15th ASA Conference

(united with 16th HITRAN Conference)

University of Reims Champagne-Ardenne

Hôtel de la Paix, Reims - FRANCE

Wednesday, 24 August – Friday, 26 August 2022

Local Organizing Committee :

Maud Rotger *(Chair)*

Alexander Alijah
Marie-Renée De Backer
Alain Barbe
Sophie Chenal
Ludovic Daumont
Bruno Grouiez
Barbara Poty
Laurence Régalia
Michael Rey
Vladimir Tyuterev
Dominika Viglaska
Virginie Zéninari

International Advisory Committee :

Iouli E. Gordon *(Chair)*

Peter F. Bernath
Manfred Birk
Vincent Boudon
Alain Campargue
Kelly Chance
Athéna Coustenis
Brian J. Drouin
Jean-Marie Flaud
Robert R. Gamache
Joseph T. Hodges
Christian Hill
David Jacquemart
Eli Mlawer
Andrei Nikitin
Valery I. Perevalov
Maud Rotger
Laurence S. Rothman
Keith Shine
Jonathan Tennyson
Geoffrey Toon
Ha Tran
Vladimir G. Tyuterev

Wednesday August 24, 2022 Program

8:30-9:00	Welcome	
	Chair : J. Buldyreva	
9:00-9:20	V. Tyuterev	p 7
9:20-9:40	A. Campargue	p 8
9:40-10:00	M. Birk	p 9
10:00-10:20	Z. Reed	p 10
10:20-10:40	J. Hayden	p 11
10:40-11:00	Coffee break	
11:00-11:40	**M.A. Martin** (*invited speaker*)	p 12
11:40-12:00	L. Manceron	p 13
12:00-12:20	O.Ben Fathallah	p 14
12:20-12:40	S. Kassi	p 15
12:40-14:00	Lunch	
	Chair : M. Rey	
14:00-14:40	**S. Yurchenko** (*invited speaker*)	p 16
14:40-15:20	**G. Mellau** (*invited speaker*)	p 17
15:20-15:40	T. Delahaye	p 18
15:40-16:00	I. Gordon	p 19
16:00-16:20	R. Hargreaves	p 20
16:20-16:40	*Exhibitor – J. Schmitt (Bruker)*	
16:40-17:00	Coffee break	
17:00-18:30	Poster session 1	p 23-44

Recent studies in ozone spectroscopy and dynamics

V. Tyuterev[1,2], A. Barbe[1], S. Mikhailenko[3], E. Starikova[2,3], O. Egorov[2,3], V. Kokoouline[4], A. Alijah[1], M. Mirahmadi[5], J. Pérez-Ríos[5,6]

[1] *Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France*
[2] *Laboratory of Quantum Mechanics and Radiative Transfer, Tomsk State University, Tomsk, Russia*
[3] *Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS 1, Akademician Zuev Sq., Tomsk, 634055 Russia*
[4] *Department of Physics, University of Central Florida, Florida, USA*
[5] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*
[6] *Department of Physics, Stony Brook University, Stony Brook, New York 11794, USA*

A brief overview of recent studies in ozone spectroscopy and dynamics will be reported.
The first part concerns an improvement of intensities [1] and positions [2] for the line parameters in the infrared range updated in recent versions of S&MPO and HITRAN databases as well as work in progress. This includes validations of *ab initio* predictions using accurate FTS [2,3,4] and atmospheric [5] measurements. New results concerns measurements and analyses of various isotopic species of ozone in the MW-THz range using SOLEIL synchrotron experimental setup [6] and FTS measurement in Reims [7].

The second part concerns the study of the vibrational dynamics of ^{18}O-enriched isotopologues near the dissociation threshold including the delocalization of vibrational states among three potential wells [8,9], calculation of life times of metastable vibrational states and of isotopic dependent dissociation channels for scattering resonances [10]. The results of the further work [11] on the formation of the ozone molecules in ternary collisions $O+O_2+M$ of the atomic and diatomic oxygen with the third body M will be also discussed. The developed theoretical approach is applied to the reaction $O+O_2+Ar$ because of extensive experimental data available. Thermally-averaged coefficients for the ozone formation rate were derived for temperatures 5-900 K. The theoretical approach combines original *ab initio* potential energy surface (PES) of the ArO_3 system, and the classical-trajectory method in hyperspherical coordinates that permitted to obtain a good agreement [11] with the experimental data for temperatures 100-900K accounting for the process of vibrational quenching of the nascent population.

GSMA Reims laboratory acknowledges support from SAMYA collaborative French-Russian program, and Tomsk groups acknowledges support from NSF grant N° 19–12–00171-П.

References

[1] Tyuterev, V., Barbe, A., Mikhailenko, S., Starikova, E., Babikov, Y. JQSRT **272**, 107801 (2021)
DOI: 10.1016/j.jqsrt.2021.107801
[2] Barbe, A., Mikhailenko, S., Starikova, E., Tyuterev, V. JQSRT **276,** 107936 (2021)
DOI: 10.1016/j.jqsrt.2021.107936
[3] Janssen, C.; Boursier, C.; Elandaloussi, et al. JQSRT **279**, 108051(*2022*)
DOI : 10.1016/j.jqsrt.2021.108051
[4] Birk, M., Wagner, G., Barbe A. , et al ESA SEOM- IAS –Measurement and line parameter database O 3 MIR region. Zenodo 2021. DOI: 10.5281/zenodo.1492542
[5] Toon, G. Ozone Spectroscopy Evaluation Update, JPL NASA, Caltech, 2021-07-14.
https://mark4sun.jpl.nasa.gov/report/O3_Spectroscopy_ Eval_2021_07_14.pdf
[6] Manceron, L., Barbe, A., Tyuterev, V., Grouiez, B., Burgalat, J., Rotger, M., Roy, P., ASA-HITRAN , Reims (2022)
[7] Barbe, A., Mikhailenko, S., Starikova, E., Tyuterev, V., Molecules**, 27** (**3**), 911 , (2022)
DOI: 10.3390/molecules27030911
[8] Kokoouline, V., Lapierre, D., Alijah, A., Tyuterev, V. Physical Chemistry Chemical Physics, **22 (28),**15885 (2020)
DOI: 10.1039/d0cp02177f
[9] Vasilchenko, S., Barbe, A., Starikova, E., Kassi, S., Mondelain, D., Campargue, A., Tyuterev, V., Physical Review A, **102 (5),** 052804 (2020)
DOI: 10.1103/PhysRevA.102.052804
[10] Kokoouline, V., Alijah, A., Tyuterev, to be published (2022)
[11] Mirahmadi, N., Pérez-Ríos, J., Egorov, O., Tyuterev, V., Kokoouline, V., Phys .Rev. Letters **128**, 108501 (2022).
DOI: 10.1103/PhysRevLett.128.108501

Water absorption spectroscopy:
Continua measurements and Validation tests of spectroscopic databases

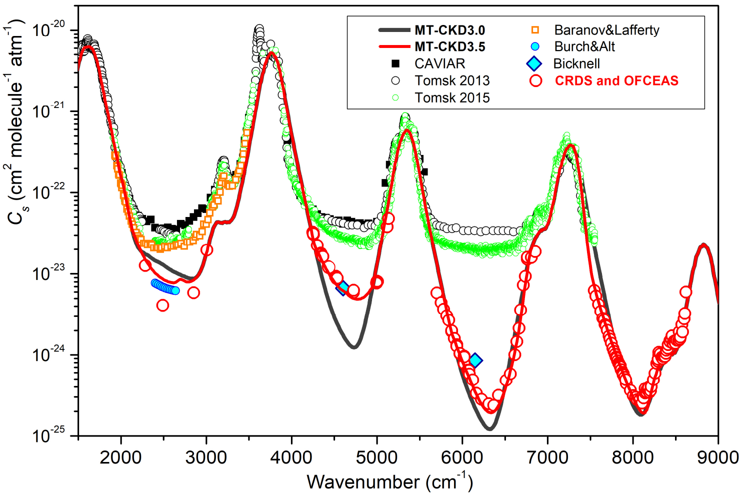
A. Campargue[1,*], S. Kassi[1], D. Mondelain[1], S. Vasilchenko[1,2], H. Fleurbaey[1], M. Toureille[1], A.O. Koroleva[1], and S. Mikhailenko[2]

1. LIPhy Université de Grenoble Alpes, UMR5588 CNRS, F-38041, France
2. V.E. Zuev Institute of Atmospheric Optics SB RAS, 1, Academician Zuev square, Tomsk 634021, Russia

** alain.campargue@univ-grenoble-alpes.fr*

In the three last years, different aspects of the water spectroscopy have been investigated in our group, mostly by cavity-enhanced absorption spectroscopy (in particular CRDS). The main results obtained will be summarized and include:

- Extensive high sensitivity recordings providing new observations and validation tests of spectroscopic databases by CRDS in the near infrared up to 750 nm [1,2] and FTS in the far infrared (50-750 cm^{-1}),
- The first detection of electric-quadrupole transitions [3],
- Self- and foreign-continuum absorption measurements in the near infrared atmospheric windows which were used as constraints of the MT_CKD model [4, 5] – see Figure.



References

[1] A. Campargue *et al*, JQSRT **276**, 107914 (2021)
[2] S. Vasilchenko, Mol Phys DOI: 10.1080/00268976.2022.2051762
[3] A. Campargue *et al*, Phys. Rev. Res. 023091 (2020)
[4] H. Fleurbaey *et al*, JQSRT **278**, 108004 (2022)
[5] A.O. Koroleva *et al*, JQSRT **286**, 108206 (2022)

Fourier-transform intensity measurements with 0.1% accuracy

Manfred Birk*, Georg Wagner, Christian Röske

German Aerospace Center (DLR), Institute for Remote Sensing Technology, Münchner Str. 20, D-82234 Wessling, Germany

* *Manfred.Birk@dlr.de*

Remote sensing of atmospheric trace gases with climate relevance requires spectroscopic data with better than 0.1% absolute intensity accuracy. This requirement poses a big challenge, especially to Fourier-transform spectroscopy (FTS).

The alternative CRDS method has the advantage of a higher sensitivity compared to FTS. CRDS is also independent from cavity length and there is no instrumental line shape. In contrast, the FTS technique has the major advantages of a broadband coverage and the entire spectral range is measured simultaneously. Both techniques are thus complementary.

The demanding metrological requirements for multireflection cell absorption path determination as well as for pressure and temperature measurement to achieve 0.1% absolute intensity accuracies will be addressed. Furthermore, the instrumental line shape characterization, the treatment of offset errors, and multipassing will be discussed. For this high accuracy application, a sophisticated multispectrum fitting software is essential. Finally, highly accurate results require several measurements under different conditions to validate the overall uncertainties. As examples CO 3-0 and CO2 1.6 µm intensity measurements will be presented.

Comb-locked Cavity Ring-down Spectroscopy for Precise Measurements of Molecular Spectra

---

Z.D Reed[1], B. Drouin[2], D.A Long[1], H, Fleurbaey[3], J.T. Hodges[1]

1. Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899 U.S.A.

2. Jet Propulsion Laboratory, NASA, California Institute of Technology, 4800 Oak Grove Drive, Pasadena CA 91109, USA

3. CNRS, LIPhy, Université Grenoble Alpes, Bat. E, 140 rue de la Physique, Grenoble, Saint-Martin d'Hères 38000, France

Precision spectroscopy is an indispensable tool for satisfying the stringent data demands of atmospheric remote sensing and for tests of theoretical models. Here we present work towards this end, involving measurements of molecular transition frequencies and line intensities of carbon dioxide which employ a Cs-clock-referenced comb-locked cavity ring-down spectrometer recently developed at the National Institute of Standards and Technology [1].

Molecular transition frequencies with relative standard uncertainties of $\sim 5\times10^{-12}$ [2] were measured for 44 transitions in the (30012) ← (00001) and (30013) ← (00001) bands of $^{12}C^{16}O_2$. Spectroscopic constants were derived from these data and a perturbing Fermi interaction of the (33301) and (30012) states was identified. We demonstrate excellent agreement with HITRAN 2020 in the (30013) ← (00001) band (average $\Delta \sim -9$ kHz; $\sigma \sim 19$ kHz), however, systematic differences as large as 300 kHz occur in the (30012) ← (00001) band.

We have also applied this technique to the determination of molecular line intensities and line shapes of carbon monoxide, demonstrating sub-permille agreement with multiple alternative experimental techniques and theoretical calculations [3]. This effort required the application of highly linear reference-grade digitizers [4] and NIST-calibrated pressure, temperature and gas mixture standards. The excellent measurement precision also us to do stringent tests of advanced lineshape models needed to extract accurate intensity values from experimental spectra.

References

[1] Z.D. Reed, D.A. Long, H. Fleurbaey, J.T. Hodges Optica, 7 (2020), pp. 1209-1220

[2] Z.D. Reed, B.J. Drouin, DA Long, J.T. Hodges J Quant Spectrosc Radiat Transf, 271 (2021), 107681

[3] K. Bielska, A.A. Kyuberis, Z.D. Reed, Gang Li, A. Cygan, R. Ciurylo, E.M. Adkins, L.Lodi, N.F. Zobov, V. Ebert, D. Lisak, J.T. Hodges, J. Tennyson, and O.L. Polyansky Phys. Rev. Letters (accepted)

[4] A. J. Fleisher, E. M. Adkins, Z. D. Reed, H. Yi, D. A. Long, H. M. Fleurbaey, and J. T. Hodges, Phys. Rev. Lett. 123, 043001 (2019).

A table-top dual-comb spectrometer in the 5 – 10 µm range for line-parameter studies with 10^{-4} cm^{-1} accuracy

Jakob Hayden[1,*], **Olivier Browet**[2], **Jean Clément**[2], **Bastien Vispoel**[2], **Pitt Allmendinger**[1], **Markus Mangold**[1] **and Muriel Lepère**[2]

1. IRsweep AG, Laubisrütistrasse 44, 8712 Stäfa, Switzerland
2. Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur, 61, Rue de Bruxelles, Namur, Belgium
** jakob.hayden@irsweep.com*

Spectroscopic line lists and databases increasingly incorporate experimental data obtained by (dual-) frequency comb spectroscopy due to the excellent spectral resolution and accuracy as well as the broad-band nature of the technique. So far, the vast majority of these measurements cover the near-infrared spectral region as well as the mid-infrared region at wavelengths below 5 µm due to the availability of laser sources and instruments in these regions.

We developed a table-top dual-comb spectrometer based on quantum cascade lasers (QCL) that covers the important spectral range from 5 µm to 10 µm. By step-wise tuning of the center frequency of the combs, we increase the spectral sampling beyond the repetition frequency of the lasers, yielding spectra covering > 50 cm^{-1} with a spectral sampling down to 2×10^{-4} cm^{-1}. By measuring the changes in optical frequency directly from the heterodyne spectrum for every step, we obtain an accurate frequency axis.

The spectrometer was thoroughly characterized in measurements of the ν_1 band of N_2O and ν_4 band of CH_4 between 1283 cm^{-1} and 1333 cm^{-1} [1]. A comparison of the found N_2O line-positions with the HITRAN 2020 database [2] revealed a wavenumber accuracy of $< 4 \times 10^{-4}$ cm^{-1}. Doppler-limited measurements of CH_4 showed no systematic broadening of the Gaussian line-shapes, indicating an instrument response function well below 1 MHz (3×10^{-5} cm^{-1}). In conjunction with the good signal-to-noise ratio, the IRis-F1 spectrometer in step-sweep mode is ideally suited for measurements of new and improved line-parameters in the 5 – 10 µm range.

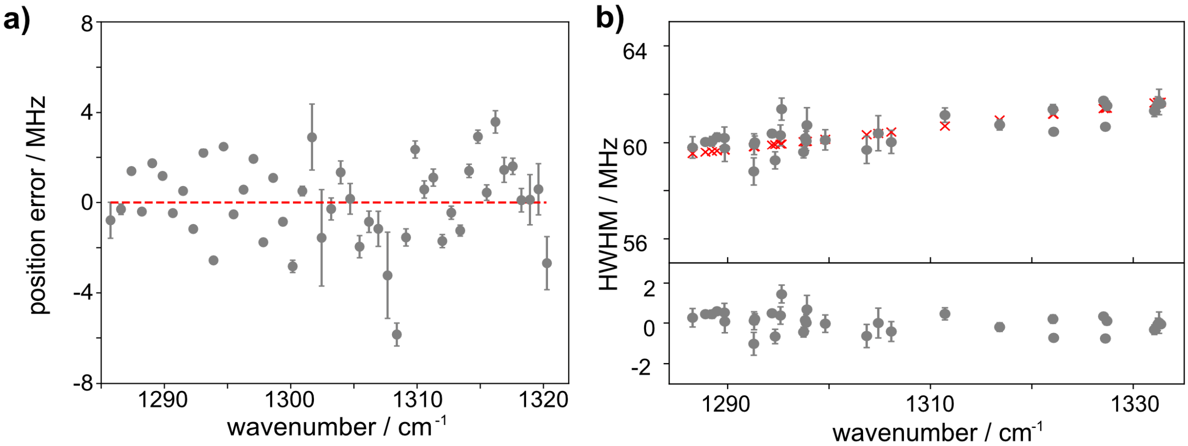


Figure 1. a) Deviation between HITRAN – listed and measured line positions of N_2O. b) Measured half-width at half-maximum (grey dots) of CH_4 lines at 0.182 mbar and their theoretical values (red crosses). Bottom panel: residuals.

References

[1] M. Lepère, M. Mangold *et al*, JQSRT **287**, 108239 (2022)

[2] I.E. Gordon, L.S. Rothman, R.J. Hargreaves et al., JQSRT **277**, 107949 (2022)

An exotic use of the HITRAN database: Predicting laser lines for optically pumped terahertz molecular laser

Marie-Hélène Mammez[1], Marie-Aline Martin-Drumel[2,*], Thomas S. Hearne[2], Dominique Mammez[1], Olivier Pirali[2], Guillaume Ducournau[3], Sophie Eliet[3], Francis Hindle[1], Stefano Barbieri[3], Pascale Roy[4], Gaël Mouret[1], and Jean-François Lampin[3]

1. LPCA, Université du Littoral Côte d'Opale, Dunkerque, F-59140, France
2. Université Paris-Saclay, CNRS, ISMO, Orsay, F-91405, France
3. IEMN, CNRS, Villeneuve d'Ascq, F-59652, France
4. SOLEIL Synchrotron, Saint-Aubin, F-91190, France
** marie-aline.martin@cnrs.fr*

Quantum cascade laser-pumped terahertz (THz) gas lasers are at the edge of revolutionizing THz science where powerful yet tunable sources have long been lacking. Maybe one of the last remaining drawbacks to a wider use of these instruments lies in the lack of available databases of potentially lasing transitions for users. We recently have proposed a new figure of merit, the molecular gain factor, which allows to discriminate transitions by their lasing potential [1]. This figure of merit relies on crucial spectroscopic parameters for the pump and laser lines that can fortunately be accessed in the HITRAN database. Demonstration of the use of this gain factor is made by experimentally observing laser lines of $^{14}NH_3$ and 5 lines of $^{15}NH_3$ up to 5.5 THz.

These THz laser lines can now be used as local oscillators for heterodyne spectroscopy with a broadband THz source, hence allowing both broadband and high resolution investigations of molecular spectra in the THz range. We are currently developing such a spectrometer exploiting both an optically-pumped ammonia laser and the bright THz synchrotron radiation extracted by the AILES beamline of the SOLEIL synchrotron [2]. Ultimately, this spectrometer will enable to cover the 1–4 THz region in 5 GHz windows at Doppler resolution.

In this talk I will present our recent advancements in the development and exploitation of both the THz molecular laser and the broadband THz heterodyne spectrometer, with particular emphasis on how we exploit the HITRAN database.

References

[1] M.-H. Mammez *et al*, Advanced Photonics Research 2100263 (2022)
[2] T. S. Hearne *et al.,* Optics Express **30**, 7372 (2022)

Far infrared spectroscopy of the ozone molecule and its isotopomers between 50 and 800 cm^{-1}

Laurent Manceron*[1,2] Alain Barbe[3], Vladimir Tyuterev[3,4], Bruno Grouiez[3], Jérémie Burgalat[3], Maud Rotger[3], and Pascale Roy[2]

1. Synchrotron SOLEIL, Beamline AILES, L'Orme des Merisiers, Saint-Aubin, France
2. MONARIS CNRS - Sorbonne Université, UMR 8233, 4 place Jussieu, Paris, F-75005 France
3. Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France
4. QUAMER laboratory, Tomsk State University, Tomsk, 634000, Russia

* *laurent.manceron@synchrotron-soleil.fr*

Far infrared spectra of ozone, with natural and ^{17}O- or ^{18}O-enriched ozone isotopologues, was recorded in the 50-850 cm^{-1} spectral range at 0.001 cm^{-1} resolution on the AILES Beamline at Synchrotron SOLEIL. This study extends previous works [1-3] devoted to the analysis of the 50–150 cm^{-1} region to higher energy range (up to 200 cm^{-1}) and permits observing a much larger number of transitions. We present the experimental set-up and a first, preliminary analysis extended to K_a values up to 29 and comparisons between observed and synthetic spectra which illustrate the quality of the analyses. We also present comparisons of the experimental and calculated values for some of the eighteen isotopic species.

References

[1] M.Carlotti *et al.*, J. Mol. Spectrosc. **107**, 84 (1984)
[2] J.M.Colmont et al. , J. Mol. Spectrosc. 233, 293–6 (2005)
[3] M.Birk *et al*, JQSRT **226**, 60-65 (2019)

Measurements of Line Intensities and self-broadening coefficients in the ν_2, ν_5 and ν_3+ν_6 Bands of Methyl Iodide

Ons Ben Fathallah[1,2*], **Fadoua Hmida**[1,2], **Arwa boughdiri**[1,2], **Laurent Manceron**[3], **Maud Rotger**[1] **and Hassen Aroui**[2]

1. *Université de Reims Champagne Ardenne, CNRS, GSMA UMR 7331, 51100 Reims, France*
2. *Université de Tunis, Laboratoire de Spectroscopie et Dynamique Moléculaire, Ecole Nationale Supérieure d'Ingénieurs de Tunis, 5 Av Taha Hussein 1008 Tunis, Tunisia*
3. *Synchrotron Soleil Ligne AILES, BP 48, 91192 Cedex Gif-sur-Yvette, France and MONARIS, UMR 8233 CNRS-UPMC, case 49, 4 place Jussieu, 75252 Cedex Paris, France*

* *ons.ben-fathallah@univ-reims.fr*

Halogenated hydrocarbons have been recognized as important species in atmospheric studies. Among these halocarbons, methyl iodide (CH_3I) is the most abundant iodine-containing compound, emitted primarily by the oceans [1]. It is likely to play an important role in the budget of tropospheric ozone, through production of iodine by photolysis.

All these reasons give a great interest to measure spectroscopic parameters of this molecule.

In this work, we present measurements of absolute intensities and self-broadening coefficients of ro-vibrational lines in the ν_2, ν_5 and ν_3+ν_6 bands of CH_3I.

The spectra were recorded with a high-resolution Fourier transform spectrometer at T = 297.6 K in the spectral region from 1280 to 1600 cm^{-1}.

To retrieve line parameters, a multi-pressure fitting technique using a Voigt profile was used to fit a series of five spectra at pressures ranging from 1. 15 to 9.98 mbar of about 1326, 900 and 225 transitions for the ν_2, ν_5 and ν_3+ν_6 bands respectively, with $2 \leq J \leq 70$ and $0 \leq K \leq 13$.

The rotational dependencies of line intensities were analyzed and used to derive the squared transition dipole moments for each line. The analysis of these moments using the theoretical model of Watson [2], allows us to derive a consistent set of line intensity parameters such as vibrational transition moments, band intensities as well as Herman-Wallis coefficients for each band. The results were compared with previous works.

The average accuracies have been estimated to be about 5 % for the three studied bands of the CH_3I line intensities. The rotational dependencies of self-broadening coefficients have been clearly observed and modeled using the Starikov empirical model [3]. The average accuracies have been estimated to be about 5 % for the ν_2 band and 7 % for the other two bands.

References

[1] Y. Yokouchi *et al*, Geophys. Res. Lett. **39**, L23805 (2012)
[2] J.K.G. Watson, J. Mol. Spectrosc. **153,** 211-24 (1992).
[3] V.I. Starikov *et al*, Optics and Spectroscopy **98,** 330-5 (2005)

The (2-0) R(0) and R(1) transition frequencies of HD at the $\Delta\nu/\nu=10^{-10}$ level of accuracy from Doppler spectroscopy at 80 K

S. Kassi[1*], C. Lauzin[1,2], J. Chaillot[1], A. Campargue[1]

1. Université Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France
2. Institute of Condensed Matter and Nanosciences (IMCN), Université catholique de Louvain, Louvain-la-Neuve,Belgium
** samir.kassi@univ-grenoble-alpes.fr*

The Doppler broadened R(0) and R(1) lines of the (2-0) vibrational band of HD have been measured at liquid nitrogen temperature and at pressures of about 2 Pa, with a comb referenced continuous-wave cavity ring-down spectrometer set-up coupled to a very stable laser source[1]. Transition frequencies of the R(0) and R(1) lines were derived from 33 and 83 recordings, with corresponding root mean squared deviation of 53 and 33 kHz, respectively. This is the first sub-MHz frequency determination of the R(0) transition frequency and represents a three order of magnitude accuracy improvement compared to literature[2]. The R(1) transition frequency is in very good agreement with previous determinations in saturation regime reported with similar accuracy [3,4,5]. To achieve such accuracy the transition frequency of a (101)-(000) 211-312 line of $H_2{}^{16}O$ interfering with the R(0) line had to be precisely determined and is reported with a standard error of 102 Hz at 214904329820.7(1) kHz. These measurement sets provide stringent reference values for validating future advances in the theoretical description of the hydrogen (and water) molecule.

References

[1] M. Casado *et al*, App. Phys. B 128 (2022)
[2] S. Kassi and A. Campargue, J.Mol.Spectrosc 267 (2011) 36
[3] F.M. Cozijn *et al*, Phys. Rev. Lett. 120 (2018) 153002
[4] L.-G. Tao *et al*, Phys. Rev. Lett. 120 (2018) 153001
[5] A. Castrillo *et al*, Phys. Rev. A 103 (2021) 022828

ExoMol 2022: Molecular data for studies of exoplanets and other hot atmospheres

Sergey N Yurchenko

Department of Physics and Astronomy, University College London, London, United Kingdom

The discoveries of exoplanets have sparked significant activity on characterizing these planets through their spectra. Broadly speaking there are three methods of observing the spectrum of an exoplanet: directly imaging the planet, transit spectroscopy which involves observing light from the host star as a planet passes in front (and behind) it, and high resolution Doppler shift spectroscopy. These techniques all have different requirements in terms of laboratory data needed to interpret observations: line positions, intensities and shapes, collision induced absorption, temperature and pressure dependent cross sections, molecular continuum data etc. We run the ExoMol project [1] which aims to provide molecular line lists, and increasingly other data, for studies of exoplanets and other astronomical atmospheres.

The unusual conditions found on most known exoplanets, involving elevated temperatures and high fluxes of stellar radiation, means the required data are missing and not readily measurable in the laboratory. Due to the limited resolution of the typical exoplanetary spectra and high temperatures of atmospheres observed, the data completeness plays a special role in the atmospheric retrievals. The recent development of the ground-based high-resolution Doppler spectroscopy techniques extended these demands to the high quality of the data [2]. In this talk I will review the data needs of the exoplanetary atmospheric spectroscopy, data availability and usage by typical atmospheric retrieval packages. The modern strategies to meet the competing demands of completeness and accuracy in these data will be reviewed.

Our group ExoMol is one of the international leaders in providing molecular spectroscopic data (line lists) for studies of exoplanets. ExoMol's techniques are based on the application of rigorous quantum mechanical methods informed by laboratory experiments, rather than on direct measurements. After ten years of the ExoMol project, 700 billion molecular transitions and two formal releases, ExoMol continues responding to the new challenges of the exoplanetary spectroscopy [3]. One of the key ExoMol activities is provision of high accuracy spectroscopic data for high resolution studies of exoplanetary atmospheres. This is done by re-factoring ExoMol line lists using high resolution laboratory measurements. Novel theoretical techniques are being used to provide similar high accuracy line lists for isotopically substituted species and to generate pressure broadening data. Finally, given the extreme conditions experienced by most observable exoplanets, namely high temperatures and huge levels of insolation, photodissociation is a major process chemical process. New methods are being developed to compute these cross sections and rates.

References

[1] J. Tennyson and S.N. Yurchenko, *Mon. Not. R. Astron. Soc.* **425**, 21 (2012)
[2] J. Tennyson and S.N. Yurchenko, *Front. Astron. Space Sci.* **8**, 218 (2022)
[3] J. Tennyson and S.N. Yurchenko, *Astronomy & Geophysics* **62**, 16 (2021)

Experimentally-accurate complete molecular line lists

Georg Ch. Mellau
Justus-Liebig-Universität Gießen, Physikalisch-Chemisches Institut, Heinrich-Buff-Ring 17, 35392 Gießen, Germany
georg@mellau.de

Molecular gas analytics is a major scientific tool for studying the atmosphere of the earth, the sun, and its planets, and is the most important extrasolar analytical method of the observable universe. It works on the principle of “measure data and compare it to a theoretical prediction”. Exact pure quantum calculations for polyatomic molecules are only possible by algebraic methods or by using quantum computers. Since such methods have not yet been invented or are possible, the high-resolution spectroscopy community must provide the basis for molecular gas analytics through spectroscopic databases. These data sets are the result of a complex merging of a large number of experimental data sets and quantum chemical calculations and cover mainly those transitions for which experimental line positions are available.

The “power” of the exponent in the Boltzmann distribution severely limits the number of transitions accessible in room temperature absorption measurements. One experimental method for measuring highly excited states is the Hot Gas Molecular Emission (HOTGAME) spectroscopy [1-2], a combination of a high sensitivity tube furnace FT-IR emission experiment and the SyMath data analysis algorithm [2]. The highly excited states can be extracted from the very dense (with hundreds of thousands of lines) emission spectra only by perfect deconvolution of the highly overlapping lines. SyMath analysis directly links the set of spectroscopic parameters of all bands to the (x,y) spectrum data points. The method has a “dynamic peaklist”, after each assigned band the extracted line positions/intensities of all lines and the spectroscopic constants of all bands are improved step by step.

HOTGAME spectroscopy allowed me to introduce the concept of the “complete eigenenergy list” [3-6], which experimentally covers the complete set of eigenenergies of a polyatomic molecular system up to a high eigenenergy limit. For the triatomic molecular system [H,C,N] it was possible to obtain a complete list of experimental eigenenergies and thus to “solve” the quantum many-body “Schrödinger equation” exactly. The main objective of this research was the study of the spectroscopic pattern of isomerization (how the eigenstate structure is connected to the transition state of the molecule) [6-7], but on the other hand, the complete eigenenergy list is an important result regarding spectroscopic databases. The transition wavenumbers generated with the eigenenergy list of this work (combined with accurate *ab inito* line intensity data) correspond to the first complete spectroscopic database and fixed for the first time “forever” the partition sum at room temperature for a polyatomic molecule.

Thanks to advances in quantum chemistry, we can now calculate the eigenenergy structure of small polyatomic molecules and the transition intensities between energy eigenstates. These calculations provide line positions much worse that the 10-digit accuracy of the measurements, but can reach the 3-4-digit accuracy of the experimental line intensities [8]. Combining *ab initio* lists with experimental data is straightforward at low excitation energies or when the *ab initio* calculations provide vibrational quantum labels. If this is not the case, automatic algorithmic mapping is very difficult at high excitation energies due to the high density of states. For complete eigenenergy list, I am developing the MAP program system [8] which merges a set of incrementally improved theoretical eigenenergy lists with the complete experimental data set. Within the MAP project an “effective Hamiltonian free” high-resolution spectrum analysis system is being developed; the assignment is based solely on *ab initio* eigenstate calculations.

In my talk, I will give an overview of these three major research topics regarding complete eigenenergy lists and the present some recent results.

References

[1] G. Ch. Mellau, *et al*, 15th Colloquium on HRMS, Glasgow (1997)
[2] G. Ch. Mellau, *et al*, J. Mol. Spectrosc. **249**, 23 (2008)
[3] G. Ch. Mellau, PICS Workshop on Local Mode Vibrations, St. Flour, France (1999)
[4] G. Ch. Mellau, J. Chem. Phys. **134**, 164303 (2010);
[5-6] G. Ch. Mellau, J. Chem. Phys. **134**, 234303, 194302 (2011);
[7] G. Ch. Mellau, *et al*, Sci. Rep. **6**, 33068 (2016)
[8] G. Ch. Mellau, *et al*, JQSRT **270**, 107666 (2021)

Evaluation and validation of spectroscopic databases: the GEISA2020 update and the preparation of GEISA2022

Thibault Delahaye[1,*], **Raymond Armante**[1], **Alain Chédin**[1], **Noëlle Scott**[1]

1. Laboratoire de Météorologie Dynamique/IPSL, CNRS, Ecole Polytechnique, Université Paris-Saclay, 91128, Palaiseau, France
** thibault.delahaye@lmd.polytechnique.fr*

The process of updating spectroscopic databases to provide users with a database that ensures optimal characterization of molecular absorption spectral properties is a complex task. Based on a solid experience of calibration/validation activities within the laboratory, and to help make the most relevant choices when developing the database, the SPARTE [1] (Spectroscopic Parameters And Radiative Transfer Evaluation) chain has been developed at the LMD, and applied for the first time for the GEISA2015 update [2]. SPARTE is based on the comparison between direct radiative transfer simulations performed by the 4AOP algorithm, using a given spectroscopic database as input, and various remote sensing observations for thousands of well-characterized atmospheric situations. Typically, clear-sky observations from two well-established instruments are used to cover a wide spectral range: data from the IASI instrument (15 to 3.7 µm) and from the ground-based Fourier Transform Fourier transform spectrometers of the TCCON network (2.5 to 0.7 µm). For the GEISA2020 update [3], the SPARTE chain has been used systematically when possible (especially for molecular species whose contribution to the atmospheric spectra is not negligible).

In this presentation, in addition to the validation chain, we'll present some examples of evaluation for the 2020 update of O_3 at 10 µm, H_2O between 1.7 and 1.2 µm and O_2 in the band at 1.27 µm. We'll also present our plan for the next update GEISA2022 and preliminary works on it.

References

[1] R. Armante et al., "Evaluation of spectroscopic databases through radiative transfer simulations compared to observations. Application to the validation of GEISA 2015 with IASI and TCCON," J. Mol. Spectrosc., vol. 327, pp. 80–192, Sep. 2016, doi: 10.1016/j.jms.2016.04.004

[2] N. Jacquinet-Husson et al., "The 2015 edition of the GEISA spectroscopic database," J. Mol. Spectrosc., vol. 327, 2016, doi: 10.1016/j.jms.2016.06.007

[3] T. Delahaye et al., "The 2020 edition of the GEISA spectroscopic database", J. Mol. Spectrosc., vol. 380, 2021, doi: 10.1016/j.jms.2021.111510

Collaborative (COVID-perturbed) transition from HITRAN2020 to HITRAN2024

Iouli E. Gordon[1,*], Frances M. Skinner[1], Robert J. Hargreaves[1], Laurence S. Rothman[1], HITRAN Community World-Wide

1. Center for Astrophysics | Harvard & Smithsonian, Atomic and Molecular Physics Division, 60 Garden Street, Cambridge, MA 02138 USA
** igordon@cfa.harvard.edu*

The HITRAN2020 edition [1] features significant expansion and improvements with respect to HITRAN2016 [2]. This talk will briefly summarize this current edition, which has already been actively employed in diverse atmospheric and astrophysical studies. Work on the 2024 edition has begun. This effort includes eliminating any errors found in the 2020 edition, validating and implementing new data, improving and extending parametrization of the spectral properties in the database, as well as improving user experience. The most important aspects of these improvements will be addressed, as well as ways the community can help with the development of the future edition.

References

[1] I. E. Gordon, *et al,* JQSRT, **277**, 107949 (2022)
[2] I. E. Gordon, *et al,* JQSRT, **203**, 3-69 (2017)

Updating the HITEMP database

Robert J. Hargreaves[1,*], **Iouli E. Gordon**[1], **Xinchuan Huang**[2,3], **Eamon K. Conway**[1,4] **and Laurence S. Rothman**[1]

1. Center for Astrophysics | Harvard & Smithsonian, 60 Garden Street, Cambridge, MA, USA
2. Carl Sagan Center, SETI Institute, Mountain View, CA, USA
3. NASA Ames Research Center, Moffett Field, CA, USA
4. Kostas Research Institute at Northeastern University, 141 South Bedford Street, Burlington, MA, USA
** robert.hargreaves@cfa.harvard.edu*

The HITEMP database [1] (www.hitran.org/hitemp) provides accurate line-by-line molecular spectroscopic parameters for eight molecules: H_2O, CO_2, N_2O, CO, CH_4, NO, NO_2, and OH [1-4]. HITEMP was established to model the radiative transfer of high-temperature environments and therefore contains substantially more transitions for each molecule than the corresponding molecule in HITRAN [5]. In recent years, HITEMP has been undergoing significant updates to improve the quality and extent of spectroscopic data, as well as adding additional molecular line lists. For CH_4 [4], the most recent addition to HITEMP, a line list compression technique was implemented. This enabled the CH_4 line list to be practical to use while remaining capable of accurately modeling high-temperature experimental spectra and astrophysical observations up to 2000 K.

A major aspect of updating the HITRAN and HITEMP databases is comparing candidate line lists and validating against experimental works. A demonstration of these validations for H_2O and CO_2 will be presented, along with a summary of the most recent updates for HITEMP.

References

[1] L.S. Rothman *et al*, JQSRT **111**, 2139 (2010). [doi:10.1016/j.jqsrt.2010.05.001]
[2] R.J. Hargreaves *et al*, JQSRT **232**, 35 (2019) [doi:10.1016/j.jqsrt.2019.04.040]
[3] G. Li *et al*, ApJS **216**, 15 (2015) [doi:10.1088/0067-0049/216/1/15]
[4] R.J. Hargreaves *et al*, ApJS **247**, 55 (2020) [doi:10.3847/1538-4365/ab7a1a]
[5] I.E. Gordon *et al*, JQSRT **277**, 107949 (2022) [doi:10.1016/j.jqsrt.2021.107949]

Key words

HITEMP
Line lists
Databases
High temperature
Spectroscopic parameters

Poster Session 1

P1-1

CO (3-0) band line intensities measured and calculated at permille level of accuracy

---

Katarzyna Bielska[1,*], **Aleksandra A. Kyuberis**[2], **Zachary D. Reed**[3], **Gang Li**[4], **Agata Cygan**[1], **Roman Ciuryło**[1], **Erin M. Adkins**[3], **Lorenzo Lodi**[5], **Nikolay F. Zobov**[5], **Volker Ebert**[4], **Daniel Lisak**[1], **Joseph T. Hodges**[3], **Jonathan Tennyson**[5], **and Oleg L. Polyansky**[5]

1. *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Toruń, Grudziadzka 5, 87-100 Torun, Poland*
2. *Van Swinderen Institute for Particle Physics and Gravity, University of Groningen, Nijenborgh 4, 9747AG Groningen, The Netherlands*
3. *Chemical Sciences Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899 U.S.A.*
4. *PTB (Physikalisch-Technische Bundesanstalt), Bundesallee 100, 38116 Braunschweig, Germany*
5. *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom*

* *kbielska@umk.pl*

Intensities from the second overtone (3-0) band of CO were independently determined with three substantially different experimental techniques by three research groups. The same set of relatively weak high-*J* lines was measured with cavity ring-down spectroscopy (CRDS) [1] at NIST and cavity mode-dispersion spectroscopy (CMDS) [2] at NCU. Stronger low-*J* lines were measured with Fourier-transform spectroscopy (FTS) [3] at PTB. The experimental results are compared to calculations performed at UCL [4] based on an *ab initio* dipole moment curve (DMC) and an empirical potential energy curve (PEC).

Relative differences between line intensities measured with CRDS and CMDS techniques are around 1‰ with similar differences between experimental and theoretical results. For the set of six lines that were considered, the average relative difference between the weighted mean experimental line intensities and the corresponding theoretical values is -0.2‰ with a standard deviation of 0.7‰. Similarly, comparisons of all line intensities measured by FTS with the theoretical values give an average relative difference of 0.7‰ with a standard deviation of 0.9‰, which for the subset of strongest transitions in the 50th percentile is 0.2‰ and 0.4‰, respectively. All experimental results together yield an average relative difference from the calculated line intensities of 0.6‰ with a standard deviation of 0.9‰ [5]. This excellent overall agreement between experiment and theory contrasts with presently available line intensities determined from laboratory measurements, which exhibit more than order-of-magnitude-larger scatter [6].

The unprecedented level consistency between theory and experimental techniques demonstrated here results in line intensity determinations that are unlikely to exhibit systematic biases much greater than 1‰. This robust and multi-faceted approach to assigning line intensities can meet a growing number of demanding applications in remote sensing that require permille uncertainties in retrieved molecular number density.

References

[1] A. J. Fleisher *et al*, Phys. Rev. Lett. **123**, 043001 (2019)
[2] A. Cygan *et al*, Opt. Express **27**, 21810 (2019)
[3] V. Werwein *et al*, Appl. Optics **56**, E99 (2017)
[4] E. Zak *et al.*, J. Quant. Spectrosc. Radiat. Transf. **177**, 31 (2016)
[5] K. Bielska e*t al*, Phys. Rev. Lett. (2022), accepted for publication
[6] V. Meshkov *et al*, J. Quant. Spectrosc. Radiat. Transf. **280**, 108090 (2022)

P1-2

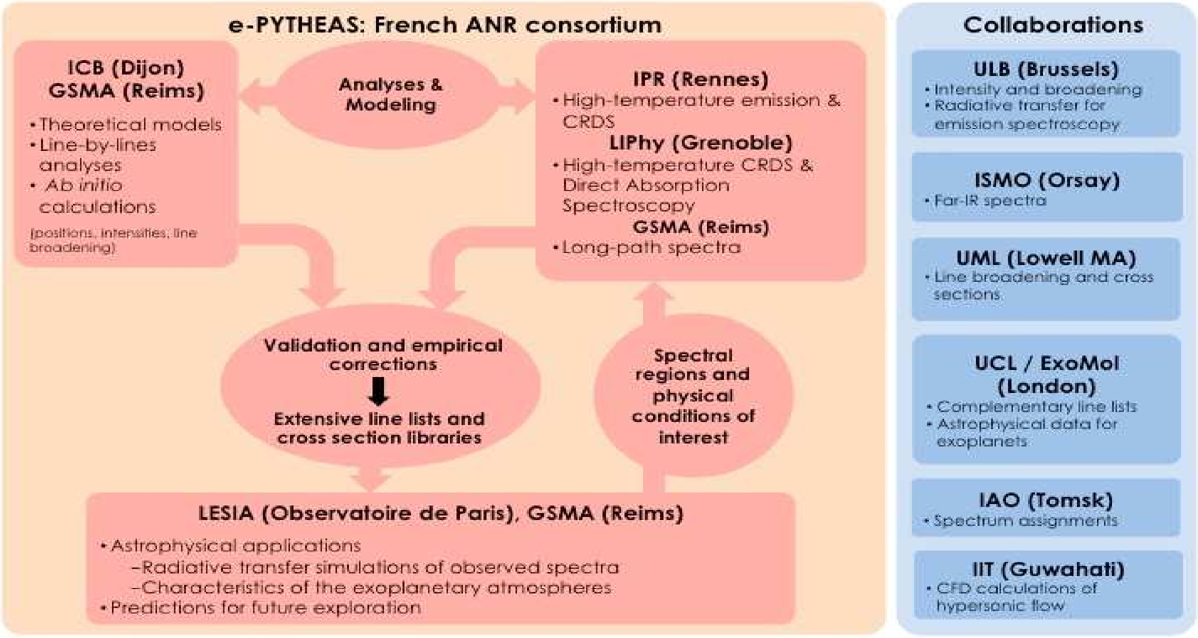
High-temperature spectroscopic data for exoplanetary studies: the e-PYTHEAS project

V. Boudon[1], A. Coustenis[2,*], A. Campargue[3], R. Georges[4], M. Rey[5] and Vl. G. Tyuterev[5] and the e-PYTHEAS Team:

G. Albora[5], B. Amyay[1], A. Benidar[4], B. Bézard[1], D. Biet[4], J. Courbe[4], L. Daumont[5], P. Drossart[2], E. Dudas[4], Th. Encrenaz[1], T. Gabard[1], E. Gallou[4], R. Gamache[8], B. Grouiez[5], S. Kassi[3], D. Lapierre[5], P. Lavvas[5], D. Mondelain[3], A. V. Nikitin[5] , O. Pirali[9], P. Rannou[5], L. Régalia[5], C. Richard[1], M. Rotger[5], J. Tennyson[6], J. Thiévin[4], G. Tinetti[6], J. Vander Auwera[7], S. Vasilchenko[3], B. Vispoel[10]

1. Laboratoire ICB, UMR 6303 CNRS/Univ. Bourgogne Franche-Comté, 9 A. A. Savary, BP 47870, F-21078 Dijon Cedex, France
2. LESIA, Observatoire de Paris, CNRS, UPMC, Univ. Paris Diderot, F-92195 France
3. LIPhy, UMR 5588 Université Grenoble 1/CNRS, F-3804, Grenoble, France
4. IPR, Campus de Beaulieu, UMR 6251 CNRS/Université de Rennes 1, F-35000 Rennes Cedex, France
5. GSMA, UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France
6. Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom
7. Service de Chimie Quantique et Photophysique, C.P. 160/09, Université Libre de Bruxelles, B-1050Brussels, Belgium
8. Univeristy of Masachusetts Lowell, University Avenue, 01854 Lowell MA, USA
9. Ligne AILES – Synchrotron Soleil, L'Orme des MerisFranceF-91192 Gif-sur Yvette, France & ISMO, CNRS/Univ. Paris Sud,France Paris-Saclay, F-91405 Orsay, France
10. Research Unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur (Unamur), 61 rue de Bruxelles, B-5000, Namur, Belgium
** Corresponding author: athena.coustenis@obspm.fr*

The e-PYTHEAS project combines theoretical and experimental work with exoplanet modelling applications. It aims to enhance our understanding of the radiative properties of hot gaseous media to allow for improved analysis and interpretation of the large mass of data available on the thousands of exoplanets and exoplanetary systems known to date. Our approach is to use theoretical research validated by laboratory experiments and to then inject it into models of the atmospheres of the giant gaseous planets in the solar system and other planetary systems. Our consortium of five French laboratories and associated partners proposes to improve the existing high-temperature spectroscopy data for several molecular species detected in exoplanets. The provision of infrared (IR) laboratory data of methane, acetylene, ethylene and ethane, between 500 and 2500 K will help to refine thermal profiles and provide information on the gaseous composition, the hazes and their temporal variability. The results will help analyze data and interpret observations of missions such as ESA's M4 ARIEL in 2029.



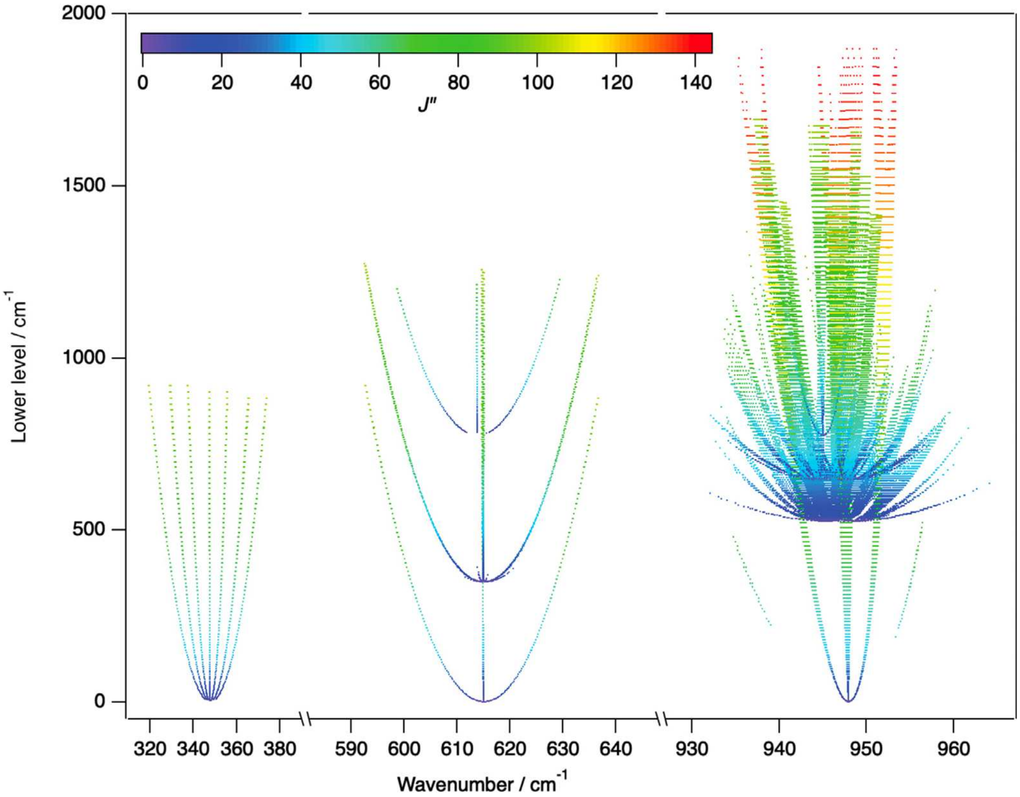
The e-PYTHEAS consortium

Calculated spectroscopic databases for the VAMDC portal: New molecules and improvements

C. Richard[1,*], **V. Boudon**[1] **and M. Rotger**[2]

1. Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS - Université Bourgogne Franche-Comté, 9 avenue Alain Savary, BP 47870, F-21078 Dijon Cedex, France
2. Université de Reims Champagne Ardenne, CNRS, GSMA UMR 7331, 51100 Reims, France
* *Cyril.Richard@u-bourgogne.fr*

We report the current status of our calculated spectroscopic relational databases [1]. They contain line lists for specific molecules, that result from recently published spectroscopic analyses. The two original databases, denoted MeCaSDa (CH_4) and ECaSDa (C_2H_4), have been greatly improved with the addition of new calculated lines. Then, five new databases, TFMeCaSDa (CF_4), SHeCaSDa (SF_6), GeCaSDa (GeH_4), RuCaSDa (RuO_4) and TFSiCasDa (SiF_4) were deployed based upon the same model. These databases are developed in the framework of the international consortium VAMDC (Virtual Atomic and Molecular Data Centre, http://vamdc.org) [2] and are also part of the Dat@OSU project (http://dataosu.obs-besancon.fr).



Representation of the lower level wavenumber for all SF_6 transitions present in the SHeCaSDa database. Colors are used to display the lower state rotational quantum number value, J''.

References

[1] C. Richard, V. Boudon and M. Rotger, JQSRT **251**, 107096 (2020)
[2] D. Albert *et al*, Atoms **8**, 76 (2020)

High-resolution spectroscopy and analysis of combination bands of SiF_4

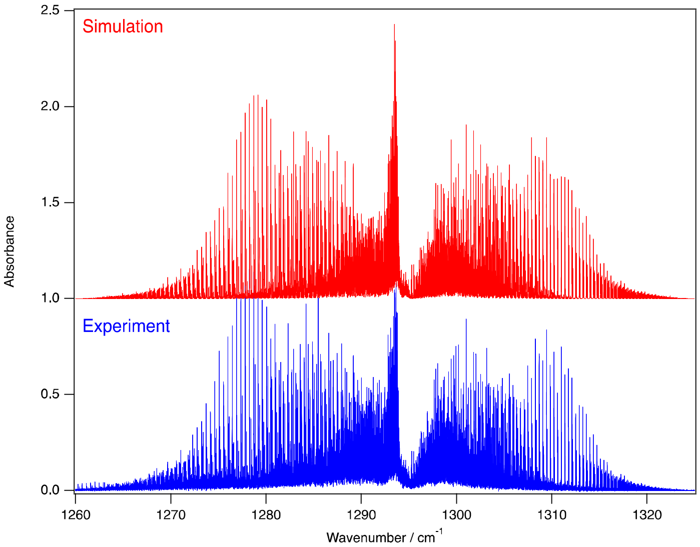
M. Merkulova[1,2*,], V. Boudon[2], L. Manceron[3,4]**

1. Research School of High–Energy Physics, National Research Tomsk Polytechnic University, Tomsk 634050, Russia
2. Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS - Université Bourgogne Franche-Comté, 9 avenue Alain Savary, BP 47870, F-21078 Dijon Cedex, France
3. Synchrotron SOLEIL, AILES Beamline, L'Orme des Merisiers, BP48, F-91192 St-Aubin Cedex, France
4. MONARIS, UMR 8233, Université Pierre et Marie Curie, 4 Place Jussieu, case 49, F-75252 Paris Cedex
** Corresponding author: mari_andrew@mail.ru, ** PhD Thesis supervised by V. Boudon in Dijon, France and O. Ulenikov in Tomsk, Russia*

Silicon tetrafluoride (SiF_4) is a trace component of volcanic gases and is gaining industrial importance. However, a better knowledge of spectroscopic parameters is needed for this molecule in order to derive accurate concentrations. Recently, we have undertaken a systematic study of its different rovibrational bands. We first published the analysis of the ν_3, ν_4 and $2\nu_4$ bands of it different isotopologues [1], followed by the fit of all fundamental levels of $^{28}SiF_4$ that led to an accurate determination of the Si–F equilibrium bond length [2].

In this poster, we present a continuation of this global investigation concerning four combination bands, namely $\nu_1+\nu_3$, $\nu_1+\nu_4$, $\nu_2+\nu_3$ and $\nu_2+\nu_4$. For this we used new spectra recorded on the AILES Beamline of the SOLEIL Synchrotron facility. The data were obtained using a cryogenic long path cell regulated at 163 K temperature along the entire optical path, set up to 93 m.

For each band, between 1000 and more than 2000 lines could be assigned for *J* values higher than 55 (up to 82 for $\nu_1+\nu_3$) and this leads to a determination of accurate molecular parameters with root mean square deviations for line positions of a few 10^{-4} cm^{-1}. In the case of the $\nu_1+\nu_3$ band, the $^{29}SiF_4$ and $^{30}SiF_4$ isotopologues could also be assigned and fitted. These results will allow the calculation of hot bands like $\nu_3+\nu_2-\nu_2$, *etc*., in the regions of strong atmospheric absorption.



Comparison between the experimental and the simulated spectrum for the $\nu_2+\nu_3$ *combination band of* $^{28}SiF_4$ *at 163 K.*

References

[1] V. Boudon, L. Manceron, C. Richard, J. Quant. Spectrosc. Radiat. Transfer, **253**, 107114 (2020).
[2] V. Boudon, C. Richard, L. Manceron, J. Mol. Spectrosc., **383**, 111549 (2022).

P1-5

An ab initio study of the rovibronic spectrum of sulfur monoxide ($^{32}S^{16}O$): diabatic vs. adiabatic representation

---

R.P. Brady[1], S.N. Yurchenko[1], G.-S. Kim[2], W. Somogyi[1], J. Tennyson[1]

1. Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, United Kingdom

2. Dharma College, Dongguk University, 30, Pildong-ro 1-gil, Jung-gu, Seoul 04620, Korea

We present an ab initio study of the rovibronic spectra of sulphur monoxide ($^{32}S^{16}O$) using internally contracted multireference configuration interaction (ic-MRCI) method using aug-cc-pV5Z basis sets. It covers 13 electronic states X $^3\Sigma^-$, a$^1\Delta$, b$^1\Sigma^+$, c$^1\Sigma^-$, A$''^3\Sigma^+$, A$'^3\Delta$, A$^3\Pi$, B$^3\Sigma^-$, C$^3\Pi$, d$^1\Pi$, e$^1\Pi$, C$'^3\Pi$, and (3)$^1\Pi$ ranging up to 66800 cm^{-1}. The ab initio spectroscopic model includes 13 potential energy curves, 29 dipole and transition dipole moment curves, 25 spin-orbit curves, and 18 electronic angular momentum curves. A diabatic representation is built by removing the avoided crossings between the spatially degenerate pairs C$^3\Pi$– C$'^3\Pi$ and e$^1\Pi$– (3)$^1\Pi$ on-the-fly through a property-based diabatisation method. We also present non-adiabatic couplings and diabatic couplings for these avoided crossing systems. Finally, an ab initio rovibronic spectrum of SO is computed. All phases for our coupling curves are defined, and consistent, providing the first fully reproducible spectroscopic model of SO covering the wavelength range up to 147 nm.

Keywords: Diabatisation, Electronic structure, transition moment, cross sections, potential energy surfaces.

A comparative theoretical study of pressure broadening parameters and their temperature dependences for symmetric tops of methane family

Jeanna Buldyreva[1,*], **Anna Dudaryonok**[2], **Larisa Troitsyna**[3] **and Nina Lavrentieva**[2]

[1] *Institut UTINAM, UMR CNRS 6213, Université Bourgogne Franche-Comté, 16 route de Gray, 25030 Besançon cedex, France*

[2] *V.E. Zuev Institute of Atmospheric Optics, 1 Akademishian Zuev square, 634021 Tomsk, Russia*

[3] *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France*

* *jeanna.buldyreva@univ-fcomte.fr*

Methyl-group containing molecules CH_3X (where X=Cl, CN, Br, F, I, D, ...) are widely known as minor constituents of the Earth atmosphere with large impact on fundamental atmospheric processes (ozone layer depletion) and human's health [1,2]. Line lists for CH_3Cl and CH_3D are available in atmospheric databases HITRAN and GEISA [3] since decades. CH_3Br was included in these databases about fifteen years ago. A line list for CH_3F was suggested in 2016 [4] for new releases. A series of measurements for CH_3I was initiated very recently [5]. While line intensities and positions are relatively well studied for some important fundamental bands, the knowledge of line-shape parameters (widths and shifts by various perturbers) is very scarce; even less data are available for their temperature dependences. This information is however of major importance for planetary atmosphere modelling and attracts much attention for reliable interpretation of remote-sounding spectra.

To provide such missing data for spectroscopic databases, we have been developing theoretical approaches for methane-derived molecules CH_3Cl, CH_3CN, CH_3I, CH_3D self-perturbed and perturbed by N_2, O_2, air, and H_2 (see, e.g. [6-10] and refs therein). The growing need for other similar active molecules and other perturbers requires however a global analysis of line-shape parameters for already studied systems to identify their main trends and attempt extrapolations to collisional partners still unstudied experimentally. The present work summarizes the main features of the CH_3X line widths and shifts studied previously for rotational quantum numbers $0 \leq J \leq 70$, $K \leq 20$ in a temperature interval of atmospheric interest 200-400 K and suggests estimation methods for other collisional pairs.

References

[1] B.J. Allan *et al.*, J Geophys Res **105(D11)**, 14363 (2000)
[2] N. Bell *et al.*, J Geophys Res **107(D17)**, 1 (2002)
[3] I.E. Gordon *et al.*, JQSRT **203**, 3 (2017); N. Jacquinet-Husson *et al.*, J Mol Spectrosc **327**, 31 (2016)
[4] D. Jacquemart, M. Guinet, JQSRT **185**, 58 (2016)
[5] E. Raddaoui *et al.*, JQSRT **232**, 165 (2019)
[6] A.S. Dudaryonok *et al.*, JQSRT **130**, 321 (2013)
[7] A.S. Dudaryonok *et al.*, Icarus **250**, 76 (2015); Icarus **256**, 30 (2015)
[8] L. Troitsyna *et al.*, JQSRT **242**, 106797 (2020)
[9] J. Buldyreva *et al.*, JQSRT **203**, 355 (2017)
[10] T. Sinyakova, J. Buldyreva, Icarus **282**, 363 (2017)

P1-7

Experimental and theoretical studies of N_2-pressure broadening parameters for $CH_3C^{14}N$ rotational transitions

---

Luyao Zou[1], **Anna Dudaryonok**[2], **Laurent Margules**[1], **François Rohart**[1], **Nina Lavrentieva**[2]**and Jeanna Buldyreva**[3,*]

[1] *Laboratoire de Physique des Lasers, Atomes et Molécules, UMR CNRS 8523, Université Lille 1, F-59655 Villeneuve d'Ascq cedex, France*
[2] *V.E. Zuev Institute of Atmospheric Optics, 1 Akademishian Zuev square, 634021 Tomsk, Russia*
[3] *Institut UTINAM, UMR CNRS 6213, Université Bourgogne Franche-Comté, 16 route de Gray, 25030 Besançon cedex, France*
* *jeanna.buldyreva@univ-fcomte.fr*

Methyl cyanide (acetonitrile) CH_3CN is a molecule of atmospheric and astronomical interest, in particular for Titan's atmosphere studies, now included in the HITRAN database [1]. However, except for some experimental studies of line intensities, positions, broadening and shifting parameters [2] (see also refs cited therein) its line broadening characteristics remain incomplete for many buffer gases. The case of N_2-broadening is the most important since nitrogen is the main perturbing gas in the atmospheres of Earth and Titan.

In the present work we report new room-temperature measurements of N_2-broadening coefficients of $CH_3C^{14}N$ rotational transitions for a wide range of rotational quantum numbers J and K requested by spectroscopic databases. Experiments were performed with a frequency-modulated spectrometer operating in the 180-1400 GHz range. It consists of a 10-20 GHz frequency synthesizer followed by a frequency multiplier chain based on solid-state devices, a 1.1 meter long absorption inox cell and a bolometric detection. Rotational lines $R(J,K)$ with $J = 9, 12, 15, 21, 27, 33, 42, 48, 63, 69, 75$ and $K \leq 15$, ranging from 184 up to 1390 GHz, have been studied in details. All recorded lines exhibit clear departures from the usual Voigt profile, so they have been analyzed using the more realistic Speed-Dependent Voigt profile. For completeness, the Voigt profile has been also employed because of its continuing use in atmospheric applications.

Measured values are compared to theoretical estimates obtained by the semi-empirical method [3] successfully applied previously to other symmetric tops CH_3X [4] and well appropriate to the CH_3CN-N_2 case because of strong electrostatic interactions due to the large dipole moment of the absorbing molecule. Being fitted on experimental J- and K-dependent values of pressure-broadening coefficients, the theoretical model parameters enable computations of line-shape parameters for enlarged ranges of rotational quantum numbers. The calculated CH_3CN-N_2 halfwidths demonstrate a very good agreement with measurements.

References

[1] L.S. Rothman *et al.*, JQSRT **130**, 4 (2013).
[2] C.P. Rinsland *et al.*, JQSRT **109**, 974 (2008).
[3] A.D. Bykov, N.N. Lavrentieva, L.N. Sinitsa, Mol. Phys. **102**, 1653 (2004).
[4] A.S. Dudarynok, N.N. Lavrentieva, J. Buldyreva, JQSRT **130**, 321 (2013).

P1-8

The water vapour selective absorption spectrum in the 8040-8630 cm^{-1} range

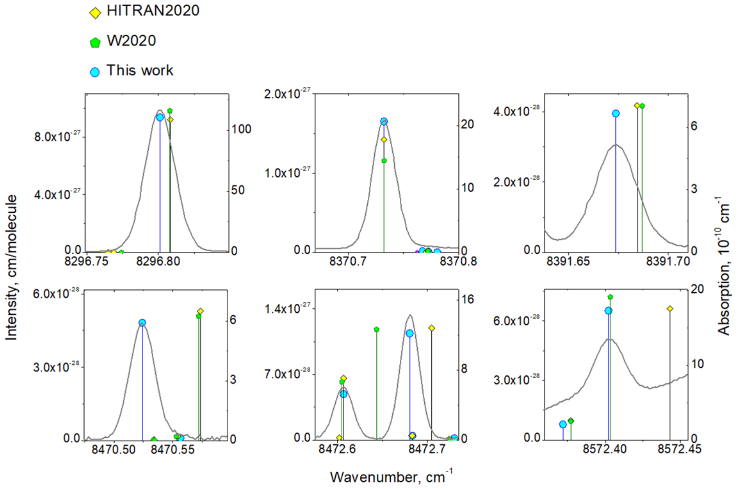
A.O. Koroleva[1], **S.N. Mikhailenko**[2], **S. Kassi**[1], **A. Campargue**[1,*]

1. LIPhy Université de Grenoble Alpes, UMR5588 CNRS, F-38041, France
2. V.E. Zuev Institute of Atmospheric Optics SB RAS, 1, Academician Zuev square, Tomsk 634055, Russia

** alain.campargue@univ-grenoble-alpes.fr*

The 1.25 µm transparency window is of importance for a number of atmospheric applications. As a continuation of our previous work on the improvement of water vapour line parameters in this spectral range [1], the room temperature absorption spectrum of water vapour in natural isotopic abundance was recorded with an unprecedented sensitivity between 8040 - 8620 cm^{-1} using comb referenced cavity ring-down spectroscopy technique [2]. The line positions and intensities of more than 5700 lines were retrieved within the 3.9×10^{-30} - 1.5×10^{-22} cm/molecule intensity range. The assignments were performed using known experimental energy levels and calculated spectra based on variational calculations by Schwenke and Partridge. The final line list contains more than 8300 transitions of six water isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, $HD^{16}O$, $HD^{18}O$ and $HD^{17}O$). The high sensitivity and low noise level of about $\alpha_{min}\approx10^{-11}$ cm^{-1} allows detecting a high number of new lines and determine their positions with an accuracy of about 10^{-4} cm^{-1} in the case of isolated lines. Observed line positions allow to found about 70 new energies of three isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$ and $HD^{16}O$) and to correct more than 60 previously reported term values of four isotopologues ($H_2{}^{16}O$, $H_2{}^{18}O$, $H_2{}^{17}O$, and $HD^{16}O$).

An overall good agreement of experimental line parameters with line parameters from HITRAN2020 [3] and W2020 [4] is observed. However some deviations are found with amplitude largely exceeding the claimed uncertainty on the W2020 transition frequencies.



References

[1] A. Campargue *et al*, JQSRT **157**, 135 (2015)
[2] M. Konefał *et al*, JQSRT **241**, 106653 (2020)
[3] I.E. Gordon *et al*, JQSRT **277**, 107949 (2022)
[4] T. Furtenbacher *et al*, J Phys Chem **49**, 043103 (2020)

P1-9

UV Spectrum and Photodecomposition of Peroxynitrous Acid (HOONO)

W. Chebbi[1,2] , T. Cours[2] , N. Derbel[1] , A. Alijah[2]
[1]Laboratoire de Spectroscopie Atomique, Moléculaire et Applications (LSAMA), Faculté des Sciences de Tunis,Tunis
[2]Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA), Université de Reims Champagne-Ardenne, France

Peroxynitrous acid HOONO was first observed in an Argon matrix. It is an unstable species and has not been seen in the gas phase at ambient pressure and temperature because of its short lifetime of a few milliseconds.

As is well known, the reaction of HO_2 and NO is a major producer of the OH radical ($HO_2+NO \rightarrow OH+NO_2$), which is considered the oxidative ‘work horse’ in the atmosphere. On other hand, OH is removed through the reaction ($OH+NO_2+M \rightarrow HNO_3+M$) yielding nitric acid and, to a less extent (about 15%), peroxynitrous acid ($OH+NO_2+M \rightarrow HOONO+M$). HOONO desintegrates readily through thermolysis and photo-decomposition. The mechanisms are not well understood. In this work, we investigate the photochemical decomposition.

The energies and structures of various conformers of peroxynitrous acid have been calculated at the CCSD(T)/AVTZ level of theory. Three configurations were found, denoted cis-cis, which is the most stable, cis-perp and trans-perp. The UV spectra are computed by DFT (M06-2X/AVTZ) using the NEWTON-X package. The principal peak does not coincide with the vertical excitation energy which can be explained as due to the slow motion of the ONOO and the NOOH torsional modes. The decay pathways of HOONO were determined using the steepest descent method. Three channels were found for the two stable conformers cis-cis and trans-perp.

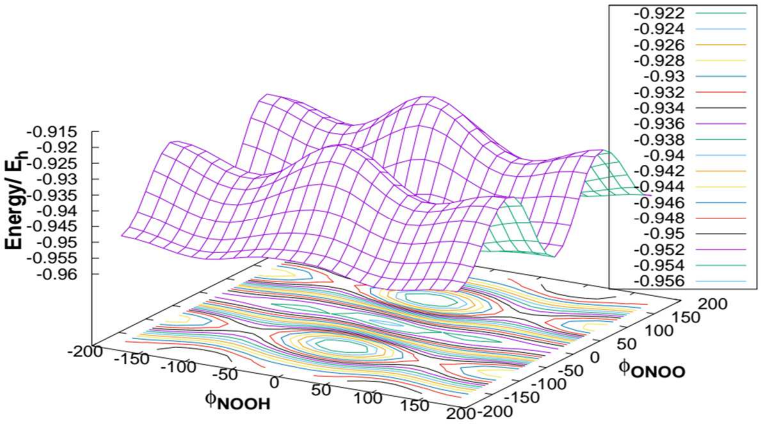


Figure 1: Variation of potential energy as a function of the two dihedral angles (NOOH) and (ONOO).

Acknowlegements: PhD grant for W.C. from the Tunisian Ministry of Higher Education and Scientific Research, CNRS IEA # 317871, P3M (Reims), ROMEO and CRIANN supercomputers.

P1-10

Increase of radiative forcing through mid-IR absorption by stable CO2 dimers?

Dennis F. Dinu[1,2,3], **Pit Bartl**[2], **Patrick K. Quoika**[1], **Maren Podewitz**[1,3], **Klaus R. Liedl**[1], **Hinrich Grothe**[3,*] **and Thomas Loerting**[2,*]

1. Institute of General, Inorganic and Theoretical Chemistry, University of Innsbruck, Innrain 80, A-6020 Innsbruck, Austria
2. Institute of Physical Chemistry, University of Innsbruck, Innrain 52c, A-6020 Innsbruck, Austria
3. Institute of Materials Chemistry, TU Wien, Getreidemarkt 9/165, A-1060 Vienna, Austria
* *thomas.loerting@uibk.ac.at, hinrich.grothe@tuwien.ac.at*

We have demonstrated that the combination of matrix isolation infrared (MI-IR) spectroscopy and vibration configuration interaction (VCI) calculations [1-3] is a feasible approach [4] to accurately assign vibrational transitions of single molecules, such as water [5], fluoroethane [6], carbon dioxide and methane [7].

Relying on our integral experimental-computational methodology, we recently investigated the carbon dioxide dimerization [8] including MI-R spectroscopy of carbon dioxide monomers CO_2 and dimers $(CO_2)_2$ trapped in neon and in air. Based on our VCI calculations accounting for mode-coupling and anharmonicity, we identify additional infrared-active bands in the MI-IR spectra due to the $(CO_2)_2$ dimer.

In a systematic carbon dioxide mixing ratio study using neon matrices, we observe a significant fraction of the dimer at mixing ratios above 300 ppm, with a steep increase up to 1000 ppm. In neon matrix, the dimer increases the IR absorbance by about 15% at 400 ppm compared to the monomer absorbance alone. This suggests a high fraction of the $(CO_2)_2$ dimer in our matrix experiments. In atmospheric conditions, such increased absorbance would significantly amplify radiative forcings and, thus, the greenhouse warming.

In the context of planetary atmospheres, our results improve understanding of the greenhouse effect for planets of rather thick CO_2 atmospheres such as Venus, where a significant fraction of the $(CO_2)_2$ dimer can be expected. There, the necessity of including the mid-IR absorption by stable $(CO_2)_2$ dimers in databases used for modelling radiative forcing, such as HITRAN, arises.

References

[1] G. Rauhut, JCP, **121**, 19 (2004)
[2] M. Neff *et al*, JCP, **131**, 12 (2009)
[3] H. J. Werner *et al*, JCP, **152**, 14, (2020)
[4] D. F. Dinu *et al*, TCA, **139**, 12, (2020)
[5] D. F. Dinu *et al*, JPCA, **123**, 38 (2019)
[6] D. F. Dinu *et al*, JMS, **367**, (2019)
[7] D. F. Dinu *et al*, PCCP, **22**, 32 (2020)
[8] D. F. Dinu *et al*, JPCA, **126**, 19, (2022)

P1-11

Air-broadened oxygen B band line shapes from cavity ring-down spectroscopy

Jolanta Domysławska*, Duc Dung Tran, Aleksandr A. Balashov, Katarzyna Bielska, Szymon Wójtewicz, Marcin Bober, Sławomir Bilicki, Roman Ciuryło, Daniel Lisak

Institute of Physics,
Faculty of Physics, Astronomy and Informatics,
Nicolaus Copernicus University in Toruń, Grudziądzka 5, 87-100 Toruń, Poland
** jolka@fizyka.umk.pl*

The oxygen B band has been investigated extensively in our laboratory, as a result the line shape parameters for self-perturbed oxygen including the speed dependence of line broadening and shifting as well as Dicke narrowing has been published [1,2,3]. However, the air-perturbed line shapes parameters for oxygen B band in the HITRAN2020 [4] are based on the Voigt profile with air-broadened half widths and pressure-shifts based in small part on experiment [5] or, for the most part, scaled values based on A-band parameters [6]. The coefficient of the temperature dependence of the air-broadened half width is a default value.

Unpublished results for over 20 selected O_2 transitions from P and R branches measured in air-like mixture in the pressure range up to 200 Torr and at temperatures from 288K to 328K will be presented. This was measured in part as the ESA founded ISOGG project [7]. Measured spectra has been fitted with the speed-dependent Nelkin-Ghatak line shape function taking into account the speed-dependence of the collisional broadening, the Dicke narrowing effect and the line asymmetry due to the speed-dependence of the collisional shifting. We will show the line positions, line intensities and other line-shape parameters together with temperature dependencies for widths and shifts.

Recent upgrade of our cavity ring-down spectrometer (CRDS) enabled for the use of the cavity mode-width spectroscopy (CMWS) [8,9] technique, complementary to CRDS, which has a different principle of the absorption determination, to validate the CRDS measurements [1]. We will show, on the example of the self-perturbed transitions from the P-branch, the influence of the input power beam on the absorption measurements at the subpercent level and the estimation of the nonlinearity of the detection system [1].

We will also mention the line mixing coefficient observed in the low pressure for the transitions at the B-band head [10].

References

[1] K. Bielska *et al*., JQSRT **144**, 107927 (2021)
[2] J. Domysławska *et al*, JQSRT **242**, 106789 (2020)
[3] J. Domysławska *et al*, JQSRT **169**, 111 (2016)
[4] I. E. Gordon *et al*., JQSRT **277**, 107848 (2022)
[5] J. E. Barnes and P. B. Hays, J. Mol. Spectr., **216**, 98 (2002)
[6] I. E. Gordon *et al*., JQSRT **112**, 2310 (2011)
[7] https://atmos.eoc.dlr.de/isogg/
[8] A. Cygan *et al*., Opt. Expr. **21**, 29744 (2013)
[9] D. A. Long, *et al*., Appl. Phys. B**. 114,** 489 (2014)
[10] J. Domysławska *et al*, J Chem Phys **156**, 084301-1 (2022)

High-resolution spectroscopy and analysis of the 3 μm region of C_2H_4 in natural isotopic abundance

Ons Ben Fathallah[1,2*], **Maud Rotger**[1], **Hassen Aroui**[2], **Vincent Boudon**[3], **Jean. Vander Auwera**[4], **Marcos. Antonio Loroño Gonzalez**[5]

1. *Université de Reims Champagne Ardenne, CNRS, GSMA UMR 7331, 51100 Reims, France*
2. *Université de Tunis, Laboratoire de Spectroscopie et Dynamique Moléculaire, Ecole Nationale Supérieure d'Ingénieurs de Tunis, 5 Av Taha Hussein 1008 Tunis, Tunisia*
3. *Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS - Université Bourgogne Franche-Comté, 9 avenue Alain Savary, BP 47870, F-21078 Dijon Cedex, France*
4. *QUARES, C.P. 160/09, Université Libre de Bruxelles, 50 avenue F. D. Roosevelt, B-1050 Brussels, Belgium*
5. *Oficina 410, Departamento Académico de Fisicoquímica, Facultad de Química e Ingenieria Química, Universidad Nacional Mayor de San Marcos, Lima, Peru*

* *ons.ben-fathallah@univ-reims.fr*

Ethylene is a natural gaseous compound present in the atmosphere of the Earth but also in the atmospheres of outer solar system planets such as Neptune and Titan [1,2]. However, a better knowledge of spectroscopic parameters is needed for this molecule to detect its presence and/or to derive accurate concentrations.

The results of such studies are of great interest to atmospheric scientists to as they help improving spectroscopic databases [3,4].

We present here a detailed analysis and modeling of the strongly absorbing ν_9 and ν_{11} fundamental bands of $^{12}C_2H_4$ observed in the 3 μm region. Due to the complexity of the observed spectrum, we have built a quite reasonable but complex polyad scheme that includes some fundamental bands previously analyzed thanks to the tensorial formalism developed in Dijon for asymmetric-top molecules [5]. A four polyad system has been settled and the last P_3 polyad contains five rovibrationnal modes: ν_9, ν_{11}, $\nu_2 + \nu_{12}$, $\nu_2 + \nu_{10}$, and $2\nu_{10} + \nu_{12}$.

A first frequency analysis has been performed providing 3323 assignments and 86 adjusted parameters with a root mean square of 5.9 10^{-3} cm^{-1} and a standard deviation of 2.0 10^{-3} cm^{-1}.

The line intensities were then fitted with a root mean square deviation is of 1.9 %, using parameters determined from the analysis of the line positions.

The band intensities were also determined and compared with previous work.

A new line list of calculated lines in the 2900 − 3300 cm^{-1} region will be proposed to be added to the ECasDa and to the HITRAN [3] and GEISA [4] databases.

References

[1] G.S. Orton *et al.*, Icarus **70**, 1-12 (1987)
[2] A. Coustenis *et al.*, Icarus **80,** 54-76 (1989)
[3] I.E. Gordon *et al*, J. Quant. Spectrosc. Radiat. Transf. **277,** 107949 (2022)
[4] T. Delahaye *et al.*, J. Mol. Spectrosc. **380**, 111510 (2021)
[5] J.P. Champion *et al.*, in "Spectroscopy of the Earth's atmosphere and interstellar medium," K.N. Rao and A. Weber (eds), Academic Press, San Diego, p. 339–422 (1992)

Self-,O_2- and N_2-Broadening Coefficients and Line Intensities of Methyl Chloride in the 10 µm Region

Ons Ben Fathallah[1,2*], **Laurent Manceron**[3], **Nawel Driddi**[1,2], **Maud Rotger**[1] **and Hassen Aroui**[2]

1. *Université de Reims Champagne Ardenne, CNRS, GSMA UMR 7331, 51100 Reims, France*
2. *Université de Tunis, Laboratoire de Spectroscopie et Dynamique Moléculaire, Ecole Nationale Supérieure d'Ingénieurs de Tunis, 5 Av Taha Hussein 1008 Tunis, Tunisia*
3. *Synchrotron Soleil Ligne AILES, BP 48, 91192 Cedex Gif-sur-Yvette, France and MONARIS, UMR 8233 CNRS-UPMC, case 49, 4 place Jussieu, 75252 Cedex Paris, France*

* *ons.ben-fathallah@univ-reims.fr*

The halocarbons derivatives of methane contribute to the destruction of the ozone layer and the greenhouse effect [1]. The most abundant of these halocarbons is methyl chloride (CH_3Cl) with an estimated lifetime in the stratosphere of about 1 to 3 years [2]. This molecule is the main source of natural chlorine in the atmosphere and was included in the global stratospheric chlorine budget [3]. High-resolution spectroscopy studies are necessary to achieve accurate concentrations of this gas. The results of such studies are of great interest to atmospheric scientists to enrich databases [4].

We performed the first systematic measurements of pressure broadening coefficients and line intensities of ro-vibrational absorption transitions of the ν_6 perpendicular band of the $^{12}CH_3{}^{35}Cl$ and $^{12}CH_3{}^{37}Cl$ isotopes. The spectra were recorded in the spectral region between 920 and 1130 cm^{-1} with a high-resolution Fourier transform spectrometer.

A multi-pressure fitting technique was used to fit a series of seven spectra at pressures of CH_3Cl ranging from 1.02 to 10.24 mbar to retrieve line intensities of about 2000 transitions with $3 \leq J \leq 55$ and $0 \leq K \leq 12$. The average accuracies have been estimated to be about 4 and 5 % for line intensities and the broadenings respectively. The rotational dependencies of the self-broadening coefficients have been clearly observed and modeled using a second-order empirical polynomial. We have also calculated the O_2- and N_2-broadenings with the Starikov empirical model [5]. To interpret these measurements, a semi-classical calculation based on the Robert and Bonamy (RB) formalism was made [6].

The rotational dependencies of line intensities were analyzed and used to derive the transition dipole moments squared for each line. The analysis of these moments using the theoretical model of Watson [7] allows us to derive a consistent set of line intensity parameters such as vibrational transition moments, band intensities as well as Herman-Wallis coefficients. The results were compared with previous works and with the HITRAN database [4].

References

[1] R.F. Sherwood, Phil. Trans. R. Soc. B **361**,769-90 (2006)
[2] AT1. Brown *et al*, Atmos. Chem. Phys. **13,** 6921-50 (2013)
[3] R. Nassar *et al*, J. Geophys. Res. **111**, D22312 1-13 (2006)
[4] Gordon IE *et al*, JQSRT **203,** 3-69 (2017)
[5] V.I. Starikov *et al*, Optics and Spectroscopy **98,** 330-5 (2005)
[6] D. Robert *et al*, J Phys. **40,** 923–43 (1979)
[7] J.K.G. Watson, J. Mol. Spectrosc. **153**, 211-24 (1992)

New line list for nine isotopologues of CO, based on semi-empirical PEF and DMF

Vladimir V. Meshkov[1], Aleksander Yu. Ermilov[1], Andrey V. Stolyarov[1], Emile S. Medvedev[2], Vladimir G. Ushakov[2], and Iouli E. Gordon[3,*]

2. Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, Leninskie gory 1/3, Russia
2. Institute of Problems of Chemical Physics, RAS, Prospect Akademika N.N. Semenova 1, 142432 Chernogolovka, Russia
3. Center for Astrophysics | Harvard & Smithsonian, Atomic and Molecular Physics Division, 60 Garden Street, Cambridge, MA 02138 USA
** igordon@cfa.harvard.edu*

The semi-empirical electric dipole-moment function (DMF) for the ground electronic state of the CO molecule has been constructed analytically in the entire range of the inter-nuclear distance by means of the simultaneous non-linear least-squares fitting (NLLSF) of the vetted experimental intensities for the principal isotopologue of CO and the ab initio dipole moment values [1]. The derived mass-invariant DMF possesses the physically correct asymptotic behavior in both the united-atom and dissociation limits as well as reproduces the majority of the measured intensities in different bands within their experimental uncertainties. The resulting DMF and the mass-corrected potential-energy function [2] were used to calculate line lists for all (including radioactive) CO isotopologues in the wide range of vibrational and rotational quanta. The predicted intensities are compared with their experimental counterparts, including the most recent ones that were not involved in the present NLLSF. We also show that discrepancies in calculated line lists and experimental measurements for minor isotopologues could primarily be attributed to uncontrolled abundances in the experimental cells and call for experiments that would involve mass-spectrometric measurements. The resultant line list [1] should be considered superior to previous efforts (including Li et al. [3] work that underlines current line lists for HITRAN and HITEMP) in terms of accuracy for both line positions and intensities.

References

[1] V. V. Meshkov, *et al,* JQSRT, **280**, 108090 (2022)
[2] V. V. Meshkov, *et al,* JQSRT, **217**, 262-273 (2018)
[3] G. Li, *et al,* Astrophys. J. Suppl. Ser., **216**, 15 (2015)

P1-15

Using machine learning to meet the need for pressure-broadening data in exoplanetary atmospheric studies

Elizabeth R Guest[1], Jonathan Tennyson[1], Sergei N Yurchenko[1], Jeanna Buldyreva[2]

1. *Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, UK*
2. *Institut UTINAM UMR CNRS 6213, Université Bourgogne Franche-Comté, 16 Route de Gray, 25030 Besançon cedex, France*

The characterisation and modelling of exoplanetary atmospheres require large volumes of laboratory spectroscopic data [1]. Simulations have demonstrated the need to deal correctly with line broadening in the atmospheres of exoplanets [2]. The provision of these line broadening parameters was deemed crucial for understanding exoplanetary atmospheres [3]. Current studies of hot atmospheres demand at least qualitative estimates of pressure-broadening parameters for many molecules and molecular ions. HITRAN [4] provides pressure broadening parameters for lines from a range of species, for a subset of the desired perturbing species (largely by 'air' and the molecule itself). The ExoMol [5] database contains many exotic species important on exoplanets, not covered by HITRAN, so an extended range of perturbers and temperatures must be considered. We would like to make complete assignments of pressure broadening values to the ExoMol species, for a range of key perturbing molecules. The molecules of interest, for example TiO, are often formed at high temperatures and pressures, and as such are difficult to study empirically. These situations also pose challenges to ab initio methods, due to the complexity of the theory of many-electron systems. An alternative approach is to use machine learning to provide good estimates of line broadening. This research collects all of HITRAN's line broadening data, and trials various machine learning tools to extrapolate pressure-broadening parameters to new species. Initial studies explore the J-dependence of line broadening, especially for diatomics. Our goal is to develop an approach for automatic, large-scale production of broadening parameters which can be transferred to new species and to a range of perturbers. These will be used to update the rather crude ExoMol pressure-broadening diet [6] and thus populate the database with these important data.

References

[1] J. Tennyson and S. N. Yurchenko, Atoms **6,** 26 (2018); K.L. Chubb *et al.*, Astron Astrophys **646**, A21 (2021)
[2] G. Tinetti *et al.*, Phil Trans Royal Soc London A **370**, 2749 (2012)
[3] J.J. Fortney *et al.*, arXiv:1905.07064 (2019)
[4] I.E. Gordon *et al.*, JQSRT **277**, 107949 (2022)
[5] J. Tennyson *et al.*, JQSRT **255**, 107228 (2020)
[6] E.J. Barton *et al.*, JQSRT **203**, 490 (2017)

P1-16

Measurement of perfluoro-n-heptane temperature-dependent absorption cross-sections between 515 and 1500cm^{-1}

Muhammad Osama Ishtiak[1,*], **Orfeo Colebatch**[1], **Karine Le Bris**[2], **Paul J. Godin**[3], **Kimberly Strong**[1]

1. Department of Physics, University of Toronto, Toronto, ON, Canada
2. Department of Physics, Saint Francis Xavier University, NS, Canada
3. Institute for Quantum Computing, University of Waterloo, ON, Canada
* *osama.ishtiak@mail.utoronto.ca*

Keywords: Absorption cross-sections, Perfluorocarbon, Global warming potential, Radiative efficiency

Perfluorocarbons (PFCs) are fully fluorinated greenhouse gases. These compounds are chemically inert due to their C-F bonds and therefore have atmospheric lifetimes of thousands of years. Although regulated under the Kyoto Protocol, PFCs with four or more carbon atoms have seen increases in atmospheric concentrations of up to 27% between 2010 and 2017 [1]. Perfluoro-n-heptane saw a 21% increase in atmospheric concentration in the southern hemisphere over the same period [1]. To quantify the climate impact of perfluoro-n-heptane, spectral data are required to calculate metrics like radiative efficiency and global warming potential. A recent review paper provided only one experimental source of spectral data at 296K for perfluoro-n-heptane [2]. Here we provide a set of absorption cross-sections in the range 515-1500cm^{-1} at 0.1cm^{-1} resolution for five temperatures between 305K and 340K. The cross-sections are in good agreement with the data provided in [3]. Preliminary radiative efficiency and global warming potential values, obtained via the updated Pinnock method [2], agree with the values presented in [3]. Therefore, our results validate previously collected experimental data and increase the range of temperatures for measured perfluoro-n-heptane cross-sections.

References

[1] E. S. Droste *et al.*, "Trends and emissions of six perfluorocarbons in the Northern Hemisphere and Southern Hemisphere," *Atmospheric Chemistry and Physics*, 20(8), 4787–4807, 2020, doi: 10.5194/acp-20-4787-2020.

[2] Ø. Hodnebrog *et al.*, "Updated Global Warming Potentials and Radiative Efficiencies of Halocarbons and Other Weak Atmospheric Absorbers," *Reviews of Geophysics*, 58, e2019RG000691, 2020, doi: 10.1029/2019RG000691.

[3] D. J. Ivy *et al.*, "Global emission estimates and radiative impact of C_4F_{10}, C_5F_{12}, C_6F_{14}, C_7F_{16} and C_8F_{18}," *Atmospheric Chemistry and Physics*, 12(16), 7635–7645, 2012, doi: 10.5194/acp-12-7635-2012.

P1-17

Recent analysis of high-absorption path FT spectra of acetylene

David Jacquemart[1,*], Oleg M. Lyulin[2], Aleksander M. Solodov[2], Tatiana M. Petrova[2], Alexandr A. Solodov[2]

1. Sorbonne Université, CNRS, MONARIS, UMR 8233, 4 place Jussieu, 75005 Paris, France.

2. V. E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Academician Zuev sq., 634055, Tomsk, Russia

** david.jacquemart@upmc.fr*

Recent acetylene spectra have been recorded at the V.E. Zuev Institute of Atmospheric Optics SB RAS from IAO (Tomsk) with a Bruker IFS-125HR Fourier transform spectrometer connected to a White type cell (absorption paths length up to 1057.95 m). The Bruker resolution is ranging from 0.005 to 0.016 cm^{-1} depending on studied spectral regions. Acetylene pressures ranging from 1 to 10 mbar have been used. This work is focused on the spectral region between 2400 and 2800 cm^{-1} where HITRAN and GEISA databases have spectroscopic data for only 5 bands whereas with present experimental spectra more than 20 bands can be observed and were analyzed by a line-by-line multispectrum fitting procedure. Also the *Q*-branch of the $\nu_1+\nu_3+3\nu_4$ cold band of $^{12}C_2H_2$ located at 8330 cm^{-1} was considered since this strong *Q*-branch is missing from spectroscopic databases. These works complete the recent updates of acetylene in HITRAN and GEISA both in the $\Delta P = 4$ (previous update in 2008) and $\Delta P = 13$ (previous update in 2020) spectral regions.

The ν$_3$ band of $^{16}O^{14}N^{18}O$: line positions and intensities

A.A. Marinina [1], **D. Jacquemart** [2], **L. Krim** [2], **P. Soulard** [2], **V.I. Perevalov** [1*]

1. V. E. Zuev Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1, Academician Zuev sq., 634055, Tomsk, Russia
2. Sorbonne Université, CNRS, MONARIS, UMR 8233, 4 place Jussieu, 75005 Paris, France.

** vip@iao.ru*

Fourier transform IR spectra of samples prepared by mixing two gaseous species $^{18}O_2/^{14}N^{16}O$ (1:2) have been recorded in the region of the ν_3 band of nitrogen dioxide. The spectra contain the lines corresponding to the ν_3 band of the $^{16}O^{14}N^{18}O$ isotopologue within the 1540-1640 cm^{-1}. In total 1795 lines of the ν_3 band of this isotopologue were assigned with the rotational quantum numbers N and K_a up to 51 and 12, respectively, what corresponds to 3487 electron spin-rotation-vibration transitions. The overall measured set of the line positions was used to fit the effective Hamiltonian parameters. The fitted set of the parameters reproduces the observed line positions with an *rms* of 3.6×10^{-3} cm^{-1}. A selected set of the measured line intensities was used to determine the effective dipole moment parameters describing the line intensities of the ν_3 band. The *rms* deviation of the fit is 5.0%. It was found that the lines with the $\Delta K_a = \pm1$ are very weak compared to those with the $\Delta K_a = 0$. At attained sensitivity only few lines with the $\Delta K_a = \pm1$ were assigned. A line list of this band has been generated for databases.

The $^{16}O^{14}N^{18}O$ is one of the most abundant daughter isotopologues of nitrogen dioxide. Its natural abundance is about 0.397%. This value is slightly larger than the value of the natural abundance of the $^{15}N^{16}O_2$ isotopologue (0.365%). In Ref. [1] it is shown that the inclusion of the $^{15}N^{16}O_2$ lines to the fitting of the atmospheric balloon spectra significantly reduces the *rms* spectral fitting residuals in the 1550 – 1650 cm^{-1} region. The addition of $^{16}O^{14}N^{18}O$ isotopologue in databases could improve the gases retrievals from the atmospheric spectra in this region.

References

[1] A. Perrin *et al*, JQSRT **154**, 91 (2015)

P1-19

Massive Gas Release Monitoring using a Quantum Cascade Laser Spectrometer with a Compact Dense Pattern Multipass Absorption Cell

Clément Jacquemin[1,2], Raphaël Vallon[1], Bertrand Parvitte[1], Guillaume Aoust[2], Grégory Maisons[2], Mathieu Carras[2] and Virginie Zeninari[*,1]

1. Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France
2. MirSense, Centre d'intégration NanoINNOV, 91120 Palaiseau, France
** virginie.zeninari@univ-reims.fr*

In many industrial and atmospheric processes, determination and monitoring over time of molecular species concentration in a gaseous media is an important element (e.g. air quality, process efficiency). Laser spectroscopic techniques based on tunable lasers provide good results for gas detection in terms of sensibility and selectivity thanks to the characteristics of these sources. The use of spectrally fine and tunable sources allows to discriminate and quantify precisely several species [1-4]. In Tunable Diode Laser Absorption Spectroscopy, sources are tuned over a spectral interval in order to record spectra. Knowing absorption lines parameters, it is possible to determine concentration of species. The mid-infrared region is particularly suitable for these measurements due to strong molecules signatures.

In the framework of an invitation to a gas release trial at CENZUB (military training area in France), a CO_2 spectrometer using a mid-IR quantum cascade laser in pulse operation coupled with a home-made dense pattern multipass absorption cell was developed. An illustration of the developed sensor is given in Fig. 1.

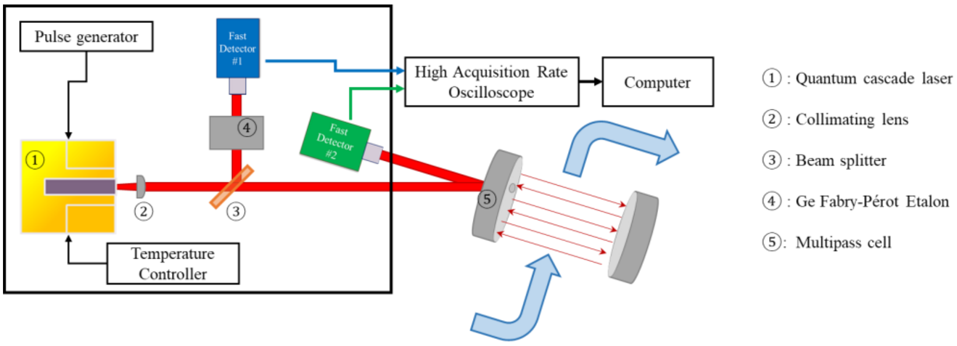


Fig. 1. Experimental setup illustration

The trial consists of massive CO_2 release in urban-like environment with different type of sensors arranged in the area. Data are used to improve flow dispersion model in this kind of environment. Members of Reims University have been invited to join the trial with their sensors.

Intrapulse measurement method and multipass cell design will be detailed. Outdoor campaign results will be also presented.

References

[1] Joly, L., Zéninari, V., Decarpenterie, T., Cousin, J., Grouiez, B., Mammez, D., Durry, G., Carras, M., Marcadet, X., & Parvitte, B. Continuous-wave quantum cascade lasers absorption spectrometers for trace gas detection in the atmosphere. Laser Physics, 21(4), 805–812. (2011)

[2] Grossel, A., Zéninari, V., Parvitte, B., Joly, L., Courtois, D., & Durry, G. (2008). Quantum cascade laser spectroscopy of N2O in the 7.9 μm region for the in situ monitoring of the atmosphere. Journal of Quantitative Spectroscopy and Radiative Transfer, 109(10), 1845–1855.

[3] Joly, L., Robert, C., Parvitte, B., Catoire, V., Durry, G., Richard, G., Nicoullaud, B., & Zéninari, V. Development of a spectrometer using a continuous wave distributed feedback quantum cascade laser operating at room temperature for the simultaneous analysis of N2O and CH4 in the Earth's atmosphere. Applied Optics, 47(9), 1206–1214. (2008)

[4] Joly, L., Decarpenterie, T., Dumelié, N., Thomas, X., Mappe-Fogaing, I., Mammez, D., Vallon, R., Durry, G., Parvitte, B., Carras, M., Marcadet, X., & Zéninari, V. Development of a versatile atmospheric N2O sensor based on quantum cascade laser technology at 4.5 μm. Applied Physics B: Lasers and Optics, 103(3), 717–723. (2011)

A Near Infrared Laser Diode Spectrometer for Ammonia Leakage

C. Jacquemin, R. Vallon, F. Defossez, B. Parvitte and V. Zéninari*

Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, Université de Reims Champagne-Ardenne, Faculté des Sciences, Moulin de la Housse, BP 1039, 51687 Reims Cedex 2 France
** virginie.zeninari@univ-reims.fr*

In industrial context, determination and monitoring over time of molecular species concentration in a gaseous media allows to control processes efficiency or prevent accident in case of chemical hazard. Several techniques exist to characterize this medium such as semiconductor sensors, chromatographic or optical methods.

Among these, laser spectrometry has many advantages. The use of spectrally fine and tunable sources allows to discriminate and quantify precisely several species [1–4]. In Tunable Diode Laser Absorption Spectroscopy, sources are tuned over a spectral interval in order to record spectra. Knowing absorption lines parameters, it is possible to determine concentration of species with any calibration step.

We developed a transportable Laser Diode Spectrometer composed of a 2µm-wavelength laser source injected in a new dense pattern multipass absorption cell. Our device is pictured below in Fig. 1.

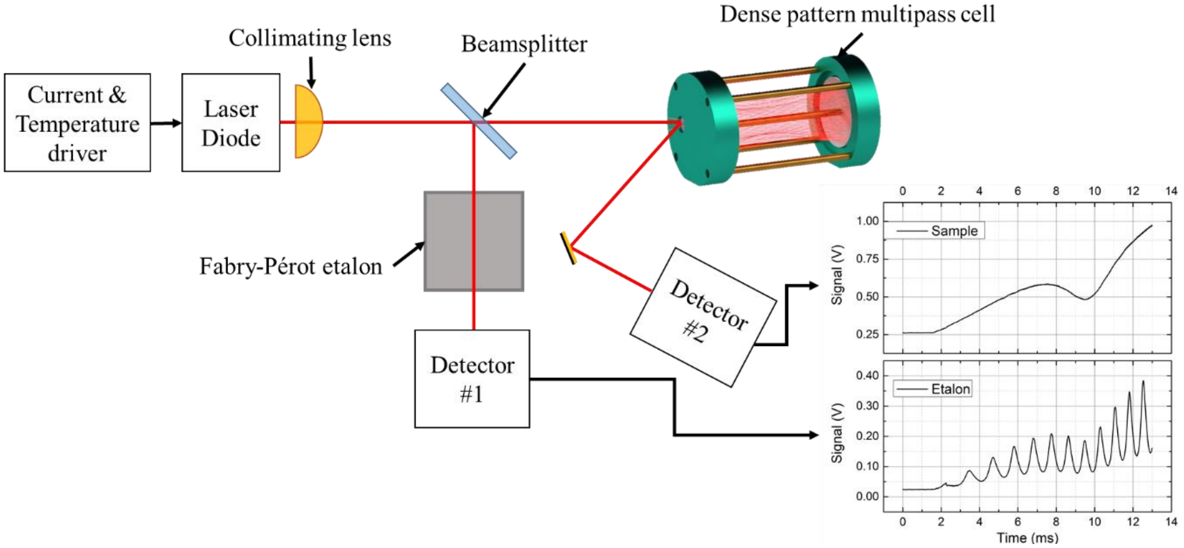


Fig. 1 Experimental setup illustration

Detection of 10-ppm-level have been performed during an outdoor measure during a simulated gas leakage of ammonia in a firefighter formation center in Belgium. Comparison with reference instrument have also been realized. Measurement method and campaign results will be detailed.

References

[1] L. Joly, B. Parvitte, V. Zeninari, and G. Durry, “Development of a compact CO_2 sensor open to the atmosphere and based on near-infrared laser technology at 2.68 µm,” *Appl. Phys. B*, vol. 86, no. 4, pp. 743–748, Feb. 2007.

[2] R. D. May, “Open-path, near-infrared tunable diode laser spectrometer for atmospheric measurements of H_2O,” *J. Geophys. Res. Atmos.*, vol. 103, no. D15, pp. 19161–19172, Aug. 1998.

[3] V. Zéninari, A. Vicet, B. Parvitte, L. Joly, and G. Durry, “In situ sensing of atmospheric CO2 with laser diodes near 2.05 µm: A spectroscopic study,” *Infrared Phys. Technol.*, vol. 45, no. 3, pp. 229–237, 2004.

[4] G. Durry and I. Pouchet, “A Near-Infrared Diode Laser Spectrometer for the In Situ Measurement of Methane and Water Vapor from Stratospheric Balloons,” *J. Atmos. Ocean. Technol.*, vol. 18, no. 9, pp. 1485–1494, Sep. 2001.

Towards a new NDACC-IRWG site at Paris: site characterization and atmospheric urban pollution monitoring

---

Hao FU, Pascal JESECK, Christof JANSSEN, Corinne BOURSIER and Yao TÉ*

Laboratoire d'Etudes du Rayonnement et de la Matière en Astrophysique et Atmosphères (LERMA-IPSL), Sorbonne Université, CNRS, Observatoire de Paris, PSL Université, 75005 Paris, France
* *yao-veng.te@sorbonne-universite.fr*

Abstract

The increase of greenhouse gases and chemically active species in the atmosphere and their impact on climate change and air quality are among the most important environmental problems. Monitoring of these atmospheric trace gases is required for understanding the climatic and atmospheric composition changes. The LERMA laboratory operates the ground-based high-resolution Fourier Transform Spectrometer (FTS-Paris) located at the Campus of Pierre et Marie Curie (Jussieu), in the center of Paris downtown. The FTS-Paris instrument [1, 2] is part of TCCON (Total Carbon Column Observation Network) [3] and provides integrated measurements of greenhouse gases. In addition, the instrument also performs measurements in the spectral ranges used by the NDACC-IRWG (Network for the Detection of Atmospheric Composition Change-Infrared Working Group) for monitoring chemically active atmospheric pollutants causing urban pollution and impacting air quality. The FTS-Paris instrument is planned to fulfil the NDACC-IRWG requirements to formally join this network. In the frame of these efforts, a characterization of the Paris megacity environment using atmospheric retrievals and back trajectory calculations is under way and first results will be presented here: climatology, pollution events, characterization of the origin of sources (local, nearby and long-distance emission sources), …

References

[1] Té *et al.*, The Fourier transform spectrometer of the UPMC University QualAir platform, Rev. Sci. Instrum, 2010
[2] Té *et al.*, Seasonal variability of surface and column carbon monoxide over megacity Paris, high altitude Jungfraujoch and Southern Hemispheric Wollongong stations, ACP, 2016
[3] Wunch *et al.*, The Total Carbon Column Observing Network, Phil. Trans. R. Soc. A, 369, 2087-2112, (2011). DOI: 10.1098/rsta.2010.0240.

P1-22

UV spectra and kinetic study of degradation of a several of first-generation oxidation products of monoterpene by atmospheric oxidants in the gas phase.

Mariam Fakih[1, *], **Estelle Roth**[1], **and Abdelkhaleq Chakir**[1]

* *mariam.fakih1@univ-reims.fr*

The Biogenic Volatile Organic Compound (BVOC) emissions are the largest land source of Total Organic Compounds in the atmosphere. Among BVOCs compounds [1], monoterpenes ($C_{10}H_{16}$), constitute an important fraction of BVOCs [2-3]. Once in the atmosphere, these compounds undergo several atmospheric reactions leading to the formation of numerous secondary products such as tropospheric ozone and secondary organic aerosol (SOA) [4-5]. Hence the importance to understand the atmospheric oxidation processes involving these compounds as well as the atmospheric fate of the main products resulting from the first generation of the monoterpenes oxidation. However, atmospheric oxidation of these products still less well understood in terms of kinetics and mechanism. In this context, this work presents a kinetic study of several first-generation oxidation products of monoterpenes with OH radicals, chlorine radicals and ozone over the temperature range 298-353 K in air and at near atmospheric pressure of 760 Torr. To find out if these compounds could be photodissociate in the atmosphere, their UV spectra were determined. The target compounds were: nopinone, myrtenal, limononaldehyde, caronaldehyde and ketolimonene.

Kinetic experiments were performed using a 63 L Pyrex atmospheric chamber, surrounded with 24 fluorescent black lamps, coupled to a PTR-MS (proton transfer reaction-Mass spectrometer) and FTIR (Fourier Transformed InfraRed Spectrometry). While, UV absorption cross section measurements were carried out using an optical system coupled to a deuterium lamp monochromator system and conducted at temperature 353 K. The UV spectrum of all five target compounds show a significant absorption above 290 nm. This indicates that their photolysis potential in the troposphere could be eliminated from atmosphere by photolysis. Rate constants for the reactions of OH and Cl with nopinone, myrtenal, limononaldehyde and ketolimonene were found to exhibit no or low temperature dependence under our experimental conditions, whereas for ozone reactions clear temperature dependence was observed.

The Results obtained in this study was used to assess the ability of these compounds to be degraded by different atmospheric process (photolysis and by reaction with OH radicals, ozone and Cl atoms) and to determine the contribution of these processes in the atmospheric removal of the compounds investigated.

Keywords: UV spectra, monoterpene, kinetic, simulation chamber, PTR-MS, rate coefficients, OH radicals, Cl radicals, ozone, atmospheric lifetime.

References

[1] A. B. Guenther and al. The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2. 1): an extended and updated framework for modeling biogenic emissions. Geoscientific Model Development, 2012, vol. 5, no 6, p. 1471-1492.

[2] K.Sindelarova and al. Global data set of biogenic VOC emissions calculated by the MEGAN model over the last 30 years. Atmospheric Chemistry and Physics, (2014), vol. 14, no 17, p. 9317-9341.

[3] P.Messina, and al. Hauglustaine. Global biogenic volatile organic compound emissions in the ORCHIDEE and MEGAN models and sensitivity to key parameters. Atmospheric Chemistry and Physics, 2016, vol. 16, no 22, p. 14169-14202.

[4] T.Sakulyanontvittaya, and al. C.Wiedinmyer. Secondary organic aerosol from sesquiterpene and monoterpene emissions in the United States. Environmental science & technology, 2008, vol. 42, no 23, p. 8784-8790.

[5] A. R. Berg, and al. The impact of bark beetle infestations on monoterpene emissions and secondary organic aerosol formation in western North America. Atmospheric Chemistry and Physics, 2013, vol. 13, no 6, p. 3149-3161.

Thursday August 25, 2022 Program

	Chair : V. Boudon	
9:00-9:40	**A.J. Fleisher** (*invited speaker*)	p 47
9:40-10:00	P. Cacciani	p 48
10:00-10:20	P. Cermak	P 49
10:20-10:40	A. Perrin	p 50
10:40-11:00	Coffee break	
11:00-11:40	**E. Mlawer** (*invited speaker*)	p 51
11:40-12:00	H. Fleurbaey	p 52
12:00-12:20	P. Chelin	p 53
12:20-12:40	C. Janssen	p 54
12:40-14:00	Lunch	
	Chair : D. Jacquemart	
14:00-14:40	**E. Fedorova** (*invited speaker-online*)	p 55
14:40-15:20	**N. Batalha** (*invited speaker-online*)	p 56
15:20-15:40	M. Lepère	p 57
15:40-16:00	S. Perot	p 58
16:00-16:20	W. Fakhardji	p 59
16:20-16:40	*Exhibitor – J. Hayden (IRsweep)*	
16:40-17:00	Coffee break	
17:00-18:30	Poster session 2	p 63-83
19:30	Banquet	

Accurate molecular line intensities: Measurements, applications, and isotope ratios

Adam J. Fleisher[1,*] **and Joseph T. Hodges**[1]

1. National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, United States
** adam.fleisher@nist.gov*

Laboratory measurements of accurate molecular line intensities require precision laser spectroscopy and a well-characterized sample. This overview will discuss recent progress on the characterization of potential biases encountered while performing cavity ring-down spectroscopy (CRDS) on gas-phase samples of carbon dioxide (CO_2) in air. Results from this work include improved accuracy for CO_2 line intensities, now reported at the 0.1 % level [1–3]. We will also introduce measurements of line intensities by dual-comb spectroscopy, using initial results on hydrogen cyanide as an example [4]. Finally, in addition to their application in remote sensing, we will introduce recent work on the accurate measurement of isotope ratios in CO_2-in-air samples using line intensities from both experiment and theory [5]. This work represents progress towards determining absolute isotope ratios for common artifacts used to realize or define isotope delta-scales like the Vienna PeeDee Belemnite (VPDB) $\delta^{13}C$ scale.

References

[1] A.J. Fleisher *et al*, PRL **123**, 043001 (2019)
[2] D.A. Long *et al*, GRL **47**, e2019GL086344 (2020)
[3] H. Fleurbaey *et al*, JQSRT **252**, 107104 (2020)
[4] P. Guay *et al*, Opt Lett **43**, 1407 (2018)
[5] A.J. Fleisher *et al*, Nat Phys **17**, 889 (2021)

New analysis of ammonia spectrum in the 4700-5650 cm^{-1} energy range. Importance of intensity transfer in case of quasi degenerated energy levels.

Patrice Cacciani[1], Peter Čermák[2], Alain Campargue[3], Jean Vander Auwera[4],

1.UMR CNRS 8523 - Université de Lille, Laboratoire PHLAM, F-59655 Villeneuve d'Ascq cedex, France,
2.Department of Experimental Physics, Comenius University, Bratislava, Slovakia;
3.UMR5588 LIPhy, Université Grenoble Alpes/CNRS, Saint Martin d'Hères, France,
4.SQUARES, Université Libre de Bruxelles, Brussels, Belgium.

Laboratory data for various molecules are necessary to understand the composition and processes which occurs in earth and exoplanets atmospheres. This is the role of feeding databases like HITRAN or GEISA. Our contribution is dedicated to ammonia molecule in the near infrared energy range. A recent high resolution FTS absorption spectrum [1] motivates the interest of new analysis with the help of high accurate ab initio calculations [2]. The 4700-5650 cm^{-1} range is the target that fills the hole of our previous works for the 3900-4700 [1] and the 5650-6350 cm^{-1} [3] ranges. The lower state combination difference technique is very powerful with such accurate spectrum as well as the ability of the ab initio calculation to reproduce position and intensity of the transitions. However, this is upset in the case of quasi degenerated energy levels and yields for the transitions to a transfer of intensity. This phenomenon has been systematically explored in this work and should be considered in future work, particularly for higher energy ranges.

References

[1] Cacciani P, Čermák P, Vander Auwera J, Campargue A . The ammonia absorption spectrum between 3900 and 4700 cm^{-1} J Quant Spectrosc & Radiat Transf 2022;277:107961. doi:10.1016/j.jqsrt.2021.107961

[2] Furtenbacher T, Coles PA, Tennyson J, Yurchenko SN, Yu S, Drouin B, et al. Empirical rovibrational energy levels of ammonia up to 7500 cm^{-1}. J Quant Spectrosc & Radiat Transf 2020;251:107027. doi: 10.1016/j.jqsrt.2020.107027.

[3] Cacciani P, Čermák P, Béguier S, Campargue A. The absorption spectrum of ammonia between 5650 and 6350 cm^{-1}. J Quant Spectrosc & Radiat Transf 2021;258:107334. doi: 10.1016/j.jqsrt.2020.107334.

Mots clefs: High resolution spectroscopy, ammonia, infrared spectra

IR Ammonia spectra: Accuracy tests around 6000 cm^{-1}

Peter Čermák[1,*], **Odřej Votava**[2], **Jozef Rakovský**[2], **Patrice Cacciani**[3], **Jean Cosléou**[3]

1. Department of Experimental Physics, Faculty of Mathematics, Physics and Informatics, Comenius University, Mlynská dolina F2, 842 48 Bratislava, Slovakia
2. Heyrovský Institute of Physical Chemistry, Dolejškova 2155/3, Prague 8, 18223, Czech Republic
3. Laboratoire de Physique des Lasers, Atomes et Molécules, CNRS, UMR 8523 Université Lille 1, 59655 Villeneuve d'Ascq Cedex, France
** cermak@fmph.uniba.sk*

Accurate reference laboratory data represents a key element for understanding any remote observations in particular astrophysical surveys. In the current contribution we focus on the accuracy check of our previously published peaklist in the 6000cm^{-1} region [1]. This comprises two complementary studies. First, the line center validation was performed by the referenced supersonic jet expansion spectra, and second, the multi-temperature analysis focused on the line intensity validation.

The jet spectra were measured in the 5980 and 6090 cm^{-1} range together with reference methane lines. These were recently recorded using the comb coherence-transfer and cavity ring-down saturation spectroscopy in the same region [2]. This analysis yielded frequency accuracy on the kHz level. In the current work we used a frequency stable zerodur étalon to transfer this accuracy to the nearby ammonia lines. At the end a list of 70 lines was produced with the line positions better than 0.0005 cm^{-1} for strong lines.

The multi-temperature analysis was performed in our cryogenically cooled Herriot cell with the same ECDL source used for jet measurements in a small one wavenumber wide range. The idea was to benefit from the measurement at low temperatures where the pressure follows the saturated vapor pressure curve [3] and is thus governed by the temperature. A set of five transitions was studied in the temperature span from 140 K up to room temperature. The measured dependance allowed to check for line intensity consistency of studied lines. Further analysis is in progress to retrieve the accurate values for absolute line intensities as well.

References

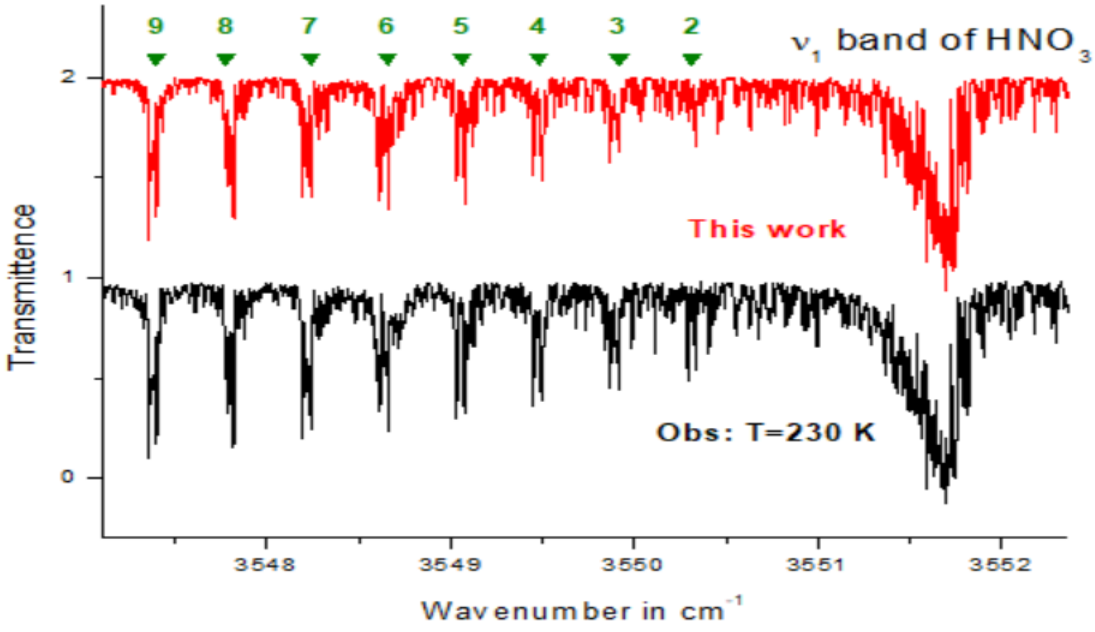
[1] P. Cacciani, *et al*, JQSRT **258**, 107334 (2021), 10.1016/j.jqsrt.2020.107334
[2] O. Votava, *et al,* PCCP 24, 4157-4173 (2022), 10.1039/d1cp04989e
[3] P. Cacciani, *et al*, J. Phys. Chem. A **123**, 3518–3534 (2019), 10.1021/acs.jpca.9b01278

First investigation of the ν_1 band of nitric acid (HNO_3) at 3551.766 cm^{-1}

A. Perrin[a,*] , L. Manceron [b,c], R.Armante [a], F. Kwabia-Tchana [d], P.Roy[b], G.C. Toon[e]

[a]*Laboratoire de Météorologie Dynamique/IPSL, UMR CNRS 8539, Ecole Polytechnique, Université Paris-Saclay, 91128 Palaiseau Cedex, France ;*
.[b] *Ligne AILES, Synchrotron SOLEIL, L'Orme des Merisiers, St-Aubin, France. ;*
[c] *Sorbonne Université, CNRS, MONARIS, UMR 8233, Paris, F-75005 France ;*
[d] *Université de Paris and Univ Paris Est Creteil, CNRS, LISA, F-75013 Paris, France ;*
[e]*Jet Propulsion Laboratory, California Institute of Technology, Pasadena California, USA*
* *agnes.perrin@lmd.ipsl.fr,*

We performed the first investigation of the ν_1 band of nitric acid ($H^{14}N^{16}O_3$) at 3551.766 cm^{-1} using high resolution Fourier transform spectra recorded in the 2.81 µm 3.23 µm and 2.5 µm spectral regions at the SOLEIL synchrotron facilities. For this highly perturbed band the analysis was very difficult because of the large value of the Doppler linewidths (~0.003 cm^{-1} HWHM in the 210K – 296K temperature range). As we can see on this figure, the 1^1 energy levels are affected by torsional splittings. The final outcome of this work is the generation of the first line by line list of the ν_1 band of nitric acid at 3551 cm^{-1} and of its first two associated hot bands ($\nu_1+\nu_9-\nu_9$ and $\nu_1+\nu_7-\nu_7$) that is presently absent in HITRAN [1] and GEISA [2].



Part of the central range of ν_1 band of HNO3. The agreement between the observed spectrum (in black) and the first linelist generated during this work (in red) is excellent.

References

[1] Gordon et al. JQSRT , **277**, https://doi.org/10.1016/j.jqsrt.2021.107949 (2022)
[2] Delahaye et al. J. Mol. Spectrosc. 380, 111510 (2021)

Recent development of the MT_CKD water vapor continuum

Eli J. Mlawer

Atmospheric and Environmental Research, Lexington MA, USA

The upcoming inclusion of the MT_CKD water vapor continuum as part of HITRAN has resulted in a substantial redevelopment of the corresponding code and data. This presentation will provide details of these modifications, along with recent significant changes in the model to the continuum absorption in the far-infrared and infrared window, as well as to the implementation of the self continuum temperature dependence. Information about potential future development will also be provided.

H_2O-CO_2 binary absorption continua in the infrared transparency windows

Hélène Fleurbaey[1], **Didier Mondelain**[1], **Jean-Michel Hartmann**[2], **Wissam Fakhardji**[2], **Alain Campargue**[1]

1. LIPhy, Univ. Grenoble Alpes, CNRS, 38204 St Martin d'Hères, France
2. LMD, ENS, CNRS, 91128 Palaiseau, France
** helene.fleurbaey@univ-grenoble-alpes.fr*

Accurate knowledge of the absorption by a gas mixture of CO_2 and water is very important for planetary sciences, as it enables a better modeling of the atmospheres of rocky planets. The absorption spectrum of such a gas mixture includes local resonant monomer lines, and binary absorption features varying more smoothly with frequency: self-continuum absorption, proportional to the squared density, and "crossed" absorption involving both species and scaling as the density product $\rho_{CO2}\rho_{H2O}$. We used highly sensitive spectroscopy techniques (CRDS and OFCEAS) to measure the absorption spectrum of H_2O+CO_2 gas mixtures in various spectral regions situated in transparency windows where the monomer absorption of both species is weak (1.5-1.53 µm, 1.68-1.75 µm, 2.06 µm, 2.2-2.35 µm, 3.5 µm). For water and CO_2, the monomer lines, modeled using HITRAN parameters, and the self-continuum absorption, calculated from literature values or measured in dedicated experiments, were subtracted from the measured absorption. The obtained "crossed binary absorption" coefficients are compared to the only available empirical model based on far wings of line shape profiles scaled by χ-factors [1]. A broad absorption peak centered at about 6000 cm^{-1} was attributed to a collision-induced simultaneous transition of H_2O and CO_2 through the ν_1 and ν_3 modes, respectively. This assignment was confirmed using humidified $^{13}CO_2$. Classical molecular dynamics simulations (CMDS) of the considered collision-induced absorption were also conducted and are found in good agreement with the experiment [2].

References

[1] Fleurbaey H, Campargue A, Carreira Mendès Da Silva Y, Grilli R, Kassi S, Mondelain D. J Quant Spectrosc Radiat Transf 282, 108119 (2022)

[2] Fleurbaey H, Mondelain D, Fakhardji W, Hartmann J-M, Campargue A. J Quant Spectrosc Radiat Transf 285, 108162 (2022)

Evaluating new settings and robustness for retrieved ammonia (NH_3) total columns from the OASIS ground-based remote sensing observatory

Pascale Chelin[1,*], **Rebecca D. Kutzner**[1,#], **Juliette Brochet**[1], **Juan Cuesta**[1], **Guillaume Siour**[1], **and Claude Camy-Peyret**[2]

1. Univ Paris Est Creteil and Université Paris Cité, CNRS, LISA, F-94010 Créteil, France
2. L'Institut Pierre-Simon Laplace (IPSL), UPMC/UVSQ, Paris, France
 # now at: LUBW, Landesanstalt für Umwelt Baden-Württemberg, Institut für Seenforschung, Argenweg 50/1, 88085 Langenargen, Germany
** pascale.chelin@lisa.ipsl.fr*

Ammonia (NH_3) is a very harmful atmospheric pollutant for ecosystems and the overall environment regarding the eutrophication and acidification of soils and water, but also a gaseous precursor of other major secondary pollutants, such as inorganic fine particles: sulphate and ammonium nitrate particles [1], which are particularly harmful to human health. Ammonia and particulate matter (PM) are responsible for severe pollution outbreaks over Île-de-France region and Europe. In France, the dominant source of atmospheric ammonia (NH_3) is attributed to agricultural activities, with contributions between 94% and 98 % [2,3].

Despite this major societal and scientific interest, ammonia is one of the least documented precursors of $PM_{2.5}$ in France which is strongly related to the crucial lack of routine ammonia observations. One of the scientific reasons comes from the difficulty to measure atmospheric (gaseous) ammonia due to its sticky, volatile, and reactive nature [4].

An innovative and very promising alternative for monitoring atmospheric ammonia is infrared remote sensing, from the ground or from space. This method is free from sampling problems and is noticeably less influenced by local sources than *in situ* observations. The first multiyear time series of atmospheric NH_3 ground-based measurements over a European megacity (Paris) was done using the moderate-cost mid-resolution Observations of the Atmosphere by Solar absorption Infrared Spectroscopy (OASIS) FTIR solar observatory located in the Paris suburbs (Créteil, France) [5]. In this paper, NH_3-OASIS retrievals were based on the scaling factor scheme using the initial MIPAS *a priori* [6] as a starting point which is then multiplied by a constant factor at each altitude to retrieve ammonia concentrations.

An alternative approach of total column concentration retrieval is the Tikhonov-Phillips (TP) method that uses user-definable height-depending constraints and provides more flexibility. We tested also another *a priori* profile (slanted) in order to investigate the impact of the *a priori* on the retrieval. Four different ammonia multiyear time series are now available. The slanted *a priori* assumes a gradual decrease in NH_3 concentrations, compared to the MIPAS that considers a vertically homogeneous NH_3 value (0.1 ppb) for the first 10 km. Using the slanted *a priori*, the representativeness of ammonia distribution is assumed to be physically more reasonable in an urban site, with higher ammonia concentrations in the atmospheric boundary layer, and then decreasing values.

Each method provides a similar seasonal cycle, and also a similar diurnal cycle by focusing on several days with high NH_3 total column concentrations during spring pollution episodes. The comparison between the FTIR measured NH_3 total columns and those from the CAMS data assimilation system [7] is showing a good consistency regarding the seasonal variability.

References

[1] J.H. Seinfeld, and Pandis, S.N., Atmospheric chemistry and physics: from air pollution to climate change, 2nd edn. John Wiley & Sons, New York (2006)

[2] J. Ringuet, J *et al*, Inventaire des émissions de polluants atmosphériques en France au titre de la convention sur la pollution atmosphérique transfontalière à longue distance et de la directive européenne relative aux plafonds d'émissions nationaux, Centre Interprofessionel Technique d'Etudes de la Pollution Atmosphérique, 2016

[3] S. Génermont *et al*, Data in Brief **21**, 1119 (2018)

[4] K. von Bobrutzki *et al*, Atmos. Meas. Tech, **3**, 91 (2010)

[5] B. Tournadre *et al*, Atmos. Meas. Tech, **13,** 3923 (2020)

[6] A.B. Burgess *et al*, Advances in Space Research, **37**, 2218 (2006)

[7] A. Inness *et al*, Atmos. Chem. Phys. **19,** 3515 (2019)

Multi-spectral ozone spectroscopy for atmospheric applications: Recent experimental results at 5 µm and 10 µm and open questions

Christof Janssen[1*], Corinne Boursier[1], Nicolas Cahuzac[1,2], Benoît Darquié[2], Hadj Elandaloussi[1], David Jacquemart[3], Pascal Jeseck[1], Dmitry Koshelew[1¶], Patrick Marie-Jeanne[1], Robin Miri[1‡], Christian Rouillé[1], Florence Thibout[4], Mélanie Vaudescal-Escudier[5†], Maxime Leuliet[1], Olivier Lopez[2], Yao Té[1] and Thomas Zanon[1]

1. LERMA-IPSL, Sorbonne Université, CNRS, Observatoire de Paris – Université PSL, 4 place Jussieu, 75252 Paris, France
2. LPL, Université Sorbonne Paris Nord, CNRS, 99 avenue JB Clément, 93430 Villetaneuse, France
3. MONARIS, Sorbonne Université, CNRS, 4 place Jussieu, 75252 Paris, France
4. LKB, Sorbonne Université, CNRS, ENS-Université PSL, Collège de France, 4 place Jussieu, 75252 Paris, France
5. INSP, Sorbonne Université, CNRS, 4 place Jussieu, 75252 Paris, France
[¶] now at Criteo, 32 rue Blanche, 75009 Paris, France
[‡] now at École Normale Supérieure de Cachan, Université de Sorbonne, 24 rue Lhomond, 75005, Paris, France
[†] now at PLACAMAT, CNRS, Univ. Bordeaux, 87 avenue Docteur Albert Schweitzer, 33600 Pessac, France
** christof.janssen@sorbonne-universite.fr*

Ozone amount of abundance measurements are strongly relying on spectroscopic techniques. Recently, the reference absorption cross section in the UV at 253.65 nm has been revised by 1.23% [1] and there has been a recent update of the HITRAN2020 database [2] taking into account new line intensities in the mid-IR from the fundamental and combination band regions at 10 µm and 5 µm, respectively.

Here, we present recently published line intensity data of FTIR measurements in these two mid-IR regions at the 1% accuracy level [3-5] as well as cross section data from the UV and VIS regions [6, 7]. We discuss in as much discrepancies [8] remain or are expected when compared to spectroscopic data from different spectral regions. We also point out how to further improve the quality of spectroscopic data in the UV and IR using new spectroscopic techniques.

References

[1] J. Hodges *et al*, Metrologia **56**, 034001 (2019)
[2] I. Gordon et al. JQSRT **277**, 107949 (2022)
[3] C. Janssen *et al*, JQSRT **279**, 108051 (2022)
[4] D. Jacquemart *et al*, JQSRT **279**, 108050 (2022)
[5] Vl. Tyuterev *et al,* JCP **150,** 184304 (2019)
[6] R. Miri *et al*, priv. communication
[7] C. Janssen *et al*, AMT **11**, 1707 (2018)
[8] Picquet-Varrault *et al*, JPC **109**, 1008 (2005)

High resolution infrared spectroscopy of Mars' and Venus' atmospheres: recent results and perspectives.

Anna Fedorova[1,*]

1. Space Research Institute RAS, 84/32 Profsoyuznaya str., Moscow 117997, Russia
** fedorova@iki.rssi.ru*

High-resolution infrared (IR) spectroscopy is a powerful tool for studying the atmosphere of terrestrial planets, especially searching for minor species. In the case of Mars and Venus, for a long time it was a prerogative of ground-based observations. Mapping of water distribution, HDO/H_2O ratio on both planets, H_2O_2 on Mars and SO_2 on Venus were included in science observations of main ground-based instruments on the Earth, like CRIRES, TEXES, SCHELL, NIRSPEC and others [1]. The first high resolution IR spectrometer SOIR onboard Venus-Express was working from 2006 to 2015 on orbit of Venus and provided information about vertical distribution of many gases in Venus' mesosphere at latitudes from 70 to 110 km as well as atmospheric density and temperature [2].

In 2016 two sets of high resolution spectrometers for remote sensing, the Atmospheric Chemistry Suite (ACS) [3] and NOMAD [4], were delivered to Mars onboard the ExoMars Trace Gas Orbiter (TGO) spacecraft. They cover the spectral range from visible to long-wavelength infrared and provide 3D spatial distribution and temporal variations of atmospheric constituents obtained from nadir and solar occultation measurements. Since the beginning of the science program on Mars in April 2018, spectrometers have provided a sensitive study of vertical structure of the Martian atmosphere by solar occultation method. Among their discoveries: the first detection of HCl and its seasonal variations in the Martian atmosphere [5], first observation of ozone in very weak IR band near 3.3 μm [6], first observation of the magnetic dipole CO_2 absorption band at 3.3 μm [7], study of carbon and oxygen isotopes in H_2O and CO_2 [8-9] and seasonal and spatial variations of HDO/H_2O ratio as a tracer of water evolution on Mars[10-11], hunting for methane and volcanic gases [12-13], study of aerosols [14-15], thermal structure and water vertical distribution in the wide range of altitudes from troposphere to thermosphere [16-18], seasonal cycles of non-condensable CO and O_2.

Last two years the focus moved to Venus and several missions were selected. The success of TGO and Venus-Express has shown that high-resolution IR spectrometers are effective tools to study the atmosphere from orbit. VenSpec-H spectrometer for EnVision (the new European mission to Venus), VIRAL (Venus InfraRed Atmospheric gases Linker) for Indian Venus Orbiter Mission, VIKA, a set of near and mid-IR spectrometers, for Venera-D will continue a study of the CO_2 atmosphere of Venus from its orbit.

References

[1] T. Encrenaz *et al*, Icarus **376**, 114885 (2022).
[2] A.-C. Vandaele *et al*, Adv. Sp. Res. **57(1)**, 443-458 (2016).
[3] O. Korablev *et al*., Space Sci.Rev. **214**, 7 (2018).
[4] A.-C. Vandaele *et al*., Space Sci.Rev. **214**, 24 (2018).
[5] O. Korablev *et al*., Sci. Adv. **7**, eabe4386 (2021).
[6] K. Olsen *et al.,* A&A **639** A141 (2020).
[7] A.Trokhimovskiy *et al.,* A&A **639**, A142 (2020).
[8] J. Alday *et al.,* A&A **630**, A91 (2019).
[9] J.Alday *et al.,* J. Geophys. Res. Planets **126**, e2021JE006992 (2021).
[10] J.Alday *et al.,* Nat Astron **5,** 943–950 (2021).
[11] G. Villanueva *et al.*, Science Advances **7(7)**, Eabc8843 (2021).
[12] F. Montmessin *et al.,* A&A **650**, A140 (2021).
[13] E. Knudsen *et al.,* Icarus **357**, 114266 (2021).
[14] G. Liuzzi *et al.*, Geophys. Res. Letters **48** (22), e95895, (2021).
[15] M. Luginin *et al.* J. Geophys. Res. Planets **125** (11), E06419 (2020).
[16] A. Fedorova *et al.* Science **367**(6475), 29 (2020).
[17] S. Aoki *et al.* J. Geophys. Res. Planets **124** (12), 3482-3497 (2019).
[18] D. Belyaev *et al.* Geophysical Research Letters **48,** e2021GL093411 (2021).

Building access and community standards for opacity data at the onset of next-generation atmosphere observations

---

Natasha Batalha[1*], Nikole Lewis[2], Katy Chubb[3], Richard Freedman[4], Ehsan Gharib-Nezhad[5], Iouli Gordon[6], Robert Hargreaves[6], Ryan MacDonald[2], Clara Sousa-Silva[6], Jonathan Tennyson[7], Jeff Valenti[8], Sergey Yurchenko[7]

1. *NASA Ames Research Center Moffett Field, CA 94035, USA*
2. *Department of Astronomy and Carl Sagan Institute, Cornell University, 122 Sciences Drive, Ithaca NY 14853 CA*
3. *Centre for Exoplanet Science, University of St Andrews, North Haugh, St Andrews, KY16 9SS, UK*
4. *SETI Institute, 339 Bernando Ave, Suite 200, Mountain View, CA 94043, USA*
5. *Bay Area Environnemental Research Institute, NASA Ames Research Park Building 18 Room 101 Moffett Field, CA 94035*
6. *Harvard Smithsonian Center for Astrophysics, Observatory Building E, 60 Garden St, Cambridge, MA 02138*
7. *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT*
8. *Space Telescope Science Institute, 3700 San Martin Dr, Baltimore, MD 21218, USA*

* *natasha.e.batalha@nasa.gov*

The characterization of a diverse set of exoplanet atmosphere observations, ranging from hot gas giants to small temperate rocky worlds, will be one of the legacies of upcoming facilities such as the James Webb Space Telescope (JWST). Our understanding and interpretation of such observations will hinge on our ability to link observations with atmospheric theoretical studies that critically rely on fundamental molecular and atomic opacities. Computing such opacities is a highly non-trivial and inaccessible process which requires several terabytes of available disk space, hours of CPU time per pressure-temperature combination, and requires users to carefully aggregate line lists data from various sources, which limits access and intercomparison of opacity data in the exoplanet community. Here we present MAESTRO (Molecules and Atoms in Exoplanet Science: Tools and Resources for Opacities) an opacity database that can be accessed by the community via a web interface and python API. MAESTRO was built with community input to create a version-controlled opacity database that is easily queryable, includes informative metadata to ensure reproducibility, and exports relevant citations for inclusion in publications. Scheduled for community release in 2022, MAESTRO will prove to be an invaluable community resource in the era of JWST and beyond.

Methane line shape parameter measurements by mid-infrared QCL dual-comb spectroscopy – first results

Muriel Lepère[1*], **Jean Clément**[1], **Bastien Vispoel**[1], **Olivier Browet**[1], **Marine Appart**[1], **Jakob Hayden**[2], **Pitt Allmendinger**[2], **Andreas Hugi**[2], **and Markus Mangold**[2]

1. *Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur, 61, Rue de Bruxelles, Namur, Belgium*
2. *IRsweep AG, Laubisrütistrasse 44, 8712 Stäfa, Switzerland*

* *muriel.lepere@unamur.be*

Accurate determination of line shape parameters has both fundamental and applied interests. It allows the understanding of inter-molecular interactions and is required for the inversion of atmospheric spectra. The state-of-the-art models have largely improved the understanding of the interactions between molecules. However, the potentials must be validated by accurate measurements. Several recent works have allowed to determine precisely the line shape parameters of a very large number of transitions thanks to the Modified Complex Robert-Bonamy (MCRB) formalism for which the potential can be validated by a limited number of accurate measurements (see for example [1]). In this way theoretical models validated by accurate measurements provide an immense amount of spectroscopic data. Elsewhere, the improvement of remote sensing mission instruments pushes the need for high accuracy spectroscopic data. The quality of the retrieved quantities from inversion methods of atmospheric spectra directly depends on the precision of the spectroscopic parameters. It has been shown that the line shape parameters are the largest sources of uncertainties in the retrieval process (see for example [2]). In view to reach the accuracy in the measurement of line shape parameters, experimental techniques must have specific characteristics such as high resolution, excellent signal-to-noise ratio, large spectral range, homogeneity in the gas mixtures.

We recently reported on the characterization of IRis-F1, our new quantum cascade laser based dual-comb spectrometer [3,4]. This table-top instrument operates in the mid-infrared (5-10 µm), with a resolution of 10^{-4} cm^{-1} on the covered range of > 50 cm^{-1}. First results putted in evidence that IRis-F1 can be used to study beyond-Voigt line shape parameters. Here, we will report on our latest measurements of N_2-pressure broadening in the ν_4 band of methane. The experimental line shape profiles were fitted using Voigt and hard-collision (Rautian-Sobel'man) profiles. Our values are compared with the available data in the literature.

References

[1] B. Vispoel, J.H. Cavalcanti, E.T. Paige, and R.R. Gamache, JQSRT **253**, 107030 (2020).
[2] J.S. Delamere, S.A. Clough, V.H. Payne, E.J. Mlawer, D.D. Turner, and R.R. Gamache, J. Geophys. Research **115** (2010).
[3] M. Lepère, O. Browet, J. Clément, B. Vispoel, P. Allmendinger, J. Hayden, F. Eigenmann, A. Hugi, and M. Mangold, JQSRT **287**, 108239 (2022).
[4] J. Hayden, O. Browet, J. Clément, B. Vispoel, P. Allmendinger, M. Mangold, and M. Lepère, ASA-HITRAN, 24-26 Sept. 2022, Reims, France.

Non-LTE Cavity Ring-Down Spectroscopy of ethylene around 1.67 µm: modelling the atmospheres of hot Jupiter exoplanets.

Solène Perot[1], **Lucile Rutkowski**[1,*], **Samir Kassi**[2] **and Robert Georges**[1,*]

1. IPR, Université de Rennes 1, UMR6251 CNRS, F-35042, France
2. LIPhy Université de Grenoble Alpes, UMR5588 CNRS, F-38041, France
** lucile.rutkowski@univ-rennes1.fr, robert.georges@univ-rennes1.fr*

The hot Jupiter exoplanets are giant gas planets orbiting very closely to their star, leading to atmospheric temperatures up to 3000 kelvins. These environments will be studied by the recently launched James Webb Space Telescope [1] and the upcoming Ariel mission [2] using infrared spectrometry. However, the quantitative analysis of the observations and the accurate modelling of the radiative properties of these atmospheres will require a major improvement of the high temperature spectroscopic databases for a series of relevant molecules. Up to now, methane [3] and acetylene [4] were already detected and the presence of other small hydrocarbons, such as ethylene (C_2H_4), is expected. Our work is therefore devoted to the high precision spectroscopy of the excited vibrational states of ethylene.

Unambiguous spectral assignment in the infrared for ethylene is only available at room temperature below 3500 cm^{-1}[5], partly due to its highly congested absorption spectrum at higher wavenumbers. The first step of this study focuses on providing accurate assignments of the ethylene cold rovibrational transitions in the 1.65-1.68 µm (5930-6070 cm^{-1}) spectral range. This region corresponds to the first overtones of the C-H stretching modes, where 160 interacting bands are expected, but only 608 lines were assigned to the $\nu_5 + \nu_9$ and $\nu_5 + \nu_{11}$ bands by Loroño Gonzalez *et al*. [6]. Our investigation is performed using a cavity ring-down spectrometer (CRDS) coupled to a supersonic slit jet, as depicted in Figure 1(a). The low temperature is obtained by expanding our gas sample contained in a high-pressure reservoir into a low-pressure chamber through an 80 mm-long and 100 µm-wide slit aperture. This process leads to a simplification of the absorption spectrum by reducing drastically the rotational temperature and by narrowing the absorption line widths. Figure 1(b) shows the cold spectrum (grey markers) that is obtained by using 20 slm of Ar buffer gas and 1 slm of C_2H_4 initially at room temperature. A translational temperature of 13 K is determined from the line widths. We recorded a second spectrum at 24 K, by injecting a larger amount of C_2H_4 (3 slm) preheated at 160°C prior to the supersonic expansion. The resulting spectrum is shown in black: hot band transitions have emerged and the ratio intensity of the two cold band transitions is reversed. This series of measurements will be later expanded towards higher vibrational temperatures using a method already applied to methane [7]. Our experimental data will be later used to validate the TheoReTS database [8] to simulate ethylene line lists at temperatures relevant to hot Jupiters.

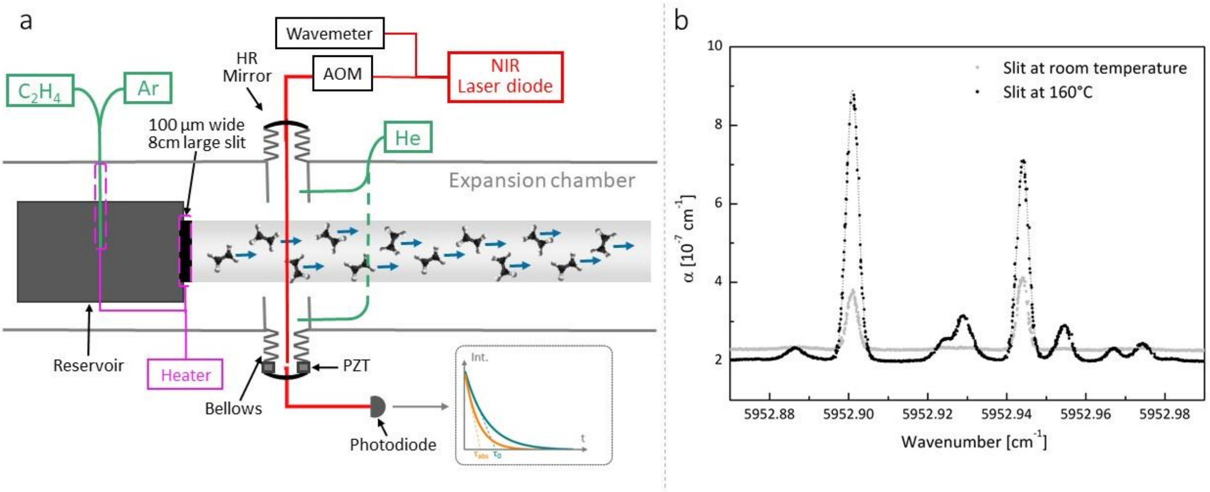


Figure 1: a) Schematic drawing of the experimental setup. b) Recorded spectra of C_2H_4 in different conditions, emphasizing hot band transitions.

References

[1] see https://wwww.jwst.nasa.gouv/
[2] Th. Encrenaz, G. Tinetti, A. Coustenis, Exp. Astron., **46**, 31-44 (2018) ; G. Tinetti *et al.,* Exp. Astron., **46**, 135-209 (2018)
[3] M. R. Swain, G. Vasisht, G. Tinetti, Nature, **463** (7281), 637-639 (2008)
[4] P. Giacobbe *et al.*, Nature, **592** (7853), 205-208 (2021)
[5] I. E. Gordon *et al.*, J. Quant. Spectrosc. Radiat. Transfer, **277**, 107949 (2022)
[6] M. A. Loroño Gonzalez *et al.*, JQRST, **111** (15), 2265-2278 (2010)
[7] E. Dudás *et al.*, J. Chem. Phys., **152**, 134201 (2020)
[8] M. Rey, A. V. Nikitin, Y. L. Babikov, and V. G. Tyuterev, J. Mol. Spectrosc., **327**, 138–158 (2016)

This work is part of the e-PYTHEAS, CECoSA and TEMMEX projects supported by the ANR.

Study of molecular absorption continua for telluric planets' atmospheres applications: calculations and measurements

---

Wissam Fakhardji[1], Ha Tran[1], Olivier Pirali[2] [3] , Christian Boulet[2], Jean-Michel Hartmann[1]

1 Laboratoire de Météorologie Dynamique/IPSL CNRS, Ecole polytechnique, Institut polytechnique de Paris, Sorbonne Université, École normale supérieure, PSL Research University, Palaiseau, F-91120, France
2 Institut des Sciences Moléculaires d'Orsay (ISMO), CNRS, Université Paris-Sud, Université Paris-Saclay, F-91405 Orsay, France.
3 AILES beamline, SOLEIL Synchrotron, L'Orme des Merisiers, Saint-Aubin, 91190, France

The development of accurate infrared spectra of H_2O, CH_4 and H_2 mixed with CO_2 is crucial for planetary sciences [1]. While the local absorptions due to the optical transitions can be relatively well predicted using parameters provided by spectroscopic databases, the continua still suffer from a lack of precision. Their role being important in the radiative budget of the atmospheres, it is necessary to accurately know them in order to constrain formation and evolution models of telluric planets' atmospheres.

A first example concerns early Mars where many evidences suggest that liquid water flowed between 4 to 2.5 billions years ago [2]. However the necessary conditions allowing the stability of liquid water are still unexplained. Among the various hypotheses that are considered, one implies an atmosphere warming initiated by the greenhouse effect in reducing atmosphere. In such conditions, collision-induced absorption (CIA) can occur for the $H_2 - CO_2$ and $CH_4 - CO_2$ pairs which are expected to absorb in the 200 – 600 cm^{-1} region.

Another example concerns the evolution of Venus which has, unlike the Earth, lost all its water [2]. It is known that during their early age, rocky planets' atmospheres were dominated by CO_2 and H_2O [3].

These only two examples show that an accurate knowledge of the infrared absorption continua in CO_2-rich atmospheres is a key to understand their evolutions. This is not limited to our solar system since, with the James Webb Space Telescope, it will be possible to directly study the atmospheres of extrasolar planets where CO_2 is abundant [4]. As part of the French ANR project COMPLEAT, we present here results for the CH_4+CO_2 CIA spectra and CO_2 -broadened H_2O far line-wings, respectively obtained from calculations and direct measurements.

The first result is computed using classical molecular dynamics simulations, which consist in modeling a gas made of 50% of CH_4 and 50% of CO_2 in a simulation box with periodic boundary conditions thanks to an accurate intermolecular potential surface [5]. The interaction-induced dipole, as expressed in [6], can then be evaluated for each dissimilar pair. The dipole autocorrelation function is evaluated at each time step which; by Fourier transform, gives the spectral density function and finally the absorption coefficient. The difference between our results and those of Turbet et al. [7] highlights the influence of the potential anisotropy as well as the need of a new accurate dipole moment surface including short-range components.

The CO_2 -broadened H_2O far line-wings are measured at room temperature in the region 1100 – 1500, 1800 – 2000 and 3100 – 3300 cm^{-1}. It is in good agreement with previous measurements [8,9] in the low frequencies part of the ν_2 band of H_2O (1100 – 1500 cm^{-1}). In addition, it confirms the quality of a previously proposed χ factor model [9] in the blue part of the ν_2 band of H_2O (1800–2000 cm^{-1}) and in the 3100 – 3300 cm^{-1} region, which are for the first time measured in this work.

References

[1] Fortney et al. 2016 (https://arxiv.org/pdf/1602.06305.pdf)
[2] R Haberle, et al., The Early Mars Climate System. Cambridge University Press; 2017, p. 497–525.
[3] LT Elkins-Tanton, et al., Earth Planet Sci Lett, 2008;271:181. doi:10.1016/j.epsl.2008.03.062
[4] M Turbet, et al., Astron Astrophys, 2018;612:A86. Doi:10.1051/0004-6361/201731620
[5] Hellmann et al. J Chem Phys 2016; 102:429–41. doi: 10.1016/j.jct.2016.07.034
[6] Li X et al. J Chem Phys 1998;109:8416–25. doi: 10.1063/1.477504
[7] Turbet et al. Icarus 2020;346:113762. doi: 10.1016/j.icarus.2020.113762
[8] Baranov, Y., 2016. J. Quant. Spectrosc. Radiat. Transf. 175, 100-106. https://doi.org/10.1016/j.jqsrt.2016.02.017.
[9] Tran, H. et al. J. Quant. Spectrosc. Radiat. Transf. 230, 75-80 https://doi.org/10.1016/j.jqsrt.2019.03.016.

Poster Session 2

First high resolution measurement and analysis of the 83.3 µm absorption of the chlorine nitrate $ClONO_2$ molecule

---

Fridolin Kwabia Tchana[1,*], **Anusanth Anantharajah**[1], **Jean-Marie Flaud**[1], **Laurent Manceron**[2,3], **Johannes Orphal**[4]

1. Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, F-75013 Paris, France
2. Ligne AILES, Synchrotron SOLEIL, L'Orme des Merisiers, St-Aubin BP48, F-91192 Gif-sur-Yvette Cedex, France
3. Sorbonne Université, CNRS, MONARIS, UMR 8233, 4 place Jussieu, F-75005 Paris, France
4. Institute of Meteorology and Climate Research (IMK), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany
** fridolin.kwabia@lisa.ipsl.fr*

Chlorine nitrate ($ClONO_2$) is a very important atmospheric "reservoir" of ClO and NO_2, destroying stratospheric ozone through catalytic cycles [1, 2]. It was detected for the first time by infrared spectroscopy [3], a detection confirmed and extended by the MIPAS [4] and the ATMOS satellite experiments [5].

Many high-resolution spectroscopic studies of $ClONO_2$ in the microwave and mid-infrared regions have been published [see Ref. 6 and references therein]. However, chlorine nitrate presents 4 fundamentals in the far-infrared region below 600 cm^{-1}, with the lowest one corresponding to the torsional mode ν_9 around 83.3 µm. Two previous studies dealt with the $\nu_9 = 1$ state of $ClONO_2$. This torsional band exhibiting at least 7 peaks has been observed at low resolution (0.3 cm^{-1}) near 120 cm^{-1} by Fleming in 1977 [7], and was reexamined at 0.06 cm^{-1} resolution by Chance and Traub in 1982 [9] but without precise determination of the band center. More recently, the analysis of the mid-infrared ν_8 and $\nu_8 + \nu_9$ band spectral regions of $^{35}ClONO_2$ allowed the indirect but accurate determination of the ν_9 band center at 123.7219 (20) [9].

In this work, the 83.3 µm region of $ClONO_2$ has been recorded at high resolution (0.001 cm^{-1}) using a Fourier transform spectrometer and the SOLEIL synchrotron light source. The spectrum corresponds to the absorption of the torsional mode, ν_9 around 123 cm^{-1} and a series of $n\nu_9$-$(n-1)\nu_9$ hot bands. In this poster, the analysis of the ν_9 bands of $^{35}ClONO_2$ and $^{37}ClONO_2$ and $2\nu_9$-ν_9 band of $^{35}ClONO_2$ will be presented. In turn, this will enable an analysis of the hot bands involving low energy levels in the mid-infrared region where $ClONO_2$ is detected and modelled.

References

[1] P. J. Crutzen, Quart. J. Royal Met. Soc. **96**, 320 (1970)
[2] M. M. Molina and F. S. Rowland, Nature **240**, 810 (1974)
[3] D. G. Murcray *et al*, Geophys. Res. Lett. **6**, 857 (1979)
[4] H. Fischer *et al*, Atmos. Chem. Phys. **8**, 2151 (2008)
[5] R. Zander *et al*, Geophys. Res. Lett. **13**, 757 (1986)
[6] J. Orphal, M. Birk, G. Wagner, and J.-M. Flaud, Chem. Phys. Lett. **690**, 82 (2017)
[7] J. W. Fleming, Infrared Phys. **18**, 791 (1978)
[8] K. V. Chance and W. A. Traub, J. Mol. Spectrosc. **95**, 306 (1982).
[9] J.-M. Flaud, W.J. Lafferty, J. Orphal, M. Birk, and G. Wagner, Mol. Phys. **101**, 1527 (2003)

Monitoring gaseous ethanol in the headspace of champagne glasses through absorption spectroscopy with an ICL infrared source

Florian Lecasse[*]**, Raphaël Vallon, Vincent Alfonso, Bertrand Parvitte, Clara Cilindre, Gérard Liger-Belair and Virginie Zeninari**

Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA), UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France
** florian.lecasse@univ-reims.fr*

Under standard tasting conditions, conveyed by the combined action of bursting bubbles and molecular diffusion through the champagne surface, gaseous species progressively invade the headspace above champagne glasses (including gas-phase CO_2, ethanol and many other volatile organic compounds) [1]. In recent years, a spectrometer based on tunable diode laser absorption spectroscopy (TDLAS) (the so-called CO_2-DLS), was developed to monitor gas-phase CO_2 in the headspace of champagne glasses [2]–[4]. Moreover, because ethanol is known to have a strong impact on wine tasting [5], micro-gas chromatography was used in the past to monitor gas-phase ethanol in the headspace of champagne glasses, but with a relatively poor temporal resolution leading to a one-minute data sampling interval [1].

Here, the idea of monitoring gas-phase ethanol with a high temporal resolution led to an update of the CO_2-DLS. Ethanol molecule is highly active in the 3µm and 9µm region with strong ro-vibrationnal transition. Nevertheless, standard soda-lime-silica tasting glasses absorb mid-infrared light above 4.5µm. Thus, the glass restricts light sources to the absorption in the 3µm region. In this spectral area, diode laser and quantum cascade laser (QCL) are less suitable [6]. Therefore, new technology laser source were used: Interband Cascade Laser (ICL), to scan few cm^{-1}, centred at 2989 cm^{-1} peak, of the ethanol broadband spectre (Figure 1). The CO_2-DLS setup was thus adapted to include the ICL in order to quantify ethanol by straightforward absorption spectroscopy.

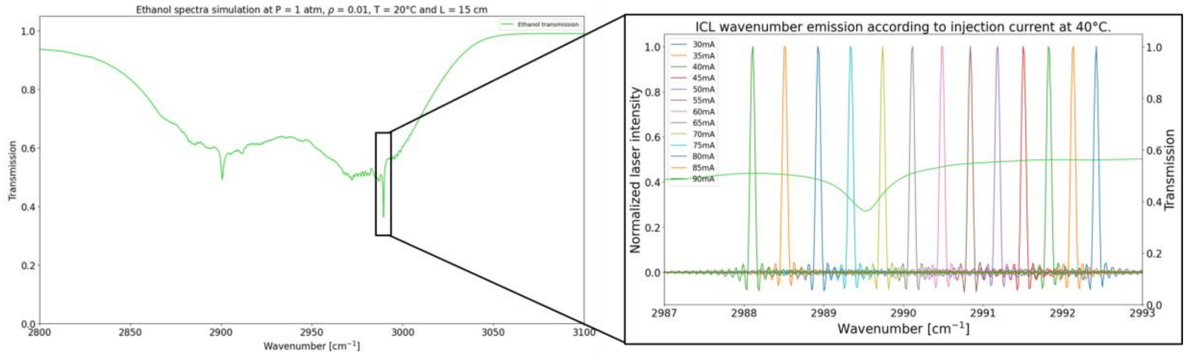


Figure 1: Ethanol spectra in transmission in the 2800-3100 cm^{-1} range and the ICL laser scanning emission around the 2989 cm^{-1} peak.

References

[1] G. Liger-Belair, M. Bourget, H. Pron, G. Polidori, and C. Cilindre, "Monitoring gaseous CO_2 and ethanol above champagne glasses: Flute versus coupe, and the role of temperature," *PLoS One*, vol. 7, no. 2, pp. 1–8, 2012, doi: 10.1371/journal.pone.0030628.

[2] A. L. Moriaux, R. Vallon, C. Cilindre, B. Parvitte, G. Liger-Belair, and V. Zeninari, "Development and validation of a diode laser sensor for gas-phase CO_2 monitoring above champagne and sparkling wines," *Sensors Actuators, B Chem.*, vol. 257, pp. 745–752, 2018, doi: 10.1016/j.snb.2017.10.165.

[3] A. L. Moriaux, R. Vallon, B. Parvitte, V. Zeninari, G. Liger-Belair, and C. Cilindre, "Monitoring gas-phase CO_2 in the headspace of champagne glasses through combined diode laser spectrometry and micro-gas chromatography analysis," *Food Chem.*, vol. 264, no. January, pp. 255–262, 2018, doi: 10.1016/j.foodchem.2018.04.094.

[4] A. L. Moriaux *et al.*, "How does gas-phase CO_2 evolve in the headspace of champagne glasses?," *J. Agric. Food Chem.*, vol. 69, no. 7, pp. 2262–2270, 2021, doi: 10.1021/acs.jafc.0c02958.

[5] R. D. Mattes and D. DiMeglio, "Ethanol perception and ingestion," *Physiol. Behav.*, vol. 72, no. 1–2, pp. 217–229, 2001, doi: 10.1016/S0031-9384(00)00397-8.

[6] B. d'Humières, É. Margoto, and Y. Fazilleau, "Cascade laser applications: trends and challenges," *Nov. In-pl. Semicond. Lasers XV*, vol. 9767, p. 97671U, 2016, doi: 10.1117/12.2212568.

P2-3

An infrared laser sensor to monitor gas-phase CO_2 in the headspace of champagne glasses under swirling conditions

Florian Lecasse[*]**, Raphaël Vallon, Anne-Laure Moriaux, Bertrand Parvitte, Clara Cilindre, Gérard Liger-Belair and Virginie Zeninari**

Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA), UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France

** florian.lecasse@univ-reims.fr*

Under standard tasting conditions, smelling the headspace of a glass is indeed one of the key step in order to experience the complexity and expression of still and sparkling wines [1]. During champagne and sparkling wine tasting, ascending and bursting bubbles convey gas-phase CO_2 and many volatile organic compounds in the headspace above the wine surface, thus progressively modifying the chemical space perceived by tasters [2]. In recent years, a tunable diode laser spectrometer (the so-called CO_2-DLS) was developed to monitor gas-phase CO_2 in the headspace of champagne glasses under static condition [3,4].

Nevertheless, it is worth nothing that enologists, sommeliers, and most of experienced tasters are commonly used to swirl their glass with the aim of increasing flavor release. Therefore, as the consequences of wine swirling are barely known on the chemical space perceived by champagne tasters, the CO_2-DLS was recently upgraded with the aim of monitoring gas-phase CO_2 in the headspace of champagne glasses under swirling conditions. The experimental setup was thus divided into two distinct parts. The first part is a convoluted tunable diode laser absorption spectroscopy (TDLAS) made of three laser sources designed to quickly switch the output beam laser into a single mode optical fiber (Figure 1a). The carbon dioxide sensing is carried out by two antimonide laser diode at 4985.93 cm^{-1} and 3728.41 cm^{-1} to reach two ranges of concentrations. The second part is a homemade optomechanical orbital shaker developed to replicate the human motion of wine swirling (Figure 1b). A structure surrounding the glass was designed to correctly hold the laser beam position immobile during the glass swirling.

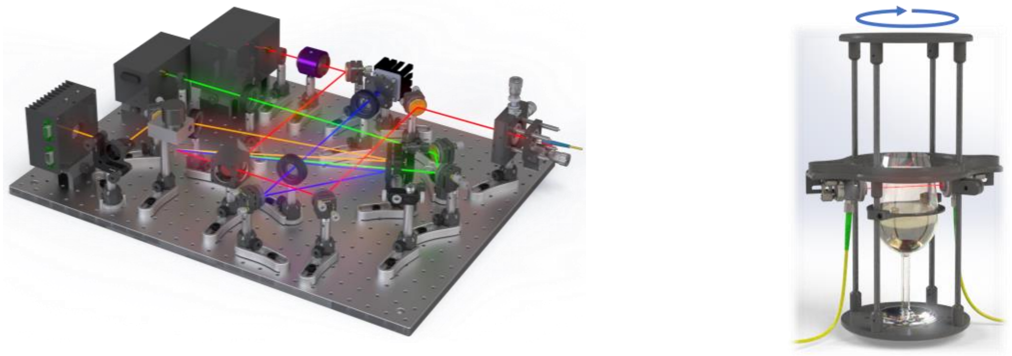


Figure 1 : Computer-aided design of the experimental setup, with the first part used to shape and guide the laser beams into an optical fiber (a), and the homemade device used to direct the laser beam through the glass headspace under rotation (b).

References

[1] C. Spence, "Just how much of what we taste derives from the sense of smell?," *Flavour*, vol. 4, no. 1, pp. 1–10, 2015, doi: 10.1186/s13411-015-0040-2.

[2] G. Liger-Belair, M. Bourget, H. Pron, G. Polidori, and C. Cilindre, "Monitoring gaseous CO_2 and ethanol above champagne glasses: Flute versus coupe, and the role of temperature," *PLoS One*, vol. 7, no. 2, pp. 1–8, 2012, doi: 10.1371/journal.pone.0030628.

[3] A. L. Moriaux, R. Vallon, C. Cilindre, B. Parvitte, G. Liger-Belair, and V. Zeninari, "Development and validation of a diode laser sensor for gas-phase CO_2 monitoring above champagne and sparkling wines," *Sensors Actuators, B Chem.*, vol. 257, pp. 745–752, 2018, doi: 10.1016/j.snb.2017.10.165.

[4] A. L. Moriaux *et al.*, "How does gas-phase CO_2 evolve in the headspace of champagne glasses?," *J. Agric. Food Chem.*, vol. 69, no. 7, pp. 2262–2270, 2021, doi: 10.1021/acs.jafc.0c02958.

P2-4

Highly accurate HF dimer ab initio potential energy surface.

Roman I. Ovsyannikov[1], **Vladimir Yu. Makhnev**[1], **Nikolai F. Zobov**[1], **Jonathan Tennyson**[2], **and Oleg L. Polyansky**[1,2*]

[1]*Institute of Applied Physics, Russian Academy of Science, Uljanov Street 46, Nizhny Novgorod, Russia, 603950*

[2]*Department of Physics and Astronomy, University College London, London, WC1E 6BT, United Kingdom*
**o.polyansky@ucl.ac.uk*

Ab initio calculations of the HF dimer tunneling-rotation-vibration spectrum have been performed [1] using variational nuclear motion program WAVR4 [2] and a full-dimensional HF dimer *ab initio* PES These calculations used some 152 000 points at CCSD(T) level of theory with a F12QZ basis set and all the major corrections, such as the higher correlation CCSDT(Q) correction, core-valence correction, as well as DBOC and relativistic correction. These corrections were calculated on a reduced grid of only 2000 points. The use of exact kinetic energy, variational nuclear motion program WAVR4 to solve the rotation-vibration-tunneling Schrodinger equation facilitated the comparison of all parameters measured for the HF dimer with *ab initio* calculated ones using the PES of Huang [3] and the our ones. Calculations over an extended range of rotationally excited states show very good agreement with the experimental data. In particular, the known empirical rotational constants B [4] for the ground vibrational states are predicted to better than about 2 MHz. B constants for excited vibrational states are reproduced several times more accurately than by the best previous calculations [3]. This level of accuracy is shown to extend to higher excited inter-molecular vibrational states v and higher excited rotational quantum numbers (J, K_a). Our calculated dissociation energy (D_0) is about 3.8 cm^{-1} above the observed value [5]. Attempts to further improve agreement will require full convergence of the zero point energy calculations independent of the particular PES used. The study of weakly bound molecular complexes with hydrogen bonds and Van der Waals bonding accounts for a large sub-branch of molecular spectroscopy. Intermolecular states with ($J, K>1$) of arguably the most important one -- $(H_2O)_2$ -- currently cannot be characterized by high resolution experiments [6]. As a consequence of the similarities of $(H_2O)_2$ to $(HF)_2$, the discrepancies in the HF dimer calculations provide a unique means of characterizing the corresponding discrepancies in calculated water dimer spectra. Hence, a high level *ab initio* model for the rotation-vibration-inversion (RVI) spectrum of the HF dimer is an important aid in constructing a similarly accurate model for the RVI spectrum of the water dimer.

References:

[1] Ovsyannikov, R. I., Makhnev, V. Y., Zobov, N. F., Koput, J., Tennyson, J., & Polyansky, O. L. (2022). Highly accurate HF dimer ab initio potential energy surface. The Journal of Chemical Physics, 156(16), 164305.

[2] Kozin, I. N., Law, M. M., Tennyson, J., & Hutson, J. M. (2004). New vibration–rotation code for tetraatomic molecules exhibiting wide-amplitude motion: WAVR4. *Computer physics communications*, *163*(2), 117-131.

[3] Huang, J., Yang, D., Zhou, Y., & Xie, D. (2019). A new full-dimensional ab initio intermolecular potential energy surface and vibrational states for (HF) 2 and (DF) 2. The Journal of chemical physics, 150(15), 154302.

[4] Polyansky, O. L., Ovsyannikov, R. I., Tennyson, J., Belov, S. P., Tretyakov, M. Yu., Makhnev, V. Yu., & Zobov, N. F. (2021). Variational analysis of HF dimer tunneling rotational spectra using an ab initio potential energy surface. Journal of Molecular Spectroscopy, 111481.

[5] Bohac, E. J., Marshall, M. D., & Miller, R. E. (1992). Initial state effects in the vibrational predissociation of hydrogen fluoride dimer. The Journal of chemical physics, 96(9), 6681-6695.

[6] Mukhopadhyay, A., Cole, W. T., & Saykally, R. J. (2015). The water dimer I: Experimental characterization. Chemical Physics Letters, 633, 13-26.

Ozone formation in ternary collisions: Theory and experiment reconciled

Marjan Mirahmadi[1], Jesús Pérez-Ríos[1,2], Oleg Egorov[3], Vladimir Tyuterev[3,4], and Viatcheslav Kokoouline[5]

[1] *Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany*
[2] *Department of Physics, Stony Brook University, Stony Brook, New York 11794, USA*
[3] *Quamer Laboratory, Tomsk State University, Tomsk, Russia*
[4]*Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France*
[5]*Department of Physics, University of Central Florida, Florida, USA*

Understanding ozone formation and further ozone-based reactions is crucial to control Earth's atmospheric dynamics and climate change. The present study shows that the formation of ozone in ternary collisions $O+O_2+M$ - the primary mechanism of ozone formation in the stratosphere - at temperatures below 200 K (for M=Ar) proceeds through a formation of a temporary complex MO_2, while at temperatures above 700 K, the reaction proceeds mainly through a formation of long-lived vibrational resonances of O_3. The present theoretical approach combines original *ab initio* potential energy surface (PES) of the ArO_3 system, obtained in this study, and the classical-trajectory method in hyperspherical coordinates [1]. At intermediate temperatures 200-700 K, the process cannot be viewed as a two-step mechanism, often used to simplify and approximate collisions of three atoms/molecules. The developed theoretical approach is applied to the reaction $O+O_2+Ar$ because of extensive experimental data available. The rate coeffcients for the formation of O_3 in ternary collisions $O+O_2+Ar$ without using two-steps approximations were computed as a function of collision energy. Thermally-averaged coeffcients were derived for temperatures 5-900 K. It is found that the majority of O_3 molecules formed initially are weakly bound. These results show for a first time a remarkable agreement [1] with the experimental data for temperatures 100-900K accounting for the process of vibrational quenching of the nascent population.

References

[1] M. Mirahmadi, J.Pérez-Ríos, O.Egorov, V.Tyuterev, V.Kokoouline, Phys.Rev.Letters **128**, 108501 (2022).
DOI: 10.1103/PhysRevLett.128.108501

P2-6

Variational calculation for COH_2 , C_2H_2 , and C_2H_6 molecules based on *ab initio* potential energy and dipole moment surfaces

Andrei Nikitin[1], Michael Rey[2], Alexander Protasevich[1], Oleg Egorov[1], Alena Rodina[1], Attila Tajti[3], Dominika Viglaska[2] and Vladimir Tyuterev[1, 2]

[1]*Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS 1, Akademician Zuev Sq., Tomsk, 634055 Russia*
[2]*Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France*
[3] *ELTE, Eötvös Loránd University, Institute of Chemistry, Laboratory of Theoretical Chemistry, P. O. Box 32, H-1518, Budapest 112, Hungary*

High-accuracy potential energy surfaces (PESs) (for example [1, 2, 3, …], and references therein) have been used in the past to extend analyses of experimental spectra and to improve line lists for various databases [4,5]. In this work, we report calculations using our PESs built for the formaldehyde [6] and acetylene molecules as well as comparisons of ro-vibrational energies with empirical values and other theoretical data for COH_2 [7] and C_2H_2 [8]. Analytical representation of the PESs and the dipole moment surfaces for both molecules will be discussed. Rovibrational spectra of four isotopologues $^{12}C^{16}OH_2$, $^{13}C^{16}OH_2$, $^{12}C^{18}OH_2$, $^{12}C^{16}OD_2$ are calculated and compared with experimental PNNL database. Recent progress in ab initio PES calculations for ethane molecule C_2H_6 is discussed. These data will be included in the database of our TheoReTS project [9] devoted to development of complete theoretical line lists for polyatomic molecules.

This work was supported by the project Russian Scientific Foundation (RSF, No. 22-42-09022) and Agence Nationale de la Recherche (ANR, French National Research Agency, Grant No. 21-CE30-0053-01)

References

1. E.Conway, I.Gordon, J.Tennyson, O.Polyansky, S.Yurchenko, K.Chance, ACP **20,** 10015 (2020). https://doi.org/10.5194/acp-20-10015-2020
2. A.Nikitin, M. Rey, V. Tyuterev, JCP **145**, 114309 (2016). https://doi.org/10.1063/1.4961973
3. H.Huang, Schwenke, T. Lee, ACR. **54**, 6, 1311 (2021) https://doi.org/10.1021/acs.accounts.0c00624Gordon
4. I. Gordon, L. Rothman, R. Hargreaves, et al., JQSRT **277**, 107949 (2022). https://doi.org/10.1016/j.jqsrt.2021.107949
5. R.Hargreaves, I.Gordon, M. Rey, A.Nikitin, V.Tyuterev, R.Kochanov, L.Rothman, APJ Suppl. Series, **247**, 55 (2020). https://doi.org/10.3847/1538-4365/ab7a1a
6. A.Nikitin, A.Protasevich, A. Rodina, M. Rey, A.Tajti, V.Tyuterev, JQSRT **260**, 107478 (2021) https://doi.org/10.1016/j.jqsrt.2020.107478
7. A. Yachmenev, S. Yurchenko, P. Jensen , W. Thiel JCP **134**, 244307 (2011). https://doi.org/10.1063/1.3599927
8. K.Chubb, A.Yachmenev, J. Tennyson, S.Yurchenko, JCP **149**, 014101 (2018). https://doi.org/10.1063/1.5031844
9. M.Rey, A.Nikitin, Y.Babikov, V.Tyuterev, JMS **327**, 138 (2016). https://doi.org/10.1016/j.jms.2016.04.006

P2-7

The 5.8 µm absorption bands for nitric acid ($H^{14}N^{16}O_3$): line positions and intensities for the ν_2 band at 1709.567 cm^{-1} and for its first associated hot bands ($\nu_2+\nu_9-\nu_9$, $\nu_2+\nu_7-\nu_7$, $\nu_2+\nu_6-\nu_6$).

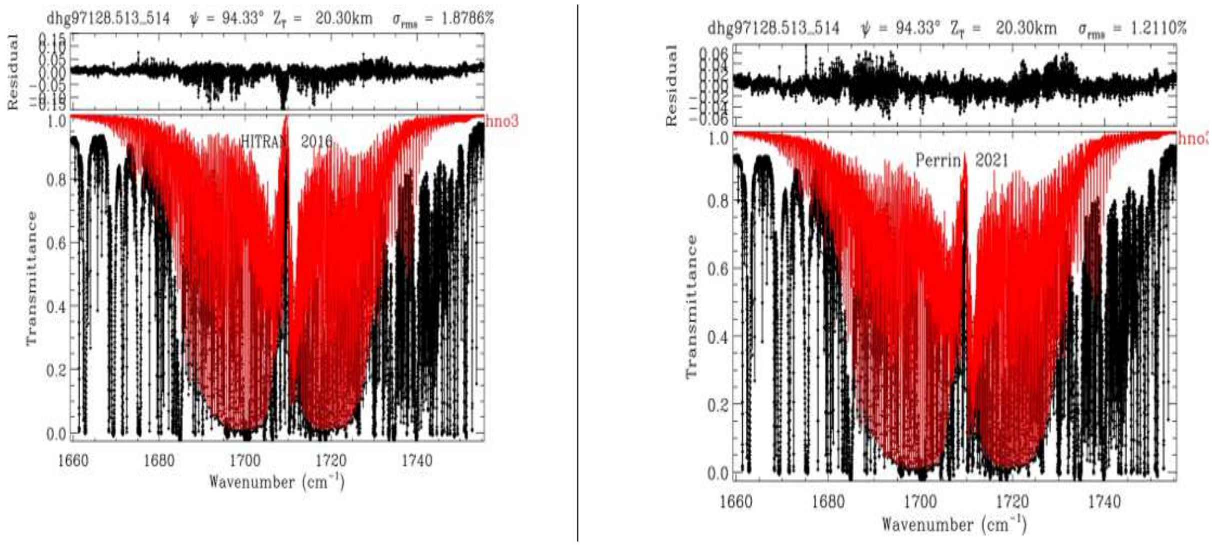
A. Perrin[a,*] , L. Manceron [b,c], R.Armante [a], F. Kwabia-Tchana [d], P.Roy[b,] G.C. Toon[e]

[a] *Laboratoire de Météorologie Dynamique/IPSL, UMR CNRS 8539, Ecole Polytechnique, Université Paris-Saclay, 91128 Palaiseau Cedex, France ;*
.[b] *Ligne AILES, Synchrotron SOLEIL, L'Orme des Merisiers, St-Aubin, France. ;*
[c] *Sorbonne Université, CNRS, MONARIS, UMR 8233, Paris, F-75005 France ;*
[d] *Université de Paris and Univ Paris Est Creteil, CNRS, LISA, F-75013 Paris, France ;*
[e] *Jet Propulsion Laboratory, California Institute of Technology, Pasadena California, USA*
* *agnes.perrin@lmd.ipsl.fr,*

The goal of this work [1,2] was to generate a more accurate linelist for the 5.8 µm absorption band of HNO_3 that includes, for the first time, lines from both the ν_2 band together with those of the $\nu_2+\nu_9-\nu_9$, $\nu_2+\nu_6-\nu_6$, and $\nu_2+\nu_7-\nu_7$ associated hot bands. For this task, high resolution Fourier transform spectra were recorded in the 5.8 µm and in the 4.2 – 4.6 µm spectral ranges.

The first study is devoted to the generation of first linelists for the $\nu_2+\nu_9-\nu_9$, $\nu_2+\nu_7-\nu_7$, and $\nu_2+\nu_6-\nu_6$ hot bands in the 5.8 µm region. Surprisingly, both $\nu_2+\nu_9$ and $\nu_2+\nu_9-\nu_9$ bands exhibit large amplitude torsional splittings of ~0.043 cm^{-1}.

The second study concerned the positions and intensities for the ν_2 band centered at 1709.567 cm^{-1}. It appears that, although the ν_2 band is mainly of B-type, it also possesses a (very) weak A-type component that cannot be ignored. Overall, the line intensities in this new database are about 8% weaker than those quoted presently in the HITRAN (https://hitran.org/) or GEISA (https://geisa.aeris-data.fr/) databases.



Example of a spectral fit to a MkIV balloon spectrum using the HITRAN 2016 HNO3 linelist (left panel) and the present work (right panel). Black diamonds represent the measured spectrum, the black line the fitted calculation, and the red lines the contribution of HNO3. The upper panels display the residuals (Obs-Calc.); note the scale change between left and right residuals. The differences between the left- and right-hand panels are entirely attributable to HNO3 spectroscopy changes.

References

[1] Perrin, Manceron, Armante, Kwabia-Tchana, Roy, Doizi, & Toon., Molecular Physics, 376, 111394, https://doi.org/10.1080/00268976.2021.1987543 (2021).
[2] Perrin et al. Molecular Physics, https://doi.org/10.1080/00268976.2021.1998931 (2021)
[3] Gordon et al. HITRAN HITRAN (https://hitran.org/) JQSRT , 277, https://doi.org/10.1016/j.jqsrt.2021.107949 (2022)
[4] Delahaye et al. J. Mol. Spectrosc. 380, 111510 (2021)

P2-8

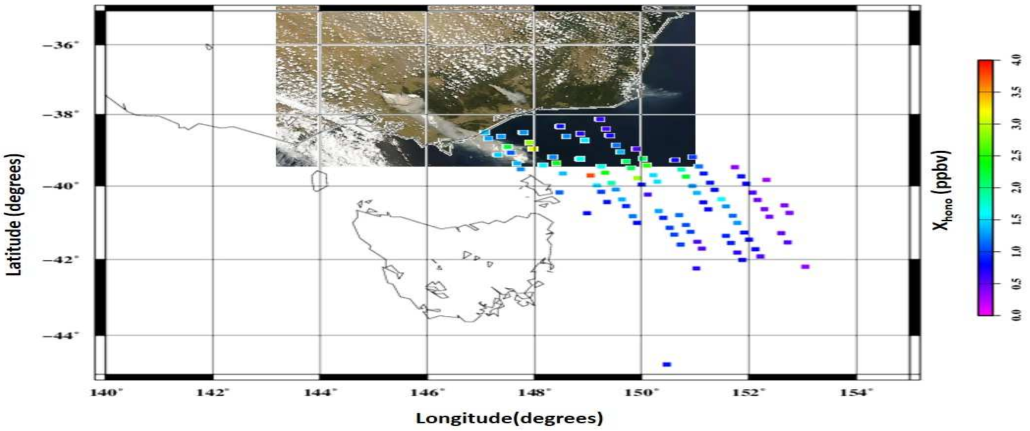
The ν_4 bands at 11 µm: linelists for the Trans- and Cis- conformer forms of nitrous acid, (HONO), in the 2019 version of the GEISA database

---

R.Armante [a], A. Perrin[a,*] , L. Manceron [b,c], F. Kwabia-Tchana [d],

[a]*Laboratoire de Météorologie Dynamique/IPSL, UMR CNRS 8539, Ecole Polytechnique, Université Paris-Saclay, 91128 Palaiseau Cedex, France ;*
.[b] *Ligne AILES, Synchrotron SOLEIL, L'Orme des Merisiers, St-Aubin, France. ;*
[c] *Sorbonne Université, CNRS, MONARIS, UMR 8233, Paris, F-75005 France ;*
[d] *Université de Paris and Univ Paris Est Creteil, CNRS, LISA, F-75013 Paris, France ;*
[e]*Jet Propulsion Laboratory, California Institute of Technology, Pasadena California, USA*
* *agnes.perrin@lmd.ipsl.fr,*

Using line positions and line intensities parameters existing in the literature for the Trans- and Cis conformer forms of nitrous acid (HONO), we generated for the first time a linelist of positions, intensities, and line shape parameters for the ν_4 bands of nitrous acid located at 790.117 cm^{-1} and 851.943 cm^{-1} for the Trans- and Cis- conformers, respectively [1]. A validation of this linelist was performed using spectra recorded by the IASI (Interféromètre Atmosphérique de Sondage Infrarouge) satellite instrument in February 2009 during the (rather) exceptional conditions of the large Australian bush fires. This list, which is now included in the 2020 version of the GEISA database [2] of potential interest for the *IASI-NG* (Infrared Atmospheric Sounding Interferometer - New Generation) instrument which will be launched on board the METOP-SG satellite in 2021.



True color imagery from the US MODIS Aqua satellite passes around 04 UTC (7 February, 3 PM EDT) on Saturday 7 February 2009 showing the smoke plumes from fires, (Image courtesy of MODIS Rapid Response Project at NASA/GSFC). The X_{HONO} inversions points (colored squares) performed for the IASI instrument (9:30 PM) on the same day, are over plotted in the range 0 to 4 ppbv and for a zone in latitude and longitude over the south of Australia and the Tasmania island.

References

[1] Armante, Perrin, Kwabia-Tchana, Manceron Molecular Physics, https://doi.org/10.1080/00268976.2021.1951860 (2021)

[2] Delahaye et al. J. Mol. Spectrosc. 380, 111510 (2021)

[3] Gordon et al. JQSRT , **277**, https://doi.org/10.1016/j.jqsrt.2021.107949 (2022)

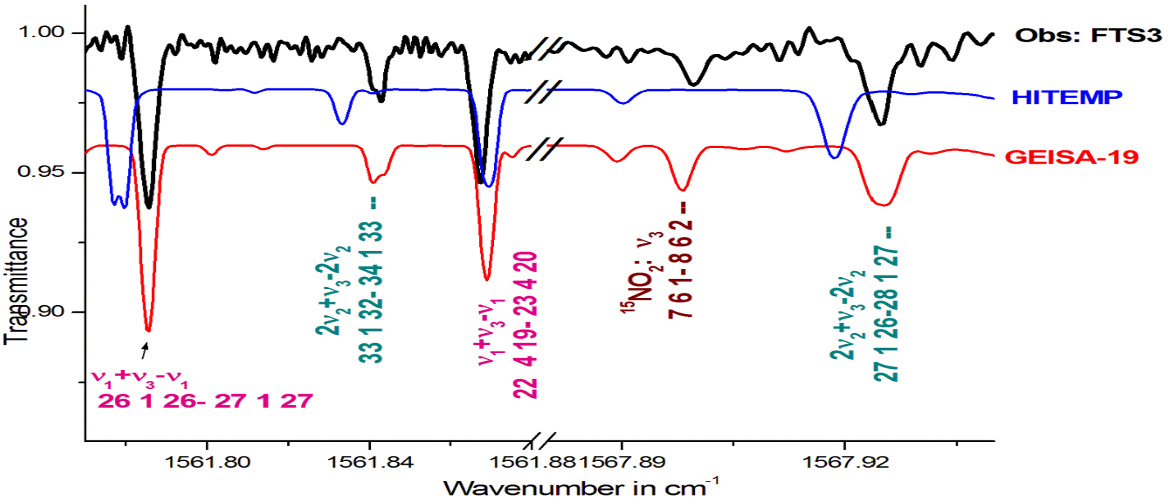
P2-9

The new NO_2 linelist in the GEISA database

A. Perrin[a,*] , L. Manceron [b,c], R.Armante [a], F. Kwabia-Tchana [d], P.Roy[b,] , D.Doizi[f]

[a]*Laboratoire de Météorologie Dynamique/IPSL, UMR CNRS 8539, Ecole Polytechnique, Université Paris-Saclay, 91128 Palaiseau Cedex, France ;*
.[b] *Ligne AILES, Synchrotron SOLEIL, L'Orme des Merisiers, St-Aubin, France. ;*
[c] *Sorbonne Université, CNRS, MONARIS, UMR 8233, Paris, F-75005 France ;*
[d] *Université de Paris and Univ Paris Est Creteil, CNRS, LISA, F-75013 Paris, France ;*
Université Paris-Saclay, CEA, Service d'Etude du Comportement des Radionucléides, 91191, Gif-sur-Yvette, France
* *agnes.perrin@lmd.ipsl.fr,*

We have generated new lists of line position, line intensity and line shape parameters of nitrogen dioxide ($^{14}N^{16}O_2$ and $^{15}N^{16}O_2$) [1], here labeled as "GEISA-19", which have been included in the) GEISA database [2]. Except for the far infrared and the 13.3 µm regions, all spectral regions of the 1153- 4775 cm^{-1} spectral domain are significantly modified by this major update of the GEISA linelist. For the 6.2 µm and 3.4 µm spectral regions, which correspond to the strongest absorption of NO_2, we proceed to a complete replacement of the lists for the first hot bands, $\nu_2 + \nu_3 - \nu_2$ and $\nu_1 + \nu_2 + \nu_3 - \nu_2$, respectively, and to the inclusion, whenever possible, of higher order hot bands involving the (1,0,0), (0,2,0) and (0,0,1), (1,1,0), (2,0,0) or (0,0,2) states as lower states. Also, the $\nu_1 + \nu_3$ linelist was improved for high rotational quantum numbers and the ν_3 and $\nu_1 + \nu_3$ bands for $^{15}N^{16}O_2$, which is the second most abundant isotopologue of NO_2, are now included in the database. Finally several weak cold bands in the 2.2 to 4.9 µm region were added for the first time to the GEISA linelist. These new vibration rotation transitions were generated using existing literature data or making use of experimental data extracted from high resolution Fourier transform spectra recorded at SOLEIL for the purpose of this study. The validation of this new NO_2 linelist was performed through a detailed comparison at 296K between computed and observed Fourier transform laboratory spectra. Finally inter-comparisons and verifications were performed using the recent versions of the HITRAN [3] and HITEMP databases [4]. Our conclusions are that, at 296K, GEISA-19 is of better quality than HITRAN2016-updated or HITEMP in the overall 1153- 4775 cm^{-1} spectral region. However, contrary to HITEMP, GEISA-19 which does not include transitions involving high rotational quantum numbers or belonging to very high order hot bands cannot be used for hot temperature conditions.



References

[1] Perrin, Manceron, Armante, Kwabia-Tchana, Roy, Doizi, J. Mol. Spectrosc. 376, 111394, (2021).
[2] Delahaye et al. J. Mol. Spectrosc. 380, 111510 (2021)
[3] Gordon et al. JQSRT , **277**, https://doi.org/10.1016/j.jqsrt.2021.107949 (2022)
[5] Hargreaves et al. JQSRT **232** 35 (2019)].

P2-10

Solar occultations observed by VIMS-IR: What haze and methane profiles reveal about Titan's atmospheric dynamics and climate.

Pascal Rannou (1,*), Maélie Coutelier (1,2), Sébastien Lebonnois (3), Luca Maltagliati (4), Emmanuel Rivière (1) , Michaël Rey (1) and Sandrine Vinatier (6)

1. *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France*
2. *LATMOS, Université Paris-Saclay, UVSQ, CNRS, 78280 GUYANCOURT, FRANCE*
3. *Laboratoire de Météorologie Dynamique, IPSL, Sorbonne Université, 75005, PARIS, FRANCE*
4. *Nature Astronomy, Springer Nature, 4 Crinan Street, N1 9XW LONDON, UNITED KINGDOM*
5. *LESIA, Observatoire de Paris, CNRS, 5 place Jules Janssen, 92195 MEUDON, FRANCE*

* *pascal.rannou@univ-reims.fr*

Titan, the largest satellite of Saturn, has a dense atmosphere mainly composed of nitrogen and methane at a percent level. These two molecules generate a complex prebiotic chemistry, a global haze, most of the cloud cover and the rainfalls which model the landscape. Methane sources are located in liquid reservoirs at and below the surface and it sink is the photodissociation at high altitude. Titan's present and past climates strongly depend on the connection between the surface sources and the atmosphere upper layers. The observations made by the Cassini orbiter and the Huygens probe have greatly improved our knowledge of Titan's system. However, some compounds of its climatic cycle remain poorly known. This is clearly the case of the methane cycle.

We reanalysed four solar occultations by Titan's atmosphere observed with the infrared part of the Visual Infrared Mapping Spectrometer (VIMS) instrument. These observations were already analysed [1,2], but here we use significantly improved methane spectroscopic data [3].

We find that the methane mixing ratio in the stratosphere is much lower (about 1.1%) than expected from Huygens measurements (about 1.4 to 1.5%). However, this is consistent with previous results obtained with CIRS. Features in the methane vertical profiles clearly demonstrate that there are interactions between the methane distribution and the atmosphere circulation. We find a layer rich in methane at 165 km and at 70°S (mixing ratio 1.45 ± 0.1%) and a dryer background stratosphere (1.1 − 1.2%). In absence of local production, this reveals an intrusion of methane transported into the stratosphere, probably by convective circulation. On the other hand, methane transport through the tropopause at global scale appears quite inhibited. Leaking through the tropopause is an important bottleneck of Titan's methane cycle at all timescales. As such, it affects the long term evolution of Titan atmosphere and the exchange fluxes with the surface and subsurface reservoirs in a complex way. We also retrieved the haze extinction profiles and the haze spectral behaviour that reveal noticeable changes in their size distribution with altitude and time.

We conclude that, to fully understand these results, Global Climate Models accounting for haze and cloud physics, thermodynamical feedbacks and convection are needed. Especially, the humidificaton of the stratosphere, at the present time and its evolution under changing conditions at geological timescale appears as a key process, and our work provide strong constraints to guide studies.

References

[1] Bellucci, A., Sicardy, B., Drossart, P., et al. 2009, Icarus, 201, 198
[2] Maltagliati, L., Bézard, B., Vinatier, S., et al. 2015, Icarus, 248, 1
[3] Rey, M., Nikitin, A., Bézard, B., et al. 2018, Icarus, 303, 114

P2-11

High-level *ab initio* calculations for the study of molecules with one large-amplitude motion: new spectroscopic line lists of NH_3, CH_3, and CH_2

Oleg Egorov[1,2], Michaël Rey[3], Andrei V. Nikitin[1,2], Dominika Viglaska[3]

1. Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS, 1, Academician Zuev square, Tomsk 634021, Russia

2. Faculty of Physics, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia

3. Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France

**oleg.egorov@iao.ru, michael.rey@univ-reims.fr, avn@iao.ru, dominika.viglaska@univ-reims.fr*

In this poster we present the results of a theoretical study of molecules exhibiting one large-amplitude motion by combining high-level *ab initio* calculations-as implemented in the MOLPRO, MRCC and CFOUR packages-to construct potential energy (PESs) and dipole moment surfaces (DMSs) with a hybrid nonrigid Hamiltonian model based on the Hougen–Bunker–Johns formalism for nuclear motion variational calculations.

The correlation energy was calculated by the single-reference coupled cluster methods including the excitations up to the pentuple level [CCSDTQP]. The convergence with respect to the orbital basis set size of CCSD(T) was analyzed employing the largest Dunning's *aug*mented *c*orrelation-*c*onsistent orbital basis sets of the *sextuple*-ζ *v*alence quality with the *c*ore-valence electron correlation [aug-cc-pCV6Z]. Moreover, the explicitly-correlated F12x{x=a, b} versions of CCSD(T) was additionally tested with the cc-pCVQZ-F12 basis set. The contributions due to Douglas-Kroll-Hess scalar relativistic Hamiltonian and diabatic Born-Oppenheimer corrections have been included to the PESs. Finally, the band origins of NH_3, CH_3, and CH_2 were predicted for the first time with a root-mean-square deviation of 0.5 cm^{-1} or lower from the developed "pure" *ab initio* PESs. New spectroscopic *ab initio* line lists for NH_3 and CH_3 will be presented.

This work is supported by the joint "TEMMEX" project between the Russian Scientific Foundation (RSF, No. 22-42-09022) and Agence Nationale de la Recherche (ANR, French National Research Agency, Grant No. 21-CE30-0053-01).

P2-12

Novel methodology for systematically constructing effective *ab initio*-based Hamiltonian and dipole moment operators

Michaël Rey[1]

1. Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France
michael.rey@univ-reims.fr

Precise knowledge of high-energy molecular states and absorption spectra is of primary importance because it gives access to the determination of the physical properties of various planetary object and clearly demonstrates the necessity of having consistent line-by-line molecular databases (e.g. like HITRAN or GEISA for the modelling of the Earth's atmosphere). The interpretation of strong spectral features requires the use of sophisticated and robust theoretical models (i) for an accurate quantum-mechanical description of highly excited molecular states and (ii) for the prediction of line intensities for reliable opacity calculations. Although empirical effective Hamiltonians have greatly contributed to the "golden age" of the high-resolution molecular spectroscopy, extensive first-principles quantum mechanical calculations are generally preferred for planetary and astrophysical applications because of their completeness.

The first necessary ingredient in variational calculations is the construction of accurate intra-molecular potential energy and dipole moment surfaces in a large range of nuclear displacements. The second one lies in the development of efficient computational methods for solving the Schrödinger equation. New symmetry-adapted contracted basis functions will be presented for solving the nuclear motion equation, even for large molecules.

Starting from selected variational eigenpairs, a novel methodology will be presented for the construction of “global” *ab initio* effective rotation-vibration spectroscopic models. The current researches in the study of various planetary atmospheres require knowledge of increasingly complex molecular systems over wide wavenumber and temperature ranges. Unfortunately, the empirical models are beginning to reach their limits for studying molecules with complex rovibrational energy-level structures and for which the successive polyads contain many vibrational bands and numerous degeneracies and quasi-degeneracies. Modelling of the « dark states » which are not directly observable is one of the major obstacles in the empirical effective approach. The model we propose turns out to be a clear alternative to the rather involved Van Vleck perturbation method. We will see how to transform first-principles calculations into a set of spectroscopic parameters to be further refined on experiment. It is demonstrated that crucial information is provided within a very short time compared to more traditional spectroscopic models (*few hours, days or weeks against few months, years or decades*). Undoubtedly, the proposed approach brings a new insight into high-resolution spectra analysis and will be of great help, not only in current or future infrared spectra analyses of polyatomic molecules but also in the modelling of hot atmospheres for which completeness is crucial.

P2-13

Measurements of H_2O line parameters and self-continuum in the spectral range 700 – 2000 cm^{-1} (ν_2 + atmospheric window)

Christian Röske[1,*], **Manfred Birk**[1], **Georg Wagner**[1]

1. German Aerospace Center (DLR), Remote Sensing Technology Institute, Oberpfaffenhofen, Münchner Str. 20, 82234 Weßling, Germany
** christian.roeske@dlr.de*

A Bruker IFS 125 HR Fourier transform interferometer in combination with a multireflection cell was used to measure pure water transmission spectra in the spectral range 700 – 2000 cm^{-1}. Various spectra with absorption path lengths between 14 and 161 m, sample gas pressures from 0.003 to 20 mbar and temperatures between 278 and 350 K were recorded.

The recorded spectra were corrected for detector non-linearity, thermal self-radiation and for deviations from an ideal instrumental line shape.

A micro-window-based multispectrum-fitting-approach was used, applying a quadratic speed-dependent Voigt model which was extended to account for line mixing.

Line positions, line intensities, self-shifts, self-broadening widths, their speed-dependence, temperature exponents, temperature shifts and in some cases line mixing were adjusted for fitting the corrected spectra.

Continuum information was extracted from baselines, which were fitted simultaneously with monomer lines during the multispectrum fits. Continua were then obtained by a combined fit of all measurements containing significant continuum information.

The self-continuum for room temperature was derived for the entire spectral range covered and is compared to measurements from other groups.

The good quality of the self-continuum and the visibility of high-resolution features in the ν_2 in-band region allows for a comparison with dimer spectra. Results are presented for different temperatures.

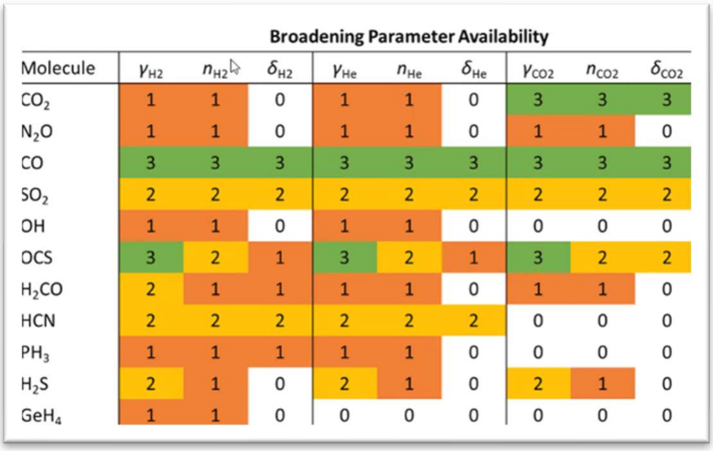
P2-14

New Planetary-Relevant Broadening Data in HITRAN2020 and their Applicability to Generate Opacities under Planetary Conditions

Frances M. Skinner[1], **Yan Tan**[1,2], **Shanelle Samuels**[1,3], **Robert J. Hargreaves**[1], **Robab Hashemi**[1], **and Iouli E. Gordon**[1]

1. Center for Astrophysics | Harvard & Smithsonian, Atomic and Molecular Physics Division, 60 Garden Street, Cambridge, MA 02138 USA
2. Department of Chemical Physics, University of Science and Technology of China, Hefei, China
3. University of Massachusetts Lowell, MA 01854, USA
** frances.skinner@cfa.harvard.edu*

The HITRAN2020 edition consists of a multitude of line-shape parameters associated with the pressure of "planetary" gases which are applicable to modeling and interpreting spectra of (exo)planetary atmospheres [1]. These new parameters comprise broadening due to the ambient pressure of H_2O [2], He, H_2, and CO_2 [3]. Planetary broadeners were initially added to the database during the HITRAN2016 edition for the line lists of SO_2, NH_3, HF, HCl, OCS, and C_2H_2 [4]. Henceforth, He, H_2, and CO_2 pressure broadening, temperature dependence, and in some cases, pressure-induced line shifts, have been added and/or updated for the line lists of CO_2, N_2O, CO, SO_2, OH, OCS, H_2CO, HCN, PH_3, H_2S, and GeH_4 [3]. Employing these planetary parameters in conjunction with the HITRAN Application Programming Interface (HAPI) [5], allows users to calculate a reliable planetary reference opacity. As a test case, we present our investigation [6] of how HITRAN broadening data can be used to model MW spectra under planetary conditions, with resultant opacities compared to available laboratory data [7 - 10]. Overall, this work demonstrates how HITRAN and HAPI along with the newly included planetary broadeners, can be utilized to generate opacities under diverse planetary conditions. The lack of data for many systems of interest is highlighted in this Figure.



Broadening Parameter Availability

Molecule	γ_{H2}	n_{H2}	δ_{H2}	γ_{He}	n_{He}	δ_{He}	γ_{CO2}	n_{CO2}	δ_{CO2}
CO_2	1	1	0	1	1	0	3	3	3
N_2O	1	1	0	1	1	0	1	1	0
CO	3	3	3	3	3	3	3	3	3
SO_2	2	2	2	2	2	2	2	2	2
OH	1	1	0	1	1	0	0	0	0
OCS	3	2	1	3	2	1	3	2	2
H_2CO	2	1	1	1	1	0	1	1	0
HCN	2	2	2	2	2	2	0	0	0
PH_3	1	1	1	1	1	0	0	0	0
H_2S	2	1	0	2	1	0	2	1	0
GeH_4	1	1	0	0	0	0	0	0	0

Figure: This figure highlights the lack of data availability for H_2, He and CO_2 broadening coefficients of different molecules. 0–no data available, 1–very few data available, 2–some measurements available, 3–relatively complete data set available.

References

[1] I. E. Gordon, *et al,* JQSRT, **277**, 107949 (2022)
[2] Y. Tan, *et al,* JGR (Atmospheres), **124**, 11580-11594 (2019)
[3] Y. Tan, *et al,* Astrophys. J. Suppl. Ser., Submitted (2022)
[4] J. S. Wilzewski, *et al,* JQSRT, **168**, 193-206 (2016)
[5] R. V. Kochanov, *et al,* JQSRT, **177**, 15-30 (2016)
[6] F. M. Skinner *et al*, MNRAS, stac1582 (2022)
[7] A. Bellotti and P. G. Steffes, Icarus, **254**, 24-33 (2015)
[8] P. G. Steffes, *et al,* Icarus, **245**, 153-161 (2015)
[9] K. Devaraj, *et al,* Icarus, **212**, 224-235 (2011)
[10] K. Devaraj, *et al,* Icarus, **241**, 165-179 (2014)

Generating collisional lineshape parameters for (vib)rotational transitions in the ExoMol database

Andrei Sokolov[1,*], Robert R Gamache[2], Ryan P Brady[1], Jeanna Buldyreva[3], Sergey N Yurchenko[1], and Jonathan Tennyson[1]
1 Department of Physics and Astronomy, University College London, London WC1E 6BT, UK
2 Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts Lowell, Lowell, MA 01854 USA
3. Institut UTINAM, UMR CNRS 6213, Université Bourgogne Franche-Comté, 16 route de Gray, Besançon cedex 25030, France
[*] *andrei.sokolov@ucl.ac.uk*

Despite ongoing efforts to provide complete and accurate information on lineshape parameters, a lot of data are still missing from spectroscopic databases. This is especially aggravating for those at high temperatures or involving more "exotic" radiators and perturbers that are missing in terrestrial atmosphere but are routinely [1] detected in certain types of exoplanets or outer regions of stars. Such data are crucial for proper molecular abundances [2] and radiative transfer calculations [3].

We present our plans to produce theoretical half-widths, half-shifts and temperature-dependent parameters for spectral line broadening in the microwave and infrared regions at high temperatures. An existing semi-classical approach, known as the modified complex Robert-Bonamy (MCRB) [4], is chosen as a compromise between accuracy (compared to more simplistic semi-classical and empirical models) and feasible computational times (compared to approaches with more sophisticated trajectory descriptions). Some results for broadening with various collisional partners are given for relatively well-known "test" systems that have astrophysical importance: acetylene, observed in cool stars [5] and nitric oxide which is thought to be a reliable tool for life detection [6]. Our plans to extend this approach to collisional partners with more complicated molecular structure are also sketched.

References

[1] J.J. Fortney *et al*, arXiv:1905.07064 (2019)
[2] C. Hedges *et al,* MNRAS **458**, 2 (2016)
[3] G. Tinetti *et al*, Philos. trans. R. Soc. Lond., A. **370**, 2749(2012).
[4] R. Gamache *et al,* JQSRT **235**, 31 (2019)
[5] K. Chubb *et al,* MNRAS **493**, 2 (2020)
[6] V. S. Airapetian *et al,* Sci. Rep **7**, 14141 (2017)

Evaluation of different parametrization of temperature dependences of the line-shape parameters based on ab initio calculations: Case study for the HITRAN database

---

Nikodem Stolarczyk[1,*], **Franck Thibault**[2], **Hubert Cybulski**[3], **Hubert Jóźwiak**[1], **Grzegorz Kowzan**[1], **Bastien Vispoel**[5], **Iouli E. Gordon**[6], **Lawrence S. Rothman**[6], **Robert R. Gamache**[4] and **Piotr Wcisło**[1]

1. *Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, Grudziądzka 5, Toruń 87-100, Poland*
2. *Univ Rennes, CNRS, IPR (Institut de Physique de Rennes)-UMR 6251, F-35000 Rennes, France*
3. *Institute of Physics, Kazimierz Wielki University, al. Powstańców Wielkopolskich 2, 85-090 Bydgoszcz, Poland*
4. *Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts Lowell, Lowell, MA, USA*
5. *Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur, 61 Rue de Bruxelles, Namur, Belgium*
6. *Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge, MA, USA*

* *Nikodem.Stolarczyk319@gmail.com*

A proper description of the temperature dependence of the line-shape parameters is important for the spectroscopic studies of both terrestrial and extraterrestrial atmospheres. We employ *ab initio* collisional line-shape calculations for several molecular systems [1] to compare the four-temperature range (4TR) representation [2], with the double-power-law (DPL) representation [3] . Besides the collisional broadening and shift parameters, we consider the most important beyond-Voigt line-shape parameters, i.e., the speed dependence of broadening and shift parameters, and real and imaginary parts of the complex Dicke parameter. We demonstrate that not only does DPL give better overall approximation of the temperature dependences, but it also requires fewer parameters than 4TR. The DPL representation was incorporated in the 2020 edition of the HITRAN database [4]. I will present the DPL parameterization for Voigt and beyond-Voigt line profiles. I will also discuss the problem of the Hartmann-Tran profile parameterization in which the correlation parameter, η, and frequency of the velocity-changing collisions parameter, ν_{vc}, diverge to infinity when collisional shift crosses zero; we provide a simple solution for this problem.

References

[1] N. Stolarczyk *et al*, JQSRT **240**, 106676 (2020)
[2] P. Wcisło *et al*, JQSRT **177**, 75 (2016)
[3] R.R. Gamache, B. Vispoel, JQSRT **217**, 440 (2018)
[4] I.E. Gordon *et al,* JQSRT **277** 107949 (2022)

P2-17

The measurements of HD rotational transitions at temperatures between 100 - 296 K

Keeyoon Sung[1], Edward H. Wishnow[2], Brian J. Drouin[1], Laurent Manceron[3], Marine Verseils[3], D. Chris Benner[5], Conor A. Nixon[4]

[1] Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA.

[2] Space Sciences Laboratory, University of California, Berkeley, CA, 94720, USA.

[3] AILES Beamline, Synchrotron SOLEIL, L'Orme des Merisiers Saint-Aubin, 91192 Gif-sur-Yvette Cedex, France.

[4] Department of Physics, The College of William and Mary, Williamsburg, VA 23187, USA
[5] Planetary Systems Laboratory, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA.

Laboratory measurements of the R(0) – R(3) pure rotational transitions of hydrogen deuteride (HD) and HD-H_2 mixtures have been performed at low pressures (< 1 bar) and temperatures between 98 and 296 K. The measurements were conducted using a Fourier transform spectrometer coupled to the Soleil synchrotron far-infrared source. The observed spectra have been fitted using a non-linear least-squares multispectral fitting program, from which line position, intensity, pressure broadening, pressure-induced frequency shifts, and their temperature dependencies have been determined simultaneously. These spectroscopic line parameters are compared to previous measurements made at higher gas pressures. Notably the present, and previous, measured H_2 broadened linewidths are smaller by a factor of five than those listed in the HITRAN 2020 database. This work is applicable to the low pressure, low temperature regimes found in the atmospheres of the giant gaseous planets[&].

High resolution absorption cross-section measurements of hydrocarbons at high temperatures and high pressures in the mid-IR spectral region

Mohamed Sy[1], **Mohammad Adil**[1], **Mhanna Mhanna**[1], **Aamir Farooq**[1,*]

1. King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center, Physical Sciences and Engineering Division, Thuwal 23955-6900, Saudi Arabia
** aamir.farooq@kaust.edu.sa*

A new high-pressure and high-temperature (HPHT) optical gas cell is designed for infrared spectroscopy. To achieve a uniform temperature distribution over the absorption path-length, the HPHT optical cell utilizes 15 cm sapphire window rods [1, 2] to minimize absorption in colder regions. The HPHT cell is placed in an insulated, temperature-controlled tube furnace that can maintain a steady and uniform desired internal temperature. Three K-type thermocouples are placed along the path-length to assure uniformity of the temperature. Gas pressure was monitored with a pressure transducer (Setra GCT-225). Along the 9 cm cell path-length, temperature is shown to be uniform within ± 4 K. High-temperature and high-pressure absorption cross-sections measurements of several C_1-C_3 hydrocarbons were performed in the HPHT cell using a continuous wavelength (cw), ultra-high resolution ($<1.5\times10^{-5}$ cm^{-1}) and narrow linewidth (<2MHz), OPO-based laser system (TOPTICA TOPO) [3]. The TOPO laser can scan a very broad wavelength range over 1.45 – 4.00 µm with a scan speed in between 6-10 cm^{-1}/s. In particular, absorption cross-sections measurements of methane, ethane, ethylene, acetylene, propane, propylene, and propyne were measured over 294 – 700 K, 0.25 – 31 atm, and 1.45 – 4.00 µm. The experimentally measured absorption cross-sections were compared with HITRAN/HITEMP databases [4].

Keywords: Optical gas cell, Absorption spectroscopy, High-temperature, High-pressure, OPO laser system.

References:

[1] Almodovar, Christopher A., et al. "High-pressure, high-temperature optical cell for mid-infrared spectroscopy." Journal of Quantitative Spectroscopy and Radiative Transfer 231 (2019): 69-78. [2] E. Starikova *et al*, JQSRT **119**, 104 (2013)
[2] Schwarm, Kevin K., et al. "High-pressure and high-temperature gas cell for absorption spectroscopy studies at wavelengths up to 8 µm." Journal of Quantitative Spectroscopy and Radiative Transfer 227 (2019): 145-151.
[3] Foote, David B., et al. "High-resolution, broadly-tunable mid-IR spectroscopy using a continuous wave optical parametric oscillator." Optics Express 29.4 (2021): 5295-5303.
[4] I. E. Gordon et al., "The HITRAN2016 Molecular Spectroscopic Database," J. Quant. Spectroscop. Radiat. Transf. 203, 3-69 (2017)

P2-19

Intensities and pressure broadening coefficients of CH_3Br lines in the THz region

Wilfried Tchana Betnga[1,2 *], Francis Hindle[2], Arnaud Cuisset[2], Jean Vander Auwera[3] and Fridolin Kwabia Tchana[1]

1. *Université Paris Cité and Univ Paris Est Creteil, CNRS, LISA, F-75013 Paris, France*
2. *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, Dunkerque, France*
3. *Spectroscopy, Quantum Chemistry and Atmospheric Remote Sensing (SQUARES), C.P. 160/09, Université Libre de Bruxelles, B-1050 Brussels, Belgium*

* *wtchana@lisa.ipsl.fr*

Methyl bromide (CH_3Br) in the Earth's atmosphere is of both natural and anthropogenic origin. Known sources include natural production from oceans (although they could also absorb it) [1] and biomass burning [2]. Methyl bromide also comes from gasoline containing brominated additives and is produced in industry since it is used for soil fumigation in agriculture [3]. In addition, CH_3Br is a greenhouse gas and contributes significantly to the global budget of atmospheric bromine, which is directly involved in the catalytic ozone destruction. From a spectroscopic point of view, CH_3Br has been the subject of several investigations, especially in the infrared region, leading to the determination of spectroscopic parameters for both $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ isotopologues [4-6].

As part of this work, pure rotational spectra of gas phase CH_3Br, self-perturbed and perturbed by N_2 and O_2, were recorded using a THz spectrometer [7] in AM and FM modes. The FM spectra exhibit hyperfine structure. A first analysis of the AM spectra was performed with a mono-spectrum fitting procedure, in order to retrieve line parameters (intensities and broadening coefficients). For example, the self-broadening coefficients measured, in the 70-110 GHz range, for the R(3,2) line of both $CH_3{}^{79}Br$ and $CH_3{}^{81}Br$ are 0.2602 (95) and 0.3688 (111) cm^{-1}/atm, respectively. These values are in good agreement with the IR measurements which are 0.2601 and 0.3610 cm^{-1}/atm, respectively [4]. For the FM spectra, a current analysis is performed with a multi-spectrum fitting procedure. All the results obtained in this work will be presented and discussed.

References

[1] J. H. Butler, Geophys. Res. Lett **21**, 185 (1994)
[2] R. J. Cicerone, Science **263**, 1243 (1994)
[3] World Meteorological Organization (WMO), "Scientific Assessment of Ozone Depletion: 1998", Report 44, WMO Global Ozone Research and Monitoring Project, Geneva, Switzerland, 1999, Chapter 2.
[4] D. Jacquemart *et al*, J. Quant. Spectrosc. Radiat. Transfer **105**, 264 (2007)
[5] L. Gomez *et al*, J. Quant. Spectrosc. Radiat. Transfer **111**, 1252 (2010)
[6] Z. Boussetta *et al*, J. Mol. Spectrosc **308/309**, 33 (2015)
[7] G. Mouret *et al*, IEEE Sens. J. **13**, 133 (2013)

Theoretical studies of the rovibrational spectrum of H_2O-HF

Dominika Viglaska[1,*], **Xiao-Gang Wang**[2],**Tucker Carrington**[2] **Jr. and David P.Tew**[3]

1. *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France*
2. *Chemistry Department, Queen's University Chemistry Department, Queen's University, Kingston, Ontario K7L 3N6, Canada*
3. *Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, UK*
dominika.viglaska@univ-reims.fr

Molecular complexes play an important role in the chemistry of planetary atmospheres. H_2O-HF is of considerable interest because of two C_s equivalent minima separated by a low inversion barrier (~70 cm^{-1}) [1] . The kinetic energy operator discussed initially by Brocks et al. [2] and written in terms of angular momentum operators defined in monomer- and dimer-fixed frames is used. A G_4 symmetry-adapted Lanczos algorithm and an uncoupled product basis are employed [3,4]. To compute the spectrum, the monomer geometries are fixed at vibrationally averaged values and therefore we treat only five inter-monomer vibrations. In this approximation, we provide rovibrational energy levels up to J =4, transitions frequencies, and intensities using a new full dimensional *ab initio* potential energy surface (PES) [5]. This work was recently extended to the 9D problem including all intra-monomer vibrations. Some preliminary results will be presented. All computed results were confronted with available experimental data [6-9]. The agreement between theory and experiments is good and we suggest a possible reassignment for two bands. Most of the experimental vibrational energies are obtained from relative intensity measurements and are rather imprecise [6]. H_2O-HF is an excellent candidate for more experimental high-resolution studies.

Keywords: Van der Waals molecule, Lanczos algorithm, rovibrational spectroscopy

References

[1] Z. Kisiel *et al,* Proc. R. Soc. Lond. Ser. A. Math. Phys. Eng. Sci , **381, 419** (1982)
[2] G.Brocks *et al,* Mol.Phys. **50,** 1023 (1983)
[3] X-G. Wang *et al,* J.Chem.Phys. **134**, 044313 (2011)
[4] X-G. Wang *et al,* J.Chem.Phys. **143**, 024303 (2015)
[5] D. Viglaska *et al*, J. Mol. Spectrosc **384**, 111587 (2022)
[6] R.K. Thomas *et al*, Proc. R. Soc. Lond. Ser. A. Math. Phys. Sci. **344**, 579 (1975)
[7] Z. Kisiel *et al,* J.Mol.Struct. **112**, 1(1984)
[8] J. Bevan *et al,* Proc. R. Soc. Lond. Ser. A. Math. Phys. Eng. Sci , **372** (1980)
[9] S . Belov *et al,* J. Mol. Spectrosc. **241**, 124 (2007)

P2-21

Impact of broadening line parameters on H_2O retrievals in CO_2 dense atmospheres

---

Séverine Robert[1], J.T. Erwin[1], R.R. Gamache[2], B. Vispoel[3], N. Orphanos[2], B. Grouiez[4] and L. Régalia[4]

[1] *Royal Belgian Institute for Space Aeronomy, Brussels, Belgium (severine.robert@aeronomie.be)*
[2] *Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts Lowell, USA*
[3] *Research unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur, Belgium*
[4] *Groupe de Spectrométrie Moléculaire et Atmosphérique, Université de Reims Champagne-Ardenne, France*

For decades, the remote sensing measurements have been made in planetary atmospheres in the Solar System and beyond. As the performances of the space instruments improve, the atmospheric science community is more and more in need of accurate spectroscopic data. The current databases offer some parameters for non-Earth atmospheres but are far from complete for all situations. For example, measured H_2O line parameters in CO_2-rich atmospheres such as Mars and Venus are missing while they are of prime importance to learn about the evolution of these atmospheres.

After the study published in 2019 by Régalia et al., we measured new Fourier Transform Spectrometer spectra in the 1.88 micron range using a Connes' type FT spectrometer built in Reims. The spectra were analysed using a multispectrum fitting procedure to obtain the line-shape parameters of H_2O broadened by CO_2. These results were used to constrain the intermolecular potential and to calculate the half-width, line shift, and their temperature dependence using the Modified Complex Robert-Bonamy formalism. The impact of these new parameters on the spectral retrievals in the atmospheres of Mars and Venus will be assessed by calculating the equivalent widths in different cases. This exercise may highlight once more that using the correct line shape and line parameters is of utmost importance now that our space instruments have high spectral resolution. More especially the impact of the Double Power law (Gamache and Vispoel, 2018) for the temperature dependence parameter is tested in the context of the scientific preparation of VenSpec-H, spectrometer part of the EnVision payload.

References

L. Régalia, E. Cousin, R.R. Gamache, B. Vispoel, S. Robert, X. Thomas
Laboratory measurements and calculations of line shape parameters of the H_2O–CO_2 collision system
Journal of Quantitative Spectroscopy and Radiative Transfer, 231, 2019, 126-135.
https://doi.org/10.1016/j.jqsrt.2019.04.012.

Robert R. Gamache, Bastien Vispoel
On the temperature dependence of half-widths and line shifts for molecular transitions in the microwave and infrared regions
Journal of Quantitative Spectroscopy and Radiative Transfer, 217, 2018, 440-452.
https://doi.org/10.1016/j.jqsrt.2018.05.019.

Friday August 26, 2022 Program

	Chair : D. Viglaska	
9:00-9:40	**D. Mondelain** (*invited speaker*)	p 87
9:40-10:00	O. Polyansky	p 88
10:00-10:20	F. Skinner	p 89
10:20-10:40	E. Panier	p 90
10:40-11:00	Coffee break	
11:00-11:40	**R. Gamache** (*invited speaker*)	p 91
11:40-12:00	J. Buldyreva	p 92
12:00-12:20	E.M. Adkins	p 93
12:20-12:40	P. Wcislo	p 94
12:40-14:00	Lunch	
	Chair : V. Tyuterev	
14:00-14:40	**K. Vodopyanov** (*invited speaker*)	p 95
14:40-15:20	**M. Spearrin** (*invited speaker-online*)	p 96
15:20-15:40	R. Georges	p 97
15:40-16:00	J. Harrison	p 98
16:00-16:20	R. Cole	p 99

CO_2 and CH_4 line shape parameters with their temperature dependence in support of satellite missions

D. Mondelain[1], A. Campargue[1], T. Delahaye[2], H. Fleurbaey[1], S. Kassi[1], H. Tran[2], S. Vasilchenko[1]

1. *Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France*
2. *Laboratoire de Météorologie Dynamique/IPSL, CNRS, École polytechnique, Institut polytechnique de Paris, Sorbonne Université, École normale supérieure, PSL Research University, F-91120 Palaiseau, France*

Several satellite instruments are currently monitoring or will monitor the column averaged atmospheric dry air mole fraction of CO_2 and CH_4 which are the two main anthropogenic greenhouse gases. These missions have high requirements in terms of uncertainties leading to strong constraints on the spectroscopic parameters and their temperature dependence. We will illustrate our contribution to this topic through two examples of line shape studies.

The first one, funded by the European Space Agency (ESA), concerns the 30013-00001 band of $^{12}CO_2$ in the 1.6 µm atmospheric transparency window. This band is especially used to monitor X_{CO2} in the Orbiting Carbon Observatory-2 (OCO-2) [1,2,3], OCO-3 [4] and GOSAT [5] missions. A relative uncertainty of less than 0.3 % (*i.e.* ~1 ppm) is required [6] to better characterize the surface CO_2 sources and sinks on regional scales and constrain the climate models. Moreover, upcoming missions like CO2M [7] will have even stronger requirements on X_{CO2} [8].

The second line shape study is dedicated to methane in air in the frame of the MEthane Remote sensing Lidar missioN (MERLIN) [9], a Franco-German (CNES-DLR) collaborative minisatellite climate mission aiming to obtain spatial and temporal gradients of atmospheric methane columns with high precision and unprecedented accuracy on a global scale. The satellite is based on a LIght Detecting and Ranging (LIDAR) instrument for which the selected vacuum wavelengths correspond respectively to the center of the R(6) manifold of the $2\nu_3$ band of $^{12}CH_4$ (λ_{ON} = 1645.5512 nm) and to λ_{OFF} = 1645.8277 nm for which there is no methane absorption. To retrieve the methane mixing ratio (X_{CH4}) with a systematic error of 3 ppb (i.e. 0.16% in relative) as required for this mission, the molecular absorption cross-section at λ_{ON} has to be known with a relative uncertainty better than 0.1%.

To fulfill the requirements on the spectroscopic parameters and their temperature dependence in both studies we recorded high signal-to-noise ratio spectra of CH_4 or CO_2 in air [10] with a cavity ring down spectrometer (CRDS) for different pressure and temperature conditions. A spectrally narrowed and stable (sub-kHz) laser source [11] was coupled into a temperature regulated high-finesse optical cavity. The frequency scale of each spectrum was accurately determined from measurements of beat note between a part of the laser light and the closest tooth of a frequency comb referenced to a rubidium clock. The recorded line profiles are reproduced using quadratic speed-dependent Nelkin-Ghatak profiles and the line-mixing effect. The retrieved parameters will be compared to the literature.

References

[1] Crisp D, *et al.* Adv Space Res **34**, 700 (2004)
[2] Crisp D, *et al.* J Appl Rem Sens **2**, 023508 (2008)
[3] Boesch H, *et al.* Remote Sens **3**, 270 (2011)
[4] Eldering A, *et al.* Atmos Meas Tech **12**, 2341 (2019)
[5] Kuze A, *et al.* Appl Opt **48**, 6716 (2009)
[6] Miller CE, *et al.* J Geophys Res: Atmos **112**, D10314 (2007)
[7] Copernicus CO_2 Monitoring Mission Requirements Document, EOP-SM/3088/YM-ymIssue 2.0, 2019. available via https://esamultimedia.esa.int/docs/EarthObservation/CO2M_MRD_v2.0_Issued20190927.pdf
[8] ISOGG project TechNote WP2100: End user requirements for relevant satellite instruments.
[9] G. Ehret, *et al.* Remote Sens **9**, 1052 (2017)
[10] D. Mondelain, *et al.* J Quant Spectrosc Radiat Transf, **288**, 108267 (2022)
[11] J Burkart , *et al.* Opt Lett **38**, 2062 (2013)

Review of the recent Progress on the *Ab Initio* Calculations of the Line Centers and Line Intensities

---

Polyansky Oleg L. [1,2*]

[1]*Institute of Applied Physics, Russian Academy of Science, Uljanov Street 46, Nizny Novgorod, Russia, 603950*

[2]*Department of Physics and Astronomy, University College London, London, WC1E 6BT, United Kingdom*
**o.polyansky@ucl.ac.uk*

In this talk I will review our recent results of the *ab initio* calculations of rovibrational energy levels and line intensities of various small molecules. Electronic problem was solved using the MOLPRO [1] package, nuclear motion problems have been solve using Duo [2] program for diatomic molecules and DVR3D [3] program for triatomic molecules.

First I will present the results of the application of coordinate dependent masses [4], calculated for the H_2 and HF molecules in [5] to the calculations of the rovibrational energy levels up to dissociation. In the case of H_2, the results obtained reproduce well the results of Komasa and Pachucki, obtained using methods, specifically applicable only to the 2-electron molecules. The method we used here is universal[3] and could be applied to any molecular system.

The calculation of the HF energy levels up to dissociation [6] of about 47 000 cm^{-1} using our coordinate dependent masses resulted in the discrepancy of less than 2 cm^{-1} for the highest energy levels[4] and the levels below 15 000 cm^{-1} have been calculated with the accuracy better[4] than 0.1 cm^{-1}.

In the second part of the talk the *ab initio* calculations of the line intensities with the sub-percent and sometimes with sub-promille accuracy will be demonstrated for H_2O [7], CO_2 [8], O_3 [9], CO [10].
The questions of the numerical accuracy of the line intensity calculations using Duo[1] programs on the exactly solvable harmonic oscillator and Morse Oscillator problems are also discussed. I will discuss the outstanding problems of universality of intensity calculations, that is the problem of the homogeneous calculations of all bands intensities within the same PES/DMS calculations.

References:

[1] H.-J Werner et. al, J. Chem. Phys., 152, 144107 (2020)
[2] S. Yurchenko, L. Lodi, J. Tennyson, A. V. Stolyarov, CPC, 202, 262 (2016)
[3] J. Tennyson, M. Kostin, P. Barletta, J. Harris, O. L. Polyansky, N. F. Zobov , CPC, 163, 85 (2004)
[4] A. Scherrer, F. Agostini, D. Sebastiani, E. Gross, R. Vuilleumier, PRX, 7, 031035 (2017)
[5] L. Lodi, R. Vuilleumier, N.F. Zobov , O. L. Polyansky ,to be submitted , 000 (2022)
[6] G. Di Lonardo and A. E. Douglas, Can.J.Phys, 51, 434 (1973)
[7] T. Rubin, M. Sarrazin, N. F. Zobov, J. Tennyson and O. L. Polyansky, Mol.Phys. e2063769 (2022)
[8] A. J. Fleisher, H. Yi, A. Srivastava, O. L. Polyansky, N. F. Zobov and J. Hodges, Nature Physics, 17, 889 (2021)
[9] Jacquemart D., Makhnev V.Yu., Zobov N. F., Tennyson J. and Polyansky O. L., JQSRT, 269, 107651 (2021)
[10] K. Bielska, A.A. Kyuberis, Z. Reed, G. Li, A. Cygan, R. Ciurlo, E. Adkins, L. Lodi, N. F. Zobov, V. Ebert, D. Lisak, J. T. Hodges, J. Tennyson and O. L. Polyansky, Physical Review Letters, accepted, 000 (2022)

Development of the HITRAN S_2 line list in the UV containing electronic transitions: $B^3\Sigma^-_u$- $X^3\Sigma^-_g$, $B''^3\Pi_u$- $X^3\Sigma^-_g$, $f^1\Delta_u$ - $a^1\Delta_g$

Frances M. Skinner[1, *], **Iouli E. Gordon**[1], **Robert J. Hargreaves**[1]

1. Harvard & Smithsonian | Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge Massachusetts, 02138, USA
** frances.skinner@cfa.harvard.edu*

Sulfur dimer is an important molecular constituent in atmospheric and cometary spectra. S_2 has been detected in the volcanic plumes on Jupiter's moon Io [1]. S_2 has also been seen in UV spectra of comet IRAS-Araki-Alcock 1983d [2], comet Hyakutake [3] and comet Shoemaker–Levy 9 [4].

An S_2 line list has been generated by using available spectroscopic constants from the literature and the program PGOPHER [5]. The line list contains the primary $B^3\Sigma^-_u$- $X^3\Sigma^-_g$ (v'=0-27, v''=0-5,7) electronic transition, with predissociated bands from v'≥10. Similar to the Schumann-Runge Bands of O_2, the S_2 predissociated bands are caused by the spin-orbit interaction with the crossing ungerade electronic states [6]. These diffuse S_2 UV bands require the inclusion of predissociated line widths in order to generate reliable cross-section spectra. HAPI is currently being modified to calculate absorption cross-sections with the inclusion of predissociated line widths. This new functionality with HAPI will allow for the calculation of spectra for any molecule with predissociated line widths. With the new predissociation calculation within HAPI we are able to accurately reproduce the available photoabsorption cross-section spectra from [7] at 370K and 823K.

The primary isotopologue $^{32}S_2$ makes up the majority of the line list, with the $^{34}S_2$ isotopologue available for a single B-X (10,0) band. The S_2 line list also includes the $B''^3\Pi_u$- $X^3\Sigma^-_g$ (v'=0-21, v''=0-5,7) electronic bands, where the B″ state strongly interacts with the B state. The $f^1\Delta_u$ - $a^1\Delta_g$ (1,2) band has also been included in the line list, its band head is visible at 35791.7 cm^{-1}. In summary, we present the new HITRAN-formatted S_2 line list and its validation against laboratory absorption and emission spectra.

References

[1] J.R. Spencer *et al*, Science **288**, 1208 (2000)
[2] M.F. A'Hearn *et al*, Astrophys J **274**, L99 (1983)
[3] C. Laffont *et al*, Geophys Res Lett **25**, 2749 (1998)
[4] K.S. Noll *et al*, Science **267**, 1307 (1995)
[5] C. Western, JQSRT **186**, 221 (2017)
[6] B.R. Lewis *et al*, J Chem Phys **148**, 244303 (2018)
[7] G. Stark *et al*, J Chem Phys **148**, 244302 (2018)

Update on RADIS: a fast line-by-line code for high-resolution infrared molecular spectra – GEISA database support and improved computation of sparse spectra

Erwan Panier[1,*], Dirk van den Bekerom[2], Nicolas Minesi[3], Corentin Grimaldi[1], and Hajime Kawahara

1. *EM2C Laboratory, CNRS UPR288, CentraleSupelec, Université Paris Saclay*
2. *Combustion Research Facility, Sandia National Laboratories, 7011 East Ave, Livermore, 94550 CA, USA*
3. *Mechanical and Aerospace Engineering, UCLA, 420 Westwood Plaza, Engineering 6, Room 336, Los Angeles, California, 90095, USA*
4. *Department of Earth and Planetary Science, The University of Tokyo, 7-3-1, Hongo, Tokyo, Japan;*
5. *Research Center for the Early Universe, School of Science, The University of Tokyo, Tokyo 113-0033, Japan*

*erwan.pannier@centralesupelec.fr

RADIS is an open source code for modelling high resolution infrared molecular spectra [1]. It aims to provide a single interface for a host of different LBL-databases and produces spectra at low computation times, even for high resolution spectra containing hundreds of millions of lines. The low computation times were first achieved through implementation of our Discrete Integral Transform algorithm [2], in which spectral lines are distributed over a "Lineshape Distribution Matrix" that provides a very efficient method for convolving the molecular lineshapes, resulting in a performance increase of 2-3 orders of magnitude over conventional broadening methods.

In the current update the computation efficiency of sparse spectra is further increased, allowing rapid computation of high resolution spectra over a wide range (e.g. 0 - 20,000 cm^{-1}). In addition GEISA was integrated in Radis. It facilitates the comparisons between the HITRAN and GEISA databases by allowing users to compute cross sections with the same line-by-line code.

References

[1] E. Pannier *et al*, JQSRT **222-223**, 12 (2019)
[2] D.C.M. van den Bekerom *et al*, JQSRT **261**, 107476 (2021)

Calculating Line Shape Data for Spectroscopic Databases

Robert Gamache[1,*]

1. Department of Environmental, Earth, and Atmospheric Sciences, University of Massachusetts Lowell, Lowell, MA, 01854, USA
** Robert_Gamache@uml.edu*

Modern spectroscopic databases often contain from hundreds of thousands to billions of transitions for each molecule. Some examples are H_2O on HITRAN2020 [1] has 486264 transitions, the 1000 K CO_2 AMES database of Huang *et al.*[2] contains 781,712,273 transitions, C_2H_2 from ExoMol [3] contains 4 347 381 911 transitions. These are far too many lines to measure in the laboratory or to do quality theoretical calculations.

Here the method of determining accurate half-widths, γ, line shifts, δ, their temperature dependence using the Gamache-Vispoel model [4], and the speed dependence of the γ and δ (Γ_2 and Δ_2) [5]. The line shape calculations use the Modified Complex Robert-Bonamy formalism [6] to generate a database of calculated values which are then used in a prediction routine developed from MCRB theory [7].

Using the calculations and prediction routines very accurate data can be added to molecular spectroscopic databases. These methods provide half-widths at the 1-5% uncertainty level and have been used to add line shape information to HITRAN, GEISA, AMES, and other databases.

References

[1] I. Gordon *et* al. JQSRT 227, 107949 (2022)
[2] X. Huang *et al*, JQSRT **119**, 104 (2013)
[3] https://www.exomol.com/db/C2H2/12C2-1H2/aCeTY/12C2-1H2__aCeTY.def
[4] R.R. Gamache, B. Vispoel, JQSRT **217**, 440, (2018)
[5] M.A. Koshelev *et al.*, JQSRT **262**, 107472 (2021)
[6] Q. Ma *et al*. JQSRT **103**, 588 (2007)
[7] R.R. Gamache, J.-M. Hartmann, JQSRT **83**, 119 (2004)

Theoretical approach to high-resolution pressure-broadening parameters for remote sensing of exoplanetary atmospheres

Jeanna Buldyreva[1,*], **Ryan Brady**[2], **Sergey Yurchenko**[2], **and Jonathan Tennyson**[2]

[1] *Institut UTINAM, UMR CNRS 6213, Université Bourgogne Franche-Comté, 16 route de Gray, 25030 Besançon cedex, France*
[2] *Department of Physics and Astronomy, University College London, Gower Street, WC1E 6BT London, United Kingdom*
* *jeanna.buldyreva@univ-fcomte.fr*

Next generation space missions, such as the James Webb Space Telescope (JWST) launched late 2021 and Atmospheric Remote-sensing Infrared Exoplanet Large-survey (ARIEL) adopted by the European Space Agency for launch in 2029 to observe about 1000 extrasolar planets simultaneously in visible and infrared regions [1], will require a large amount of spectroscopic data for already detected and expected molecules. A new and the most important need appears for high-resolution data, in particular line-broadening parameters [2] which contribute to absorption in atmospheric transparency windows and spectral wings and influence the continuum modelling. Given elevated temperatures, optically active species to be considered include not solely neutral "exotic" molecules but also molecular ions. In addition, because of a wide variety of exoplanet atmospheres to be probed, the concerned perturbing gases are hydrogen and helium (as for gas giants) as well as carbon dioxide, nitrogen, oxygen, water vapor, carbon monoxide, nitric monoxide, methane and ammonia.

Several spectroscopic databases (HITRAN [3], GEISA [4], ExoMol [5], TheoReTS [6], MoLList [7], etc.) contain extensive line lists of positions and intensities but pressure broadening and shifting parameters as well as their temperature dependences for required "exo"-molecules are extremely scarce or (more often) completely missing. The specific conditions of hot atmospheres and chemical reactions occurring in them are hardly reproducible in laboratory, so that experimental studies of line-shape parameters are also deficient. Therefore, theoretical approaches offer the only alternative to produce a large amount of essential but missing data on line-shape parameters for wide ranges of temperatures and pressures, and for large variety of perturbers.

We present theoretical recipes for getting estimates of isolated-line pressure-broadening parameters with temperature dependences for transitions relevant to infrared/microwave (vibrational/rotational transitions) and ultraviolet (vibronic transitions) domains. Examples of neutral (NO, OH) and ionic (NO^+, HCO^+) molecules are considered for which some available experimental data enable comparisons and validation of our theoretical models. These models will be incorporated into ExoMol diet [8] update to furnish default values of line-shape parameters when no refined-calculation results are available and will be used in developing automatic large-scale production of collisional widths/shifts for billions of transitions in molecules of interest for exoplanetary atmospheres.

References

[1] https://arielmission.space/
[2] J.J. Fortney *et al.*, arXiv:1905.07064 (2019)
[3] I.E. Gordon *et al.*, JQSRT **277**, 107949 (2022)
[4] N. Jacquinet-Husson *et al.*, J Mol Spectrosc **327**, 31 (2016)
[5] J. Tennyson *et al.*, JQSRT **255**, 107228 (2020)
[6] A.V. Nikitin *et al.*, J Mol Spectrosc **327**, 138 (2016)
[7] P.F. Bernath, JQSRT **240**, 106687 (2020)
[8] E.J. Barton *et al.*, JQSRT **203**, 490 (2017)

Application of theoretical constraints to model the measured temperature and wavelength dependence of collision-induced absorption in the 0.76 µm and 1.27 µm O_2 Bands

Erin M. Adkins[1,*], **Helene Fleurbaey**[1,2], **Tijs Karman**[,3], **David A. Long**[1], **Alain Campargue**[2], **Didier Mondelain**[2] **and Joseph T. Hodges**[1]

1. Material Measurement Laboratory, National Institute of Standards and Technology Gaithersburg, MD U.S.A.
2. LIPhy Université de Grenoble Alpes, UMR5588 CNRS, F-38041, France
3. Radboud Universidy Nijmegen, Netherlands
** erin.adkins@nist.gov*

Oxygen is well-mixed in the atmosphere and provides a mechanism to measure air mass for satellite and remote sensing missions. Atmospheric oxygen column retrievals rely on accurate spectroscopic modeling of the narrow rovibronic transitions superimposed on the broadband collision induced absorption (CIA) across the range of atmospherically relevant pressures and temperatures. While spectroscopic line shape models have long been used for modeling resonant transitions, there are no established line shape models for CIA. Experimental measurements of the CIA are traditionally defined as the remaining absorption after accounting for baseline, resonant absorption, and other physical effects. Theoretical constraints on the shape of the CIA could aid in decoupling the resonant and broadband features. In this work, we evaluate the theoretical CIA model reported by Karman et al. [1] using cavity ring-down spectroscopy measurements collected at multiple temperatures in both the 1.27 µm [2-4] and 0.76 µm O_2 bands. In addition to a qualitative comparison between experiment and theory, this work explores parameterization of the CIA model reported by Karman et al. [1] for future inclusion in integrated multi-spectrum analyses incorporating advanced line shape models and line-mixing.

References

[1] T. Karman *et al*, Nat. Chem. **10** (2018)
[2] S. Kassi S *et al*,. J. Geophys, Res. Atmos. **126** (2021)
[3] D. Mondelain *et al,* J. Geophys, Res. Atmos. **124** (2019)
[4] H. Fleurbaey *et al,* JQSRT **270** (2021)

Keywords
Collision induced absorption, oxygen, validiating theoretical models

Ab Initio Calculations of Line-Shape Parameters for Spectroscopic Databases

Piotr Wcisło

Institute of Physics, Faculty of Physics, Astronomy and Informatics, Nicolaus Copernicus University in Torun, Grudziadzka 5, 87-100 Torun, Poland
piotr.wcislo@fizyka.umk.pl

Our project aims at calculating comprehensive datasets of the beyond-Voigt line-shape parameters for molecular systems that are relevant for the atmospheres of Earth and other planets. We calculate the values of the line-shape parameters in a wide range of temperatures and we use a simple phenomenological representation (double power law [1]) to parametrize their temperature dependencies [2]. We will present our results for the systems relevant to gas giants' atmospheres (He- and H_2-perturbed H_2 and HD). Recently, we reported comprehensive beyond-Voigt line-shape parameter datasets for the He-perturbed H_2 [3] and He-perturbed HD [4] that will be incorporated into the HITRAN database [5]. The calculations for the H2-perturbed H_2 and HD are in progress. We will present our recent results for the Earth's atmosphere relevant systems: N_2-perturbed [6] and O_2-perturbed [7] CO, N_2-perturbed O_2 [8], and several other systems.

Our approach is based on fully quantum collisional calculations performed by employing ab initio potential-energy surfaces. We use the generalized Hess method to determine the values of the line-shape parameters and their temperature dependencies [9]. The results are projected on a simple structure of the quadratic speed-dependent hard-collision profile, so that they can be directly used to populate the HITRAN database [2].

References

[1] R.R. Gamache, B. Vispoel JQSRT **217**, 440 (2018)
[2] N. Stolarczyk, et al., JQSRT **240**, 106676 (2020)
[3] P. Wcisło, et al. JQSRT **260**, 107477 (2021)
[4] K. Stankiewicz, et al., JQSRT **276**, 107911 (2021)
[5] I.E. Gordon, et al., JQSRT **277**, 107949 (2022)
[6] H. Jóźwiak, et al. J. Chem. Phys. **154**, 054314 (2021)
[7] A. Zadrożny, et al. (in preparation)
[8] M. Gancewski, et al., J. Chem. Phys. **155**, 124307 (2021)
[9] P. Wcisło, et al., JQSRT **213**, 41 (2018)

High-resolution (<50 kHz) frequency-comb molecular spectroscopy in the mid-IR to terahertz spectral range

Konstantin Vodopyanov[*], **Dmitrii Konnov, and Andrey Muraviev**

CREOL, The College of Optics & Photonics, University of Central Florida, 4304 Scorpius St., Orlando FL 32816

** vodopyanov@creol.ucf.edu*

Frequency combs – manifolds of evenly-spaced phase-coherent narrow laser lines, originally conceived for precision UV spectroscopy, are now widely used for massively parallel spectroscopic measurements in the mid-IR. Dual-comb spectroscopy (DCS), also referred to as coherent multi-heterodyne spectroscopy, is an advanced spectroscopic technique based on a pair of mutually coherent frequency combs with slightly different line spacing (pulse repetition rate) allowing real-time broadband spectroscopic measurements in the Fourier domain with superior resolution, sensitivity, and absolute optical frequency referenced to an atomic clock.

In our first generation DCS setup, we used a broadband (3.2-5.4 µm) dual frequency comb source based on two subharmonic optical parametric oscillators (OPOs) pumped by two stabilized Tm-fiber-laser (λ≈2µm) combs. Parallel detection of ten trace gases in a gas mixture (OCS, N_2O, NO, CO, CH_4, C_2H_6, C_2H_4, C_2H_2, CO_2, and H_2O) in N_2 buffer gas at 3-mbar total pressure, including isotopologues containing isotopes ^{13}C, ^{18}O, ^{17}O, ^{15}N, ^{34}S, ^{33}S and deuterium (D), with part-per-billion sensitivity and sub-Doppler resolution was demonstrated [1]. Using the same setup, we recorded high-resolution mid-infrared spectrum of carbon disulfide (CS_2) and its three isotopologues [2] (Fig. 1). This highly accurate CS_2 data is now included in the HITRAN2020 molecular spectroscopic database.

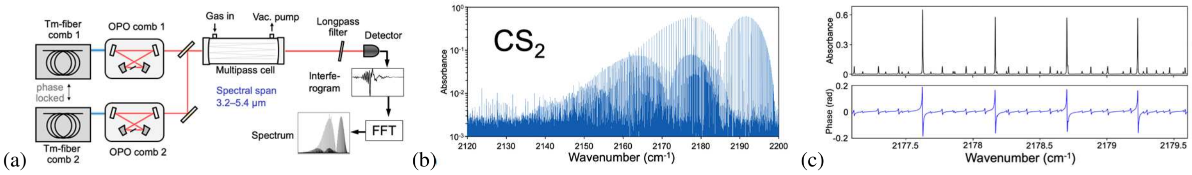


Fig. 1. Schematic of the dual-comb spectroscopy setup based on a pair of Tm-fiber laser combs as a pump. (b) High-resolution (15 MHz) spectrum of the $\nu_1+\nu_3$ band of CS_2. (c) Magnified view of the CS_2 spectrum showing absorbance (top) and phase (bottom) of the Doppler-broadened spectral lines.

.Our next generation DCS setup is based on mode-locked Cr:ZnS lasers (center λ=2.35 µm) as the pump source. We use two approaches to down convert 2.35-µm combs to the longwave range. *In the first approach*, we pump two separate subharmonic OPOs by two phase-locked Cr:ZnS lasers to produce combs spanning two octaves (3–12 µm) with about 1M comb lines. The beams of the 'sensing' and 'sampling' comb are combined on a fast (50 MHz) mid-IR detector to produce an interferogram. Here we can produce comb-line resolved spectra over the whole 3–12 µm range with the sampling interval equal to the comb-line spacing of 80 MHz. By making consecutive measurements with gradually shifted comb lines, the sampling interval (and spectral resolution) can be reduced to < 50 kHz, which is limited by the spectral width and stability of the comb lines. *In the second approach*, the first Cr:ZnS laser produces an ultra-broadband (about an octave wide) frequency comb in the long-wave infrared (4-20 µm) or terahertz (0.5-5 THz) range via intrapulse difference frequency generation in ZGP or GaSe nonlinear crystals, while the second Cr:ZnS laser produces, via second harmonic generation, a near-IR few-cycle pulse serving as a probe for electrooptic (EO) detection. In EO detection, the electric field of the mid-IR/THz transient is sampled via induced polarization change of the probe pulse in an EO crystal, where the two beams spatially overlap. This polarization change is turned (using a waveplate and a polarizer) into a signal from a balanced near-IR photodetector. The main advantage of EO detection method is that there is no need for cryogenically cooled detectors typically required for mid-IR/THz range. In all the above scenarios, the spectrum is recovered via fast Fourier transform of the time-domain detector signal.

Our DCS system, capable of generating highly precise spectral data over wide frequency spans and with absolute frequency referencing, can contribute to high-resolution molecular spectra databases such as HITRAN.

References

[1] A. V. Muraviev, V. O. Smolski, Z. E. Loparo, and K. L. Vodopyanov, Massively parallel sensing of trace molecules and their isotopologues with broadband subharmonic mid-infrared frequency combs, Nature Photon. 12, 209 (2018).

[2] A. V. Muraviev, D. Konnov, and K. L. Vodopyanov, "Broadband high-resolution molecular spectroscopy with interleaved mid-infrared frequency combs", Sci Rep 10, 18700 (2020).

Molecular line mixing effects at high temperatures and pressures: laboratory studies and sensing applications

---

R. Mitchell Spearrin*, Fabio Bendana, Daniel Lee, Kevin Schwarm, Jidong Li, and Chuyu Wei

Laser Spectroscopy and Gas Dynamics Laboratory, University of California Los Angeles, Dept. of Mechanical and Aerospace Engineering, Los Angeles, CA 90095 USA
**spearrin@ucla.edu*

Line mixing effects on select molecular spectra have been studied over a wide range of temperatures and pressures up to 3,500 K and 100 bar within target vibrational bands of CO, CO_2, and CH_4. Unique laboratory facilities have been developed to enable controlled spectroscopic measurements with Fourier transform infrared spectroscopy and laser absorption spectroscopy at such high-temperature conditions. Such facilities include (1) a high-pressure gas cell for absorption spectroscopy studies up to 8 μm at 200 atm and 1200 K [1], and (2) a high-enthalpy shock tube facility that provides near-instantaneous heating at higher temperatures up to and above 4,000 K. Temperature-dependent line mixing in the rovibrational bandheads of CO and CO_2 near 2.3 μm [2] and 4.2 μm [3], respectively, has been characterized experimentally and captured with modified exponential gap models. Additionally, high-temperature line mixing behavior was studied for 15 R-branch line manifolds in the ν_3 band of methane from 3.14 to 3.28 μm [4]. Notably, such line mixing effects have been utilized to enable new quantitative sensing and imaging applications based on laser absorption spectroscopy to study high-temperature and high-pressure combustion systems [5].

References

[1] K. Schwarm *et al*, JQSRT **227**, 145 (2019)
[2] F. Bendana *et al*, JQSRT **239**, 106636 (2019)
[3] D. Lee *et al*, JQSRT **253**, 107135 (2020)
[4] J. Li *et al*, JQSRT **255**, 107271 (2020)
[5] D. Lee *et al*, Proc. Comb. Inst. **38** 1685 (2021)

Non-LTE spectroscopy of the Tetradecad region of methane recorded in a hypersonic flow

Eszter Dudás[1,2], **Bastien Vispoel**[3], **Robert R. Gamache**[4], **Michaël Rey**[5], **Vladimir G. Tyuterev**[5], **Samir Kassi**[6], **Nicolas Suas-David**[1] **and Robert Georges**[1,*]

1. IPR, Université de Rennes 1, UMR6251 CNRS, F-35042, France
2. The von Karman Institute for Fluid Dynamics, Waterloosesteenweg 72, B-1640 Sint-Genesisus-Rode, Belgium
3. Research Unit Lasers and Spectroscopies (LLS), Institute of Life, Earth and Environment (ILEE), University of Namur, B-5000, Namur, Belgium
4. Department of Environmental, Earth, and Atmospheric Sciences University of Massachusetts Lowell, Lowell, MA 01854 USA
5. Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, BP 1039, Reims Cedex 2, F-51687, France
6. LIPhy Université de Grenoble Alpes, UMR5588 CNRS, F-38041, France
** robert.georges@univ-rennes1.fr*

This work is motivated by the need to extend to high temperatures the spectroscopic databases necessary for the modeling of hot gaseous exoplanets such as hot Jupiters. It is part of the e-PYTHEAS and TEMMEX projects supported by the ANR which aim to produce experimental data to feed and validate *ab initio* theoretical models capable of generating reliable rotation-vibration line lists at high temperature. This work focusses on non-local thermodynamic equilibrium (non-LTE) cavity ringdown spectroscopy (CRDS) of methane in the Tetradecad region between 1.7 and 1.65 µm (5880-6060 cm^{-1}). Non-LTE conditions ($T_{rot} = 39$ K; $200 < T_{vib} < 1130$ K) have been obtained by expanding a pre-heated mixture of argon and methane through a hypersonic contoured de Laval nozzle [1]. A close comparison of the recorded CRD spectrum with the TheoReTS database reveals an inefficient vibrational relaxation between polyads but an efficient vibrational relaxation between vibrational states forming a polyad. Both effects result in over populating the lowest vibrational energy level of each polyad. A series of new hot band transitions starting from the Pentad and Octad polyads are provided.

References

[1] E. Dudás *et al.*, J. Chem. Phys., **152**, 134201 (2020)

Quantitative spectroscopic measurements of atmospherically important fluorinated species

Kirill Berezkin[1], **Jeremy J. Harrison**[2*], **Alexandra Domanskaya**[1], **Gang Li**[1], **Henning Bohlius**[1], **Mi Eon Kim**[1] **and Volker Ebert**[1†]

1. Physikalisch-Technische Bundesanstalt, 38116 Braunschweig, Germany
2. National Centre for Earth Observation, Space Park Leicester, University of Leicester, Leicester LE1 7GH, United Kingdom
** jh592@leicester.ac.uk*
† volker.ebert@ptb.de

The EMPIR project "Metrology for climate relevant volatiles organic compounds" (MetClimVOC) [1] aims to improve the quality of reference gas standards for priority oxygenated VOCs, terpenes and halogenated VOCs, and provide SI-traceable spectral parameters for remote sensing applications. The focus of the spectroscopy work is on the fluorinated species trifluoromethane (CHF_3, a.k.a. HFC-23) [2], sulfur hexafluoride (SF_6) [3], and carbon tetrafluoride (CF_4) [4], all of which are present in the Earth's atmosphere, predominantly originating from industrial activity. These species are relatively unreactive with atmospheric lifetimes of hundreds of years and longer, and their abundances continue to grow in the atmosphere due to ongoing emissions. These species are also very strong greenhouse gases, with global warming potentials many times higher than that of carbon dioxide.

Satellite infrared limb sounders, such as the Atmospheric Chemistry Experiment – Fourier Transform Spectrometer (ACE-FTS), and ground-based FTS instruments such as those available in the Network for the Detection of Atmospheric Composition Change (NDACC) record atmospheric spectra from which the abundances of fluorine species can be retrieved, however this first requires accurate spectroscopic data.

Some of the difficulties encountered in laboratory quantitative spectroscopic measurements of these species arise because of their strong absorbance, particularly for CF_4 [5]. It is necessary to work with small concentrations and/or use very small absorption paths in order to avoid saturation. Small concentrations are more difficult to control and maintain, especially in small absorption cells. Other encountered problems include adsorption on cell walls, dead volumes, and unstable mixtures with air. For the latter, we can achieve better concentration stability and mixing reproducibility by using a state-of-the-art Sonimix 2106 gas mixer which utilises sonic nozzle technology.

FTIR measurements are performed with a Bruker IFS 125HR spectrometer at PTB using EUMETRISPEC infrastructure [6], specially tuned to the measurements of the gases of atmospheric interest [7,8]. This presentation will outline first measurements and their derived absorption cross sections. The ultimate aim is to reduce the uncertainties in the integrated band intensities to below 1%. Results will be compared with previous absorption cross sections (now in HITRAN) [2-4] which were scaled using PNNL spectra to calibrate the intensities.

Keywords: infrared absorption cross sections, laboratory measurements, remote sensing, greenhouse gases

References

[1] Metrology for Climate Relevant VOCs, https://www.metclimvoc.eu
[2] J. J. Harrison, JQSRT **130**, 359-364 (2013)
[3] J. J. Harrison, JQSRT **254**, 107202 (2020)
[4] J. J. Harrison, JQSRT **260**, 107432 (2021)
[5] M. Carlos et al., JQSRT **201**, 75-93 (2017)
[6] Spectral reference data for atmospheric monitoring, https://www.eumetrispec.org
[7] A.V. Domanskaya et al., JQSRT **235**, 209-216 (2019)
[8] V. Werwein et al., Appl. Opt. **56**, E99-E105 (2017)

Improving optical absorption models for CO_2 at high pressure and temperature using dual frequency comb absorption spectroscopy up to 1000 K and 25 bar

---

Ryan K. Cole[1], Ha Tran[2], Nazanin Hoghooghi[1], Gregory B. Rieker[1*]

1. *Precision Laser Diagnostics Laboratory, Department of Mechanical Engineering, University of Colorado Boulder, 1111 Engineering Drive, Boulder CO, USA 80309*
2. *Laboratoire de Météorologie Dynamique (LMD/IPSL), Sorbonne Université, ENS, PSL Research University, Ecole Polytechnique, Institut Polytechnique de Paris, CNRS, Paris, France*

* *greg.rieker@colorado.edu*

Accurate absorption models for gases at high pressure and temperature are needed as inputs to radiative transfer models for exotic planetary atmospheres and to support optical sensors for combustion, propulsion, and energy conversion systems. Improving absorption models for these conditions requires both accurate, temperature-dependent databases of absorption parameters as well as models for collisional effects that become more significant at elevated pressures (e.g. line mixing). Here, we present the results of a systematic study aimed at improving absorption models for CO_2 at high pressures and temperatures. The spectra for this study were measured using a broadband, high-resolution (0.0066 cm^{-1}) dual frequency comb absorption spectrometer in a specialized gas cell capable of generating high-pressure, high-temperature conditions with high uniformity and low uncertainty [1]. Using this experimental configuration, we measured spectra for pure CO_2 between 6800 and 7000 cm^{-1} over a matrix of pressure and temperature conditions up to 25 bar and 977 K. We fit a low-pressure subset (<0.8 bar) of these measurements using a multispectrum fitting approach [2] to determine temperature-dependent broadening and pressure shift coefficients for transitions in the 6800-7000 cm^{-1} range using both Voigt and speed-dependent Voigt profiles [3]. We use this database of temperature-dependent line shape parameters along with our spectra measured at high pressure and temperature to test and evaluate line mixing models for pure CO_2. We focus specifically on the approach developed by Tran *et al.* [4] that models line mixing in pure CO_2 using the energy-corrected sudden (ECS) scaling law. We compare our measured spectra to spectra calculated using the ECS model, and report updated model parameters that significantly improve agreement between measured and modeled spectra for pressures up to 25 bar and temperatures up to 977 K. Our results significantly improve absorption models for CO_2 across a wide range of pressure and temperature conditions relevant to planetary science and laser-based sensing.

References

[1] R. K. Cole *et al*, JQSRT **268**, 107640 (2021)
[2] D. C. Benner *et al,* JQSRT **53**, 6 (1995)
[3] R. K. Cole *et al*, JQSRT **276**, 107912 (2021)
[4] H. Tran *et al.* JQSRT **112**, 6 (2011)