

# Multiplex Molecular Fingerprinting with a Mid-Infrared $\text{Cr}^{2+}:\text{ZnSe}$ Femtosecond Laser

E. Sorokin

*Institut für Photonik, TU Wien, Gusshausstrasse 27/387, A-1040 Vienna, Austria. E-mail: e.sorokin@tuwien.ac.at*

I. T. Sorokina

*Department of Physics, Norwegian University of Science and Technology, N-7491 Trondheim, Norway*

J. Mandon, G. Guelachvili, N. Picqué

*Laboratoire de Photophysique Moléculaire, CNRS, Université Paris-Sud, Bâtiment 350, 91405 Orsay Cedex, France*

**Abstract:** A 130-fs  $\text{Cr}^{2+}:\text{ZnSe}$  laser is used to record, in 13 s, molecular spectra covering simultaneously 135 nm at 3.6 GHz resolution. The high signal-to-noise ratio of 3800 suggests 0.2 ppbv detection level for HF molecule.

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The solid-state modelocked lasers have now become reliable sources of broadband radiation, possessing unique features such as high spectral power, brightness and perfect beam quality. This makes them attractive for high resolution spectroscopy, as frequency combs [1-3] or as broadband sources with excellent beam quality [4,5]. Trace gas detection or molecular spectroscopy of weak gas lines puts a number of specific requirements to the apparatus: (i) the measurement setup should provide the highest possible sensitivity and signal-to-noise ratio (SNR) to detect faint lines; (ii) the bandwidth coverage should be sufficient to observe sets of lines for accurate identification of different constituents; (iii) the resolution and frequency accuracy must be sufficient to resolve individual lines, and (iv) for quantitative measurements, the complete line profile must be resolved (this also improves the SNR). The traditional measurements techniques meet difficulties in achieving these requirements simultaneously. Especially in the most interesting molecular fingerprint region, the spectral irradiance of the incoherent thermal sources and their poor focusability do not allow high sensitivity measurements.

In this paper, we report the implementation of a new spectrometric method based on a femtosecond laser taking the full benefit of the direct access to the mid-infrared wavelength range. We apply the femtosecond  $\text{Cr}^{2+}:\text{ZnSe}$  mode-locked laser in the molecular fingerprint region to high resolution spectroscopy. The radiation of a  $\text{Cr}^{2+}:\text{ZnSe}$  mode-locked laser is absorbed by the gas sample and analysed by a commercial Fourier transform (FT) spectrometer. Examples of ammonia spectra covering up to 135 nm in the 2400 nm region are shown.

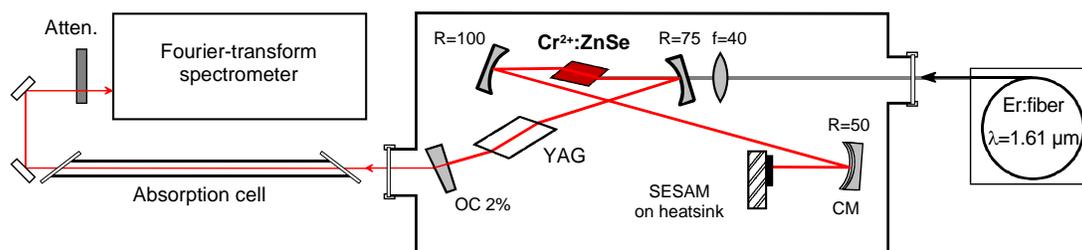


Figure 1: Experimental set-up. CM: chirped mirror. OC: output coupler.

The first sub-ps mode-locked operation of  $\text{Cr}^{2+}:\text{ZnSe}$  lasers has been reported recently [6], with pulse duration down to 80 fs at 80 mW of output power [7, 8]. In the present experiment, we have set up a prismless femtosecond laser following the design of Ref. [8], optimized for long-term hands-free stable operation. The laser is based on a 4 mm thick Brewster-cut  $\text{Cr}^{2+}:\text{ZnSe}$  crystal (Fig. 1), maintained at 20.5 °C by a recirculating water chiller system. The astigmatically compensated X-fold cavity consists of 75-mm and 100-mm radius-of-curvature dichroic mirrors, a 50-mm radius of curvature chirped mirror focusing the light onto a InAs/GaSb semiconductor saturable absorber mirror (SESAM), and an output coupler with transmission of 2 % at 2450 nm. Optical pumping is achieved with a 1607 nm Er-doped fiber laser, focused onto the crystal by an uncoated lens of 40 mm focal length. The self-starting mode-

locking results from the use of the SESAM, which has several hundreds of picoseconds relaxation time. Dispersion compensation is provided by a combination of a 6.5 mm thick uncoated YAG plate and the spherical chirped mirror. This provides about  $-1500 \text{ fs}^2$  round-trip group delay dispersion (GDD), which is almost flat over 300 nm. In order to get rid of the strong absorption lines of water vapor, the oscillator is placed inside a sealed enclosure. The enclosure is first evacuated under primary vacuum conditions and then filled with dry nitrogen.

With 1.9 W of pumping power, stable mode-locked operation is supported during hours with  $\sim 50 \text{ mW}$  average output power. The main stability limitation has been identified as arising from temperature increase of the SESAM heatsink, which was not attached to the cooling circuit, and resulted in slow decrease of the output power (and pulse broadening) during the laser operation. Fig. 2 provides a low resolution (30 GHz) spectrum and an interferometric autocorrelation trace of the laser pulses. The full width at half maximum (FWHM) of the autocorrelation trace is 250 fs, which leads to a pulse width of the order of 130 fs, consistent with the 44 nm measured FWHM of the corresponding spectrum, which has almost perfect  $\text{sech}^2$  profile. The pulse duration could be decreased by dispersion optimization [7], but we opted to improve the operation stability by providing some additional negative GDD. The laser emission is centered at 2405 nm. As compared to the open-air operation, the emission peak is not shifted towards longer wavelengths. This is different from our previous observation of the non-stationary continuous-wave operation of the Cr:ZnSe laser under secondary vacuum [9], where the decrease of the water absorption (growing towards longer wavelength) after air removal resulted in a shift of the laser wavelength by  $\sim 50 \text{ nm}$  to the red. More surprisingly, the pulse spectral width also doesn't increase when the air humidity absorption disappears. Our explanation is that the high losses of the modelocked setup (12% unsaturated absorption in the SESAM alone) significantly exceed the integrated absorption in the narrowband water vapor lines, thus making the setup almost insensitive to the air humidity.

After the exit window, the laser pulses pass through a 70 cm-long single-pass absorption cell, filled with the gas of interest, and 5 m of open-air propagation before finally reaching the spectrometer. The laser radiation is analyzed by a commercial FT spectrometer (max. resolution 3.6 GHz) equipped with a thermoelectrically cooled InAs detector. The laser beam has to be attenuated in order not to saturate the detector.

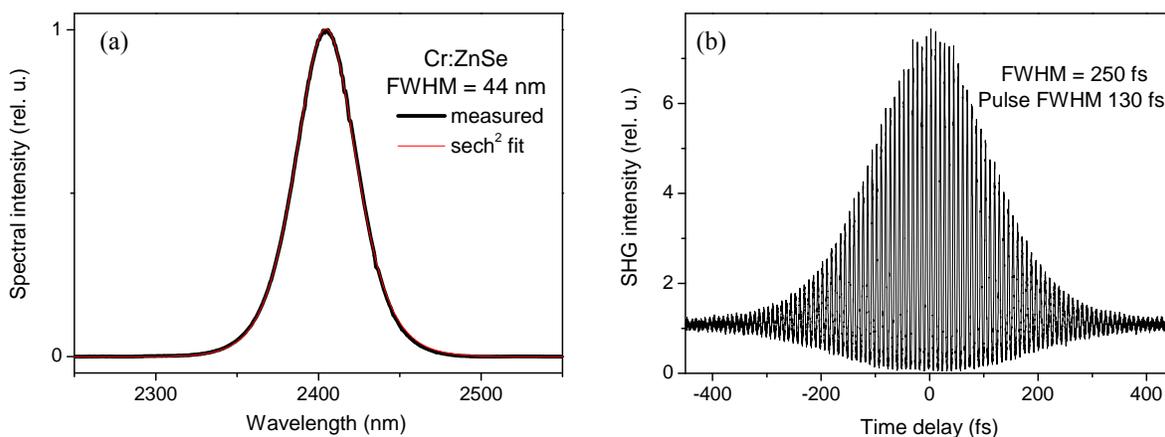


Figure 2: Spectrum (a) and interferometric autocorrelation (b) of a 130-fs pulse of the  $\text{Cr}^{2+}$ :ZnSe mode-locked laser. Pump power: 1.9 W, output power: 50 mW, repetition rate 200 MHz.

As a first demonstration of the capabilities of the source for broadband absorption spectroscopy, the rovibrational spectrum of ammonia has been recorded between 2341 and 2475 nm. Figure 3 gives an illustration of the  $\text{NH}_3$  spectrum. The  $\text{NH}_3$  pressure is 261 hPa (196 Torr). The full width at half maximum of the spectrum is 38 nm. Resolution is limited by the spectrometer to 3.6 GHz, giving the number of spectral elements  $M = 1916$ . With the total recording time  $T = 13 \text{ s}$  we observe SNR better than 3800. The spectral lines of ammonia belong to the  $\nu_1 + \nu_2$  and  $\nu_2 + \nu_3$  rovibrational combination bands. As the spectrum is complex and crowded, high resolution is useful to discriminate against the various lines.

In these spectra, the noise equivalent absorption coefficient (NEA) is  $3.7 \times 10^{-6} \text{ cm}^{-1}$  and the NEA at one second averaging per spectral element is  $3 \times 10^{-7} \text{ cm}^{-1} \cdot \text{Hz}^{-1/2}$ . This figure corresponds to detecting of 160 parts per billion by volume (ppbv) of  $\text{NH}_3$ , and it can be further improved by tuning the central wavelength to the stronger lines within the enormous bandwidth of the Cr:ZnSe laser. For hydrogen fluoride HF (1-0 band, with intensity of the R(2) line equal to  $2.3 \cdot 10^{-18} \text{ cm} \cdot \text{molecule}^{-1}$ ), the corresponding detection level is as low as 0.2 ppbv.

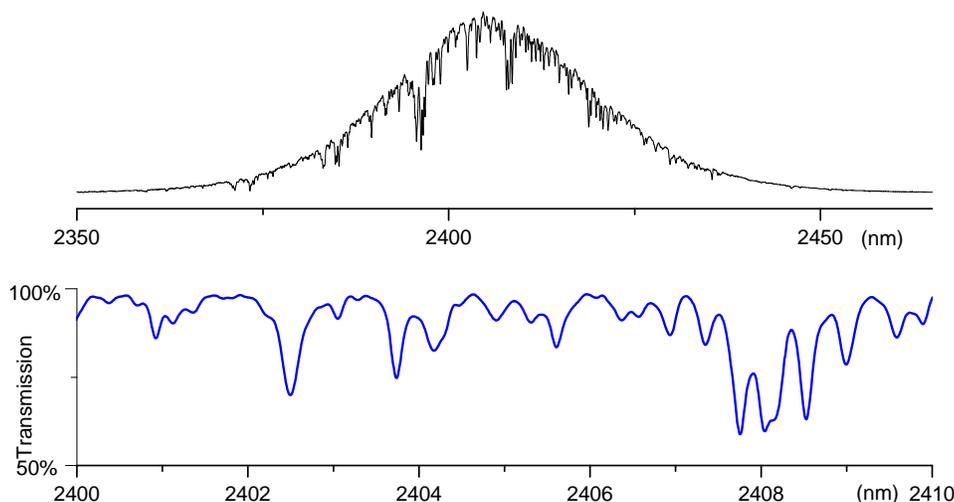


Figure 3: Spectrum of  $\text{NH}_3$  in the  $2.4 \mu\text{m}$  region illustrating the spectral bandwidth and SNR capabilities of the spectrometric technique. The  $\nu_1 + \nu_2$  and  $\nu_2 + \nu_3$  combination bands are observed. The upper part of the figure shows the whole spectral domain covered in a single recording while the lower part shows a portion expanded in wavenumber and intensity scales.

For a fair comparison, we recorded a spectrum using a traditional tungsten lamp. Under identical experimental conditions, the SNR was degraded by about 17. The recording time would have then been 300 times longer, i.e. over 1 hour, to get identical results. This is not surprising as this 50 mW femtosecond laser source has a spectral radiance which is about  $2.8 \cdot 10^5$  times stronger than a 3000 K blackbody source. Actually, a signal-to-noise ratio enhancement of about 500 should be achieved, but since the 50 mW power of the laser saturates the detector, we had to attenuate the beam by more than one order of magnitude. To make a proper use of the abundant power, one should e.g. employ a classical multipass cell. In this case increase of the absorption path by up to two orders of magnitude would then improve the sensitivity without lowering the SNR.

Summarizing, we have demonstrated the first spectroscopic application of a mid-infrared femtosecond mode-locked laser used as a broadband infrared source with a high resolution FT spectrometer. This simple experimental set-up already exhibits high sensitivity and resolution over a broad spectral domain. Sub-ppb detection levels should be easily obtained for a large panel of molecules thanks to absorption path length enhancement and high frequency detection. The frequency resolution is limited by the pulse repetition rate of 0.2 GHz. Further improvements in resolution and acquisition time are also in progress: this will include taking advantage of the comb structure of a stabilized mode-locked  $\text{Cr}^{2+}\text{ZnSe}$  laser by combination of the complementary experimental principles developed in [3, 4].

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