TUNABLE DIODE LASER BASED MID-INFRARED SOURCES FOR SPECTROSCOPY

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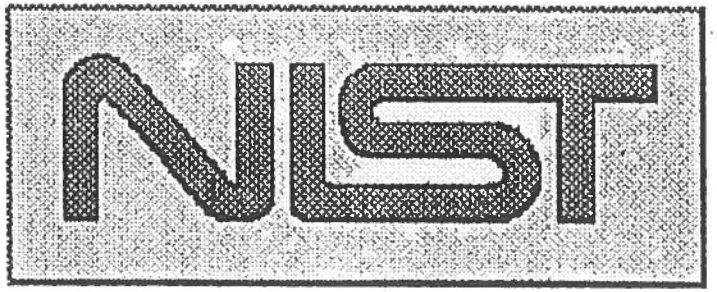


MOTIVATION

WHY USE MID-INFRARED LASERS FOR GAS DETECTION?

- high sensitivity
  (typical peak absorption 0.1 - 4.0 % for the column density of 1 ppm·m)
- high selectivity (narrow linewidth)
- real-time detection in ambient air

WHAT LASER SOURCES ARE AVAILABLE?

- microwave-sideband gas lasers: He-Ne, CO(Δv=2), CO, 2-CO_2, CO_2, NH_3
- lead-salt diode lasers
- color-center lasers
- optical parametric oscillators (OPO)
- difference-frequency-generation (DFG)

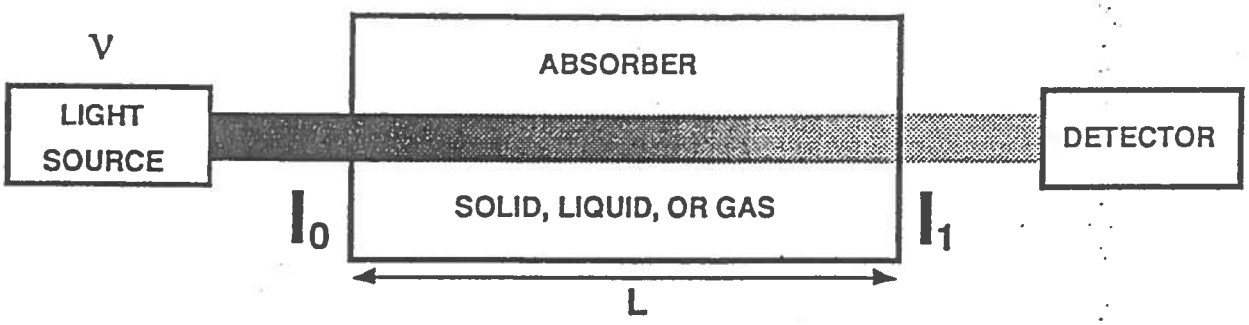
WHY USE DFG?

- broad tunability (2 - 18 μm)
- narrow linewidth (less than 50 MHz)
- continuous wave or pulsed operation at room temperature
- no pump threshold
- compact diode and solid-state pump lasers are available
- DRAWBACK: low conversion efficiency

HOW CAN DFG BE IMPROVED?

- cavity enhancement
- semiconductor power amplifiers
- quasi-phase-matched mixing crystals
- quasi-phase-matched waveguides
- fiber-coupled pump

SPECTROSCOPIC DETECTION



BEER'S LAW

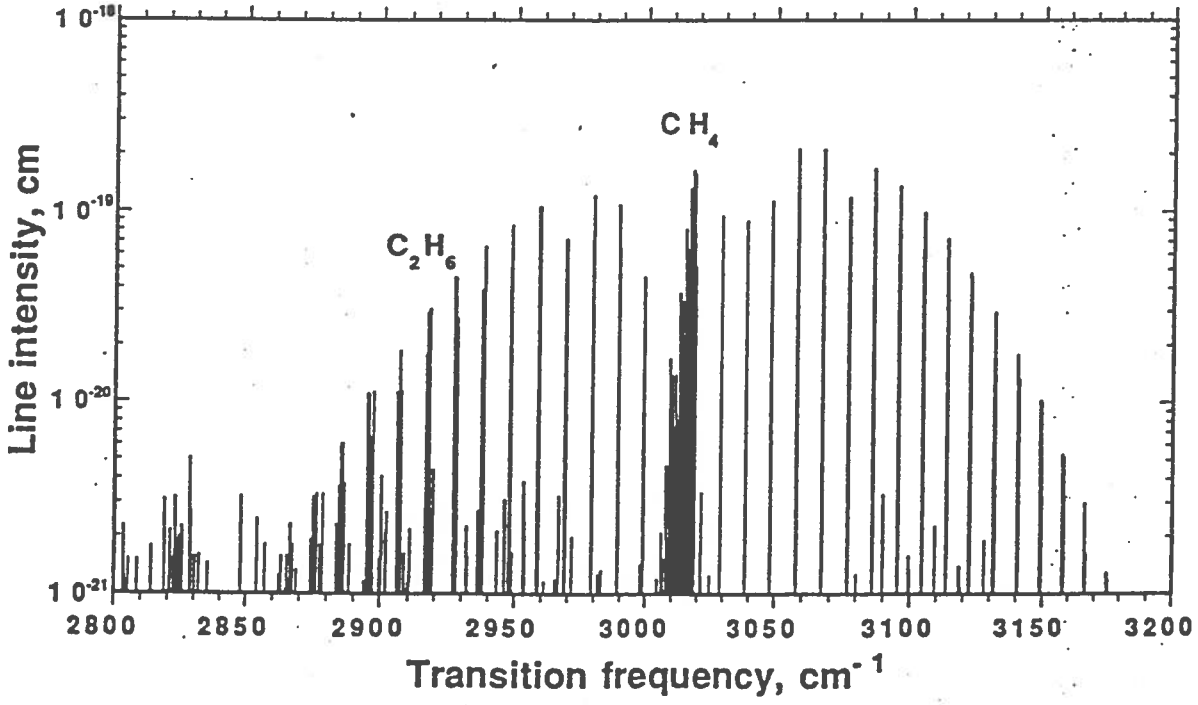
$$I_1 = I_0 \cdot e^{-\alpha(\nu)\cdot L}$$

$\alpha(\nu)$ - absorption coefficient (cm^{-1}), L - path length (cm), ν - frequency (cm^{-1})

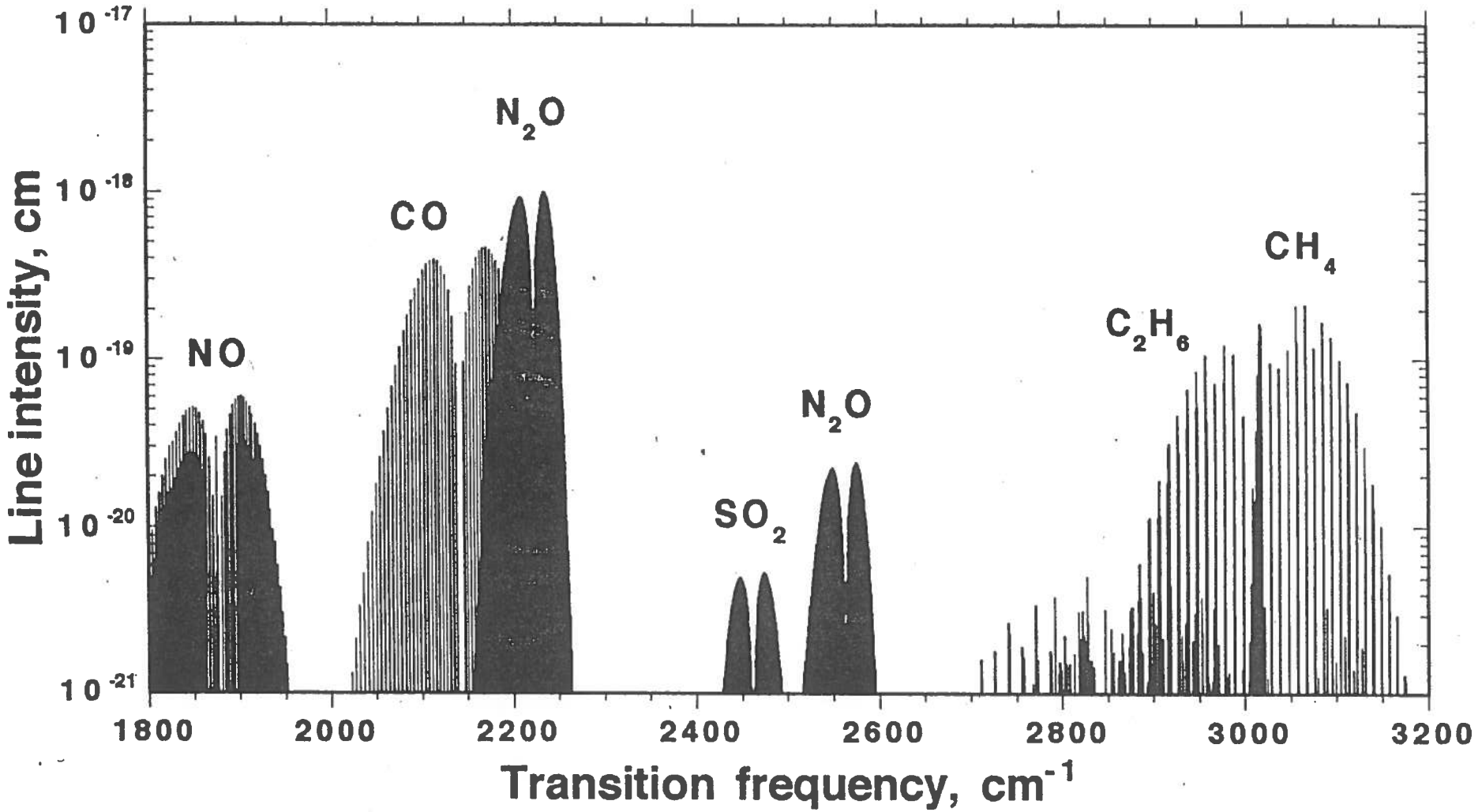
MOLECULAR ABSORPTION COEFFICIENT

$$\alpha = C \cdot \frac{S}{\Delta\nu} \cdot g(\nu)$$

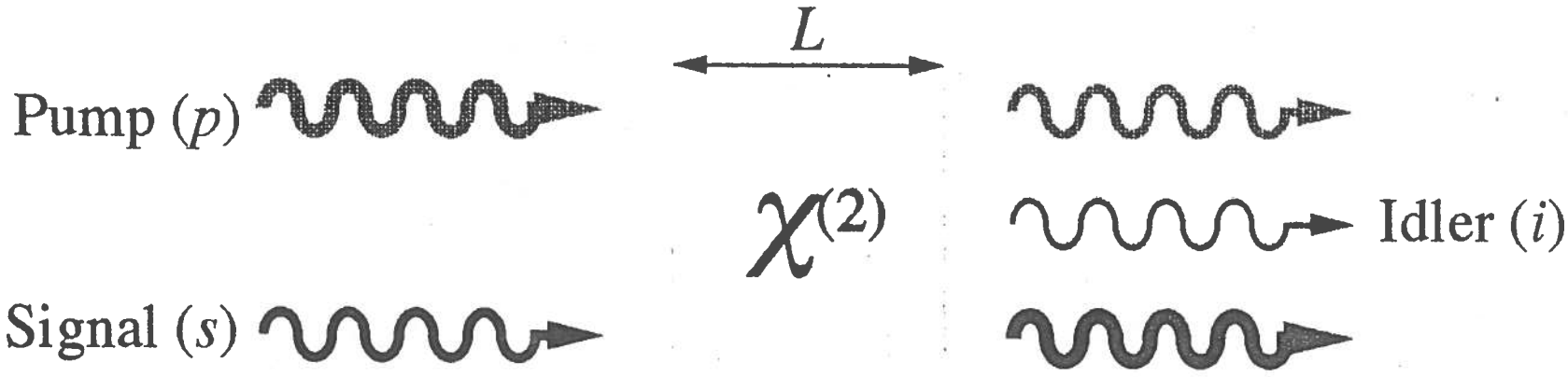
C - gas concentration (cm^{-3}), S - line intensity (cm), $\Delta\nu$ - linewidth (cm^{-1}),
$g(\nu)$ - numerical line profile: Gaussian, Voigt, or Lorentzian



SURVEY ABSORPTION SPECTRA OF SOME ATMOSPHERIC TRACE GASES



Difference-Frequency Generation



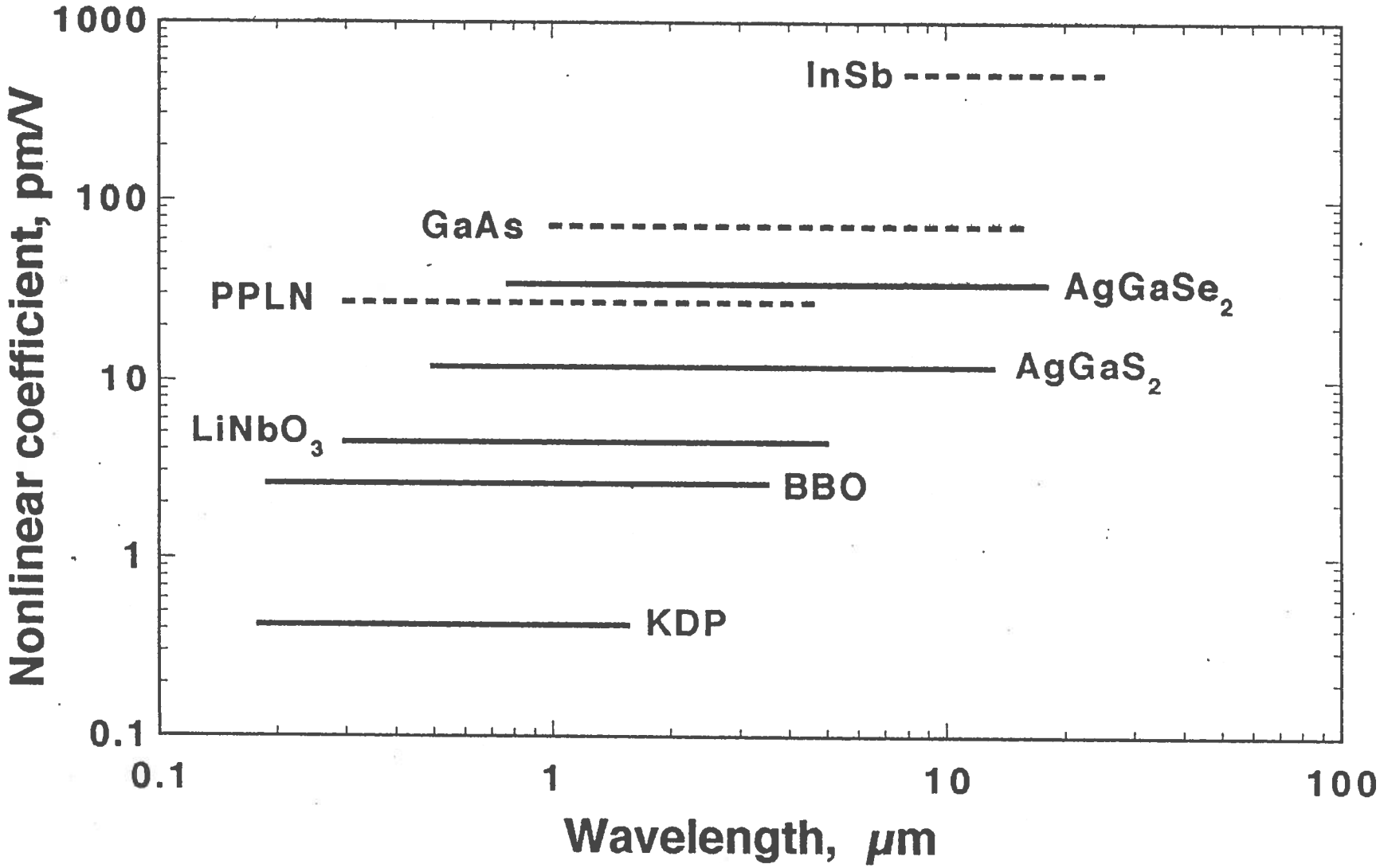
Energy and Momentum Conservation

$$\omega_p = \omega_s + \omega_i \qquad \boldsymbol{k}_p = \boldsymbol{k}_s + \boldsymbol{k}_i$$

Phase Matching Condition

$$|(k_p - k_s - k_i)L| < 2\pi$$

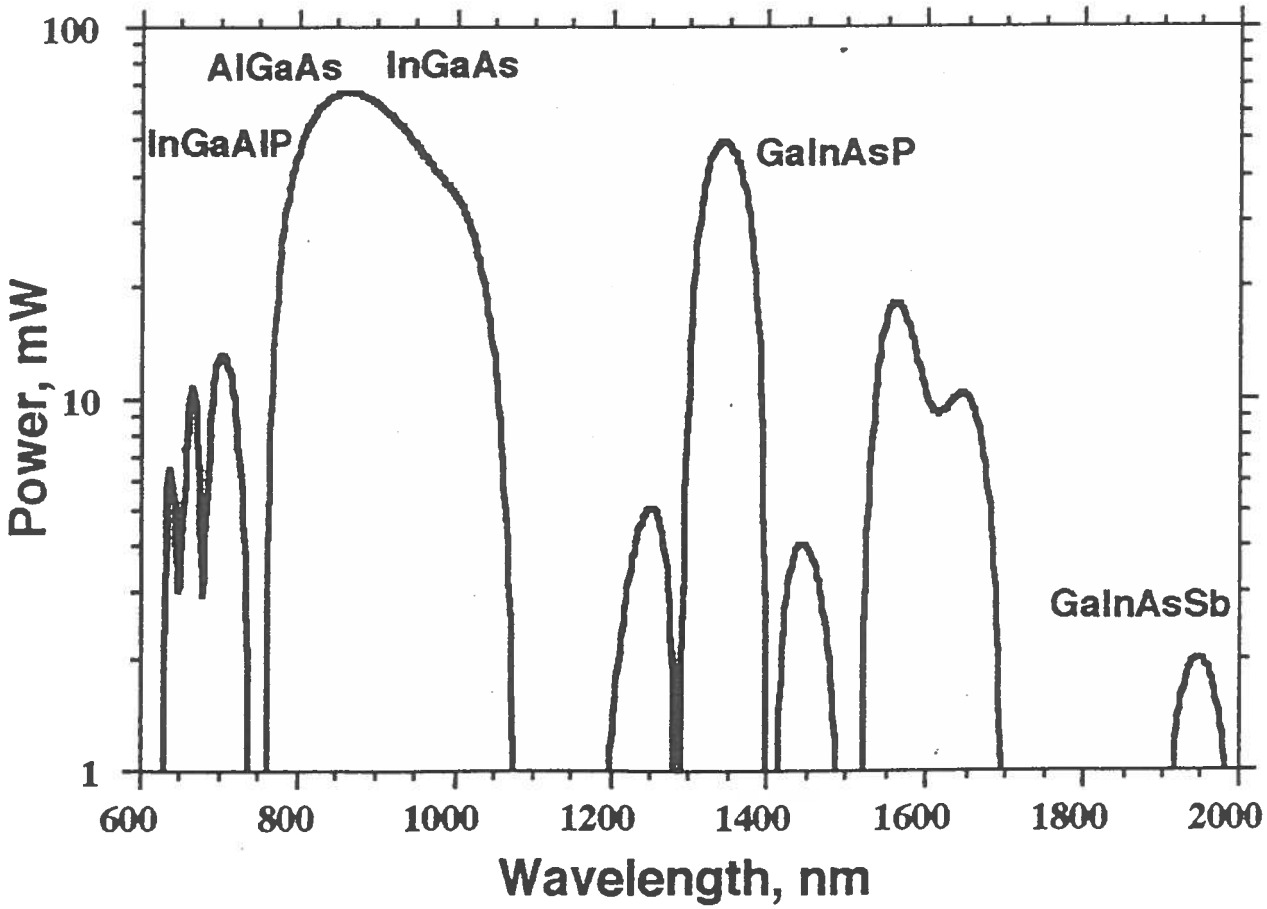
Properties of various IR nonlinear materials



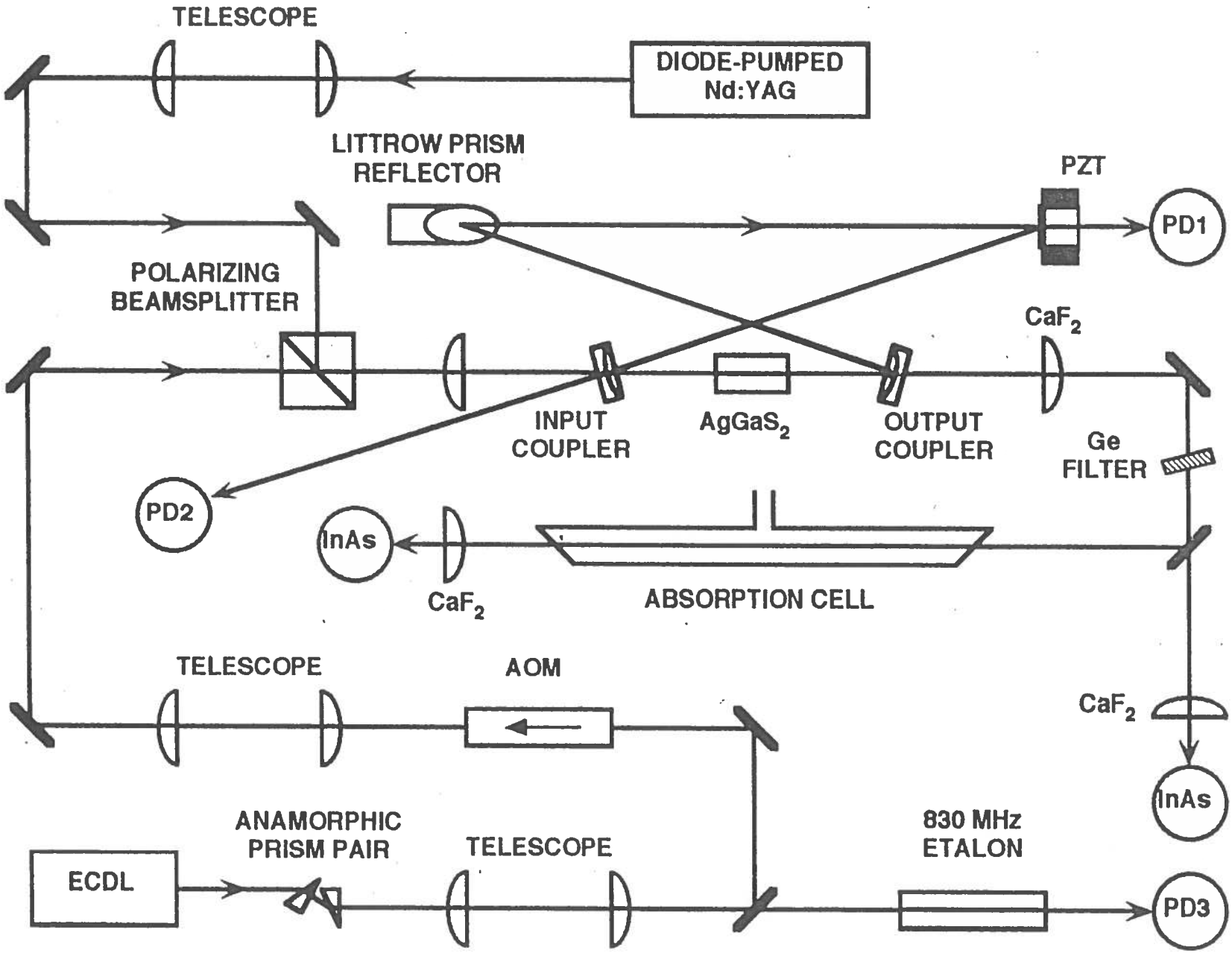
DIODE LASERS

SPECTROSCOPIC ADVANTAGES:
- wavelength coverage
- tuning range and frequency control
- single-frequency operation
- high output power
- near-diffraction-limited beam
- high sensitivity to feedback

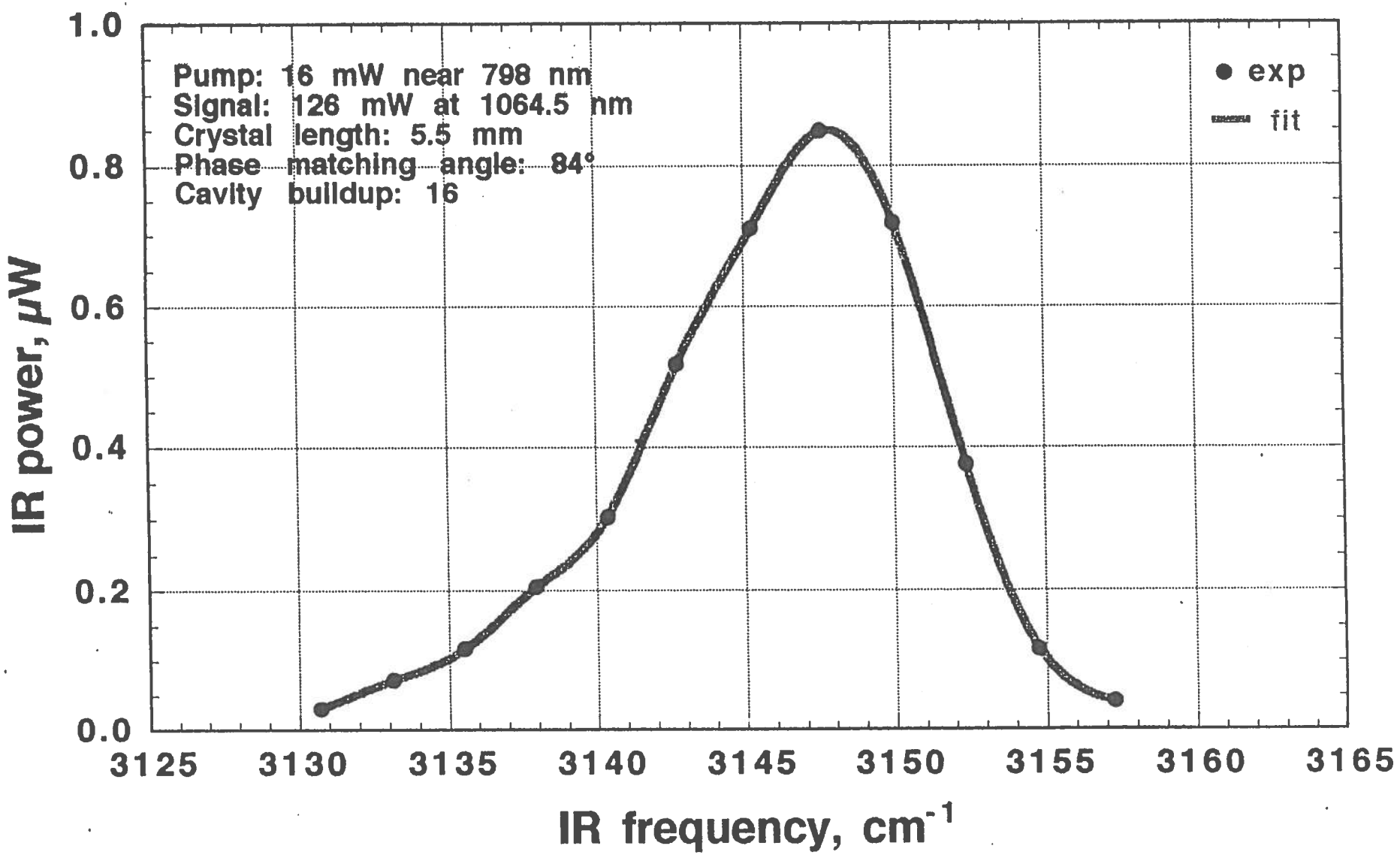
DESIGN ADVANTAGES:
- direct electric excitation
- compact size
- high efficiency
- reliability
- low cost



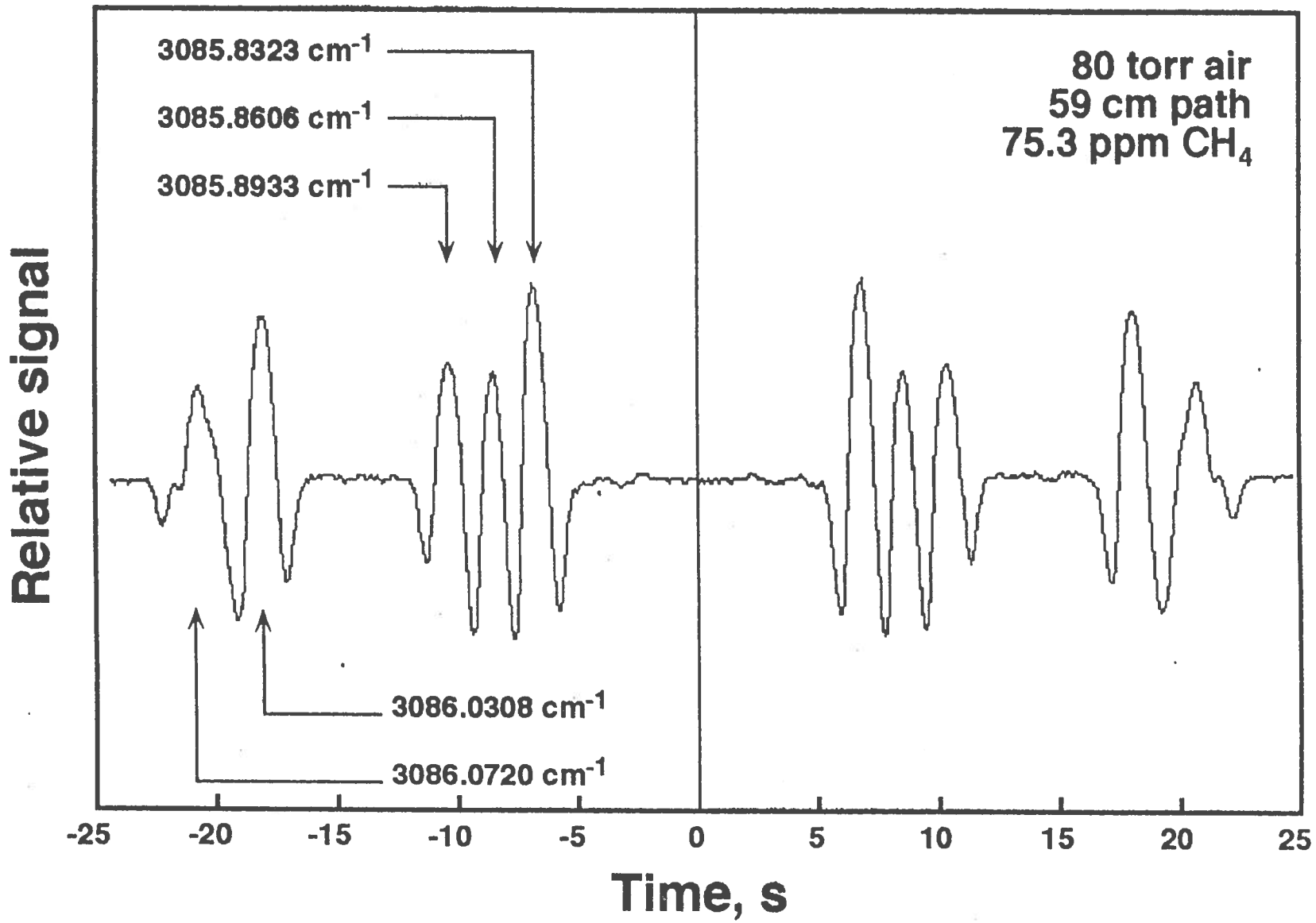
CAVITY-ENHANCED 3.2 μm TUNABLE CW DFG SOURCE



PHASE MATCHING BANDWIDTH OF $AgGaS_2$

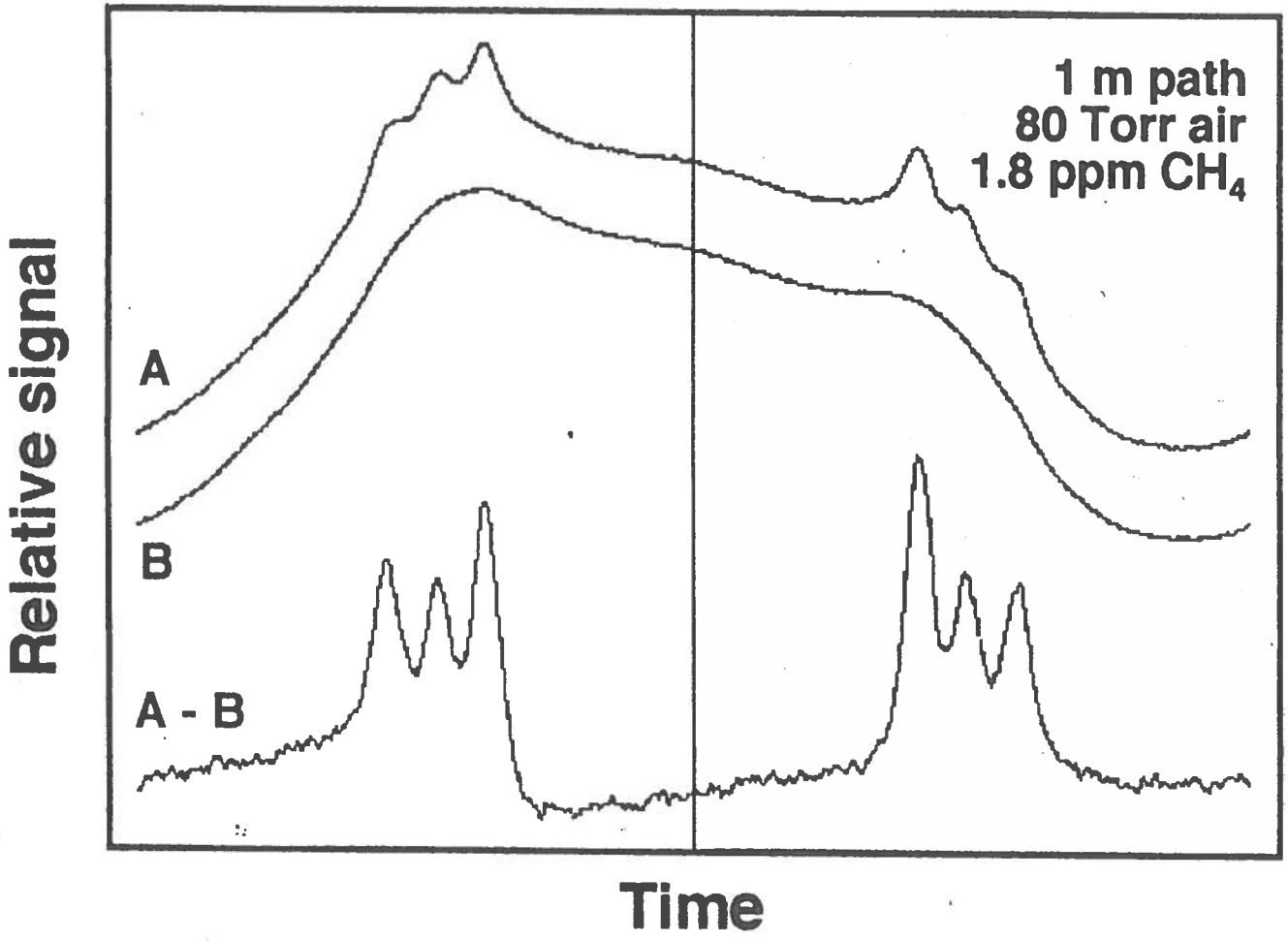


WAVELENGTH-MODULATION 2*f* SPECTRUM OF METHANE IN AIR NEAR 3086 cm^{-1}



SPECTRUM OF THE METHANE IN NATURAL AIR

1 μW @ 3086 cm^{-1}, 1 Hz noise bandwidth



LASER-BASED CH_4 DETECTION REPORTED TO DATE

1. Third combination-overtone

band: $3\nu_1+\nu_3+\nu_{2,4}$ and $2\nu_1+2\nu_3$
line intensity: not known
source: 790 and 860 nm diode laser (Lucchesini *et al*, 1993)

2. Second combination-overtone

band: $\nu_1+2\nu_3$
line intensity: not known
source: Nd:YAG laser at 1.34 μm (Scott *et al*, 1992)

3. First overtone

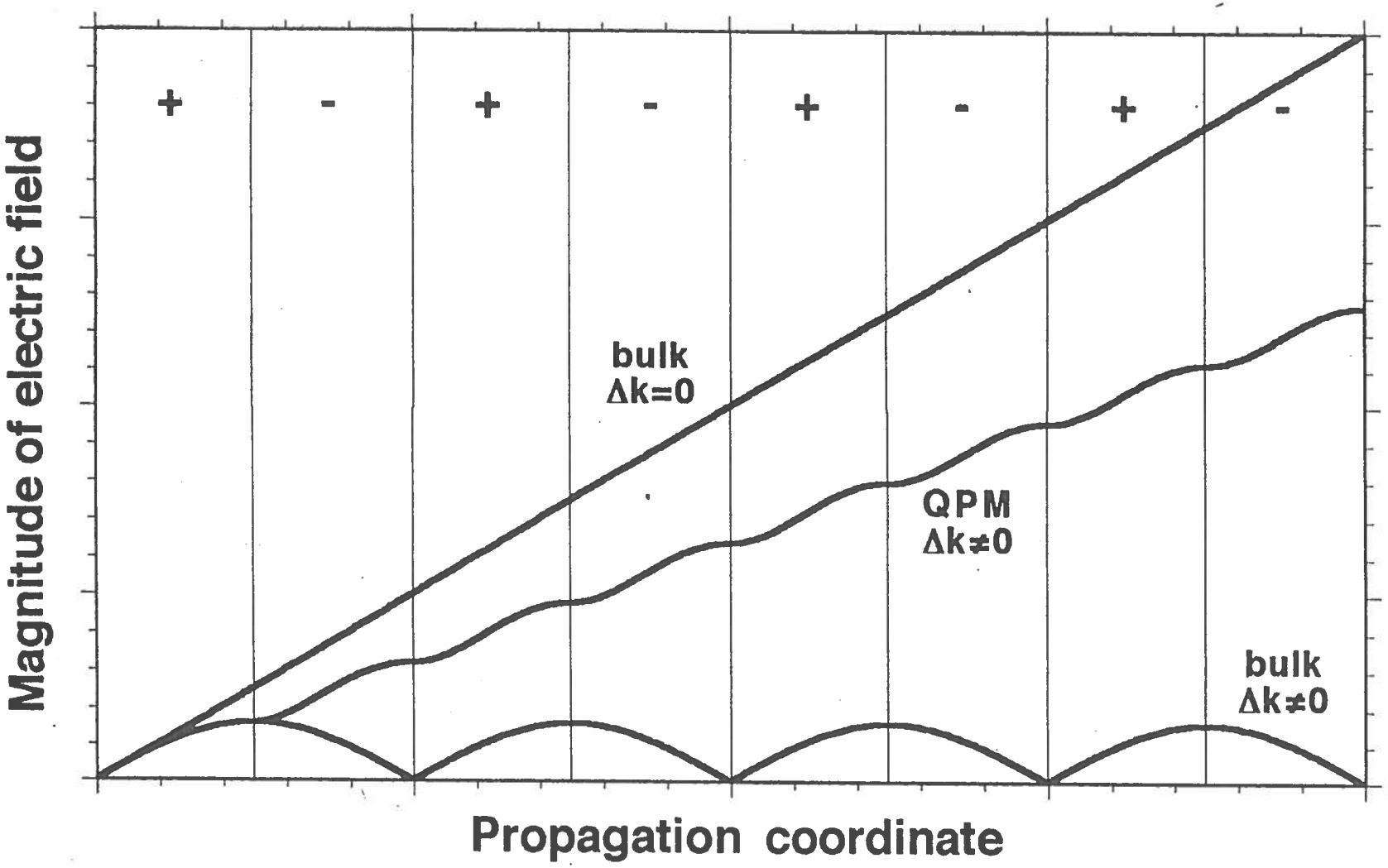
band: $2\nu_3$
line intensity: max. $1.33 \cdot 10^{-21}$ cm
source: diode laser at 1.66 μm (Uehara and Tai, 1992)
sensitivity: 600 ppb·m/$\sqrt{\text{Hz}}$

4. Fundamental

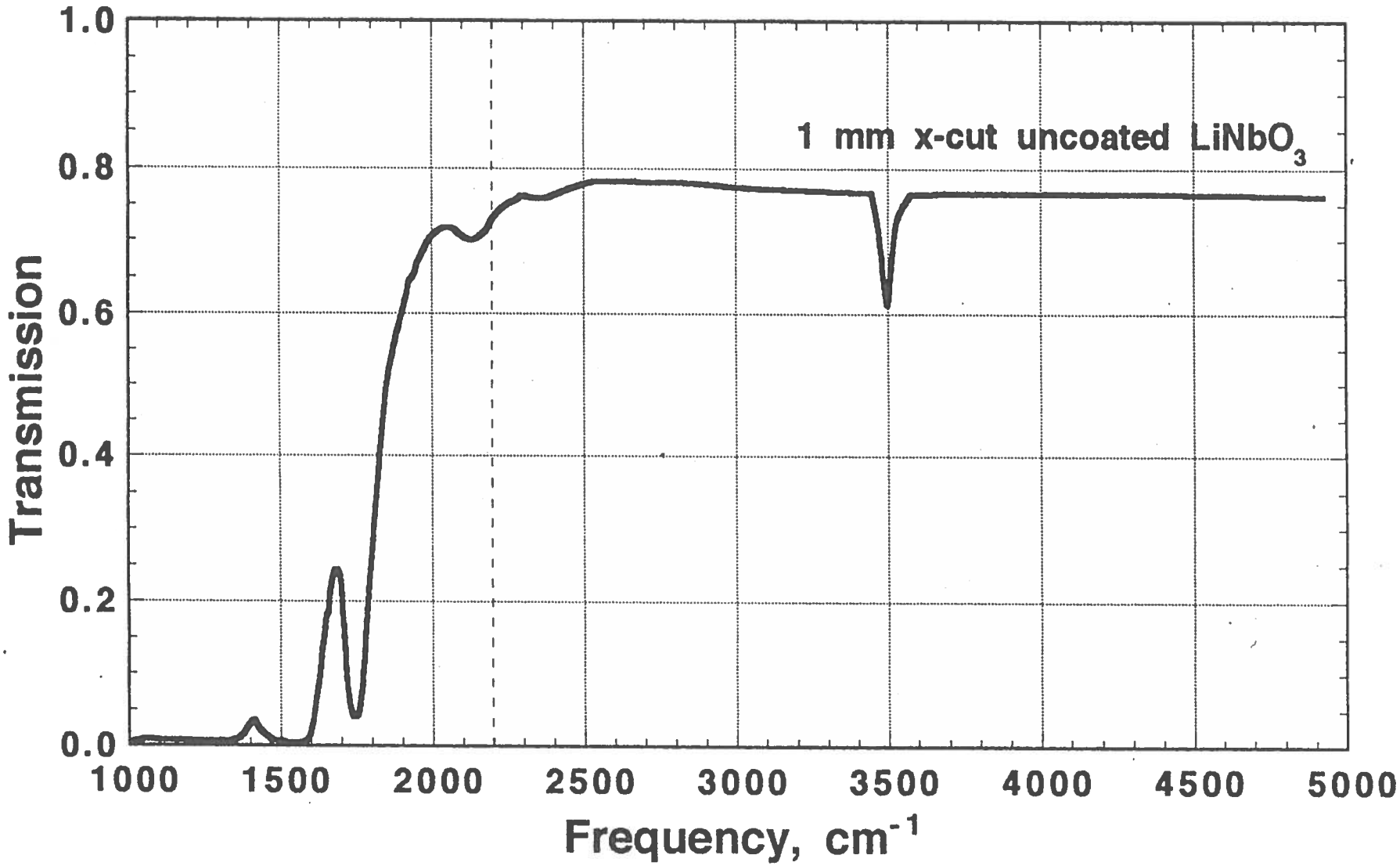
band: ν_3 (CH asymmetric stretch)
line intensity: max. $2.13 \cdot 10^{-19}$ cm
source: diode-laser-pumped 3.2 μm DFG (Petrov *et al*, 1995)
sensitivity: 12 ppb·m/$\sqrt{\text{Hz}}$

band: ν_1 (CH bend)
line intensity: max. $0.97 \cdot 10^{-19}$ cm
source: lead-salt diode laser at 7.8 μm (Webster *et al*, 1994)
sensitivity: 14 ppb·m/$\sqrt{\text{Hz}}$

OPTICAL ELECTRIC FIELD BUILDUP
BULK vs QUASI-PHASE-MATCHED



Transmission of unpolarized light by $LiNbO_3$

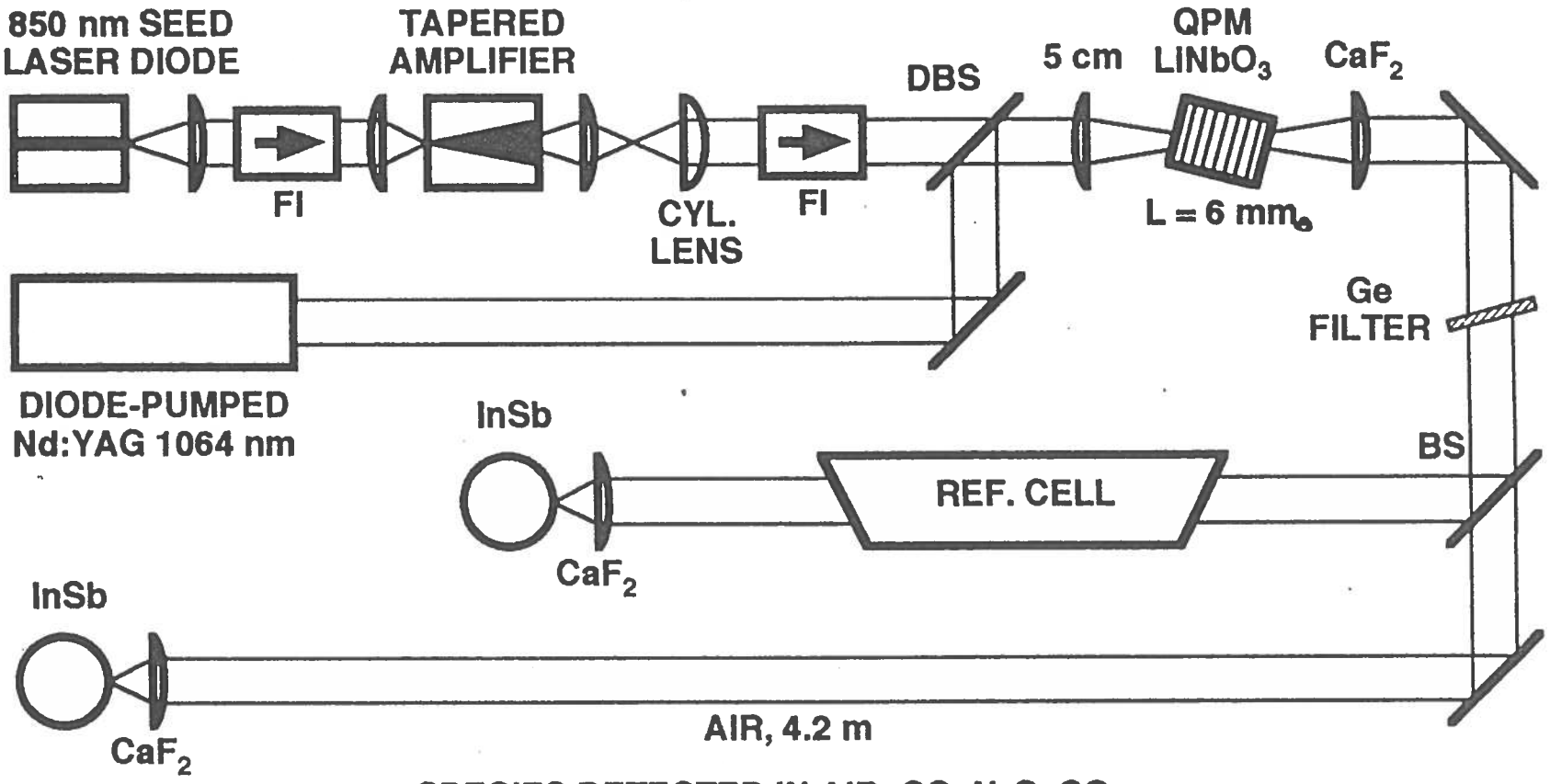


ALL-DIODE-PUMPED 4.6 μm TUNABLE CW DFG SOURCE

INPUT: 560 mW @ 860 nm, 220 mW @ 1064 nm; OUTPUT: 8 μW

TUNING RANGE: 4.3 - 4.6 μm; LINEWIDTH: < 50 MHz

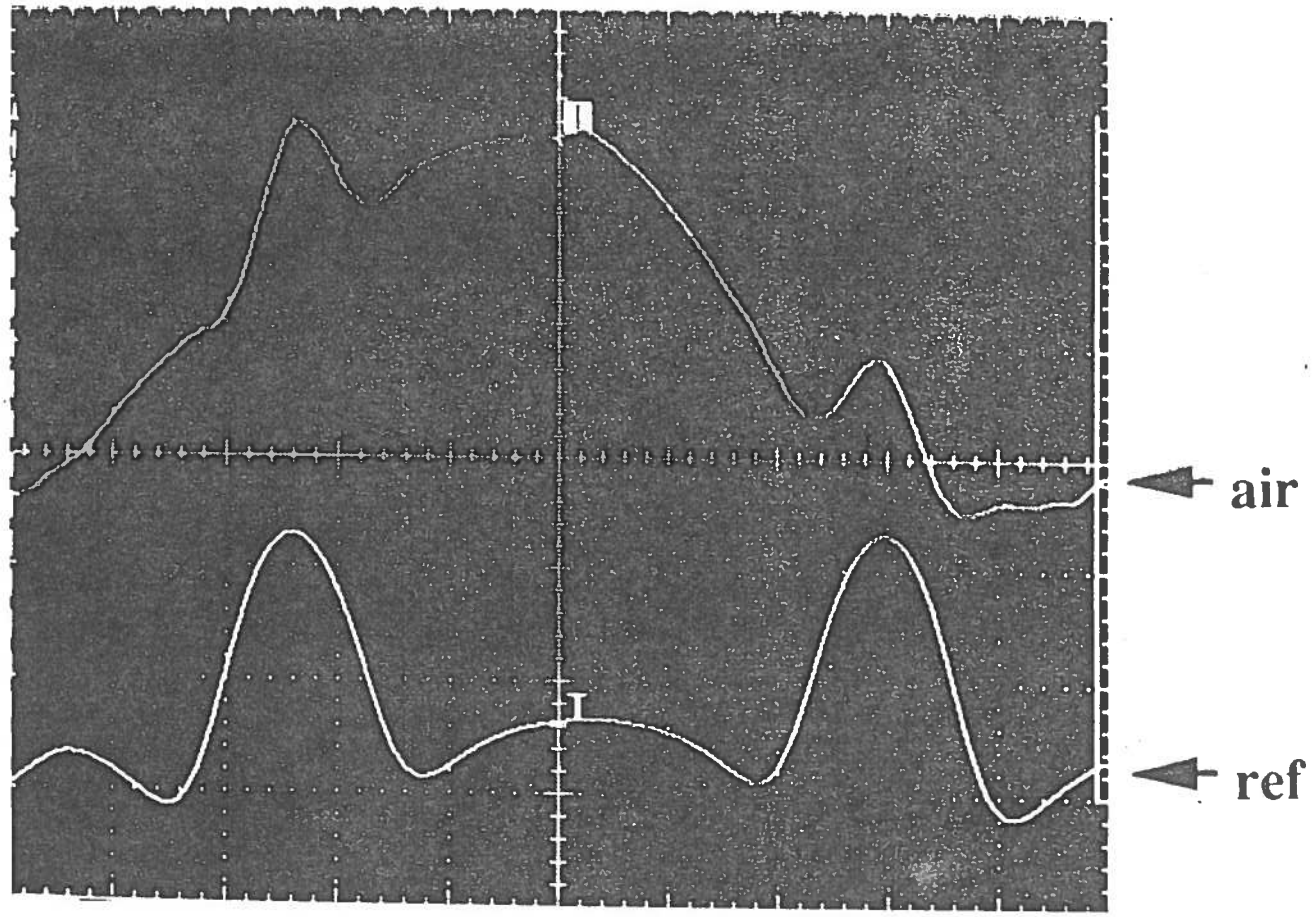
INTENSITY NOISE: $3 \cdot 10^{-5}$ rms/$\sqrt{Hz}$



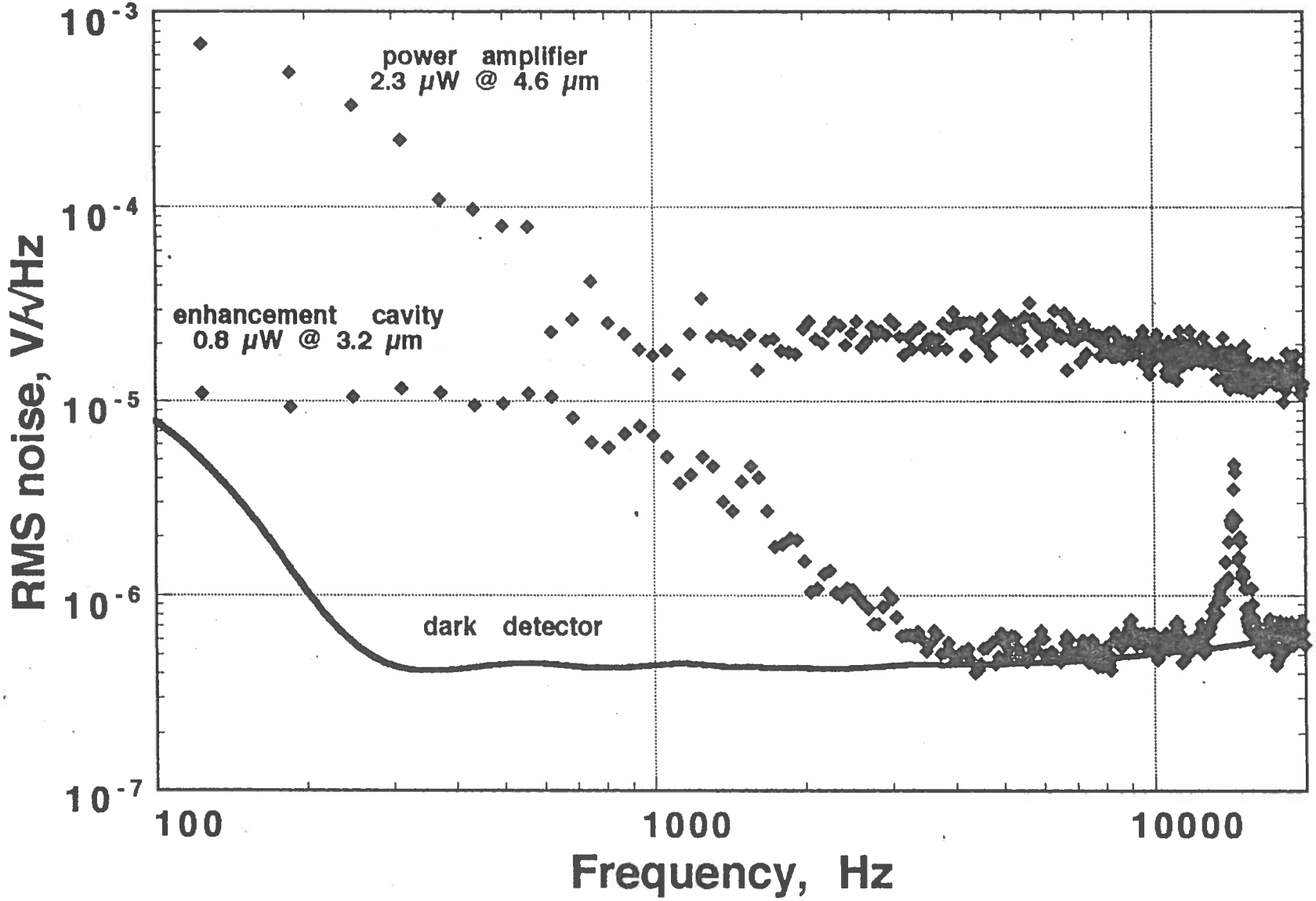
SPECIES DETECTED IN AIR: CO, N_2O, CO_2

WAVELENGTH-MODULATION 2f SPECTRUM OF THE CARBON MONOXIDE IN AMBIENT AIR

3 μW @ 2169 cm^{-1}, 2.5 Hz noise bandwidth, 4.2 m ambient air, ~360 ppbv CO



DFG INTENSITY NOISE



SUMMARY

ALL-DIODE-PUMPED CW DIFFERENCE-FREQUENCY GENERATION WAS PERFORMED NEAR 3.2 μm AND 4.6 μm AT ROOM TEMPERATURE

BULK PHASE-MATCHED $AgGaS_2$ AND QUASI-PHASE-MATCHED $LiNbO_3$ WERE USED FOR FREQUENCY MIXING

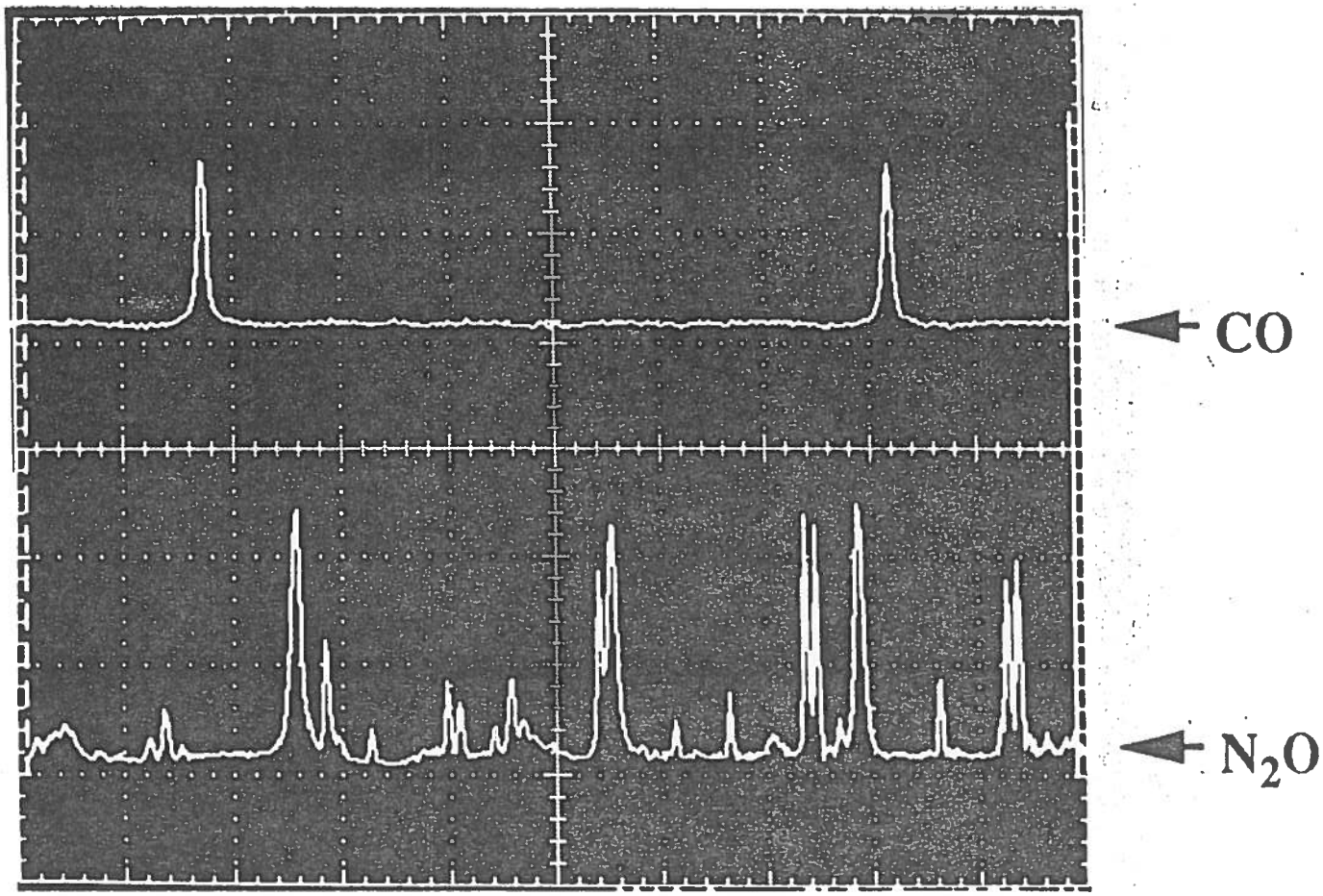
THE USE OF AN EXTERNAL BUILDUP CAVITY OR A TAPERED AMPLIFIER CAN PROVIDE OUTPUT IR POWER OF ~10 μW

IR TUNING RANGE OF 200 cm^{-1} WAS OBSERVED WITH < 50 MHz LINEWIDTH

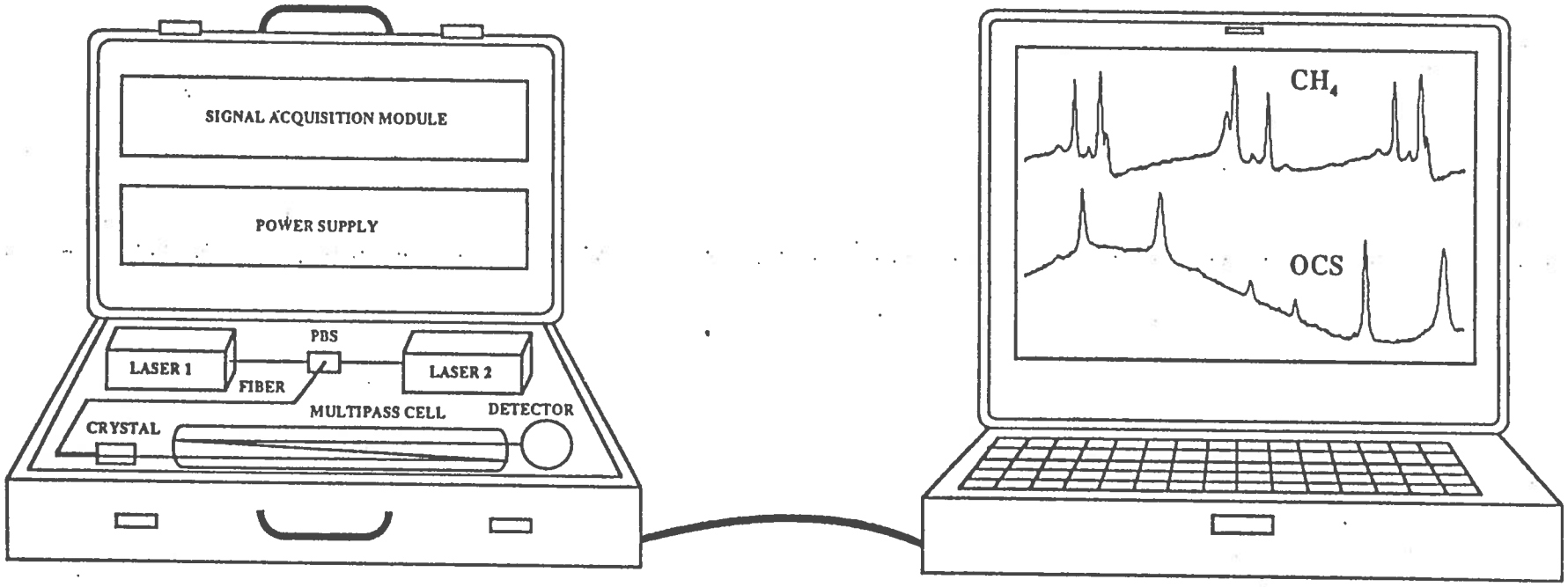
DIRECT ABSORPTION AND WAVELENGTH-MODULATION 2f SPECTROSCOPY OF CH_4, CO, N_2O, AND CO_2 WAS PERFORMED IN AMBIENT AIR

DETECTION SENSITIVITIES OF 5 ppb·m/√Hz FOR CO AND 12 ppb·m/√Hz FOR CH_4 WERE LIMITED BY IR INTENSITY NOISE AND DETECTOR NOISE, RESPECTIVELY

COMPACT ALL-SOLID-STATE ROOM-TEMPERATURE INFRARED GAS SENSORS CAN BE DESIGNED FOR DETECTION OF HCN, OCS, C_2H_2, C_2H_6, SO_2, NO, and C_2H_4

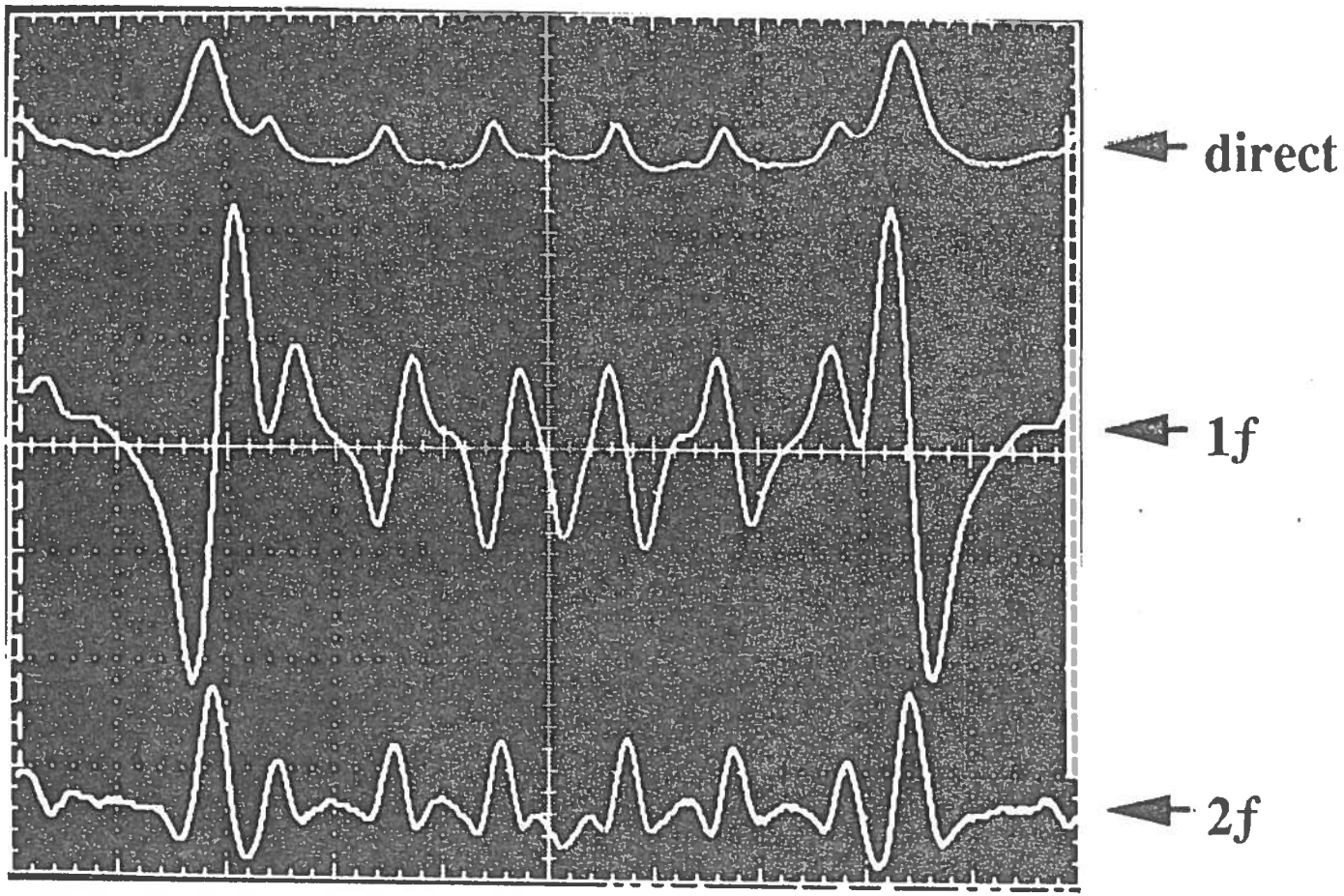

CO
N_2O

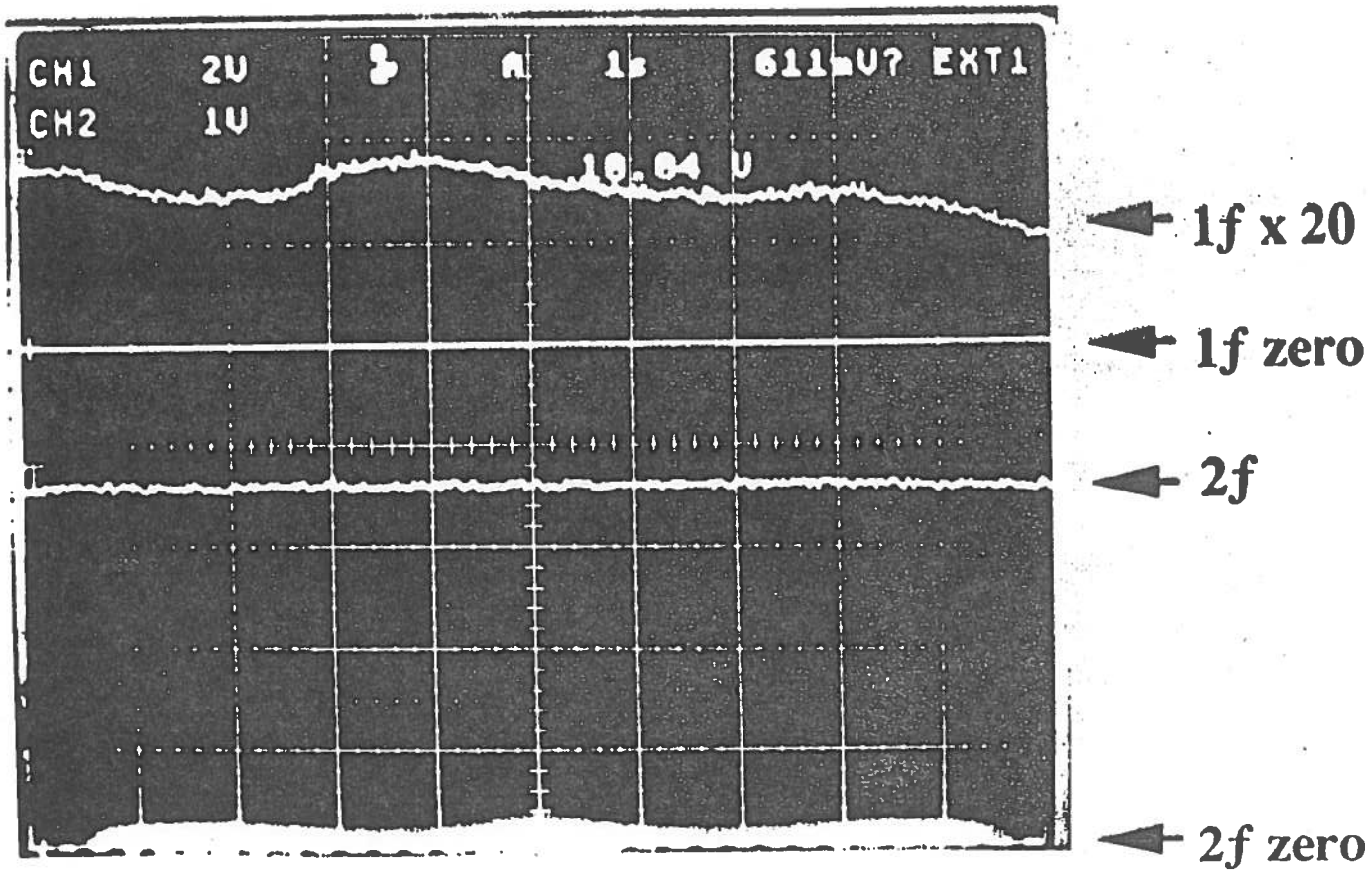
PORTABLE PROTOTYPE INFRARED LASER GAS SENSOR



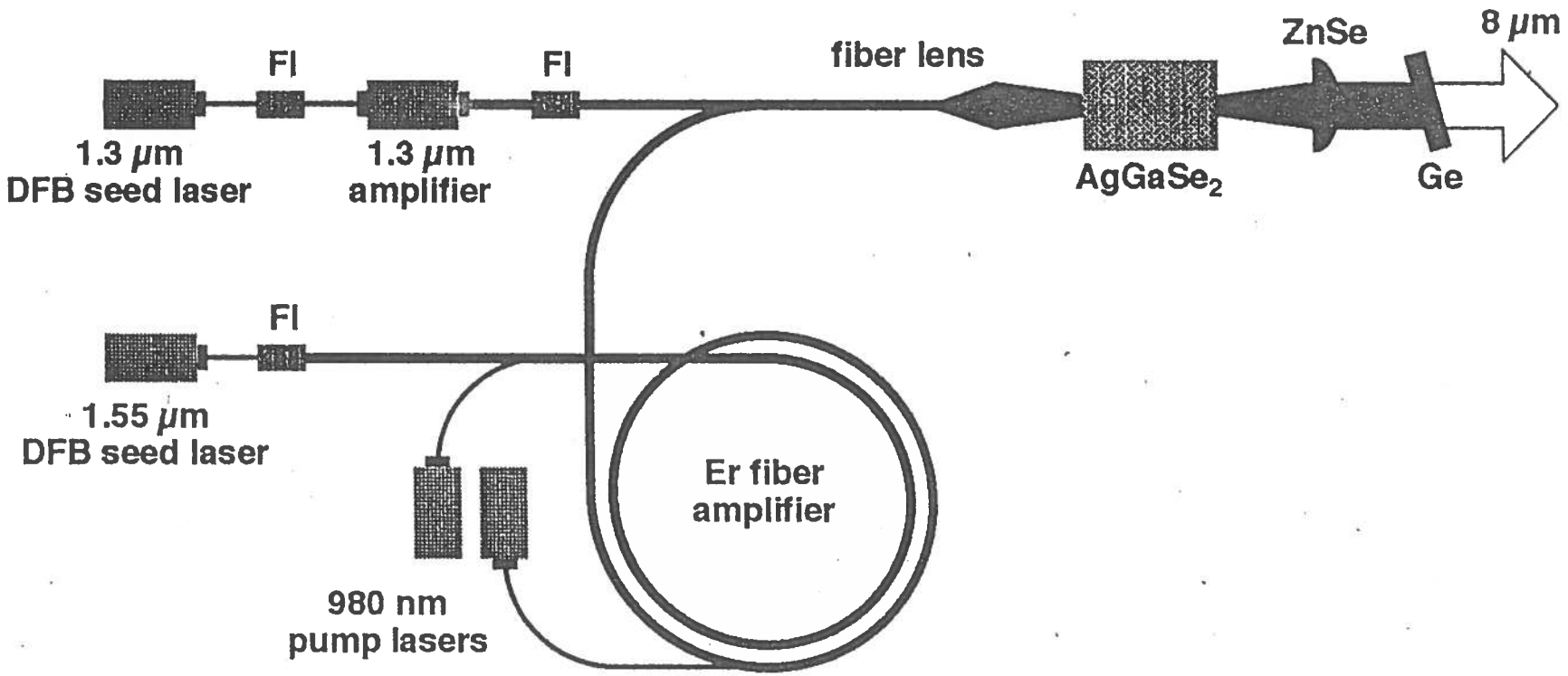
SENSOR MODULE

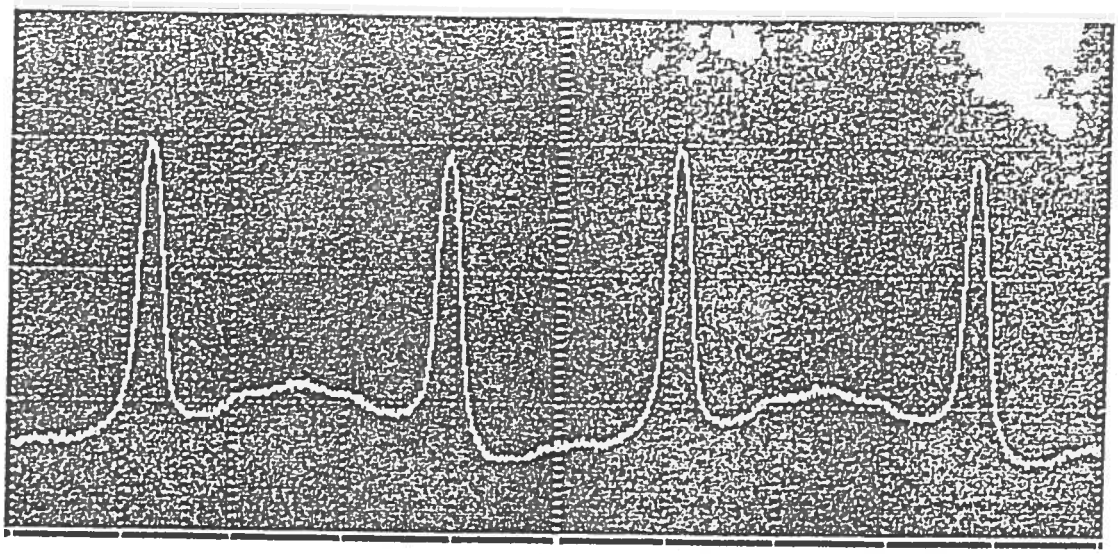
LAPTOP COMPUTER

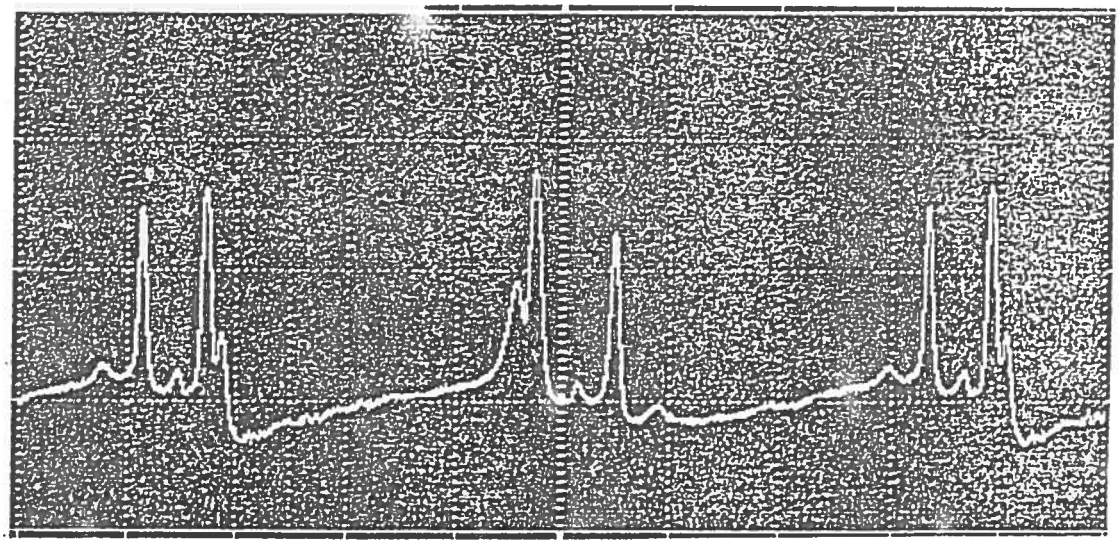

direct
1f
2f

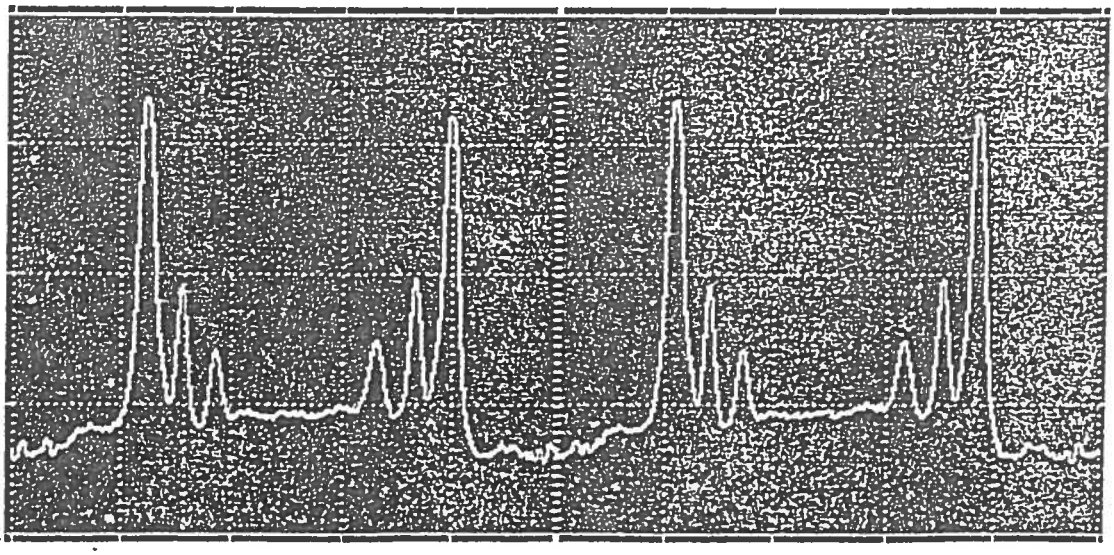

CH1 2V
CH2 1V
611mV? EXT1
1f x 20
1f zero
2f
2f zero

Tunable 8 μm DFG source using $AgGaSe_2$ and pigtailed diode lasers at 1.3 μm and 1.55 μm









1. TITLE 00:30

Good afternoon! My name is Constantine Petroff and I am here on behalf of Dr. Frank Tittel of Rice University. I will present a summary of research and development in the area of laser spectroscopy, done by Rice University in close collaboration with NIST Boulder and Naval Research Laboratory. The purpose of our joint effort was to develop all-solid-state, tunable infrared laser source that would be suitable for high resolution molecular spectroscopy and detection of trace gasses in air, in the 3 to 5 micron region. We also wanted to make it compact and operated at room temperature. (00:30)

2. LASER-BASED DETECTION 01:30

This is a cartoon of the basic principle of laser absorption spectroscopy and detection. Ideally one would send a monochromatic light beam through an absorber and measure optical transmission as a function of wavelength. In the absence of particle-size-dependent scattering and intensity-dependent processes, the transmission is determined by Beer's law. In the case of molecular absorption, the extinction coefficient alpha is given by the sum of terms that look like this. This is an individual molecular transition which has line intensity S, and line width $\Delta\nu$. Line intensity, measured in centimeters, is basically an integral of absorption cross-section per molecule over all frequencies. It is an important quantum-mechanical characteristic of a transition which only depends on temperature. Shown below for example are line intensities of the carbon-hydrogen stretch band of methane, near 3 microns. (02:00)

3. SURVEY 00:30

The wavelength region between 3 and 5 microns contains strong fundamental absorption bands of several important air pollutants, such as carbon monoxide, SO2, hydrocarbons, HCN, and many others. These bands are much stronger than their overtones in the near-infrared, and therefore can be used for sensitive gas detection. This was one of the motivating factors in our investigations. See, laser-based detection in the mid-infrared has been attempted many times with different degrees of success, mainly beacause the sources used were not quite suitable. (02:30)

4. MOTIVATION 01:30

It's easy to see why people have been trying to use mid-infrared lasers for gas detection. This technique is potentially very fast, selective, and very sensitive. For example, there is about 2 parts per million of methane in this air. Over one meter path, this amount of methane will absorb about one percent of probe light at 3 microns. This absorption can be easily measured, in fact the detection sensitivity can be as high as parts per billion. Now these are the most important lasers used for mid-infrared spectroscopy: gas lasers and their harmonics, lead-salt diodes, FCL, OPO, and DFG. We believe that DFG is a very attractive technique because it offers this combination of features: broad continuous tunability, narrow line-width, and it can be pumped with a variety of commercial diode and solid-state lasers which also makes it very quiet. The only major drawback is low conversion efficiency. However this can be improved by using new efficient mixing materials and higher pump power. In this work we used optical cavity enhancement and quasi-phase-matched lithium niobate pumped by high-power semiconductor amplifier. (04:00)

5. DFG 01:00

This cartoon explains the basic principle of difference-frequency generation. Two plane waves called pump and signal interact in a second-order nonlinear medium to generate a third wave called idler, which has frequency equal omega pump minus omega signal. For the interaction to be efficient, the nonlinear polarization generated at the beat-note between pump and signal waves must always be in-phase with the idler wave, which can be expressed as this momentum conservation. In practice however, plane waves do not exist, the beams are not mono-chromatic, and the mixing crystal has finite length. In this situation, some phase mismatch can be tolerated, and the idler wave would

still appear. These equations represent the well known case of bulk phase matching. Later on we will look at so-called bulk quasi-phase-matching. (05:00)

6. CRYSTALS 01:30

For DFG to be practical, several issues need to be considered. First of course, the mixing crystal must be reasonably transparent at all the three participating wavelengths. Second, it should be phase matchable. Third, it should have large nonlinear coefficient. Then it should have high damage threshold, be mechanically and environmentally stable and so on, at least that's the way scientists look at it. If you ask a manufacturer, the first thing he'll tell you is life-time, the second is life-time, and phase matching will probably come in as number eight. This is a diagram featuring nonlinear coefficient and transparency range of several well known infrared nonlinear materials. Those indicated by dashed lines can not be phase-matched in bulk, but can potentially be quasi-phase-matched. In our experiments we used silver gallium sulfide mainly because it is available in good optical quality, and has very attractive phase-matching properties in the mid-infrared. For example, it can be pumped with a variety of visible and near-infrared diode lasers. (6:30)

7. DIODES 00:30

There is a number of advantages diode lasers can offer, from the standpoint of both spectroscopy and design. They are small, cheap, efficient, quiet, reliable, very narrow-band, and tunable. The graph here shows wavelength coverage of commercial diode lasers, based on catalog data from different vendors. These are built as Fabry-Perot lasers or distributed feedback lasers which operate in single longitudinal mode with up to 100 milliwatt output power, or even more. (07:00)

8. 3.2 μm SOURCE 01:00

In one of our experiments, we mixed a commercial 100 milliwatt diode laser at 800 nano-meters, with a compact diode-pumped neodymium yag laser at 1064 nano-meters, to generate tunable infrared light at 3 microns. Initially, we used an anti-reflection-coated diode chip in an extended cavity configuration to obtain wide tuning range, then we replaced it with a solitary laser which had smaller tuning range but more output power. The mixing crystal was 5 milli-meter long, non-critically phase matched silver gallium sulfide. We put it into a bow-tie buildup cavity which was locked to resonance at 1064 nano-meters. It recirculated the unused signal photons and increased effective power by a factor of 20. With 230 milliwatt incident yag power in front of the cavity, and 40 milli-watt pump power in front of the crystal, we have measured 6 micro-watts at 3 microns. (08:00)

9. DFG BANDWIDTH 01:30

The idea was to use this light to detect methane in its asymmetric C-H stretch band. This band is about 300 wave-numbers wide, and typical rotational separation is approximately 10 wave-numbers. So it was essential that the source be capable of tuning at least 10 wave-numbers, preferably without crystal rotation. This would allow us to quickly and reliably locate strong absorption line of methane, regardless of the initial center frequency. This graph shows measured infrared output power as a function of wavelength, at a fixed phase-matching angle. The width of the curve is close to 13 wave-numbers, that is, just what we need. Based upon the plane-wave approach to DFG, one would expect to see a sink-squared function here. Instead, we see a somewhat asymmetric bell shaped curve with poorly resolved side-lobes. This is a consequence of pumping with focused Gaussian beams. (09:30)

10, 11. METNAHE SPECTRA 01:30

This is a second-harmonic wavelength-modulation spectrum of methane in air, acquired for calibration purposes. The methane content in this sample was 75 parts per million, very close to what it is in a Space Shuttle cabin environment after ten days of flight time. We pumped the air down to 80 torr for the lines to become resolved, so we

could match them to a database. The pump laser in this case was a solitary diode which tuned over more than 30 giga-Hertz without mode hops, by current control. This was an encouraging result, so we went on, to look at another sample. This air was sampled on a mountain ridge in Colorado, the methane content is 1.8 parts per million, and these are direct absorption spectra we're looking at. The top trace was taken at 80 torr pressure, the middle trace was taken at vacuum, and the bottom trace is the difference between the two. The reason we used background subtraction is that methane was present in laboratory air surrounding the cell, and you can see these two humps. The noise-equivalent column density here is 12 parts per billion meter per radical Hertz, limited only by detector noise. (11.00)

12. METHANE COMPARISON 01:30

From the standpoint of laser-based detection, is this number good or is it bad? Let us look at other experiments, and see how DFG compares to overtone detection and lead-salt diodes. These, in our opinion, are the mile-stone experiments on methane detection reported to date. People have looked at higher vibrational overtones and hot-bands of methane, using direct emission of near-infrared diode lasers. The most significant experiment in this area, was done by the Japanese researchers Uehara and Tai. They report the detection limit of 600 parts per billion, using the lowest vibration overtone at 1.66 microns. Webster and company have detected the fundamental bending mode near 8 microns using a cryogenically cooled lead-salt-diode laser. They report the detection limit of 14 parts per billion. DFG-based spectroscopy I have just talked about, gives a comparable detection limit of 12 parts per billion, using no cryogenic components. This tells us two things. First, mid-infrared detection using fundamental bands is indeed more sensitive than overtone, and it can also detect molecules that overtone detection can not. Second, DFG offers about the same sensitivity as lead-salt diode lasers, but it works at room temperature. (12:30)

13. QPM vs BULK 01:00

DFG has one practical disadvantage. Even if the phase matching can be achieved in the desired range, sometimes the pump and signal wave-lengths happen to be very odd, and there are no good lasers at these wave-lengths. One solution is to use quasi-phase-matching that has been recently demonstrated in lithium niobate. In a quasi-phase-matched crystal, the sign of nonlinear coefficient is reversed every co-herence length, thus forming a series of domains. Electric field generated in each domain, adds constructively to the field from other domains, so the total field keeps growing along the crystal. By choosing the domain period, one can phase-match any two wavelengths at any polarizations. In QPM materials, one can use the nonlinear tensor elements that are normally not accessible in bulk material. In lithium niobate for example, we can use d33 which is six times larger than commonly used d31. That is an over-all gain of 16 in conversion efficiency. (13:30)

14. 4.6 μm SOURCE 0:30

This is a schematic diagram of another experiment, where we mixed a diode-pumped monolithic neodymium yag laser, and a high-power tapered amplifier at 860 nano-meters. The mixing crystal was 6 milli-meter long lithium niobate with 23 micron grating period. The output infrared power was 8 micro-watts, and it tuned from 4.3 to 4.6 microns without crystal rotation. The tuning range was limited by the seed laser. We used this source to detect carbon monoxide and nitrous oxide in air. (14:00)

15. PPLN TRANSMISSION 00:30

One of our concerns was that lithium niobate would absorb heavily beyond 4.5 microns, but it turns out that it works out to about 5.3 microns, so gasses like N O can be detected as well.(14:30)

16. CO SPECTRUM 01:00

This is a wavelength-modulation spectrum of CO which we have acquired using 3 micro-watts infrared power over 4 meter path in air, that is the top trace. The bottom trace comes from the reference cell which we filled with a lot of carbon monoxide and added room air, so the line-width is comparable. The peak height here corresponds to about 360 parts per billion of CO, and the detection limit is about 5 parts per billion meter per radical Hertz, based on the measured signal-to-noise ratio. The sensitivity was found limited by the technical noise in the amplifier injection current. You can also see a rolling baseline in the top trace. We found out where it comes from and how it can be eliminated. I will not talk about it here because it's a long story. (15:30)

17. NOISE 01:00

We have also obtained intensity noise spectra of our DFG sources. In this graph, the black solid trace is the dark noise of an indium antimonide detector. The blue and red dots represent intensity noise of the 3.2 and 4.6 micron sources, respectively. In the case of 3.2 micron source, we used feedback stabilization of infrared power in order to obtain detector-noise-limited performance. We did not try to stabilize the other source, so the detection sensitivity was limited by intensity noise in the tapered power amplifier. This noise can be reduced by using a better driver. (16:30)

18. CONCLUSION 01:00

In summary, we have performed real-time sensitive detection of several trace gasses in ambient air, using all-diode-pumped, room-temperature DFG sources, based on silver gallium sulfide and quasi-phase-matched lithium niobate. They were pumped by diode and solid-state lasers at 800, 860, and 1064 nano-meters, and generated up to 10 micro-watts of narrow-band light near 3.2 and 4.6 microns. The species detected to date include: methane, carbon monoxide, nitrous oxide, CO2, and carbonyl sulfide. The typical tuning range was about 200 wave-numbers, and can be extended for the detection of nitric oxide and sulfur dioxide. The best sensitivity observed for CO in air was 5 parts per billion meter per radical Hertz, limited by intensity noise. (17:30)

19. HIGH RESOLUTION SPECTRA 01:30

The objective of my talk was to demonstrate spectroscopic advantages of DFG and compare it to other laser-based detection techniques. Let us now look at potential applications of DFG to spectroscopy and gas detection. The continuous wave DFG pumped by diode lasers, offers four features that are of great value to spectroscopy: narrow line-width, wide tuning range, low noise, and possibility of frequency modulation. These are Doppler-limited infrared spectra of carbon monoxide and nitrous oxide, acquired in a single-pass cell at room temperature. The bottom trace shows that the transitions are clearly resolved, the signal-to-noise ratio is quite impressive, and there is no background. This is to demonstrate how useful DFG can be for high-resolution spectroscopy of molecules and free radicals. (19:00)

20. SUITCASE 01:00

Another attractive feature of DFG, is that a practical device can be built using off-the-shelf diode lasers, optics, and nonlinear materials, and it will not require cryogenic cooling or high voltage electronics. In fact, the analytical instrumentation necessary for DFG spectroscopy is quite primitive, and can be packaged, along with the optical elements, into a medium size suitcase. Add a spectroscopic database to it and you have a portable mid-infrared gas detector. Thank you very much for your attention! (20:00)