

# INFRARED KINETIC SPECTROSCOPY OF FREE RADICALS USING DIFFERENCE FREQUENCY GENERATION

C. E. Miller, U. Simon, W.C. Eckhoff, R. F. Curl, and F. K. Tittel  
Department of Chemistry and Rice Quantum Institute,  
Rice University, Houston, Texas 77251-1892 USA

## ABSTRACT

A laser source based on difference frequency generation (DFG) in AgGaS<sub>2</sub> has been developed for high resolution infrared kinetic spectroscopy of free radicals. Continuously tunable infrared radiation has been generated between 4 and 9  $\mu\text{m}$  (2500 - 1100  $\text{cm}^{-1}$ ) by mixing two single frequency visible lasers in a 90° Type I phasematching configuration. Spectra of the free radicals HOCO, DOCO, and HCCN were obtained using this source.

Concurrently, we have explored the suitability of visible cw diode lasers for DFG of tunable infrared radiation with the goal of producing a portable version of the AgGaS<sub>2</sub> source. Approximately 1  $\mu\text{W}$  of tunable, narrow band infrared light near 5  $\mu\text{m}$  has been generated by mixing a single-mode III-V diode laser with a tunable single-frequency Ti:sapphire laser. We also mixed two single-mode diode lasers (690 and 808 nm, 12 mW total power input) to produce several nanowatts of infrared power in the first demonstration of diode laser DFG.

## INTRODUCTION

There exists a need for continual improvement of convenient laser-based sources for high resolution spectroscopy. Since virtually all fundamental vibrational modes of molecules, free radicals, and molecular ions lie in the 2 to 20  $\mu\text{m}$  wavelength region, tunable monochromatic sources in this range are particularly desirable. CW laser sources present the greatest potential for an optimum combination of spectral control and frequency stability. Although tunable cw laser sources such as color center lasers, lead-salt diode lasers, and CO and CO<sub>2</sub> sideband lasers emit in this spectral region, each type suffers from one or more practical drawbacks: the requirement of cryogenic cooling, operational wavelength ranges which do not reach regions of great interest, incomplete coverage of their nominal operational wavelength range, and lack of portability and ruggedness.

Difference frequency generation (DFG) in a suitable nonlinear optical medium offers a viable alternative to traditional infrared laser sources, especially when wide tunability is desired. The DFG source originally developed by Pine<sup>1</sup> in which an Ar<sup>+</sup>-laser is mixed with a cw dye laser in LiNbO<sub>3</sub> has proved very useful for high resolution spectroscopy but is limited to wavelengths shorter than 4  $\mu\text{m}$  by the transmission characteristics of LiNbO<sub>3</sub>. Using LiIO<sub>3</sub> as the nonlinear medium, Oka and coworkers extended the long wavelength limit for cw DFG spectroscopic sources to nearly 5  $\mu\text{m}$ .<sup>2</sup> Recently, we demonstrated the operation of a continuously tunable cw DFG spectrometer in the 4 to 9  $\mu\text{m}$  (2500 to 1100  $\text{cm}^{-1}$ ) region based on Type I 90° noncritical phasematching in a AgGaS<sub>2</sub> crystal pumped by two tunable single-frequency ring lasers<sup>3,4</sup>. This spectrometer extends the advantages of DFG sources into the chemically interesting "fingerprint" region of the IR, greatly increasing its applicability. This source is the essential element of an infrared kinetic spectroscopy apparatus designed to observe new free radicals. In the following we discuss the AgGaS<sub>2</sub> DFG spectrometer; the observation of HOCO, DOCO, and HCCN; and experiments involving DFG in AgGaS<sub>2</sub> using III-V diode lasers as the pump and signal beam sources.

## EXPERIMENTAL

The AgGaS<sub>2</sub> DFG spectrometer, shown in Figure 1, has been described previously (see reference 4 for details). Two single frequency ring lasers,  $\text{d}\lambda < 1 \text{ MHz}$ , were pumped by the all-lines output of

an Ar<sup>+</sup> laser (Coherent Innova 200), typically operated at ~19 W. One ring laser (Coherent 899-21) operated in a dye cavity configuration lasing on DCM dye and generated the pump beam ( $\lambda = 620\text{--}690$  nm). The second ring laser (Coherent 899-29) operating with a Ti:sapphire cavity configuration generated the signal beam ( $\lambda = 700\text{--}840$  nm). The pump and signal laser polarizations were adjusted for 90° Type I ( $e \rightarrow o + o$ ) phasematching by rotating the polarization of the Ti:sapphire laser 90° and spatially overlapping the two beams with a polarization cube. The copropagating visible beams were focused into a 45 mm long AgGaS<sub>2</sub> crystal (Cleveland Crystals, Inc.) to a beam waist of ~40  $\mu\text{m}$ . The infrared radiation generated in the crystal was collimated and propagated through a ZnSe beamsplitter. A portion of the IR light passed through a 20 cm reference gas cell and was monitored by a liquid nitrogen cooled HgCdTe detector. The other portion of the IR traversed a multipass absorption cell (White cell<sup>5</sup>) with a base pathlength of 1.00 meters and was monitored by a second liquid nitrogen cooled HgCdTe detector. The excimer laser radiation used to create the transient radical population entered one end of the White cell, overlapped the IR, and was terminated in a beam trap at the opposite end. Germanium filters with antireflective IR coatings were placed in front of each HgCdTe detector to eliminate the residual visible and UV laser light.

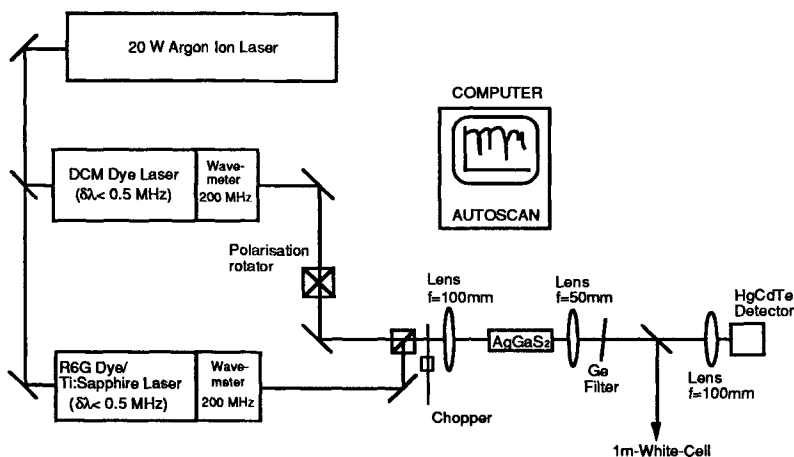


Fig.1 Schematic of AgGaS<sub>2</sub> DFG Spectrometer

The 193 nm photolysis of acetic acid, CH<sub>3</sub>COOH and CH<sub>3</sub>COOD (98% D) produced HOCO and DOCO radicals, respectively. HCCN was generated by the 193 nm photolysis of dibromoacetonitrile, Br<sub>2</sub>HCCN. Precursor compounds were introduced into the White cell by gently bubbling He carrier gas through liquid samples. The sample gas mixture and additional He buffer gas flowed through the cell so that their steady-state pressures were typically 300 millitorr and 8 Torr, respectively. Gas samples were replenished between every excimer laser pulse. The White cell was adjusted for 24-32 passes and there was an effective physical overlap of ~28 cm per pass in the middle of the cell.

## RESULTS AND DISCUSSION

The DFG spectrometer provides the resolution and brightness necessary to investigate the infrared spectra and reaction dynamics of transient free radicals. To demonstrate the capabilities of the spectrometer, we reinvestigated the  $\nu_2$  C=O stretching spectra of HOCO and DOCO near 1860  $\text{cm}^{-1}$  recently reported by Sears and coworkers.<sup>6</sup> The spectra in Figures 2 and 3, showing portions of the HOCO and DOCO  $\nu_2$  Q branches, illustrate that Doppler limited resolution was achieved. Line

positions and relative intensities are in excellent agreement with those recorded previously using lead salt diode lasers.<sup>6</sup> Closer inspection suggests that the DFG spectra exhibit slightly better resolution characteristics than the diode laser spectra even though Doppler broadening is the limiting factor in both cases.

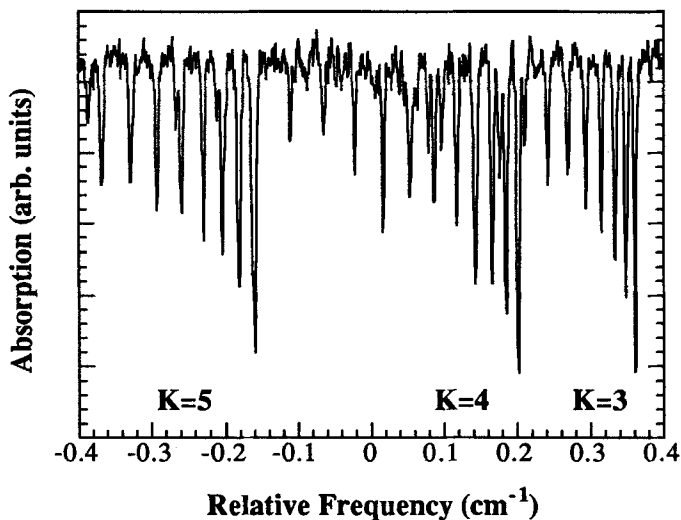


Fig.2 HOCO  $\nu_2$  Q Branch near 1852  $\text{cm}^{-1}$

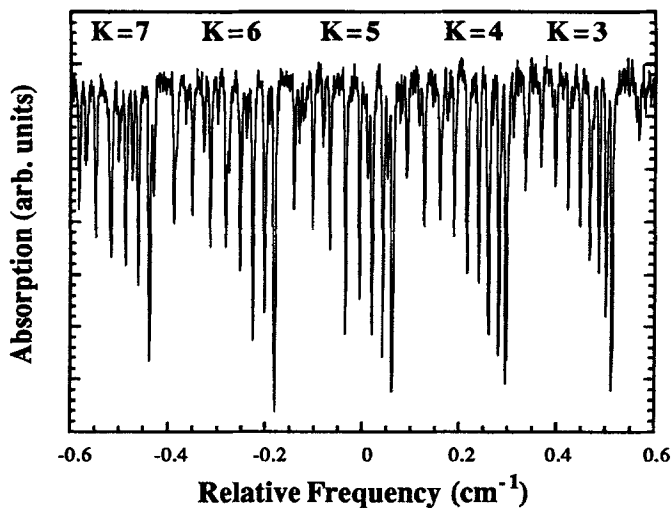


Fig.3 DOCO  $\nu_2$  Q Branch near 1850  $\text{cm}^{-1}$

Although we successfully observed the free radicals HOCO and DOCO, their spectroscopy was previously known. Therefore, we searched for the  $\nu_2$  CCN antisymmetric stretching mode spectrum of the HCCN radical. HCCN is especially interesting due to the debate over its equilibrium geometry. High level *ab initio* calculations indicate that the lowest energy structure has an HCC bond angle of  $138^\circ$ <sup>7,8</sup> while virtually all experimental results favor a linear structure<sup>9-11</sup>. The calculated barrier to linearity ranges from 300 to 800  $\text{cm}^{-1}$ <sup>7,8</sup>, suggesting a large amplitude HCC bending motion and possible quasi-linearity in this radical. Very recently, our group has observed the  $\nu_1$  CH stretching mode spectrum of this radical using the color center laser spectrometer<sup>12</sup> and found evidence for a small barrier to linearity ( $\sim 100 \text{ cm}^{-1}$ ) based on the values for  $\nu_4$ ,  $\nu_5$ , and  $2\nu_5$  determined from various hot band series. The  $\nu_2$  spectrum should be even more sensitive to the HCCN quasi-linearity since the *ab initio* structure calculations indicate that the CCN antisymmetric stretching motion, CC bond compression and CN bond elongation, is strongly coupled to the bent-to-linear transformation.<sup>7,8</sup>

IR matrix studies<sup>11</sup> located the HCCN  $\nu_2$  transition at  $1735 \text{ cm}^{-1}$ . We scanned this area and found numerous transient absorption lines. Figure 4 shows a characteristic  $3 \text{ cm}^{-1}$  wide segment of this spectrum. We have observed HCCN lines throughout the region between  $1715$  and  $1765 \text{ cm}^{-1}$ , but data analysis has been hampered by the large number overlapping spectral series due to transitions originating from vibrational levels above the ground state. A detailed interpretation of this spectrum will be the subject of a future report.

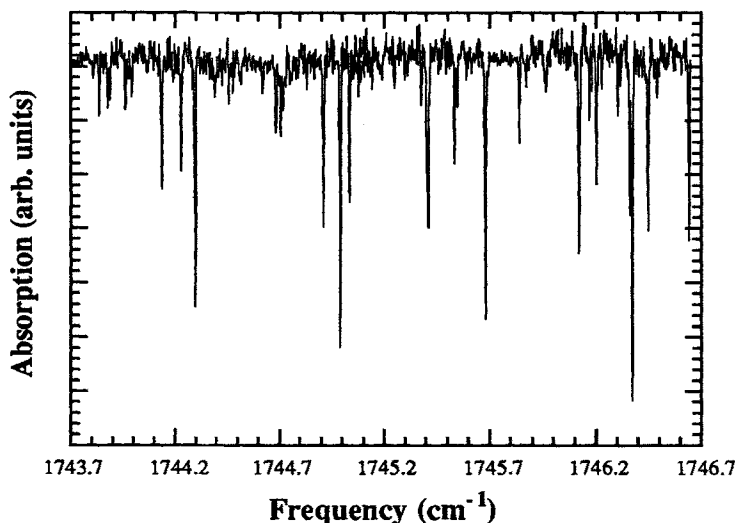


Fig.4 A  $3 \text{ cm}^{-1}$  portion of HCCN  $\nu_2$  CCN antisymmetric stretching mode spectrum

### DFG USING III-V DIODE LASERS

Recent advances in high-power single-mode III-V diode laser technology<sup>13</sup> now offers the possibility of employing diode lasers as pump sources in DFG. Efficient, compact, robust, and portable spectrometers especially suitable for applications in selective environmental monitoring of trace species can be constructed using a diode laser based DFG source. Potentially, IR radiation from 3

to 6  $\mu\text{m}$  by DFG in  $\text{AgGaS}_2$  using Type I noncritical phasematching can be generated by mixing  $\text{AlGaInP}$ ,  $\text{AlGaAs}$ ,  $\text{InGaAs}$ , and/or  $\text{InGaAsP}$  III-V diode lasers.<sup>14</sup>

In the development of a compact DFG spectrometer based on two single-mode diode lasers, we made use of the already existing DFG spectrometer.<sup>4</sup> In the first step the DCM dye laser was replaced by a single-mode diode laser which was then mixed with the Ti:sapphire laser. Finally, two single-mode diode lasers were mixed in the  $\text{AgGaS}_2$  crystal.<sup>15</sup> The diode lasers used in this work were free-running commercial index-guided devices. By varying the temperature and current of these devices, their emission wavelength could be tuned conveniently over  $\sim 2$  nm. The collimated diode laser beam which had a rectangular beam shape of  $1 \times 5 \text{ mm}^2$  cross-section was converted to a square-shaped beam with a beam dimension of approximately 5 mm using an anamorphic prism pair. A 3:1 telescope transformed the diode laser to a  $\sim 2$  mm diameter beam. The diode laser output has a polarization ratio of about 100:1; the appropriate polarization direction for 90° Type I phase-matching was chosen by proper mounting of the diode lasers.

For a signal and pump wavelength of 808.3 nm (Ti:sapphire laser) and 690.3 nm (Toshiba TOLD 9140(s) diode laser), respectively, an idler wavelength of 4.73  $\mu\text{m}$  was detected. Figure 5 shows the generated DFG power as a function of the input signal power. In this measurement the diode laser power was fixed at 12.1 mW. The Ti:sapphire laser power was varied using metallic neutral density filters. Laser powers were measured using a photodiode calibrated against factory standards. Fig. 5 shows that for low powers the idler power increased linearly with the signal power as expected. Inexact spatial overlap of the pump and signal beams was probably responsible for most of the IR power fluctuations. Thermal loads in the crystal created conversion inefficiencies for input powers above about 500 mW. Up to 1.4  $\mu\text{W}$  of DFG power was measured for 1 W of Ti:sapphire laser power and 12.1 mW of diode laser power. The phasematching bandwidth of the diode/Ti:sapphire pump laser configuration was observed to be as large as  $20 \text{ cm}^{-1}$  (600 GHz). This is much larger than the  $1 \text{ cm}^{-1}$  (30 GHz) phasematching bandwidth observed for the dye/Ti:sapphire configuration. The poor spatial coherence of the diode laser beam apparently results in reduced power, but extended phasematching range.

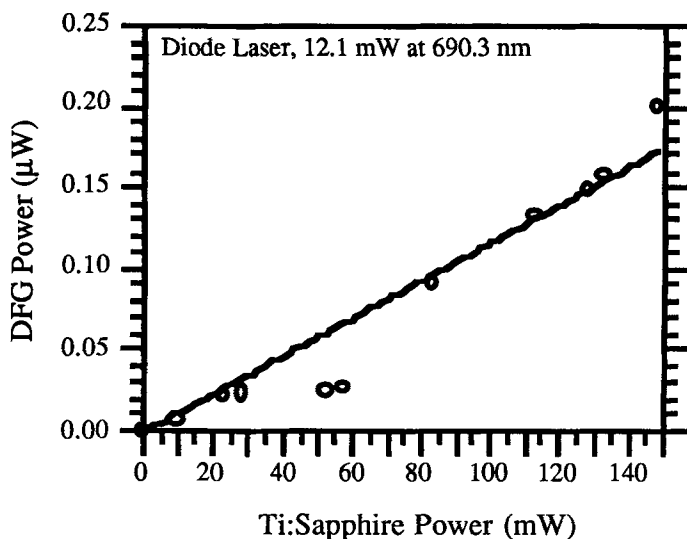


Fig.5 DFG output power for the 690.3 nm diode laser / 808.3 nm Ti:sapphire laser mixing experiment: the line represents a least squares fit to the measured data

Another laser diode (Toshiba TOLD 9215(s)) emitting up to 9 mW in a single mode at 671.4 nm was phase-matched with the Ti:sapphire laser at 772.8 nm. Approximately 1.2  $\mu$ W of IR power at 1963  $\text{cm}^{-1}$  was measured from input power levels of 5.2 mW and 1.15 W from the diode and Ti:sapphire lasers, respectively. To investigate the effect of the non-Gaussian diode laser beam on the DFG conversion efficiency, the experiment was repeated using the DCM dye laser set to the same wavelength and power level as the diode laser. The infrared output of the dye/Ti:sapphire laser combination, like the diode/Ti:sapphire laser combination, showed a linear dependence of IR power upon the input signal power but the slope was a factor of three greater. Thus, as might be expected, the non-Gaussian diode laser mode does not mix as effectively with the pure TEM<sub>00</sub> Gaussian mode of the Ti:sapphire signal source as does the pure TEM<sub>00</sub> Gaussian mode from the ring dye laser.

Finally, we performed the first successful diode laser DFG experiment by mixing two single-mode diode lasers in AgGaS<sub>2</sub> to generate tunable infrared radiation.<sup>15</sup> A Toshiba TOLD 9140(s) diode laser (690nm and 10.1 mW) and a Sharp LT010MD diode laser (808 nm and 1.93 mW) were mixed to generate up to 3.3 nW of infrared radiation around 2115  $\text{cm}^{-1}$ . By optimizing the spatial overlap of both diode laser beams in terms of the size and location of the beam waists in the crystal we expect much higher visible-to-infrared conversion efficiencies. Moreover, by using high power diode lasers in combination with diode amplifiers as pump sources and by placing the AgGaS<sub>2</sub> crystal in an external enhancement cavity, we expect to achieve a significant increase of the infrared output power.

This work has been supported by the Robert A. Welch Foundation and the National Science Foundation. The authors acknowledge notable contributions of C.C. Bradley and R.G. Hulet to the diode laser mixing experiments. CEM is a Robert A. Welch Fellow. US is a Feodor Lynen Fellow of the Alexander von Humboldt-Foundation. WCE is a Robert A. Welch Pre-Doctoral Fellow.

## REFERENCES

1. A. S. Pine, *J. Opt. Soc. Am.* **64**, 1683 (1974).
2. M. G. Bawendi, B. D. Rehfsuss, and T. Oka, *J. Chem. Phys.* **93**, 6200 (1990); L. W. Xu, C. Gabrys, and T. Oka, *J. Chem. Phys.* **93**, 6210 (1990).
3. P. Canarelli, Z. Benko, R. F. Curl, and F. K. Tittel, *J. Opt. Soc. Am. B*, **9**, 197 (1992);
4. A. H. Hielscher, C. E. Miller, D. C. Bayard, U. Simon, K. P. Smolka, R. F. Curl, and F. K. Tittel, *J. Opt. Soc. Am. B*, **9**, 1962 (1992).
5. J. U. White, *J. Opt. Soc. Am.* **32**, 285 (1942).
6. T. J. Sears, W. M. Fawzy, and P. M. Johnson, *J. Chem. Phys.* **97**, 3996 (1992).
7. P.-A. Malmquist, R. Lindh, B. O. Roos, and S. Ross, *Theor. Chim. Acta* **73**, 155 (1988).
8. E. T. Seidl and H. F. Schaefer III, *J. Chem. Phys.* **96**, 4449 (1992) and extensive experimental and theoretical references therein.
9. S. Saito, Y. Endo, and E. Hirota, *J. Chem. Phys.* **80**, 1427 (1984).
10. F. X. Brown, S. Saito, and S. Yamamoto, *J. Mol. Spectrosc.* **143**, 203 (1990).
11. A. Dendramis and G. E. Leroy, *J. Chem. Phys.* **66**, 4334 (1977).
12. C. L. Morter, S. K. Farhat, and R. F. Curl, *Chem. Phys. Lett.*, accepted.
13. C. E. Wieman, and L. Hollberg, *Rev. Sci. Instrum.* **62**, 1 (1991).
14. K. Nakagawa, M. Ohutsu, C. H. Shin, M. Kourogi, and Y. Kikunaga, *Laser Spectroscopy* (Tenicols '91), M. Ducloy ed. (Singapore:World Scientific, 1992), pp. 353-358.
15. U. Simon, C. E. Miller, C. C. Bradley, R. G. Hulet, R. F. Curl, and F. K. Tittel, *Opt. Lett.* **18**, 1 (1993).