Detection of Nitric Oxide Using Difference Frequency Generation in PPLN near 5.3 μm

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ABSTRACT

Periodically poled lithium niobate (PPLN) was used as a convenient nonlinear optical material to generate narrow-band mid-infrared radiation at wavelength up to $5.4~\mu m$. This source was applied to detect NO in air and to measure pressure broadening coefficients of some NO rovibrational transitions.

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Nitric oxide, NO, is an environmentally and biomedically important trace gas [1]. Considerable work has been done to investigate the spectrum of this molecule and develop methods of measuring trace concentrations of this species. Detection of nitric oxide using tunable diode laser spectroscopy (TDLAS) has been reported by Schmitke et.al. [2]. A sensitivity of 300 ppt was obtained that demonstrated the potential of high-resolution IR spectroscopy for NO detection. However, the absence of compact and room temperature tunable IR sources in the NO absorption region (5.1 to 5.7 µm) limits the use of laser spectroscopy for potential applications.

In this work difference frequency generation (DFG) is suggested as a convenient means to develop such a spectroscopic source [3]. Periodically poled lithium niobate (PPLN) is selected as the nonlinear optical crystal of choice. This medium can be engineered for noncritical (90°) quasi-phase matching of any combination of visible or near-IR lasers to produce DFG within its transparency range. It also features such properties as a large nonlinear optical coefficient and a optical transparency at wavelengths from the visible to 5.4 µm.

A 2 cm long multi-grating period PPLN crystal was pumped by a CW single-frequency Ti:Sapphire operating from 850 to 890 nm and a fixed wavelength diode-pumped Nd:YAG laser

operating near 1.0645 μ m. The power of each laser was approximately 0.5 W. The DFG output power as a function of wavelength is shown on Fig. 1. A quantum conversion efficiency of $2 \cdot 10^{-5}$ (~2 μ W) was achieved at 5.25 μ m despite a PPLN absorption of ~95% per cm at this wavelength. The optimum grating period for 90° quasi-phase matching PPLN is 22.0 μ m.

This infrared spectroscopic source was used for the detection of trace amounts of NO. A schematic diagram of the experimental setup is shown in Fig. 2. The detectors are balanced so that the signal in the absence of absorption is zero. This technique strongly reduces the noise caused by DFG power fluctuations. Trace amounts of NO in air are introduced into a 1m long multipass White cell configured for 24 passes. The strongest IR transitions $R(15/2)^{-2}\Pi_{1/2}^{-2}\Pi_{1/2}$ (e,f) and $R(15/2)^{-2}\Pi_{1/2}^{-2}\Pi_{1/2}$ (e,f) at ~1903 cm⁻¹ were chosen for NO detection.

The absorption spectra of $2.8(\pm0.3)$ ppm and $5.6(\pm0.3)$ ppm nitric oxide in 34 Torr of air are depicted in Fig. 3. From these data, it is seen that the noise level is 20 times smaller than the absorption signal. Hence the detection limit can be deduced to be 300 ppb for the present experimental configuration. The responsivity and the noise of the detector are 2.7 A/W and 1.20 pA/ $\sqrt{\text{Hz}}$, respectively. A detection limit of 100 ppt for a SNR=1 can be estimated for an IR power of 2 μ W, assuming that laser noise is completely balanced out. Hence further experimental improvements of the setup should lead to sensitivity levels necessary for NO concentration measurement in ambient air (~5ppb in urban areas) and human breath (~30ppb).

Accurate concentration measurements require a precise knowledge of pressure broadening coefficients. The apparatus was also used to measure NO pressure broadening coefficients in a mixture with N₂ since previously reported data are in 30% disagreement with each other. The shape of lines $R(15/2)^2\Pi_{1/2}^{-2}\Pi_{1/2}$ (e,f) and $R(15/2)^2\Pi_{1/2}^{-2}\Pi_{1/2}$ (e,f) was measured at nitrogen gas pressures of 0, 10,

30, 50, and 100 Torr at 296K with 10 MHz resolution. The partial pressure of NO was ~0.01 Torr. The obtained line envelopes were fitted with a Voigt function to extract the pressure broadening effect.

The present high-resolution mid-IR laser spectrometer can be developed into a compact gas sensor by replacing the Ti:Sapphire and, possibly, as well the Nd:YAG laser by commercial diode and diode pumped solid state lasers.

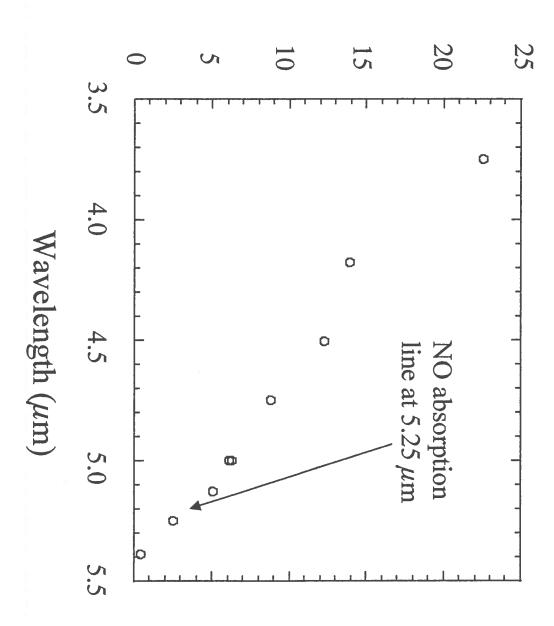
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- 2. G.Schmidtke, W.Kohn, U.Knocke, M.Knothe, W.J.Riedel, and H.Wolf, Appl. Phys., 28, 3665 (1989).
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FIGURES CAPTIONS

- Fig. 1. DFG power as a function of wavelength.
- Fig. 2. Optical arrangement of the DFG based sensor for NO detection. The length of the multipass cell is 1 meter, 24 passes.
- Fig. 3. Absorption spectra of NO in air at 34 Torr.

Infrared power (µW)



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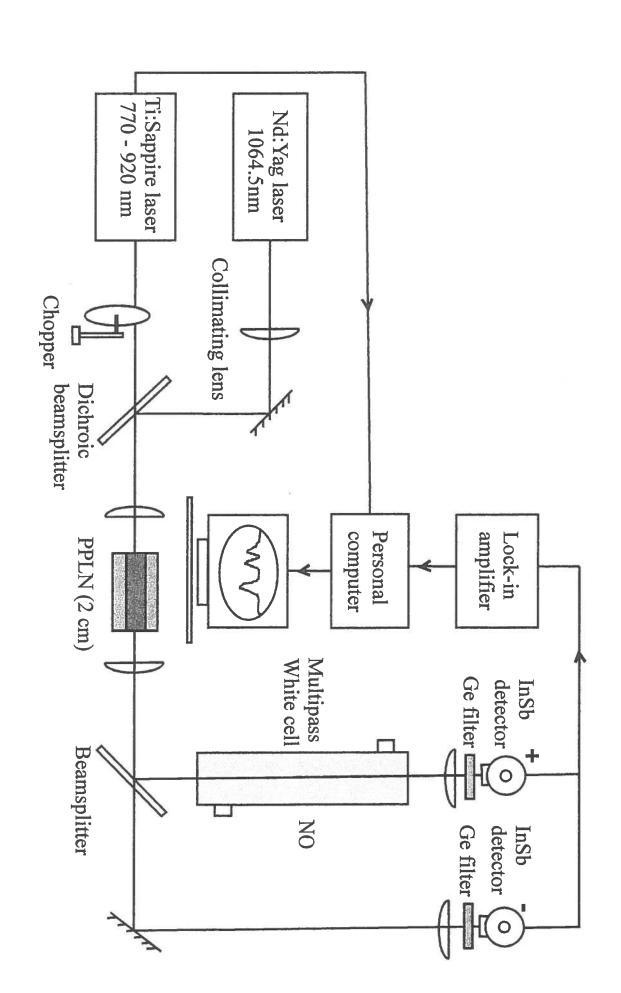


Figure: 2

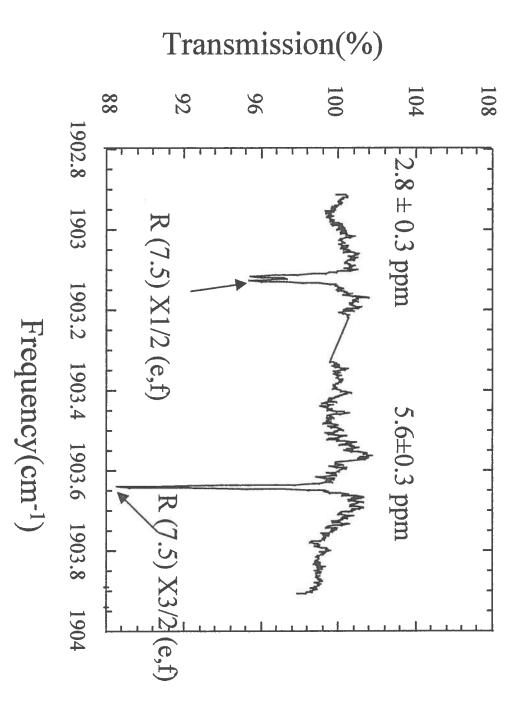


Figure: 3