

Fast scanning IR–spectrometer to measure transient molecules in a pulsed supersonic jet

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Continuous wave (cw) narrow bandwidth Quantum Cascade lasers (QCL) with enhanced output powers (50–100 mW) and with large tuning ranges at infrared wavelengths (1–20 μm) allow for new spectroscopic applications. Fast IR–detector systems of up to 1 GHz response time became commercially available, enabling fast scanning and fast recording techniques. We have used a QCL–spectrometer at 10 μm to record spectra of transient molecules formed in a pulsed supersonic jet.

The molecules were produced by laser ablation of a target rod (e.g. aluminum or titanium) with the addition of a gaseous oxygen donor (O_2 or N_2O). The pulsed Nd:YAG laser ablation source produces molecular absorption signals of 10 μs duration time and with 20 Hz repetition rate. Scanning the infrared laser frequency at a tuning rate of 100 kHz allows the recording of the complete spectrum within 10 μs . At 1 GHz detector bandwidth the sample recording speed is set to 10 000 samples per scan (1 GS/s). A fast digitizer is used to store the spectra in a computer where single spectra are automatically calibrated and co-added in order to significantly improve the signal-to-noise ratio.

We used the new fast scanning spectrometer to record spectra in the 10 μm region of titanium monoxide (TiO). These TiO data, but also other infrared spectra of molecules formed from refractory elements (e.g., Al, Fe, C, Si), can be used for possible future astronomical observations of these species in the dust forming regions of late-type stars. The new generation of high resolution IR instruments (e.g. EXES/SOFIA or TEXES/Gemini North) with spectral resolution of 100 000 will allow to record spectra of small dust forming molecules and will give new insights to the fundamental processes leading to stellar dust formation. Despite their high importance, laboratory data of these molecules are still rather sparse to date.

Wide bandwidth mid-IR spectroscopy with comb-referenced EC-QCL: application to the ν_1 fundamental band of $^{14}\text{N}_2^{16}\text{O}$

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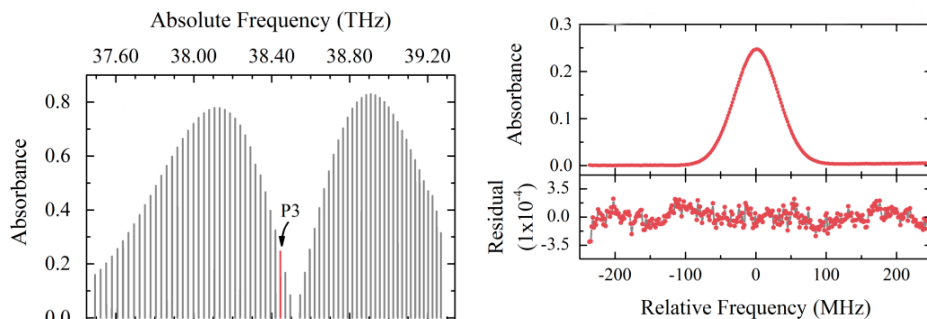
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Molecular line parameters collected in spectroscopic databases such as HITRAN are mainly retrieved from Fourier Transform spectroscopy with uncertainties that cannot overcome the MHz level. An improvement of four orders of magnitude is possible employing optical frequency combs to calibrate the frequency axis of a probe laser. In the extremely interesting spectral region of mid-ir, the only laser source suitable for wideband spectroscopy is represented by extended cavity quantum cascade lasers (EC-QCLs) with tunability that could exceed 100 cm^{-1} . Unfortunately, these lasers suffer from a large amount of frequency noise [1] preventing the possibility to lock it against a frequency comb synthesizer.

In this work we overcome this limitation and describe a spectrometer that relies for the first time on the frequency locking of an EC-QCL tunable in the $1217\text{--}1328\text{ cm}^{-1}$ range to a $1.9\text{ }\mu\text{m}$ Tm: Fiber comb exploiting a sum frequency generation scheme [2].

It is applied to the first comb-calibrated direct characterisation of the ν_1 fundamental band of N_2O , specifically of nearly 70 lines in the $1240\text{--}1310\text{ cm}^{-1}$ range, from P(40) to R(31) [3]. An overview of the measurements is presented in Fig. 1. Each line results from the average of 10 spectra acquired in 6 minutes at slightly different pressures, from 0.01 to 0.04 mbar. Such low-pressure regime allows to use a Gaussian profile for the fitting. Fig. 2 reports a 10-times averaged spectrum of the P(3) line together with the residuals. Line centers are retrieved with an uncertainty between 62 and 180 kHz.

The spectroscopic constants of the upper state are derived from a fit of the line centers with an average rms uncertainty of $4.8 \times 10^{-6}\text{ cm}^{-1}$ (144 kHz). The coupling of the spectrometer to a high-finesse optical cavity to the purpose of enhancing its sensitivity and addressing weaker absorbers, is also discussed.



[1] Opt. Express 2012,20,12432

[2] Sci. Rep. 2018,8,1292

[3] J. Quant. Spectrosc. Radiat. Transfer 2018,211,172

Endless frequency-swept comb-calibrated spectrometer

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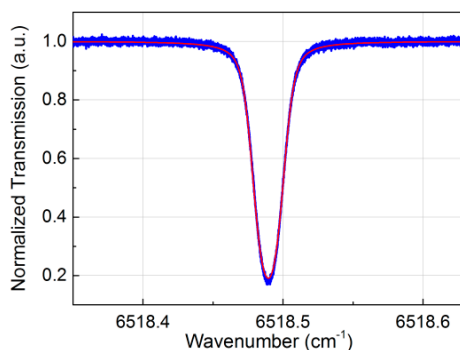
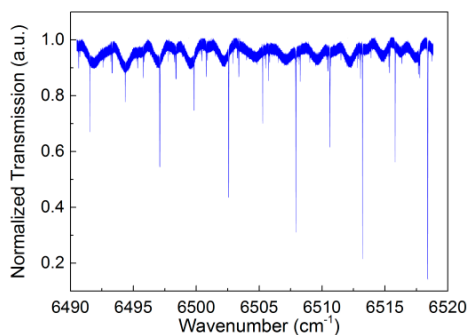
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The absolute frequency calibration afforded by optical frequency combs has enormously improved accuracy and comparability of spectroscopic measurements. Frequency combs are used either as a direct probe of molecular absorption, with the advantage of broad spectral coverage but at the price of spectral points separated by the comb repetition frequency, or in combination with a cw probe laser, which returns a very dense frequency axis and thus a high level of precision but in combination with speed and tuning range limitations given by the cw laser and/or by the referencing strategy.

Here we overcome these trade-offs by a new approach that bins the endless frequency shifting concept of an optical frequency comb proposed years ago by Rohde et al. [1] with the large and fast mode-hop-free tunability of a single-mode laser. Peculiarly, the laser remains phase-locked to the comb while being dragged by the comb itself over spectral ranges as large as a few THz at rates even beyond the THz/s.

As a proof-of-principle experiment, we measured the transmission spectrum of an acetylene cell in the range from 1533 to 1541 nm (about 1 THz in the frequency domain), encompassing 11 lines of the P-branch of the $\nu_1+\nu_3$ band. Figure 1 reports the normalized transmission spectrum acquired upon a frequency sweep of 400 GHz/s. The line centres retrieved from the fitting of the individual lines, as compared to HITRAN values, are affected by a statistical uncertainty of 1.5 MHz, which is remarkable if one considers a 2-ms scanning time per line and consistent with the current signal-to-noise-ratio of the measurement. Figure 2 reports the transmission spectrum of the 12P15 line (blue trace) together with the corresponding fitting profile (red trace). A line-by-line comparison between repeated sweeps does not show, at this level of precision, any bias, thus attesting a highly calibrated and repeatable frequency scan. A discussion about systematic and speed-dependent errors will be given together with preliminary results on the coupling of such system with a high-finesse optical cavity [2], in view of primary thermometry approaches and accurate testing of spectral line-shape models.



[1] Opt. Lett., 2014, 39, 4080

[1] J. Quant. Spectrosc. Radiat. Transfer, 2015, 154, 35

Broadband complex gas spectroscopy with sub-kHz level resolution comb spectrometer

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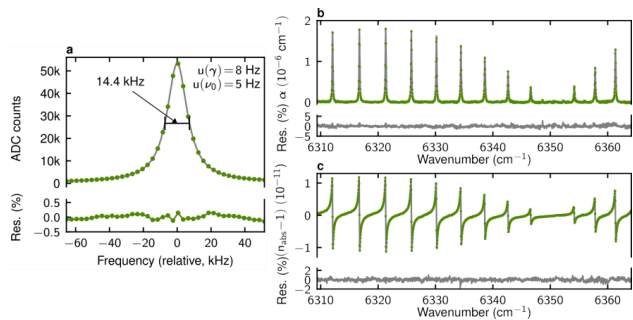
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Cavity mode-width spectroscopy [1] and cavity mode-dispersion spectroscopy [2] techniques provide a way to simultaneously determine absorption and dispersion of a sample by measuring widths and positions of enhancement cavity resonances. While these techniques were originally developed with continuous-wave lasers, they can also be efficiently combined with optical frequency combs (OFCs) [3,4]. We present broadband measurements of complex spectra of CO second overtone transitions, obtained from positions and widths of 7-kHz-wide cavity resonances determined at Hz-level precision. To the best of our knowledge, the cavity resonances shown in this work are the narrowest spectral features measured directly with a comb-based or non-comb-based broadband spectrometer. Moreover, the presented system is capable of retrieving shapes of such cavity modes in several seconds, enabling future ultra-precise, broadband and time-resolved spectroscopic measurements.

A near-infrared OFC with the repetition rate of 250 MHz is coupled into a high-finesse optical cavity ($F=18500$) and locked to the cavity modes. The controlled mismatch between the repetition rate of the OFC and the free spectral range of the cavity causes part of the comb to be filtered and produces a new OFC after the cavity with 4 GHz spacing between comb modes. The OFC is then transferred to a VIPA spectrograph with 600 MHz spectral resolution and 20 nm bandwidth to resolve the comb modes and retrieve their individual intensities. The shapes of the cavity modes are retrieved by measuring the transmitted spectrum as a function of the detuning between the OFC modes and the cavity modes.

Each cavity mode shape is fitted to a Lorentzian function (shown on Figure) to obtain its width and position. The mode widths and positions are converted to absorption coefficient and refractive index, respectively, and fitted to the complex Voigt profiles of probed transitions. We obtain signal-to-noise ratio of 190 for absorption spectrum and of 380 for dispersion spectrum with expected better performance for longer averaging times.

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- [2] A. Cygan, P. Wcisło, S. Wójtewicz, P. Masłowski, J. T. Hodges, R. Ciuryło, and D. Lisak, *Opt. Express* **23**, 14472 (2015)
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Empirical potential energy surface and bending angle probability densities for the electronic ground state of HCO^+

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In molecular spectroscopy parlance, a linear molecule is defined as one whose potential energy minimum is at a linear geometry. The nature of the *average* structure of a linear triatomic molecule – linear or bent? – has given rise to much discussion recently. We contend that the average structure of a linear triatomic molecule is bent. The purpose of the present work is to underpin this argument with results from Coulomb Explosion Imaging (CEI) experiments for the linear DCO^+ ion [R. Wester et al., *J. Chem. Phys.*, 2002, 116, 7000]; these experiments allow a direct experimental measurement of the bending angle probability density. We aim at simulating theoretically the CEI experiments for DCO^+ . The possibility of obtaining a detailed simulation is hampered by the fact that the DCO^+ ions investigated in the CEI experiment populate very highly excited vibrational states. This creates numerical problems for the theoretical calculations. We can conclude, however, that the results of the CEI experiment are in support of the average structure of a linear molecule being bent.

Torsion rotation program for nitromethane CH₃NO₂

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Nitromethane, CH₃NO₂, is the simplest representative of molecules with a C_{3v} symmetric top rotating relative to a C_{2v} frame. A very low six-fold barrier to internal rotation makes the torsional label *m* an almost good quantum number. The rotational quantum number *K_a* is much worse as a label because nitromethane is an asymmetric top closer to the oblate limit ($\kappa=0.25$). The PI symmetry group, G₁₂, is isomorphic to C_{6v} point group which possesses 6 irreducible symmetry species. However, a permutation of two oxygen atom ¹⁶O of nuclear spin equal to 0 allows only for a half of the species, namely A₁, A₂ and E₂. In the ground vibrational state the torsion-rotation functions must fulfill a strict condition $m+K_a = \text{even}$. If nitromethane is in a vibrational state of B₁, B₂ or E₁ the required condition is $m+K_a = \text{odd}$. Each torsion-rotation state is additionally labeled with *J* quantum number and a symmetry species in C_{6v} group.

The presented program allows for a determination of the condition "even or odd" for $m+K_a$. Furthermore, the torsion-rotation basis functions are derived using a full symmetry of G₁₂ group which results in relatively easy assignment of *m* and *K_a* as approximate labels to torsion-rotation energy levels. The Hamiltonian is similar to that used by Ilyushin [1] – it introduces the ρ constant which minimizes the torsion – rotation coupling and all interaction terms with $\cos 6\alpha$, $\sin 6\alpha$, $\cos 3\alpha$, $\sin 3\alpha$ functions. The detailed expressions will be shown.

This approach is closer to the Sørensen's program [2] than to the Ilyushin's approach [1] where *K_a* is no longer a label for the torsion-rotation states. On the other hand Sørensen did not use a full expansion on *m* but included limited interactions with neighboring torsional states in a range [*m*-6 to *m*+6]. The new program allows for calculation of transitions between different torsional states and facilitates determination of combination states where torsional transitions overlap a vibrational excitation.

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