EUMETRISPEC Newsletter 4

Research highlights

Preparation of reference gas mixtures for the intercomparisons

Within the EUMETRISPEC project intercomparisons are organized to demonstrate equivalence of the spectroscopic measurements at the different NMIs and the central facility at PTB. The comparisons focus on either the determination of line strength (Intercomparison 2: *Molecular reference lines*, task 3.5) or the amount of substance (Intercomparison 3: *Mole fraction*, task 3.5). The aim of Intercomparison 2 (defined in protocol deliverable D3.4.2) is to critically evaluate the capabilities of JRP partners in determination of spectral line data – here linestrength – in identical target species and spectral ranges (CH_4 R(0) line near 3.3 μm or 3028 cm^{-1} was selected for this intercpomparison). The aim of Intercomparison 2 (protocol deliverable D3.4.3) is to demonstrate that traceably established molecular line data (linestrength) enables accurate determination of molecular gas concentration (N_2O lines near 3.53 μm or 2825 cm^{-1} were selected respectively). These intercomparisons rely on reference CH_4 and N_2O mixtures in air prepared respectively by VSL and SMU partners.

For these comparisons gas mixtures are distributed among the different project partners. VSL and SMU provide gas mixtures prepared by gravimetric methods (ISO 6142) with a small uncertainty in the composition. The small uncertainty is obtained by:

- precise weighing of the amounts of the individual gas components filled into a 5-liter aluminium cylinder
- a rigorous purity analysis of the individual gas components

After the preparation mixtures are analyzed by comparison with standard gas mixtures using gas chromatography or other techniques. Partners analyze the gas mixtures using spectroscopic techniques and therefore any variation in isotopic composition of gases can cause significant errors in the results of analyses. In the past there have been a number of cases in which NMIs found that the isotope ratio of gases deviated from the normal ratios. A well-known example is ^{13}C depleted CO in some regions of the world as ^{13}C is removed for delivery into ^{13}C labelled chemical market.

VSL doesn't currently have the facility to determine isotope ratios. Therefore the Isotope Research Centre in Groningen, the Netherlands analysed the methane used for the preparation of the mixtures. The methane used for the comparison has a $\delta^{13}C$ value of -37.42 ± 0.10 ‰ VPBD which is typical for methane obtained from natural gas.

Figure 1: *Automatic weighing device for gas cylinders at VSL.*

SMU prepared batch of cylinders and sent 5 mixtures nitrous monoxide (N_2O) in synthetic air to the partners at the beginning of April 2014. For the static gravimetric preparation and validation two filling stations with built-in dry evacuation system for the preparation of nitrous monoxide in synthetic air gas mixtures were used. The amount-fractions of N_2O/synthetic-air cylinders were adapted to the satellite facilities laser spectrometry

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methods (0.1 mol/mol for direct absorption method used at LNE-CNAM, PTB and DFM and 10 µmol/mol for CRDS method used at VSL and MIKES).

Figure 2: *Equipment for the validation and purity analysis of the nitrous monoxide mixtures at SMU.*

Traceable determination of line centre frequencies of R(8) multiplets of CH_4

In the previous newsletter n°3 we presented the successful measurements on absolute line centre frequencies of the P(7) multiplets (3.39µm) belonging to the ν_3 band of methane performed by LNE-CNAM (in collaboration with their CNR-INO partner) using frequency comb-assisted direct saturated absorption spectroscopy. The results of the absolute frequency measurements agreed to within ~1 MHz with recently published measurements (details in preliminary Report D1.3.03 on traceable measurement of absolute line centre frequency). Preliminary results of the absolute line positions of R(7) components of methane were performed at MIKES by the same time using comb-assisted CRDS spectroscopy. However due to a failure of the Rubidium maser to which the MIKES optical frequency comb was referenced, only low-accuracy measurements using a wavemeter could be obtained. With the Rb maser operating again, these measurements have now been improved by MIKES for the R(8) components of CH_4 using a fully traceable comb-assisted absolute frequency measurements .

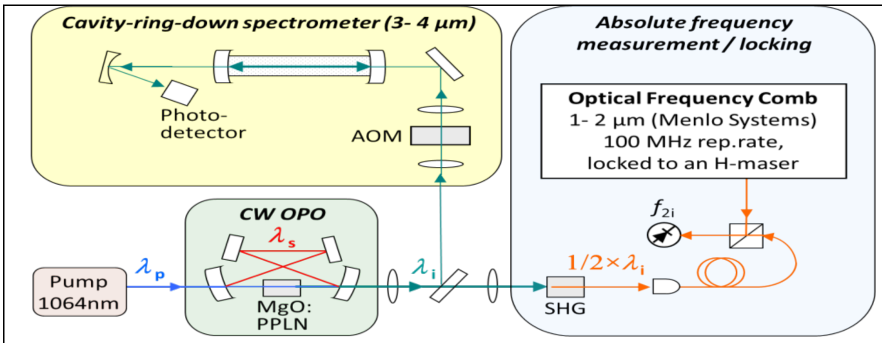

Figure 3: *Optical Frequency-comb (OFC) assisted CRDS spectrometer set-up. The beatnote between the doubled-idler from the OPO with the nearest comb tooth is used to lock the OPO to the OFC by feeding back the error signal to the pump frequency.MIR frequency scan is performed via the repetition rate of the OFC.*

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The OPO-driven CRDS spectrometer used at MIKES is depicted in Figure 3. Compared to the direct saturation spectrometer used by LNE-CNAM, where the OPO idler wave was actively frequency-locked to the saturation dip of the molecular transitions, the method used at MIKES consists in locking the MIR frequency of the OPO (idler wave) to the frequency comb, and subsequently scanning the MIR frequency by scanning the comb repetition frequency. The absorption spectrum of CH_4 was simultaneously recorded with the cavity-ring-down setup. The absolutely calibrated spectra displaying a central dip at low pressure was then fitted to a Doppler lineshape (discarding the dip zone) and the dip fitted to a Lorentzian pattern to derive the line center frequency (Figure 4).

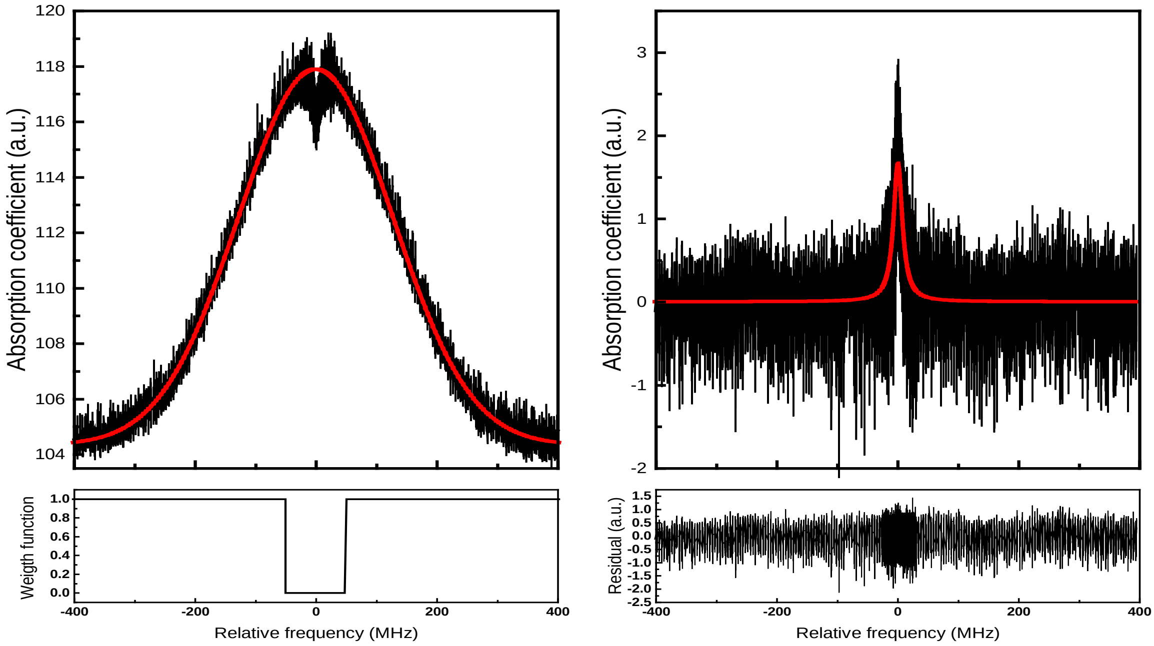

Figure 4: Left panel - Observed Lamb dip of the $F^{(2)}_1$ component of the R(8) multiplet at P=1 mbar. Right: Central saturation dip feature captured by the CRDS spectroscopy. The retrieved line center frequency is $\nu =$ 93 064 093 016.9 kHz.

The detailed results of the line center frequencies of the R(8) multiplets will be updated in the D1.3.03 report.

In May 2014, MIKES and LNE-CNAM collaborated in Helsinki on the OFC-assisted CRDS setup in order to cross-ckeck the value of the P(7) $F^{(2)}_2$ component line center position previously measured by LNE-CNAM using direct saturated absorption spectroscopy (note that this component is one of the MIR CIPM recommenced frequency standard). This involved tuning the MIR idler wave of the OPO from 3.22 μm to 3.39μm. However at twice this idler frequency, the comb power near 1695 nm was to weak to obtain a beatnote with a signal-to-noise ratio greater than 30 dB to lock securely (without cycle slips in the beatnote count) to allow a traceable measurement of the P(7) component, hindering thus the cross-check with the LNE-CNAM measurement. The use of a tracking voltage-controlled oscillator (VCO) phase-locked to the weak beatnote (S/N ~20 dB) to regenerate the beatnote S/N ratio would help to lock the OPO to the OFC and solving thus the absolute frequency measurement of the P(7) components.

Accurate measurements of N_2O $2\nu_3$-band (λ~2.25 μm) line parameters

At the PTB Central Facility, accurate line parameters (linestrengths, self-broadening and self-shift) of the whole R-branch of the first overtone of the fundamental ν_3 band ($2\nu_3$ band between 4418-4442 cm^{-1}) of pure N_2O have been performed using the infrared measurement setup based on the high-resolution Fourier-Transform (FT) spectrometer Bruker IFS 125HR (nominal resolution better than 0.002 cm^{-1}). Self-broadening coefficients for this band reported in HITRAN 2012 data base are actually based on interpolation from previous low-resolution measurements of other bands, hence the need for these new high-accuracy self-broadening coefficients (estimated uncertainty <1%, Figure 5). Furthermore Self-shift coefficients have been measured for first time in the $2\nu_3$-band for the lines R0e-R40e with a current uncertainty estimate of 3.2%.

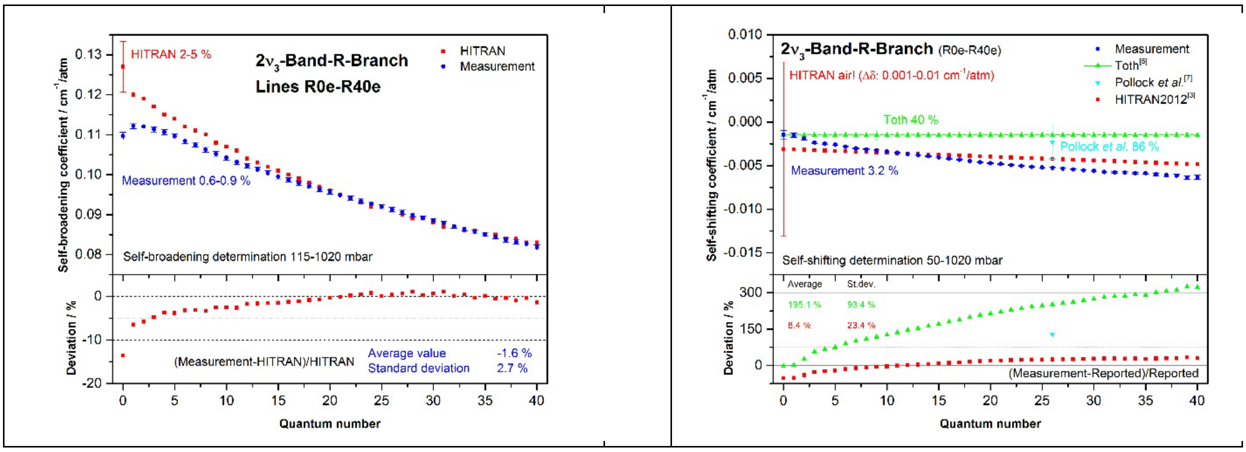

Figure 5: Left panel – Self-broadening coefficients of the R(J) branch of the $2\nu_3$ band of N_2O versus the rotational quantum number J. Right: Self pressure shift coefficients.

Measurements of linestrengths and nitrogen pressure broadening and shift coefficients in the ν_3 band of CH_4

Two satellite partners with OPO-based spectrometers (VSL and LNE-Cnam) have measured some linestrengths of methane's transitions in its fundamental ν_3 band (C-H strech bond). At VSL linestrengths measurements used standard CRDS technique with nitrogen-diluted mixtures (with amount of substance levels within the range of 10-500 nmol/mol). The lines targeted at VSL were the 2 overlapping components (F2-component at 2998.994 cm^{-1} and E-component at 2999.060 cm^{-1}) of the P(2) doublet and the R(0) singlet line (A1 symmetry) at 3028.7522 cm^{-1}. LNE-CNAM used direct absorption spectroscopy on pure methane and focused the measurements on 3 singlet lines P(1), R(0) and R(1) at 3009.011 cm^{-1}, 3028.752 cm^{-1}, and 3038.498 cm^{-1} respectively. The common R(0) linestrength measurement provides a comparison between the VSL and LNE-Cnam results. Figure 6a shows the results measured by LNE-CNAM for R(0) ($S(T_0)=(9.05\pm0.40)\times10^{-20}$ cm/molecule) compared with previous measurements by Pine (using a DFG spectrometer), Dang-Nhu (FTIR) and HITRAN value ($S_{HITRAN}=(9.21\pm0.69)\times10^{-20}$ cm/molecule). The value of LNE-CNAM (with a relative uncertainty of ~7% (at the same level as the HITRAN uncertainty), lies within the latter's uncertainty bar. The value derived at VSL, $S(T_0)=(8.1\pm0.2)\times10^{-20}$ cm/molecule (<3% uncertainty), is -13% lower than the HITRAN value and lies outside the range of the figure plot. The reason of this discrepancy is still yet unknown. Figure 7 and Figure 8 show the LNE-CNAM results for the nitrogen-induced pressure broadening and lineshift coefficients, respectively.

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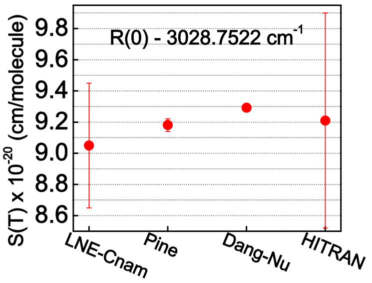

Figure 6: Comparison of linestrength values for the R(0) singlet. Pine [JQSRT **57**, 1997], Dang-Nhu [J. Mol. Spec. **77**, 1979].

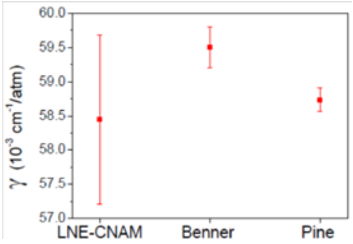

Figure 7: Comparison of N2-broadening coefficient for R(0). Benner [JQSRT 50, 1993], Pine [JQSRT **57**, 1997].

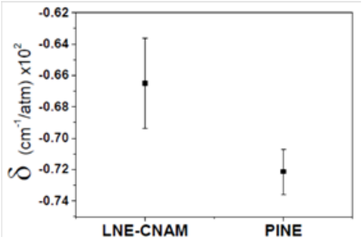

Figure 8: Comaprison of N_2 line shift coefficient. Pine [JQSRT **57**, 1997].

Announcement: 2nd Stakeholder Workshop (9-10 Oct 2014, PTB-Braunschweig)

The 2nd Stakeholder Workshop on "Traceability of Spectral Reference Line Data" will be held on 9-10 October 2014 at Physikalisch-Technische Bundesanstalt, Bundesallee 100, 38116 Braunschweig, Germany (see official announcement flyer and further information at http://wwww.eumetrispec.org).

The workshop aims to establish a European spectroscopy infrastructure enabling measurements of traceable spectral line data under well controlled conditions at a central FTIR facility (CF) and at laser based satellite facilities (SF) as well as to foster the development, application and expansion of metrological codes which aim to provide well-defined uncertainties for all measured spectral parameters. The workshop goal is to get together and mutual exchange of information and expertise between stakeholders in the atmospheric and environmental monitoring community, lab spectroscopists for spectral line data, and metrologists participating in the EURMETRISPEC project. Outcomes of the EUMETRISPEC project will be presented. The workshop language will be English (presentations, posters, discussions, proceedings).

In addition to invited presentations, the workshop can host a limited number of oral and poster presentations of contributed papers on a limited scale. The poster sessions will allow the researchers to discuss their most recent work in a relaxed atmosphere. All contributed papers will be published in a proceedings volume and will be made available to the participants in digital form after the meeting.

Registration and abstract submission

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New Consortium Publications and upcoming conference presentations

J.A. Nwaboh, O. Werhahn, V. Ebert, "Line strength and collisional broadening coefficients of H_2O at 2.7 μm for natural gas quality assurance applications", Molecular Physics (2014) DOI 10.1080/00268976.2014.916823.

J. A. Nwaboh, O. Witzel, A. Pogány, O. Werhahn, V. Ebert, "Optical path length calibration: a standard approach for use in absorption cell-based IR-spectrometric gas analysis", Int. J. Spectroscopy (2014) DOI 10.1155/2014/132607.

V. Werwein, J. Brunzendorf, A. Rausch, A. Serdyukov, O. Werhahn, V. Ebert, ”First measurements of N2O-self-broadening coefficients in the 0001-0000- and 0002-0000-bands,” in preparation.

M. P. Moreno, M. Cadoret, M. Jahjah, L. Nguyen, F. C. Cruz, J.-J. Zondy, ”Line intensity measurements of methane’s ν_3-band using a cw-OPO”, Appl. Phys. B: Lasers and Optics, online version (June 2014), DOI 10.1007/s00340-014-5883-1.

M. Jahjah, M. P. Moreno, M. Cadoret, L. Nguyen, J.-J. Zondy, “Measurements of N_2-broadening and pressure-shift coefficients in the ν_3-band of $^{12}CH_4$ using a cw-OPO”, J. Quant. Spectrosc. Rad. Transf. (accepted on oct 2nd, 2014).

V. Werwein, D. Balslev-Clausen, J. Peltola, M. Valkova, J. Brunzendorf, T. Fordell, T. Hieta, A. Rausch, A. Serdyukov, M. Vainio, J. C. Petersen, O. Werhahn, V. Ebert, “Measurements of N_2-broadening and pressure-shift coefficients in the ν_3-band of $^{12}CH_4$ using a cw-OPO”, abstract submitted to HRMS 2014 conference (Bologna, Sept 2-7, 2014).

M. Jahjah, M. P. Moreno de Souza, L. Nguyen, M. Cadoret, F. C. Cruz and J.-J. Zondy, “Line Intensity, N_2-Broadening and Pressure Shift Measurements in the ν_3-band of $^{12}CH_4$ using a cw-OPO”, oral presentation (presentation ID: LF2A.5) at *Latin America Optics & Photonics conference* (LAOP 2014, an OSA meeting, 16-21 nov 2014), Cancun, Mexico.

Contact and further information

This is a newsletter about on-going work and development of the EUMETRISPEC project, which is carried out by the following partners / institutions:

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Additional information on EUMETRISPEC and the partners can be found on the project homepage www.EUMETRISPEC.org, where our contact details and a registration access are available to get access to the stakeholder area where additional information will be made available.

Please forward this newsletter to your colleagues. They can send an email to any of the project's representatives with subject ‘register EUMETRISPEC newsletter’ to register for this 6-monthly newsletter.