorption cell, which provided greatly enhanced sensitivity and allowed for more stringent evaluation of the laser spectrometer. This cell consisted of 3 spherical concave gold mirrors (R1 = 100.662 cm; R2 = 100.420 cm; R3 = 100.336 cm) which are spaced 1 m apart. By adjusting the angular arrangement of the mirrors, the effective path length of the cell was varied between 4 and 60 meters in 4 meter increments. The spectra reported here were recorded with a 32 meter path length with an N₂O gas sample pressure of 300 mTorr. The widths of the individual absorption lines in this spectrum were limited by the room temperature Doppler width to about 110 MHz. The spectral width of the difference frequency source itself is less than 1 MHz.

As an example of a transient infrared absorption obtained with this system, Figure 4 shows the transient infrared absorption signals from CO produced by flash photolysis of acetone in various vibrational states. The signals from CO in the v=1 and v=2 states decay with time as a result of vibrational relaxation by the acetone present.

Further information

For further information about this source, please see the previous technical report (December 1991) and the papers:

1. A Continuous Wave Infrared Laser Spectrometer Based on Difference Frequency Generation in AgGaS₂ for High Resolution Spectroscopy, P. Canarelli, Z. Benko, R. F. Curl, and F. K. Tittel, J. Opt. Soc. Am. B **9**, 197-202 (1992).
2. Optimization of a midinfrared high-resolution difference-frequency laser spectrometer, A. H. Hielscher, C. E. Miller, D. C. Bayard, U. Simon, K. P. Smolka, R. F. Curl, and F. K. Tittel, J. Opt. Soc. B, **9**, 1962-1967 (1992).

Figure Captions

- Fig. 1: Schematic diagram of the DFG laser spectrometer
- Fig. 2: Experimental 90° phase matching curve of AgGaS₂ from 1550 to 2100 cm⁻¹. The solid lines correspond to the calculated curves based upon the Sellmeier parameters of Yuan Xuan Fan, R.C. Eckardt, R.L. Byer, R.K. Route, R.S. Feigelson, Appl. Phys. Lett. **45**, 313 (1984).
- Fig. 3: Survey absorption spectrum of the 01¹₁ - 00⁰₀ band of N₂O. The N₂O pressure is 300 mTorr and the path length ~ 32 m. Data points were taken at 20 MHz intervals. For comparison the calculated line positions are indicated. N₂O lines with an asterisk do not belong to the Q-branch.
- Fig. 9: Time dependent absorption intensities observed for the production of CO from 193 nm acetone photodissociation. The spectra show CO products in the $v=0$ (upper panel), $v=1$ (middle panel), and $v=2$ (lower panel) vibrational states

Fig. 1

Fig. 2

Fig. 3

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