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A Mid-infrared QEPAS sensor device for TATP detection

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Abstract. Recent developments of external cavity quantum cascade lasers (EC-QC lasers) enable new applications in laser spectroscopy of trace gas species in the mid-infrared spectral region. We report the application of quartz enhanced photo acoustic spectroscopy (QEPAS) with widely tuneable EC-QC lasers as excitation sources for chemical sensing of different species such as triacetone triperoxide (TATP). A pulsed EC-QC laser operating at ν~1120cm^{-1} and a cw EC-QC laser operating at ν~950cm^{-1} are used for the detection of the explosive TATP which is a mid infrared broad band absorber. The detection limit of our present setup is ~1ppm TATP at atmospheric pressure.

1. Introduction

The use of an EC-QC laser for sensing broad band absorbers in the mid-infrared spectral region opens new possibilities in laser spectroscopy. Explosives have strong absorption features in the mid-infrared region especially between λ=7µm and λ=11µm. As an example a vapor phase FTIR-spectrum of TATP is given in figure 1. Different laser based methods have been used for the detection of explosives and the mid-infrared spectral region offers several possibilities for their sensing [1,2]. Since recent developments on QC laser technology this spectral region is covered by EC-QC lasers [3-5]. Recently a cw EC-QC laser with a tuning range covering 182cm^{-1} combined with the output power of P=20mW for sensing different species was realized by Wysocki et al. [6]. In our sensing scheme we use two different commercially available EC-QC lasers: a pulsed laser operating between 1155cm^{-1} and 1220cm^{-1} and a cw laser operating between 925cm^{-1} and 975cm^{-1}. The tuning ranges of both systems are marked in the TATP spectrum in the figure 1 as a reference. QEPAS has been used extensively in order to detect different species in the near infrared (NIR) spectral region and also in the mid-infrared region. Details of this technique are given in [7, 8]. The sensing of broad band absorbers (for example acetone) with QEPAS was also reported earlier by Lewicki [9]. TATP is a peroxide based explosive which is also a broad band absorber in the mid-infrared region [10]. In this report we present for the first time a QEPAS based sensor approach with a QCL for the detection of TATP.

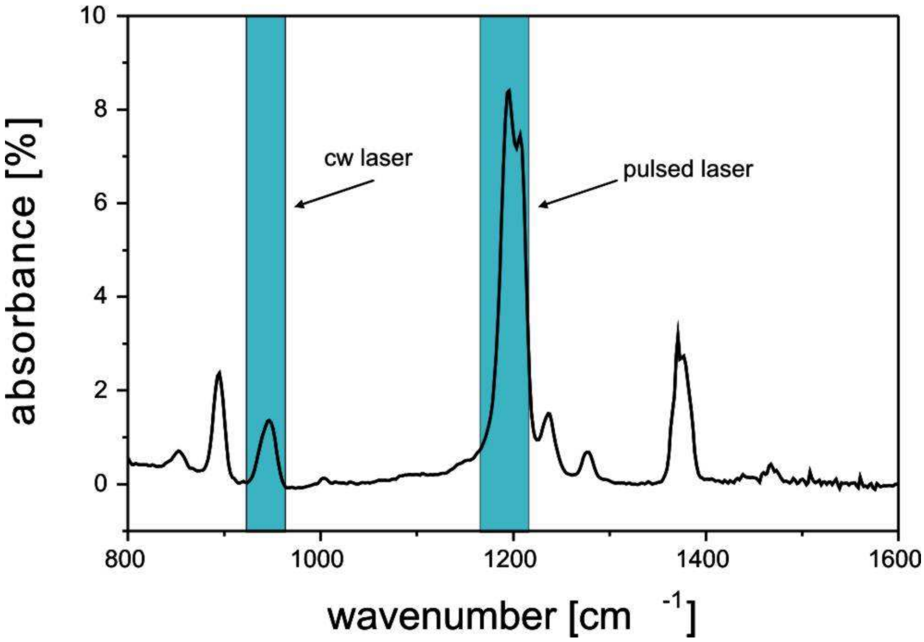

Figure 1. FTIR vapor spectrum of TATP and the tuning ranges of the used EC-QC lasers.

2. Experimental Setup

2.1. Quartz Enhanced Photo Acoustic Spectroscopy (QEPAS)

QEPAS has proven its applicability in sensing of different species. In this report we only give a brief introduction to this technique. The modulated laserlight is focused between two prongs of a quartz tuning fork (TF). Due to the vibration-translation energy transfer in the target molecule an acoustic wave is generated. If the laserlight is modulated at the resonance frequency of the TF a current signal can be measured due to the piezoelectric properties of the quartz material. The generated signal depends largely on the concentration and the absorption coefficient of the molecule and the optical power of the laser. For signal to noise (SNR) enhancement an acoustic micro-resonator (figure 2a) is extremely useful. As reported earlier the detection sensitivity can be increased if a micro resonator is used (for details see [11]). In our setup a QEPAS cell with two tubes (diameter: 600µm, length: 5mm) acting as an acoustic micro resonator is used (figure 2b-2d). The acoustic micro resonator is increasing the SNR by a factor ~7. The laserlight is coupled through a 1mm thick zinc selenide window into the cell.

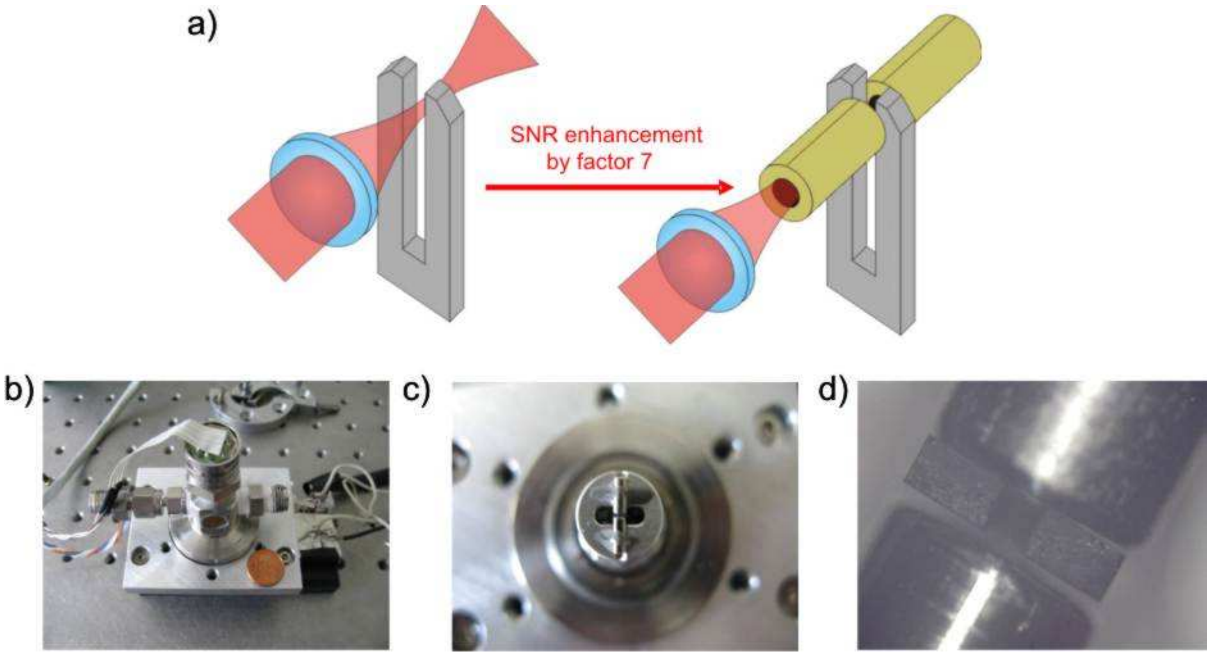

Figure 2. A QEPAS cell for sensing different species in the mid-infrared region: (a) principle of QEPAS and SNR enhancement with an acoustic micro-resonator. (b) The cell with zinc selenide windows. (c) The acoustic micro-resonator consists of two small tubes. (d) The quartz TF is placed between the tubes.

2.2. External Cavity Quantum Cascade Laser (EC-QC laser)

A fabry perot QC laser with AR-coated end facets is used as a gain medium with an external cavity in littrow configuration. This combination results in a widely tunable mid-infrared laser source with a high output power.

In this work two commercially available external cavity lasers (daylight solutions) are used. The laser housing is compact and in case of a pulsed laser no additional water cooling is needed. The tuning range of the pulsed laser (λ=8.4µm) is around $\Delta\nu$=75cm^{-1} (figure 3b) while the mode hop free cw laser (λ=10.5µm) can be tuned $\Delta\nu$=60cm^{-1} (figure 3c).

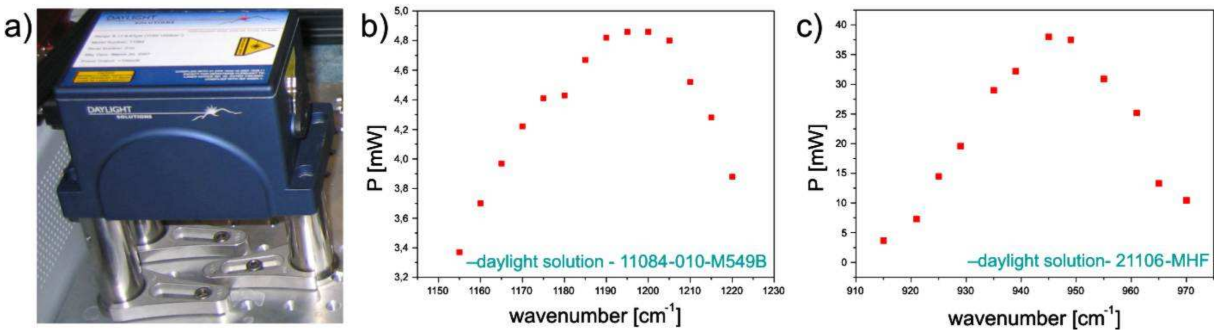

Figure 3. (a) laser housing of the EC-QC laser. (b) Tuning range of the pulsed laser at λ=8.4µm. (c) Tuning range of the mode hop free cw EC-QCL at λ=10.5µm.

For QEPAS a modulation of the laserlight at the resonance frequency of the TF is needed as well as the capability of scanning the wavelength. For coarse tuning of the wavelength the scanning option of the EC QC lasers can be used. A good agreement between measured emission wavelength and reading on the laser driver was found. For fine tuning, a piezo at the laserhead can be used. For calibration purposes of the used QEPAS cell different spectra of NH_3 were taken. For example a spectra of NH_3 with a concentration of 100ppm and at an ambient pressure of p=9torr is given in figure 4. A fine tuning coefficient of $6.75 \cdot 10^{-3}$ cm^{-1}/V_{pp} is derived from these measurements. A single absorption line at ν~932.88cm^{-1} was recorded also in order to show the small linewidth of the cw laser (figure 4b). The linewidth of the cw EC-QC laser is Δν <0.001cm^{-1}.

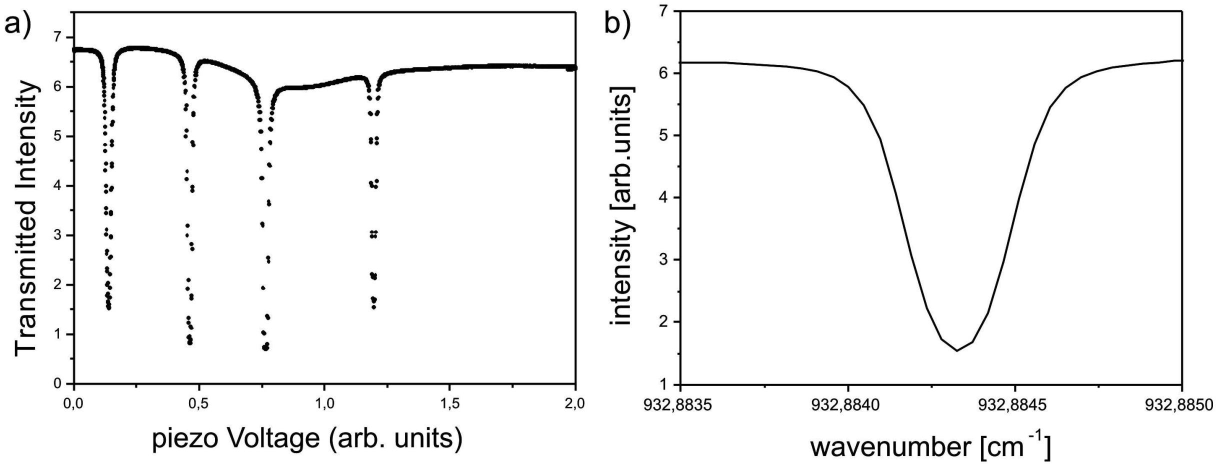

Figure 4. (a) "Piezo scan" for high resolution spectroscopy of ammonia at ν~932cm^{-1}. (b) A resolved single absorption line of ammonia at ν~932.88cm^{-1}.

For modulation of the laserlight three different approaches are used:

(1) amplitude modulation by application of an external trigger signal at f=32.756kHz. This is only possible with the pulsed EC-QC laser.
(2) amplitude modulation by use of a second tuning fork. The second tuning fork is placed into the beampath and driven into oscillation by application of an external voltage. Due to the vibrations of the prongs, the TF acts like a chopper. This method is used for the amplitude modulation of the cw EC-QC laser.
(3) frequency modulation for 2f-WMS. This method can only be applied for narrow linewidth absorbers and is therefore not suitable for broad band absorbers like TATP.

3. Results

The pulsed laser system (λ=8.4µm) was used for sensing TATP with a QEPAS sensor and for amplitude modulation the laser was triggered at f=32.756kHz at a duty cycle of 5% which results in an output power of P=5mW. The TATP was synthesized as described by Wolfenstein [12]. A small amount of TATP (<500µg) was placed inside the cell. TATP has an extremely high vapor pressure that corresponds to an equilibrium concentration of 65ppm at ambient air [13] and after a short time (few seconds) the TATP could be detected via QEPAS. Figure 5 shows the recorded TATP spectrum at ambient air. The two C-O stretch bands near ν=1200cm^{-1} can clearly be seen. Assuming the equilibrium concentration of ~65ppm for TATP at ambient air a theoretical detection limit of 1ppm TATP can be estimated with this setup.
For sensing the O-O stretch band of TATP at ν=945cm^{-1} the cw EC-QC laser was used. For amplitude modulation a second "chopper" TF was used. The SNR of the QEPAS signal is not as high as for the previously described measurement because of the lower absorption coefficient and due to the fact, that the modulation depth of the signal was only ~70%.

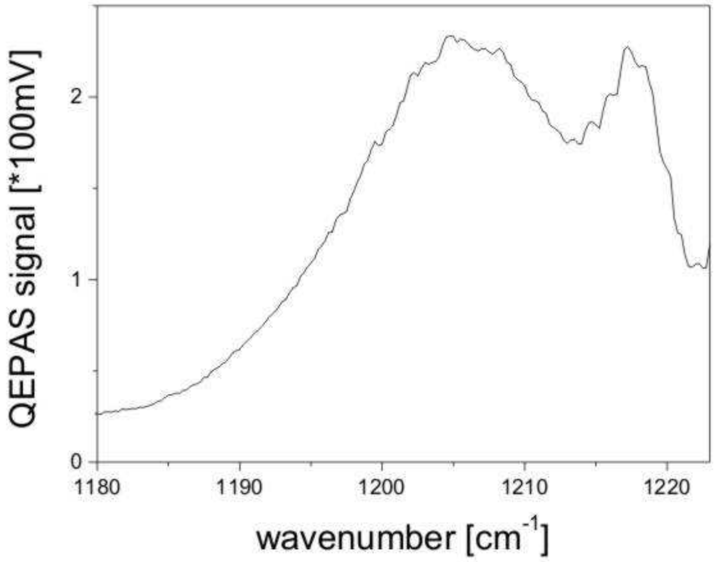

Figure 5. QEPAS signal from the complete C-O stretch band of TATP at around λ=8.4μm.

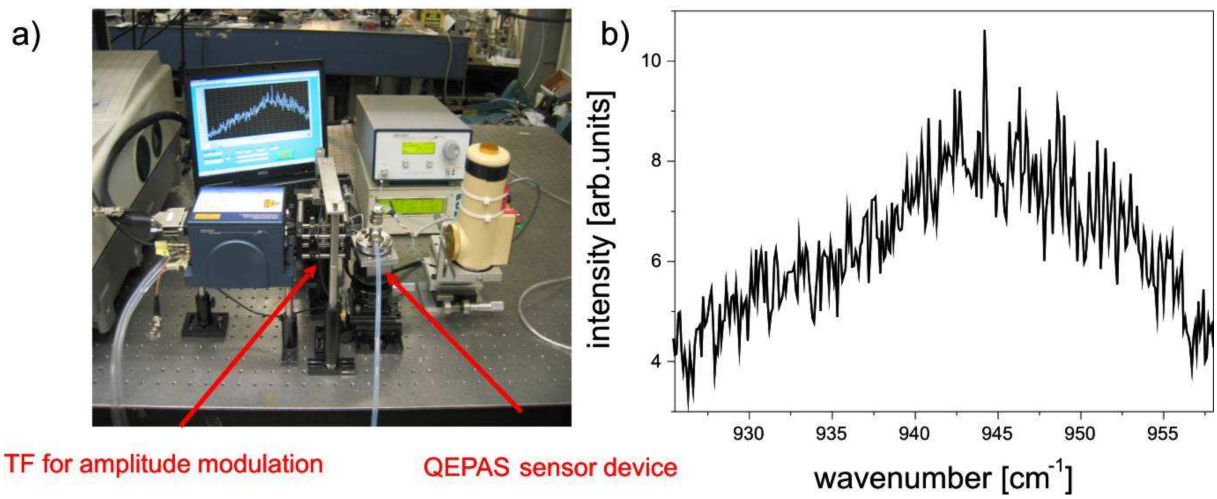

Figure 6. (a) The setup with a second quartz TF as chopper device. (b) The recorded QEPAS signal from the O-O band of TATP at around λ=10.5μm.

4. Conclusion and outlook

In this report we present a QEPAS sensor for the detection of the explosive TATP. Two different widely tunable EC-QC lasers are used. A pulsed one at λ=8.4μm in combination with a QEPAS cell enables a detection limit of 1ppm TATP in ambient air. Next steps are the integration of a QEPAS based sensor setup inside an existing security system (e.g. interlocks at airports) and the development of a fiber coupled QEPAS-TATP sensor system. With a mode hop free cw EC-QC laser it is possible to sense broad band absorbers like TATP but also small molecules with a resolved spectrum like NH_3. Narrow linewidth, high output power and wide tuning range are achieved with a mode hop free EC-QC laser. The setup of a multi species sensor system for the detection of several explosives is one of the upcoming challenges in homeland security and in our opinion mid-infrared spectroscopy will be one key technology in a multi sensor system.

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