

A Widely Tunable cw Laser Difference-Frequency Source for High-Resolution Infrared Spectroscopy

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Abstract—The development of a continuous-wave (cw) laser difference-frequency generation (DFG) spectrometer is reported. A broadly tunable cw laser-based infrared source was generated from 8 to 19 μm by laser difference frequency mixing in a gallium selenide (GaSe) crystal. The spectral performance of the DFG spectrometer was evaluated by using the Doppler limited resolution spectrum of benzene in the ν_4 band near 662 cm^{-1} . High spectral purity and wide tunability make this novel frequency conversion-based infrared source not only a powerful tool for spectroscopy, but also a useful alternative to a semiconductor laser-based detection system for highly sensitive and highly selective measurement of multicomponent trace gas at room temperature operation in the middle infrared region.

INTRODUCTION

There is considerable interest in developing a tunable continuous-wave (cw) infrared laser source for a wide range of applications, such as high-resolution and high-precision absorption spectroscopy, optical frequency metrology, study of the terrestrial atmosphere, analysis of atmospheric pollutants and environmental trace gases monitoring by the spectroscopic method. In recent years, advances in the quantum-mechanically designed cascade structure have led to a revolutionary progress in semiconductor laser technology for the mid-infrared ranging from 3.4 to 17 μm [1]. But to date, these attractive laser sources still require cooling to $\sim 100\text{ K}$ for continuous-wave operation.

Over the last decade, there has been rapid progress in new nonlinear optical materials phase-matchable for the mid-infrared up to $\sim 20\text{ }\mu\text{m}$, in novel phase-matching schemes, and in laser technology: single-mode, room temperature diode laser, diode pumped solid-state lasers, and broadly tunable Ti : Sapphire lasers are commercially available for the spectral region from 0.65 to 2 μm . It provides new opportunities in the development of laser sources based on nonlinear frequency down-conversion. This room temperature laser-based infrared source offers the unique advantage of high spectral purity and wide frequency tunability in the mid-infrared (3–20 μm) as compared with semiconductor lasers [2–4], which makes it not only a powerful tool for high-resolution spectroscopy, but also a useful alternative to the semiconductor laser-based monitoring system for high sensitive and high selective detection of multicomponent trace gas at room temperature operation in the middle infrared region.

DIFFERENCE FREQUENCY INFRARED SPECTROMETER

A widely tunable continuous-wave (cw) mid-infrared spectrometer was developed, which was aimed at spectroscopic investigation of trace species measurement by laser absorption spectroscopy [5–7]. The spectrometer was based on laser difference-frequency generation (DFG) in a gallium selenide (GaSe) crystal. As effective nonlinear material suitable for frequency conversion, it should be optically transparent to the frequencies of all the interacting waves, phase matchable with a relatively large nonlinearity and a high optical damage threshold. GaSe, a negative uniaxial crystal ($n_o > n_e$), is optically transparent from 0.65 to $\sim 20\text{ }\mu\text{m}$ [8]. The nonlinear effective coefficient for type I interaction can be written as

$$d_{00e} = d_{22} \cos^2 \theta \sin(3\phi). \quad (1)$$

GaSe exhibits a large nonlinear coefficient (54 pm/V vs. 13 pm/V for AgGaS₂). Its nonlinear figure of merit (d^2/n^3) is even almost 10 times higher than the corresponding value for AgGaS₂ [9]. The GaSe crystal is very attractive for DFG at a long wavelength of up to $\sim 20\text{ }\mu\text{m}$.

A schematic arrangement of the DFG-based spectrometer is shown in Fig. 1. The pump and signal lasers were argon ion laser-pumped cw single-frequency Ti : Sapphire lasers (899-29 Autoscan, Coherent Inc.), which were tunable from 700 to 800 nm and from 800 to 900 nm, respectively. Laser polarizations were matched to be orthogonal in order to realize type I

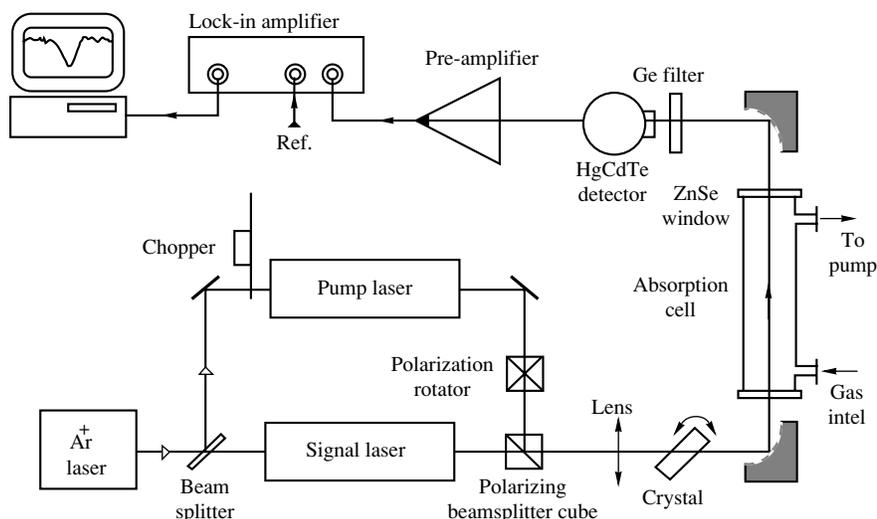


Fig. 1. A schematic arrangement of the DFG-based laser spectrometer: A polarization rotator was used to rotate the polarization of the pump laser by 90° . The orthogonally polarized laser beams were then combined in a polarizing beamsplitter cube and focused in the crystal with an $f = 350$ mm lens.

phase matching condition. The laser beams were spatially overlapped with a polarizing beamsplitter cube and focused in a GaSe crystal to generate infrared radiation at the difference frequency of the lasers by $\chi^{(2)}$ nonlinear frequency conversion. The used GaSe crystal was z -cut 5 mm thick and 10 mm in diameter (EKSMA Co.), and mounted on a rotation stage. Under type I birefringently phase-matching interaction, the infrared emission was continuously tunable from 8 to 19 μm in wavelength by laser wavelengths tuning associated with the angle tuning of the crystal z -axis orientation. Figure 2 plots the experimental type I phase matching characteristics of the GaSe at room temperature, which

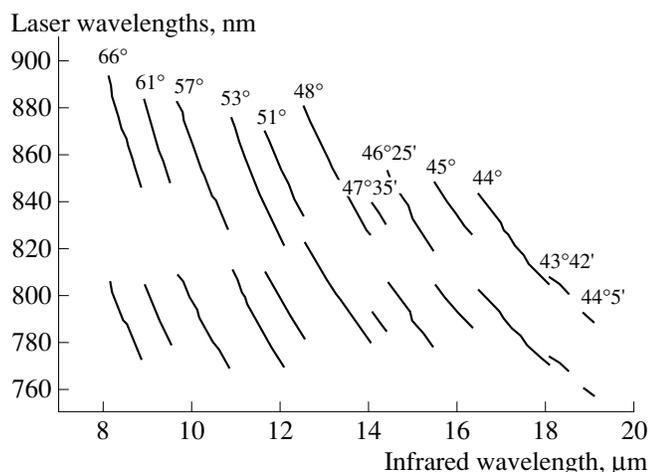


Fig. 2. Experimental type I phase matching curves of GaSe for the infrared generation from 8 to 19 μm , birefringently phase-matched by laser wavelengths tuning and crystal external angle tuning.

gives the phase-matchable laser wavelengths and corresponding crystal external angle for the infrared DFG from 8 to 19 μm . The infrared generation at a long wavelength near 19 μm was limited by the crystal absorption edge, as shown in Fig. 3. At the short wavelength, we could extend the spectral tuning range down to about 6 μm with crystal external angle greater than 66° , but this was limited by the used crystal mount and the crystal dimension. Pumped with a total laser power of ~ 500 mW, the infrared power was in the range of 0.1 μW near 9 μm and decreased with the cube of the infrared wavelength. The spectral purity of the infrared emission was ~ 1 MHz. The absolute accuracy and reproducibility of the frequency measurement of the spectrometer, determined actually by Autoscan's wavelength meter, are 7×10^{-3} and $2 \times 10^{-3} \text{ cm}^{-1}$ respectively.

The infrared beam was then collimated with a parabolic mirror into a ~ 10 -mm diameter beam, and directed towards an absorption cell. The infrared light emerging from the cell was collected by an 90° off-axis parabolic mirror and focused onto a liquid-nitrogen-cooled HgCdTe photoconductive detector with a $1 \times 1 \text{ mm}^2$ active area.

DOPPLER-LIMITED HIGH-RESOLUTION SPECTROSCOPY OF BENZENE IN THE ν_4 BAND

The benzene molecule plays an important role in the organic chemistry. As a heavy molecule, the spectra of benzene (C_6H_6) are very dense. In order to evaluate the spectroscopic performance of the DFG-based spectrometer, high-resolution spectrum of gaseous benzene was scanned near 15 μm . In this region, the absorption

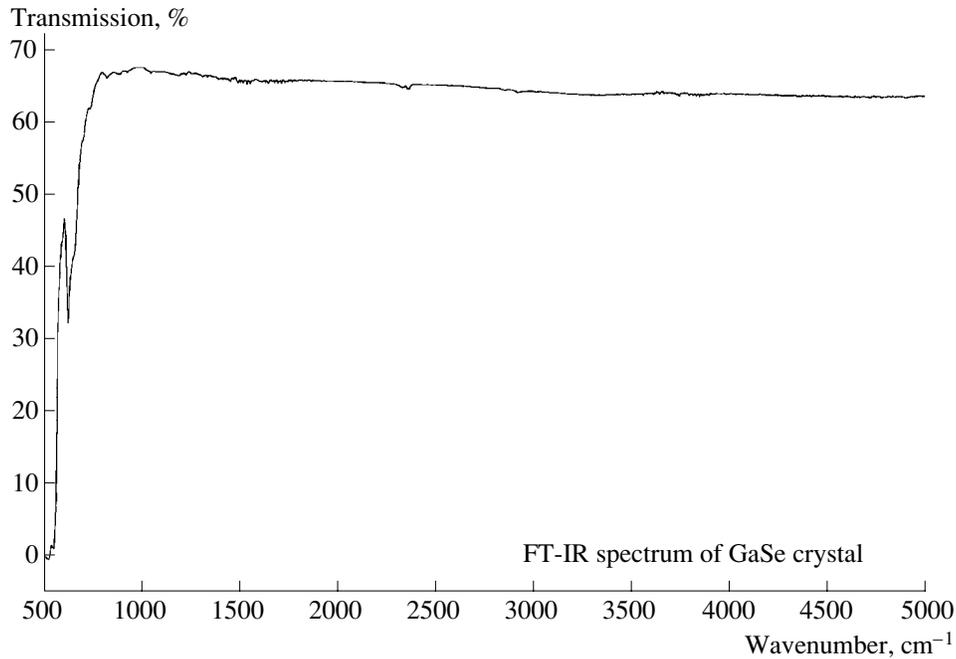


Fig. 3. FT-IR transmission spectrum of GaSe crystal.

of benzene is due to the intense ν_4 c-type parallel infrared band which presents the strongest absorption in the infrared. Benzene vapor was obtained from vaporization of liquid benzene. A direct absorption spectrum of ~ 1 mbar gaseous benzene is shown in Fig. 4 (lower trace). The spectrum was recorded by fixing the signal laser and the crystal external angle at 12000 cm^{-1} and $\sim 45^\circ$, respectively, and scanning the pump laser frequency from 12662 cm^{-1} in 10 MHz steps. The absorption cell was made of stainless steel and ended with ZnSe windows forming an optical-length of $\sim 12\text{-cm}$. The cell was pumped out and scanned to provide zero spectrum for normalization. This DFG spectrum was compared to the FT-IR spectrum (upper trace in Fig. 4) obtained with a resolution of 0.2 cm^{-1} (Perkin Elmer, System 2000 FT-IR).

Figure 5 shows a DFG spectrum of benzene of the ν_4 P(31) branch near 662 cm^{-1} , which is a $\sim 0.15\text{ cm}^{-1}$ blowup of the spectrum shown in Fig. 4. At a benzene vapor pressure of ~ 1 mbar the experimental linewidth was found to be $\sim 0.0018\text{ cm}^{-1}$, slightly greater than the theoretical Doppler linewidth ($\sim 0.00094\text{ cm}^{-1}$). With this quasi-Doppler limited resolution, the K structure of the ν_4 parallel band was resolved for $K \geq 7$. The intensity variation with the most intense transitions occurring at $K = 6n + 3$ were clearly observed, which is so useful for line transition assignment.

The P(31) transition was assigned using the usual energy expressions for a symmetric top with terms up to the quartic level [10]. Infrared frequency was directly deduced from the difference of laser frequen-

cies measured by the internal wavemeter of the laser autoscan system. The infrared wavenumber calibration was experimentally checked by using the atmospheric CO_2 R(10) 01¹0–00⁰ line at reduced pressure [11]. No additional frequency calibration etalon has been

Observed P(31) transitions of the ν_4 band of benzene

| J' | K' | J'' | K'' | $\nu_0\text{ (cm}^{-1}\text{)}$ | $\nu_0 - \nu_c\text{ (cm}^{-1}\text{)}$ |
|------|------|-------|-------|---------------------------------|---|
| 30 | 7 | 31 | 7 | 662.0964 | +0.0001 |
| 30 | 8 | 31 | 8 | 662.0988 | +0.0002 |
| 30 | 9 | 31 | 9 | 662.1018 | +0.0002 |
| 30 | 10 | 31 | 10 | 662.1048 | +0.0001 |
| 30 | 11 | 31 | 11 | 662.1084 | +0.0002 |
| 30 | 12 | 31 | 12 | 662.1122 | +0.0002 |
| 30 | 13 | 31 | 13 | 662.1164 | +0.0002 |
| 30 | 14 | 31 | 14 | 662.1208 | +0.0001 |
| 30 | 15 | 31 | 15 | 662.1254 | -0.0001 |
| 30 | 16 | 31 | 16 | 662.1308 | +0.0001 |
| 30 | 17 | 31 | 17 | 662.1361 | -0.0001 |
| 30 | 18 | 31 | 18 | 662.1418 | -0.0002 |
| 30 | 19 | 31 | 19 | 662.1481 | 0.0000 |
| 30 | 20 | 31 | 20 | 662.1545 | -0.0001 |
| 30 | 21 | 31 | 21 | 662.1618 | +0.0004 |

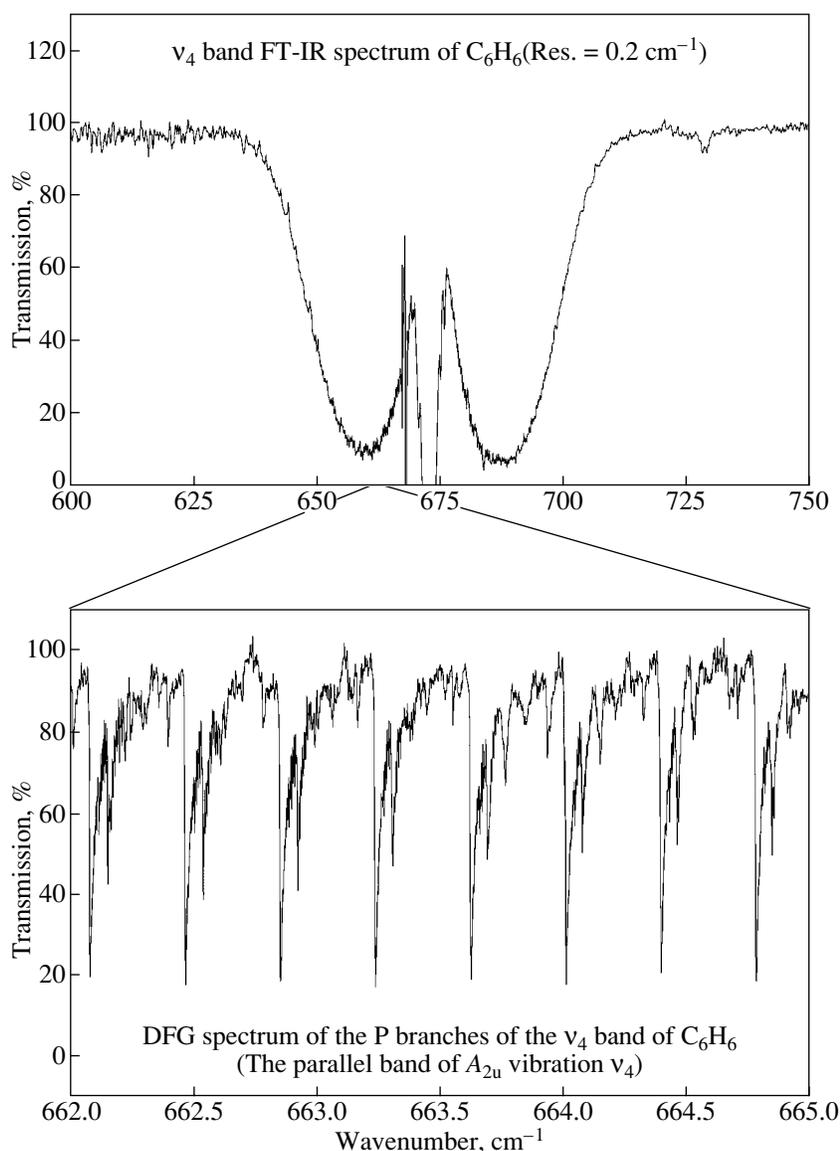


Fig. 4. Spectra of gaseous benzene in the ν_4 band near $15 \mu\text{m}$. Upper spectrum: ν_4 band FT-IR spectrum, obtained from a Fourier transform spectrometer with a resolution of 0.2 cm^{-1} (Perkin Elmer, System 2000 FT-IR); Lower spectrum: DFG spectrum of P branches of the ν_4 band.

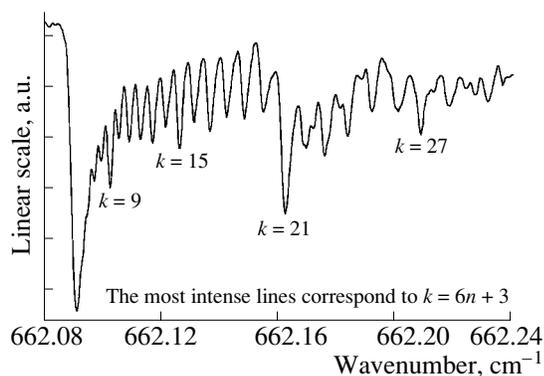


Fig. 5. DFG spectrum of the P(31) transition of the ν_4 band of benzene at near Doppler-limited resolution.

employed. The results are shown in the table. The jet cooling technique should be necessary to attain sub-Doppler resolution [12].

CONCLUSION

We reported a broadly tunable cw infrared laser spectrometer based on the difference frequency generation in a GaSe crystal. This kind of the frequency conversion-based spectrometer is very attractive for high-resolution spectroscopy and the monitoring of volatile organic compounds (VOCs) constituents in the atmosphere by using high-resolution laser absorption spectroscopy.

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REFERENCES

1. Capasso, F., Gmachl, C., Sivco, D.L., and Cho, A.Y., 1999, *Phys. World*, **12**, 27.
2. Eckhoff, W., Putnam, R., Wang, S., *et al.*, 1996, *Appl. Phys.*, **63**, 437.
3. Putnam, R. and Lancaster, D., 1999, *Appl. Opt.*, **38**, 1513.
4. Chen, W., Burie, J., and Boucher, D., 1999, *Spectrochimica Acta A*, **55**, 2057.
5. Chen, W., Burie, J., and Boucher, D., 1996, *Rev. Sci. Instrum.*, **67**, 3411.
6. Chen, W., Przygodzki, C., Delbarre, H., *et al.*, 1998, *Infrared Phys. Technol.*, **39**, 415.
7. Chen, W., Mouret, G., and Boucher, D., 1998, *Appl. Phys. B*, **67**, 375.
8. Dmitriev, V.G., Gurzadyan, G.G., and Nikogosyan, D.N., 1997, *Springer Series in Optical Science*, **64**, 166.
9. Vodopyanov, K.L., 1993, *J. Opt. Soc. Am. B*, **10**, 1723.
10. Mai Dang-Nhu and Josef Pliva, 1989, *J. Molec. Spectrosc.*, **138**, 423.
11. Kauppinen, J., Jolma, K., and Horneman, V.-M., 1982, *Appl. Opt.*, **21**, 3332.
12. Junttila, M.-L., Domenech, J.L., Fraser, G.T., and Pine, A.S., 1991, *J. Molec. Spectrosc.*, **147**, 513.