

Application of molecular spectroscopic databases for certification of calibration gas mixtures

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Available molecular spectroscopic databases and catalogues were created without the involvement of the metrological community. This is the reason why modern spectral optical methods are not fully implemented in gas analysis. However, it is possible to use the available spectroscopic databases for high-precision measurements. In this paper, we present our approach to measuring the concentrations of gas components (HCl, CO, NO, SO₂) in gas mixtures using the HITRAN or GEISA molecular spectroscopic databases. Metrological traceability is usually implemented through the comparison of gas mixtures with high precision (comparison standards (CS)) made with the use of the National Primary Measurement Standard of Mole Fraction and Mass Concentration of Components in Gas Media (GET 154–2016) and working standards used to calibrate gas analyzers.

Methods of UV absorption[1], FTIR[2], and CRD[3] spectroscopy were developed and investigated to transfer units of mole fraction of gases to the working gas standards, to reduce the required number of CS and improve the accuracy of measurements.

The calculated spectra differ from the measured spectra taken for the same concentration of gas due to the inaccuracy of the absorption cross-section or inaccuracy of the spectral line parameters, presented in the molecular spectroscopic databases and catalogues. This is the reason why modern spectral optical methods are not fully implemented in gas analysis.

Also, for any spectral instrument, it is necessary to have a precise knowledge of the instrument function and the other technical parameters. Only one special gas cell is used to control the instrument function.

For the successful application of the existing molecular spectroscopic databases in the absorption spectroscopy, it was necessary to identify the most accurate data and attribute uncertainty to it, based on our own experimental studies conducted with the use of the metrologically assured CS. In the future, the measurement of concentrations can be done without the use of the CS.

In the case of CRD spectroscopy, for the gas mixtures in which the matrix gas differs from the air, the broadening of spectral lines associated with interactions between molecules leads to significant inaccuracy of measurement[3].

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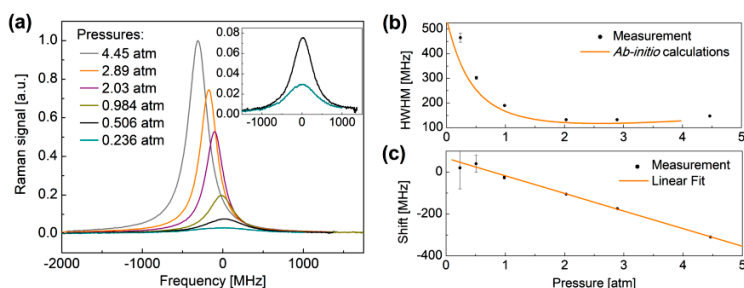
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Comb-calibrated coherent Raman spectroscopy of molecular hydrogen

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Highly accurate measurements of H₂ transition frequencies is fundamental for testing the quantum electrodynamics and physics beyond the standard model [1–3]. However, the retrieval of the unperturbed line positions is very challenging since it compels to work in low pressure conditions: the achievement of high signal-to-noise ratios is then hindered by the weakness of quadrupole transition moments and by the low molecular density. Alternatively, the distortion of the line profile at higher pressure could be carefully modelled in order to compensate for speed-dependent collisional effects and for the strong Dicke narrowing. High accuracy measurements of the Q(1) transition of the pure H₂ 1–0 band at 4155.25 cm⁻¹ have been performed from 0.2 to 5 atmosphere using stimulated Raman spectroscopy. An Er: fiber frequency comb has been used to calibrate the frequency difference between the pump and Stokes cw lasers involved in the Raman process. The pump laser emits at 737.8 nm and is kept fixed while the Stokes laser is scanned over 3 GHz around 1064 nm. The two beams are spatially superimposed and travel through a multipass cell filled with H₂. Figure 1 (a) displays the line profiles measured at seven different pressures (the measurements at the two lowest pressures are displayed in the inset). As it can be noticed from panel (b) the retrieved widths are in a good agreement with *ab-initio* values based on H₂–H₂ quantum scattering calculations. The frequency shift, plotted in panel (c), is proportional to pressure above 1 atm and the retrieved pressure coefficient agrees well with previous results [4]. The strength of the approach which provides high signal-to-noise ratio and frequency accuracy at the same time enables the use of more advanced profile models, such as the Hartmann–Tran profile, for line shape investigation.



- [1] Phys. Rev. A 1991,43,6075
- [2] Phys. Rev. Lett. 2013, 110, 193601
- [3] J. Mol. Spectrosc. 2014, 300, 55
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Design and fabrication of a high-resolution Fourier-transform spectrometer with a supercontinuum laser source

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The perfect instrument in spectroscopy consists of a broadband instrument that measures spectra with high resolution and high sensitivity in a small amount of time. Fourier transform spectrometers allow for both high resolution and broadband measurements thanks to their multiplex advantage [1]. By coupling an optical cavity to a coherent light source, the sensitivity of the instrument, that is the ability to measure small concentrations, is considerably improved because the interaction length of the light with the sample is increased by several orders of magnitude [2].

The poster presents the first results regarding the design and fabrication of a homemade instrument that will embody all these features. This spectrometer is designed for the analysis of molecules and molecular complexes in the gaseous phase from the near infrared to the UV ranges with a resolution down to 0.0035 cm^{-1} . The homemade Fourier transform spectrometer has the particularity to employ a supercontinuum laser as the broadband light source.

Several measurements were performed to validate the experimental setup. Those are direct absorption spectra of the hyperfine transitions in Rubidium around 780 nm, of forbidden electronic transitions $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ in O_2 around 766 nm, and absorption of H_2O and CO_2 between 1.3 and $1.6 \mu\text{m}$.

[1] P. R. Griffiths, Fourier transform infrared spectrometry (2007) (Vol. 171).

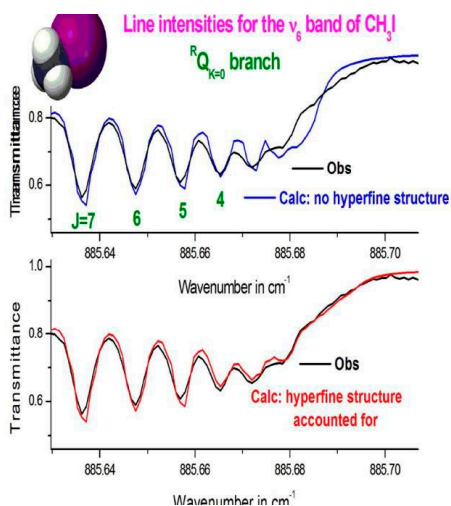
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Line intensities for the ν_6 and $2\nu_3$ bands of Methyl Iodide ($^{12}\text{CH}_3\text{I}$)

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The goal of this study is to measure for the first time absolute line intensities for the ν_6 band of methyl iodide (CH_3I) centered at 892.918 cm^{-1} . High-resolution Fourier transform spectra were recorded for the whole $500\text{--}1450\text{ cm}^{-1}$ spectral range at various pathlength-pressure products. Using these spectra, a large set of CH_3I individual line intensities was measured for the ν_6 band and least squares fit to derive the expansion of the ν_6 transition moment operator. For both line positions and intensities, the theoretical model accounts for the hyperfine structure in the 6^1 and ground states and for the vibration-rotation resonances that couple the 6^1 energy levels with those of the 3^2 and 2^1 vibrational states [A. Perrin *et al.*, *J. Mol. Spectrosc.* 324 (2016) 28 – 35]. As the $2\nu_3$ band is extremely weak, its associated transition moment operator was estimated from band strength collected in the literature. A comprehensive list of line positions and intensities was generated at $10\text{ }\mu\text{m}$ for the ν_6 and $2\nu_3$ bands of CH_3I .



Automatic assignment and fitting of spectra with PGOPHER

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This poster describes the latest version of the pgopher program [1] (<http://pgopher.chm.bris.ac.uk>), which includes two new tools for computer assisted assignment of spectra. The first tool tries many different assignments, and a preliminary version of this has already been presented [2]. The second tool, a nearest lines plot, provides a clear indication as to whether a trial calculation is plausible, and gives good results even for dense spectra with no obvious structure and in the presence of interfering absorptions and/or perturbations. The effectiveness of these tools is demonstrated by the analysis of high resolution IR spectra of several bands of *cis*- and *trans*-1,2-dichloroethene, including hot bands and isotopologues in many cases. For these spectra, the tools working together allow up to 10,000 lines to be rapidly assigned for each band.

C7.5.

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