Spectroscopy and Dynamics of Ozone and Related Atmospheric Species

Reims, October 4 – 6, 2017

Program and abstracts

Wednesday October 4, 2017 Program

	10:30 - 12:00	**Arrival / Registration**
	12:15 – 13:45	Lunch
	14:15 – 14:30	**Opening**
Ozone theory **Chair : O. Dulieu**	**14:30 – 15:10**	W1 - R. Dawes
	15:15 – 15:45	W2 - V. Kokoouline
	15:50 – 16:10	W3 - D. Lapierre
	16:15	End of session
	16:15 – 16:45	Coffee break
Ozone theory and dynamics **Chair : P. Honvault**	**16:45 – 17:05**	W4 -S. Ndengué
	17:10 – 17:30	W5 -C. Janssen
	17:35 – 18:15	W6 -V. Tyuterev
	18:20	End of session
	19:30	**Banquet at Restaurant "Excelsior" (Brasserie Flo)** **96 place Drouet d'Erlon**

Investigation of the ozone formation reaction pathway: Comparisons of Full Configuration Interaction Quantum Monte Carlo and Fixed-Node Diffusion Monte Carlo with contracted and uncontracted MRCI

R. Dawes

Missouri University of Science and Technology, Rolla, MO 65409
dawesr@mst.edu

The association/dissociation reaction path for ozone ($O_2 + O \leftrightarrow O_3$) is notoriously difficult to describe accurately using ab initio electronic structure theory, due to the importance of both strong and dynamic electron correlation. Experimentally, spectroscopic studies of the highest lying recorded vibrational states combined with the observed negative temperature dependence of the kinetics of oxygen isotope exchange reactions confirm that the reaction is barrierless, consistent with the latest potential energy surfaces. Previously reported potentials based on Davidson-corrected internally contracted MRCI, suffer from a spurious reef feature in the entrance channel even when extrapolated towards the complete basis set limit. Here, we report an analysis of comparisons between a variety of electronic structure methods including internally contracted and uncontracted MRCI (with and without Davidson corrections), as well as full configuration interaction quantum Monte Carlo, fixed-node diffusion Monte Carlo and Density Matrix Renormalization Group.

In addition, some recent results of variational vibrational calculations for various isotope combinations will be presented. Tunneling splittings and gateway states for isomerization (located well below the isomerization barrier) are characterized and discussed.

Spectroscopic and dynamical properties of the ozone molecule in the dissociation region

V. Kokoouline[1], A. Alijah[2], R. Kochanov[3], D. Lapierre[2], V. Tyuterev[2]

[1] *Department of Physics, University of Central Florida, Orlando, Florida, USA*
[1] *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France*
[3] *Harvard-Smithsonian Center for Astrophysics, Molecular Physics Division, USA; QUAMER laboratory, Tomsk State University, Russia InstitutionTrois*

Energies of vibrational states near the lowest dissociation limit of $^{16}O_3$ were determined using the hyperspherical coordinates. For the vibrational resonances with energies above the dissociation limit, lifetimes were also computed using the method of the complex absorbing potential. The calculations are based on the previously developed potential energy surface of O_3 determined with a spectroscopic accuracy. The effect of permutational symmetry on rovibrational dynamics and the density of resonance states in O_3 is discussed in detail. Correspondence between quantum numbers appropriate for short and long range parts of wave functions of the rovibrational continuum is established. For bound levels, good agreement with experimental energies is found: The RMS deviation between observed and calculated vibrational energies is 1 cm^{-1}. Rotational constants were determined and used for a simple identification of vibrational modes of calculated levels.

Predissociation resonances of O_3

D. Lapierre[1], A. Alijah[1], R. Kochanov[3], V. Kokoouline[2], V. Tyuterev[1]

[1] *Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences Exactes et Naturelles, BP 1039 - 51687 Reims Cedex 2, France*
[2] *Department of Physics, University of Central Florida, Orlando, Florida, USA*
[3] *Harvard-Smithsonian Center for Astrophysics, Molecular Physics Division,USA; QUAMER laboratory, Tomsk State University, Russia InstitutionTrois*

The new potential energy surface of ozone recently developed[1,2] is used to determine energies of vibrational bound states and predissociation resonances of O_3. Results obtained in this study agree with previous calculations and reproduce the experimental energies up to the 8000 cm^{-1} region. Coupling between the three potential wells of the ozone molecule is taken into account, using hyperspherical coordinates as decribed in Ref[2]. This is important for the correct description of excited vibrational levels and resonances. Symmetric and asymmetric isotopologues can be treated. For symmetric isotopologues, levels of all possible irreducible representations have been calculated and widths of the resonances in the region 0-1500 cm^{-1} above dissociation have been determined.

The widths are mostly between 0.1 cm^{-1} and 10 cm^{-1}, depending on the nature of the short-range part of the resonance wave functions: Resonances may differ by the degree of vibrational excitation and also by the relative angular momentum of the dissociating O-O_2 system, which can also be viewed as motion between the three potential wells. Wave functions of the predissociation resonances obtained for asymmetric molecules provide information about the exchange reaction $^{x}O + {}^{y}O^{y}O \rightarrow {}^{y}O + {}^{x}O^{y}O$.

References

1. Vl.G. Tyuterev, R.V. Kochanov, S.A. Tashkun, F. Holka, P. Szalay, New analytical model for the ozone electronic ground state potential surface and accurate *ab initio* vibrational predictions at high energy range. *J. Chem. Phys,* **139** , 134307 (2013)
2. D. Lapierre, A.Alijah, R.Kochanov, V. Kokoouline, and V. Tyuterev, Lifetimes and wave functions of ozone metastable vibrational states near the dissociation limit in a full-symmetry approach, Phys. Rev. A, A94, 042514 (2016)

Resonance and inelastic scattering calculations to understand the ozone isotopic anomaly

S. Ndengué

Missouri University of Science and Technology, Rolla MO

The ozone isotopic anomaly has been the focus of many scientific studies and debates. While the selectivity observed in the photodissociation process is now relatively well understood, thanks to sufficiently accurate PESs and recent quantum dynamics calculations, the selectivity in ozone formation remains unanswered as no accurate and reliable ozone recombination calculations have yet been performed. It is known that the ozone recombination process proceeds in 2 steps. First molecular oxygen collides with an oxygen atom to form ozone in an excited rovibrational state. Then through collision with a third body, excited ozone loses energy to achieve stabilization to the ground or weakly excited vibrational states. Two approaches have been proposed in the literature to determine ozone isotopic enrichment from the rates of the recombination process:

- One is statistical based on the determination of the collisional rates by computing ozone resonance positions and widths
- An alternative method would probe the dynamics more directly by performing inelastic collisions of highly excited ozone with a 3rd body (usually Argon) to obtain the relevant rates.

In this talk we will present recent calculations of resonances of HCO and ozone and the inelastic scattering of a triatomic molecule with an atom using the MCTDH program. These are some preliminary methodology benchmarks in preparation for accurate isotopic ozone recombination calculations.

Mass independent isotope effects in simple triatomic reactions

D. Simone [1,2], L.M. Joelsson[3], M.S. Johnson[3], M. Minissale[1],[4,5], P. Jeseck', T. Zanon[1], C. Janssen[1]

[1] LERMA-IPSL, Sorbonne Universités, UPMC Univ. Paris 6, Observatoire de Paris, PSL Research University, CNRS, F-75005, Paris, France
[2] now at : INFN - Sezione di Bari, Physics Department, Via E. Orabona 4, 70126 Bari, Italy 3 Department of Chemistry, University of Copenhagen, Denmark
[3] Department of chemistry, University of Copenhagen, Denmark
[4] now at : Aix Marseille Université, CNRS, PIIM UMR 7345, 13397 Marseille, France
[5] now at: Aix-Marseille Université, CNRS, Centrale Marseille, Institut Fresnel UMR 7249, 13013 Marseille, France

Molecular self-shielding and symmetry selection in thermochemical reactions" are molecular processes invoked to explain mass-independent isotope signatures in nature. The thermochemical reaction of ozone formation" in the gas-phase

$O + O_2 + M \rightarrow O_3 + M$ (1)

is the most prominent example for a large mass independent oxygen isotope fractionation, but fundamental questions on the nature of this isotope fractionation effect remain. For example, it was reported that the reverse process of ozone decomposition

$O_3 + M/S \rightarrow O_2 + O + M/S$ (2)

on a wall surface (S) would also show an anomalous effect," while ozone formation on the wall would not." Here we present first results from kinetic studies on ozone decomposition using laser absorption spectroscopy (TDLAS) which suggest that ozone decomposition on Teflon coated metal surfaces lacks the large symmetry selection which is associated with the formation reaction (1).

We also report on an experimental/modeling study on the spin forbidden recombination

$O + CO + M \rightarrow CO_2 + M$ (3)

which is thought to show an ozone-like isotope anomaly. We find that this reaction is slow compared to other CO_2 production pathways under most experimental conditions and claim that, so far, reaction (1) is the only well-established thermochemical reaction associated with a large symmetry driven oxygen isotope effect and that the surface reactions (ozone formation and thermal dissociation) also lack a large symmetry effect. Further experimental avenues and the link with a puzzling bath gas dependence of reaction (1) are discussed.

Ab initio dipole moment surfaces of ozone: variational predictions of line intensities for isotopic species and comparison with experiments

V. Tyuterev [1], R. Kochanov [2,3], S. Tashkun [2,4] and A. Barbe[1]

[1]Groupe de Spectrometrie Moléculaire et Atmosphérique, University of Reims, France,
[2]QUAMER laboratory, Tomsk State University, Tomsk, Russia,
[3]Harvard-Smithsonian Center for Astrophysics, Atomic and Molecular Physics Division, Cambridge MA 02138, USA.
[4]LTS, V.E. Zuev Institute of Atmospheric Optics SB RAS, Tomsk, Russia.

The state-of-the-art in *ab initio* calculations of the dipole moment surfaces (DMS) and global variational predictions of line intensities for ozone isotopic species will be reviewed. An accurate description of the complicated shape of the potential energy surface [1], of dipole moment surfaces and that of the highly excited vibration states [2] is of crucial importance for various unsolved issues in the spectroscopy and dynamics of ozone and remains a challenge for the theory. We shall present new ab initio dipole moments surfaces [3] of the ozone molecule as well as the results of first-principles variational calculations for lines intensities in the far infrared range. The comparisons of predicted spectra with experimental ones [4], with data included in S&MPO information system [5] and in HITRAN database will be presented. These calculations reveal that several weak bands are yet missing from available spectroscopic databases. The remaining issues will be discussed both for cold and hot band transitions. This work permitted to obtain for the first time a good agreement of ab initio ozone band intensities with observations in a wide range of overtone and combination bands. This includes high overtone and combination bands up to $\Delta V=6$. A particular challenge was a correct description of the B-type bands (even ΔV_3 values) that represented major difficulties for the previous ab initio investigations and for the empirical spectroscopic models. The major patterns of various B-type bands were correctly described without empirically adjusted dipole moment parameters. For the 10 μm range, which is of key importance for the atmospheric ozone retrievals, our ab initio intensity results are within the experimental error margins. The theoretical values for the strongest lines of the ν_3 band lie in general between two successive versions of HITRAN empirical database that corresponded to most extended available sets of observations. The consistency of calculated and measured intensities in 10 μm and 5 μm range range will be discussed. We acknowledge the support from LEFE CHAT CNRS program and from Mendeleev funding TSU grant.

References

[1] V. Tyuterev, R.V. Kochanov, S.A. Tashkun, et al, JCP, **139** , 134307 (2013)
[2] V. Tyuterev et al, PRL 113, 143002 (2014)
[3] V. Tyuterev, R.V. Kochanov, S.A. Tashkun, JCP, **146** , 064304 (2017)
[4] A. Barbe, S. Mikhailenko, E. Starikova, et al, JQSRT,**130**,172 (2013)
[5] Y. Babikov, S.Mikhailenko, A.Barbe and V.Tyuterev, JQSRT (2014)

Thursday October 5, 2017 Program		
Ozone dynamics **Chair : R. Dawes**	**9:15 – 9:35**	T1 - G. Guillon
	9:40 – 10:20	T2 - P. Honvault
	10:25	End of session
	10:25 – 10:55	Coffee break
Ozone spectroscopy	**10:55 – 11:15**	T3 - A. Barbe
	11:20 – 11:40	T4 - E. Starikova
	11:45 – 12:05	T5 - D. Mondelain
	12:10	End of session
	12:15 – 13:45	Lunch
Atmosphere **Chair : C. Janssen**	**14:15 – 14:55**	T6 - J. Cuesta
	15:00 – 15:35	T7 - Ha Tran
	15:40 – 16:10	T8 - V. Yankovsky
	16:15	End of session
	16:15 – 16:45	Coffee break
Ozone spectroscopy and atmosphere **Chair : A. Perrin**	**16:45 – 17:00**	T9 - M. Minissale
	17:05 – 17:20	T10 - C. Janssen
	17:25 – 17:40	T11 - Mikhailenko
	17:45 – 18:00	T12 - M.-R. De Backer
	18:05 – 18:20	T13 - M. Zoran
	18:25 – 18:40	T14 - C. Kalalian
	18:45	End of session
	19:00	**Reception at the Mairie de Reims (Reims Town hall)**

Permutation symmetry in quantum dynamics: examples with O + O_2 reactions

G. Guillon[1] and P. Honvault[1,2]

[1]*Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS/Université de Bourgogne, 21078 Dijon Cedex, France*

[2]*UFR Sciences et Techniques, Université de Franche-Comté, 25030 Besançon Cedex, France.*

Scattering between groups of identical particles, or identical fragments, deserves special attention. While always correctly accounted for in the realm of particle and nuclear physics, it seems that the proper inclusion of permutation symmetry of the nuclei has been missing in many studies in quantum molecular dynamics. The most direct way to take this fact into account would be the use of a scattering formalism entirely based on second quantization, in which symmetry requirements to be satisfied by indistinguishable entities would be incorporated from the outset [1,2]. But in the case of relatively small systems, like three-body (possibly reactive) collisions, it is possible to adapt the specific method used in explicitly computing the cross sections (like the time-independent formalism we are using, based on hyper spherical coordinates for rearranging collisions) in incorporating the correct permutation symmetry, or even to post-symmetrize the cross sections obtained when neglecting the identical character of the three nuclei, by any method.

We present various examples of scattering observables for three-body systems with two (like the ^{16}O + $^{17}O^{17}O$ [4] or ^{17}O + $^{16}O^{16}O$ [3] processes) or three identical nuclei either with zero spin, such as ^{16}O + $^{16}O^{16}O$ [5] and ^{18}O + $^{18}O^{18}O$ [6], or nonzero spin like ^{17}O + $^{17}O^{17}O$. These systems are all treated by a full quantum-mechanical time-independent formalism. To this end, we use a recent global potential energy surfaces for the ground electronic state [7]. This kind of study is computationally intensive and takes properly into account the indistinguishability of the three identical atoms, yielding accurate cross sections and rate constants as functions of collision energy and temperature.

References

[1] J. R. Taylor, *Scattering theory: the quantum theory of nonrelativistic collisions*, Dover Publications Inc. New York (1972, 2000).

[2] K. Hepp, « *On the connection between Whightman and LSZ quantum field theory* », in *Axiomatic field theory*, ed. by Chretien & Deser, Gordoan & Breach, New York (1965).

[3] G. Guillon and P. Honvault *J. Phys. Chem. A* **120**, 8254 (2016).

[4] G. Guillon and P. Honvault *Chem. Phys. Lett.* in press (2017).

[5] T. Rajagopala Rao, G. Guillon, S. Mahapatra, P. Honvault, *J. Phys. Chem. Lett.* **6**, 633 (2015).

[6] G. Guillon, T. Rajagopala Rao, S. Mahapatra, P. Honvault, *J. Phys. Chem. A* **119**, 12512 (2015).

[7] R. Dawes, P. Lolur, A. Li, B. Jiang, H. Guo, *J. Chem. Phys.* **139**, 201103 (2013).

Quantum dynamics study of the O + O_2 collisions

P. Honvault, G. Guillon

Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS/Université de Bourgogne Franche-Comté, 21078 Dijon Cedex, France

Molecular oxygen O_2 is the most important molecule in Earth's atmosphere and stratospheric ozone O_3 protects us from the UV radiation. The abundance in ^{16}O being 99.8%, O_2 and O_3 exclusively formed from it are dominant, thereby giving a reference for any process involving oxygen. A strong enrichment (about 10%) of O_3 in both ^{18}O and ^{17}O (the so-called mass-independent fractionation MIF), has been observed decades ago [1] and reproduced in laboratory experiments [2].

Although this phenomenon remains globally unexplained, the three-body recombination $O + O_2 + M \rightarrow O_3 + M$ is believed to be the main process leading to this enrichment. At sufficiently low pressures, it can be partitioned into two steps: the formation of O3 in a highly excited rovibrational state, from reaction $O + O_2 \rightarrow O_3^*$ (step 1), and its subsequent stabilization by collision with an energy absorbing partner M (say N_2), $O_3^* + M \rightarrow O_3 + M$ (step 2). Thus, the efficiency of the exchange reaction $O + O_2 \rightarrow O_3^* \rightarrow O_2 + O$, involving O_3^* as an intermediate, is one of the key parameters to understand ozone formation. We have shown [3] that this reaction, initiated by step 1, is very fast with three identical ^{16}O atoms involved. Consequently, it competes ferociously with step 2 described above, the latter becoming in this way much less effective.
We have reproduced experimentally observed negative temperature dependence for the reaction rate constant when ^{18}O is involved, along with other groups [4]. We will sum up results of a computationally intensive full-quantum investigation of the dynamics of the $^{16}O + {}^{32}O_2$ [3], $^{18}O + {}^{32}O_2$ [5] and $^{17}O + {}^{32}O_2$ [6] processes supported by a recent global potential energy surface for the O_3 ground state [7,8].

References

[1] K. Mauersberger, Geo. Res. Lett. 8 935 (1981).
[2] M.H. Thiemens, J.E. Heidenreich III, Science 219 1073 (1983).
[3] T.R. Rao, G. Guillon, S. Mahapatra, P. Honvault, J. Phys. Chem. Lett. 6 633 (2015).
[4] Z. Sun, D. Yu, W. Xie, J. Hou, R. Dawes, H. Guo, J. Chem. Phys. 142 174312 (2015).
[5] T. Rajagopala Rao, G. Guillon, S. Mahapatra, P. Honvault, J. Chem. Phys. 142, 174311 (2015).
[6] G. Guillon, P. Honvault, J. Phys. Chem. A 120 8254 (2016).
[7] R. Dawes, P. Lolur, A. Li, B. Jiang, H. Guo, J. Chem. Phys. 139 201103 (2013).
[8] G. Tyuterev, R.V. Kochanov, S. A. Tashkun, F. Holka, and P. Szalay, J. Chem. Phys. 139, 134307 (2013).

Analyses of ^{17}O isotopic species of ozone in the 5 and 10 microns spectral ranges

A. Barbe[1], M.-R. De Backer[1], V. Tyuterev[1]
[1]*Groupe de Spectrométrie Moléculaire et Atmosphérique*
UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France
E-mail: alain.barbe@univ-reims.fr mr.debacker@univ-reims.fr vladimir.tyuterev@univ-reims.fr

E. N. Starikova [2]
[2] *Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS*
1, Akademician Zuev square, 634021 Tomsk, Russia
E-mail: starikova_e@iao.ru

The high resolution infrared spectra of ozone isotopic species have been recorded with the GSMA[1] FTS at 0.002 cm^{-1} resolution in the 950-1250 cm^{-1} and 1900-2250 cm^{-1} regions .The bands ν_3 and $\nu_1+\nu_3$ are observed and the analyses performed accounting of Coriolis and Fermi resonances for the states corresponding to the diad [(001),(100)] and those of the triad [(002),(101),(200)].
In addition to improvements of the $^{16}O^{16}O^{17}O$ and $^{16}O^{17}O^{16}O$ species [2], 4902 new transitions corresponding ν_3($^{17}O^{17}O^{18}O$ and $^{17}O^{18}O^{17}O$) and $\nu_1+\nu_3$ ($^{17}O^{17}O^{18}O$,$^{17}O^{17}O^{16}O$,$^{17}O^{16}O^{17}O$ and $^{17}O^{17}O^{17}O$) are assigned .
We report Hamiltonian parameters, statistics for positions, comparison of band centres and rotational constants with predictions [3,4] ,as well as estimations of transition moment parameters .
Created line-lists allow to perform presented synthetic spectra in very good agreement with the observed ones.

References

[1]. Plateaux J-J, Régalia L, Boussin C, Barbe A. «Multispectrum fitting technique for data recorded by Fourier transform spectrometer: application to N_2O and CH_3D». J. Quant. Spectrosc. Radiat. Transfer 2001;68: 507–20.
[2].A Barbe ,E Starikova,M-R De Baker « High resolution infrared spectra of the $^{16}O^{16}O^{17}O$ and the $^{16}O^{17}O^{16}O$ ozone isotopic species. The 5 and 10 micron spectral ranges revisited J. Quant. Spectrosc. Radiat. Transfer 2017,http://dx.doi.org/10.1016/j.jqsrt.2017.03.034
J. Quant. Spectrosc. Radiat. Transfer 2001; 68:507–20.
[3] Tyuterev VlG, Kochanov RV, Tashkun SA, Holka F, Szalay P. New analytical model for the ozone electronic ground state potential surface and accurate *ab initio* vibrational predictions at high energy range. J Chem Phys 2013;139:134307.
[4] Tyuterev VlG, Kochanov RV, Tashkun SA. Analytical representation for the ozone electronic ground state potential function in the spectroscopically accessible range and extended vibration predictions. In: Proceedings of XVII international symposium HighRus-2012 high resolution molecular spectroscopy. http://symp.iao.ru/ru/hrms/17/proceedings

FTS high resolution spectra of $^{16}O^{16}O^{18}O$ in 900-3500 cm^{-1} range: Analyses and theoretical modeling for the polyads of coupled states.

A. Barbe[1], M.-R. De Backer[1], V. Tyuterev[1]

[1]Groupe de Spectrométrie Moléculaire et Atmosphérique
UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France
E-mail: alain.barbe@univ-reims.frmr.debacker@univ-reims.frvladimir.tyuterev@univ-reims.fr

Evgeniya N. Starikova[2],[3]

[2] QUAMER Laboratory, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia
[3] LTS, V.E. Zuev Institute of Atmospheric Optics SB RAS, 1, Akademician Zuev square, 634021 Tomsk, Russia, E-mail: starikova_e@iao.ru

The high resolution infrared spectra of ^{18}O enriched ozone isotopologues have been recorded in the 900-3500 cm^{-1} spectral range with the Reims Fourier Transform Spectrometer [1,2] allowing to assign 12 bands of the most abundant isotopic species in the atmosphere, $^{16}O^{16}O^{18}O$.

In the cases when all bands of corresponding polyad interacting states were observed, we used for their analyses the theoretical approach that has early been applied in the case of the main isotopologue of ozone [3]. This approach is based on the determination of all resonance coupling parameters of the polyad effective Hamiltonian model via very accurate predictions from the molecular potential energy surface (PES) [4,5], using high-order Contact Transformation (CT) method [6,7]. Some of these parameters were adjusted during the fit of observed transitions. In the other cases, only “necessary”resonance parameters were introduced in the effective Hamiltonian models.

We report here the Hamiltonian and transition moment parameters, statistics for observed transitions and corresponding energy levels, the comparison of rotational constants and band centers with the recent predictions from ozone potential energy surface [4,5], some examples of mixing coefficients and of agreements between observed and synthetic spectra. The data will be included in the S&MPO information system [8] (http://www.ozone.univ-reims.frand http://www.ozone.iao.ru).

References

[1] Plateaux J-J, Barbe A, Delahaigue A. «Reims high resolution Fourier transform spectrometer data reduction for ozone». Spectrochim.Acta Part A 1995; 51:1153–69.

[2] Plateaux J-J, Régalia L, Boussin C, Barbe A. «Multispectrum fitting technique for data recorded by Fourier transform spectrometer: application to N2O and CH3D». J Quant SpectroscRadiat Transfer 2001; 68:507–20

[3] Barbe A, De Backer-Barilly M-R, Starikova E, Taskun SA, Thomas X, TyuterevVlG, «FTS high resolution of 16O3 in 3500 and 5500 cm-1 regions. First example of new theoretical modelling for a polyad of strongly coupledstates». J. Quant. Spectrosc. Radiat. Transfer 2012; 113:829–39.

[4] TyuterevVlG, Kochanov RV, Tashkun SA, Holka F, Szalay P. New analytical model for the ozone electronic ground state potential surface and accurate *ab initio* vibrational predictions at high energy range. J ChemPhys 2013; 139:134307.

[5] TyuterevVlG, Kochanov RV, Tashkun SA. Analytical representation for the ozone electronic ground state potential function in the spectroscopically accessible range and extended vibration predictions. In: Proceedings of XVII international symposium HighRus-2012 high resolution molecular spectroscopy. http://symp.iao.ru/ru/hrms/17/proceedings

[6] TyuterevVlG, Tashkun SA, Seghir H. High-order contact transformations: General algorithm, computer implementation and triatomic tests. SPIE Proc Ser 2004; 5311:164–75.

[7] TyuterevVlG, Tashkun SA, Rey M, Kochanov RV, Nikitin AV, Delahaye T. Accurate spectroscopic models for methane polyads derived from a potential energy surface using high-order Contact Transformations. J PhysChem A. 2013; 117:13779–805.

[8] Babikov Y, Mikhailenko S, Barbe A, Tyuterev V, «S&MPO – An information system for ozone spectroscopy on the WEB. J Quant SpectroscRadiat Transfer », 2014; 145:169– 191.

Highly excited levels of the $^{16}O/^{18}O$ ozone isotopologues by CRDS near the dissociation energy

D. Mondelain, A. Campargue, S. Kassi

Laboratoire Interdisciplinaire de Physique, UMR CNRS 5588, Univ. Grenoble 1/CNRS-38041 Grenoble, France.

We are involved in a long term effort aiming at characterizing highly excited rovibrational states of ozone isotopologues in the electronic ground state towards the dissociation limit (D_0 ~8480 cm^{-1}). In the recent years, the very weak vibrational bands in the 5850-7920 cm^{-1} spectral range were detected and analysed by high sensitivity Cavity Ring Down Spectroscopy (CRDS). The homogeneous isotopologues ($^{16}O_3$ and $^{18}O_3$) were first studied followed by the symmetric and asymmetric ^{18}O-enriched isotopomers. Using energy predictions and normal mode assignment of vibrational levels from the ground state potential energy surface (PES) and an effective Hamiltonian model several tens of bands were rovibrationally assigned by the GSMA group in Reims [1].

In this talk, we will review the rovibrational bands analysed for the different species. As a result of the extreme sensitivity of the CW-CRDS recordings, unexpected broad features due to the $^3A_2$ (000)- X^1A_1(110) hot band were also detected between 7700 and 7920 cm^{-1} for the $^{18}O_3$ species permitting to investigate the spectroscopy and predissociation of the $^3A_2$(000) state. Finally, new experiments planned to further approach the dissociation limit by using a CRD spectrometer based on an external cavity diode laser (ECDL) will be described.

This work was performed under the ANR project "IDEO" (NT09_436466) and is presently supported by the LEFE-ChAt programm (INSU, CNRS).

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[1] V.G. Tyuterev et al., PRL 113 (2014) 143002.

Satellite observation of lowermost tropospheric ozone by multispectral synergism of IASI thermal infrared and GOME-2 ultraviolet measurements

J. Cuesta[1], M. Eremenko[1], X. Liu[2], G. Dufour[1], G. Foret[1], A. Coman[1], Z. Cai[3], M. Beekmann[1],
M. Höpfner[4], T. von Clarmann[4], J. Orphal[4], K. Chance[2] and J.-M. Flaud[1]

[1]LISA, UMR 7583 CNRS, UPEC, UPD, Créteil, France
[2]Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts, USA
[3]IAP, Chinese Academy of Sciences, Beijing, China
[4]IMK, KIT, Karlsruhe, Germany

Tropospheric ozone is currently one of the air pollutants posing greatest threats to human health and ecosystems. Monitoring ozone pollution at the regional and global scale is a crucial societal issue. Only spaceborne remote sensing is capable of observing tropospheric ozone at such scales. However, current spaceborne observations of operational systems use single-band measurements (either UV or IR), which only offer sensitivity to ozone at the free troposphere at lowest and thus with limited application for air quality.

Recently, we have developed an innovative multispectral approach, so-called IASI + GOME2[1], which combines IASI and GOME-2 spectral measurements, respectively in the IR and UV. The approach simultaneously fits both spectra for retrieving a single ozone vertical profile for each satellite pixel. In order to do so, consistent spectral databases of ozone in the IR and the UV are needed. Among several tests performed with different spectroscopic databases, we have only obtain good agreement between IASI + GOME2 retrievals in the troposphere and ozonesondes when using HITRAN 2004 and Brion et al., 1993[2].

The first analyses of the new multispectral ozone observations are focused on a typical ozone pollution event under anticyclonic conditions, over Europe and East Asia during the summer of 2009. We have compared IASI+GOME-2 with single-band methods (IASI, GOME-2 and OMI). Only IASI+GOME-2 depicts ozone plumes located below 3 km of altitude (both over land and ocean). Indeed, the multispectral sensitivity in the LMT in terms of degrees of freedom is greater by 40% and its maximum peaks at 2 to 2.5 km of altitude over land, at least 0.8 to 1 km below that for the single-band methods. Comparisons with ozonesondes show a low mean bias (3%) and a 20 % precision for IASI+GOME2. Good agreement is also found with chemistry-transport model simulations. Moreover, IASI+GOME2 retrievals allow an innovative estimation of LMT ozone production along transport across the continental scale, as used in combination with other pollutant retrievals such as carbon monoxide.

In this presentation, we will show an overview of the IASI+GOME2 method that has allowed the observation of ozone plumes in the lowermost troposphere (LMT, below 3 km of altitude), for the first time from space.

[1] Cuesta, J., et al.: Satellite observation of lowermost tropospheric ozone by multispectral synergism of IASI thermal infrared and GOME-2 ultraviolet measurements over Europe, Atmos. Chem. Phys., 13, 9675-9693, doi: 10.5194/acp-13-9675-2013, 2013
[2] Brion, J., et al., C.: High-resolution laboratory absorption cross section of O3: Temperature effect, Chem. Phys. Lett., 213, 610–612, doi: 10.1016/0009-2614(93)89169-I, 1993.

Line-shape problems in modelling laboratory and atmospheric spectra

Ha Tran

Laboratoire de Météorologie Dynamique, UMR CNRS 8539

Université Pierre et Maries Curie, 4 Place Jussieu, 75252 Paris Cedex 05

ha.tran@lmd.jussieu.fr

It is now well known that the widely-used Voigt profile does not well describe absorption line shapes of molecular gases. This is due to several collision effect which are neglected by the use of the Voigt profile such as the Dicke narrowing, the speed dependences of the collisional parameters, the collisional interferences between lines (line-mixing). Examples of the influence of these non-Voigt effects on the extraction of spectral line parameters from laboratory measured spectra as well as on atmospheric spectra analysis will be given. A short review on the recent theoretical approaches, models and results on the topic of isolated line shapes and of line-mixing will be presented.

Model of electronic-vibrational kinetics of the products of ozone and molecular oxygen photodissociation in the mesosphere and lower thermosphere of the Earth

V. A. Yankovsky*, vyankovsky@gmail.com; v.yankovsky@spbu.ru

**Saint-Petersburg State University, 7/9 Universitetskaya nab., St. Petersburg, 199034 Russia*

The model of photodissociation of ozone and molecular oxygen YM2011 in the mesosphere and the lower thermosphere of the Earth in daytime [1], developed at the Department of Atmospheric Physics of the St. Petersburg State University, considers the populations of 44 electronically-vibrationally excited levels of the three lower electronically excited states of the oxygen molecule.

The concentrations of the molecules $O_2(X^3\Sigma_g^-, v = 1 – 35)$, $O_2(a^1\Delta_g, v = 0 – 5)$, $O2(b^1\Sigma_g^+, v = 0, 1, 2)$ are calculated from the solution of the system of 44 kinetic equations for these excited levels. The system of kinetic equations can be solved analytically, taking into account the hierarchical location of the excited levels as a function of energy.

In the formation of altitude distributions of the vibrational level populations of the oxygen molecule in the ground electronic state $O_2(X^3\Sigma_g^-, v = 1 – 35)$ we took into account not only the direct excitation channel in photolysis of ozone in the bands of Hartley, Chappuis, Huggins and Wulf (200 – 900 nm), but also transfer of energy from excited levels of $O_2(a^1\Delta_g, v = 0 – 5)$, $O_2(b^1\Sigma_g^+, v = 0, 1, 2)$ which are populated both as a result of ozone photolysis in the Hartley band, and as due to energy transfer from the excited oxygen atom $O(^1D)$.

For different atmospheric conditions (season, latitude, zenith angle of the Sun, etc.), the altitude distributions of volume emission rates are calculated not only for traditional oxygen bands of 1.27 µm IR Atm (0, 0) and 0.762 µm Atm (0, 0), but also for the system of atmospheric bands $O_2(b^1\Sigma_g^+, v' \rightarrow v'')$ for v' and v'' equal to 1 or 2.

An analysis of the uncertainties of solutions of the direct and inverse problems (on the retrieval of the altitude profiles of ozone and atomic oxygen) was carried out using the sensitivity analysis of the entire model YM2011, performed in the form of analytical formulas. In the model YM2011, we use a specially compiled by us database of the reaction rate coefficients and quantum yields of the reaction products for all the electronically-vibrationally excited oxygen molecules [1].

1. Yankovsky V. A., Martyshenko K. V., Manuilova R. O., Feofilov A. G. (2016) Oxygen dayglow emissions as proxies for atomic oxygen and ozone in the mesosphere and lower thermosphere. J. Molecular Spectroscopy, V.327, P.209-232, DOI:10.1016/j.jms.2016.03.006.

Non-linear frequency-sweep correction of quantum cascade lasers and laser based shift measurement of molecular lines of ozone at 9.54 µm

M. Minissale[1,2,3], T. Zanon-Willette,[1] I. Prokhorov,[4] H. Elandaloussi,[1] P. Jeseck,[1]
Corinne Boursier[1], and C. Janssen[1]

1) LERMA –IPSL, Sorbonne Universités, Univ Paris 06, Observatoire de Paris, PSL Research University, CNRS, UMR 8112, Paris, France.

2) Aix Marseille Université, CNRS, PIIM UMR 7345, 13397 Marseille, France

3) Aix-Marseille Université, CNRS, Centrale Marseille, Institut Fresnel UMR 7249, 13013 Marseille, France

4) Institute of Environmental Physics, Heidelberg University, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany

Tunable electromagnetic sources, such as voltage controlled oscillators (VCO) or diode lasers are often required to be linear during frequency-sweep modulation. Unfortunately theses sources suffer from non-linearities that require special attention and in molecular spectroscopy one often employs a post-analysis based on local frequency markers. We present here a simple and universal method, based on a pre-distortion voltage ramp, which minimizes the non-linear frequency response of tunable electromagnetic sources. Using a current-driven Quantum Cascade Laser (QCL) as an example, we demonstrate that the non-linearity can easily be reduced by a factor of ten when using a single distortion parameter. We show that in the case of IR absorption spectrum of ozone at 9.54 µm, we obtain a reduction of the frequency scale error by two orders of magnitude.

Additionally, we present measurements of the pressure shift of ozone molecular lines. Using the second harmonic detection technique, we obtain the pressure shift parameter of 4 intense rovibrational transitions in the υ_3 fundamental band of ozone induced by the noble gases He, Ar, and Xe. The high density of transitions in the υ_3 spectral region of ozone make this region particularly difficult to study with more commonly used techniques in high resolution molecular spectroscopy, such as Fourier transform spectroscopy (FTS). The comparatively high spectral resolution of the QCL in the MHz range, on the contrary, allows to measure molecular shifts at relatively low pressures (from 2 to 80 mbar), thus reducing the impact of spectral congestion due to pressure broadening of molecular lines. A systematic use of this technique could be very useful to make up for the lack of shift parameters for υ_3 lines in molecular spectral databases. A subsequent stabilization of the QCL onto an optical frequency comb will open up possibilities to perform metrological measurements of Doppler-free molecular lines.

New quantitative ozone spectroscopic studies over multiple spectral regions

C. Janssen,[1] H. Elandaloussi,[1] P. Jeseck,[1] Corinne Boursier,[1] Y. Té,[1] J. Gröbner[2]

1) LERMA-IPSL, UPMC Univ Paris 06, CNRS, Observatoire de Paris, PSL Research University, Sorbonne Universités, Paris, France.
2) Physikalisches Meteorologisches Observatorium Davos, World Radiation Center, Davos Dorf, Switzerland

Remote sensing of atmospheric ozone is based on spectroscopic data using a variety of different instruments, techniques and platforms, covering several regions of the electromagnetic spectrum. Two spectral regions are of particular interest, the Huggins bands in the UV as well as the ν_1-ν_3 spectral region in the atmospheric window. But other regions, such as the regions at 5 or 3.3 µm have also gained recent in planetary remote sensing.

Here we present first room temperature measurements of the absolute absorption cross section of ozone at the HeCd laser line position at 325 nm in the Huggins band. The highly accurate data with uncertainty in the 0.2 percent range might serve as a calibration standard or reference point for available and newly upcoming UV-VIS spectra that are used in satellite missions.

We also report on a recent atmospheric multi-spectral study using the ground based FTS in Paris where we compare the ν_1+ν_3 spectral region at 5 µm with the region at 10 µm. Depending on the data base used, different ozone columns are retrieved. This points towards differences in the spectroscopic data, which we discuss in detail.

Finally, we give an overview on ongoing multi-spectral activities at the Reims and Paris laboratories.

Study of the (004) / (103) / (310) ozone system: current status

A. Barbe[a], S. Mikhailenko[b]

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

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

The first analysis of the (004)/(103)/(310) interacting states of $^{16}O_3$ molecule was done in the 2.5 micron spectral range by A. Perrin et al. [1], using KIT PEAK FTS recorded spectra, at a resolution of 0.010 cm^{-1}. Overall 552 rotation-vibration energies (J_{max} = 46, $K_{a\ max}$ = 17) were fitted with an *RMS* = 0.0033 cm^{-1}.

Later a set of observed data in Reims was extended by A. Barbe et al with a 0.004 cm^{-1} resolution and much larger pressure × length amount [2]. Up to about 1300 energies with maximum values of the rotational numbers J_{max} = 57 and $K_{a\ max}$ = 19 were assigned.

The analysis of this extended data set requires to add vibrational states in the fitting procedure: The analyzed system includes now eight interacting states: (004)/(103)/(310)/(032) + (211)/(140) + (202)/(131).

We report in this talk the last results of the extended system analysis.

References
[1] A. Perrin et al., *J. Mol. Spectrosc*. 149, 519-529 (1991)
[2] A. Barbe et al., *JQSRT*, 130, 172-190 (2013)

Ozone absorption cross-section measurements in the UV-Hartley band

G. Albora[1], A. Alkadrou[1], M-R. De Backer[1], B. Grouiez[1], M. Rotger[1], L. Daumont[1], N. De Oliveira[2], K. Ito[2], D. Joyeux[2]

[1]*Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, Université de Reims, 51100 Reims, France*

[2]*Synchrotron SOLEIL, L'Orme des Merisiers, 91192 GIF-sur-YVETTE, France*

Ozone is an important minor constituent of the Earth's atmosphere. It plays a significant role in atmospheric radiative transfer and tropospheric chemistry as it is the third largest contributor to greenhouse radiative forcing after CO_2 and CH_4. So, long-term measurements of tropospheric ozone have been performed globally for more than 30 years with UV photometers (ground based instruments as Dobson and/or Brewer and balloons).

In the UV-Visible range, 240–790 nm region, the O_3 absorption cross-sections can be separated into four systems: the Hartley band, the Huggins bands, the Chappuis band, and the Wulf bands. For all these bands, there exists a large number of laboratory measurements using different spectrometers and experimental conditions. Many measurements have been published in the past 20 years (see IGACO website [1] and [2]) and recently, studies have been performed by Viallon et al. [3] and Serdyuchenko et al. [4-5].

As the ozone laboratory data available today do not fill all the requirements of the last ACSO report 2015 [6], this committee recommends continuing the different efforts in measuring Ozone Absorption cross-sections in different laboratories.

For the first time, we have used the DESIRS Beamline of the French SOLEIL synchrotron to record the absorption cross-sections of ozone in the 200-300 nm range.

Additional measurements are also due to be done in the frame of an ESA contract using a new crossed cell built at GSMA and the BRUKER IFS 125HR of the laboratory. The set-up is tested with measurements of SO_2 cross sections before it is applied to the O_3 molecule. The results will be compared to the "BDM" cross sections recorded at GSMA some decades ago using a grating spectrometer.

References

[1] http://igaco-o3.fmi.fi/ACSO

[2] J. Orphal "A critical review of the absorption cross-sections of O_3 and NO_2 in the ultraviolet and visible", Journal of Photochemistry and Photobiology A: Chemistry 157, 185-209 (2003)

[3] J. Viallon, S. Lee, P. Moussay, K. Tworek, M. Petersen, and R.I. Wielgosz, "Accurate laser measurements of ozone absorption cross-sections in the Hartley band", Atmos. Meas. Tech. Discus. 7, 8067-8100, 2014

[4] V. Gorshelev, A. Serdyuchenko, M.Weber, W. Chehade, and J. P. Burrows, "High spectral resolution ozone absorption cross-sections – Part 1: Measurements, data analysis and comparison with previous measurements around 293K", Atmos.Meas. Tech., 7, 609–624, 2014

[5] A. Serdyuchenko, V. Gorshelev, M.Weber, W. Chehade, and J. P. Burrows, "High spectral resolution ozone absorption cross-sections – Part 2: Temperature dependence", Atmos. Meas. Tech., 7, 625–636, 2014

[6] J. Orphal, J. Staehelin, J. Tamminen, G. Braathen, *et al.* "Absorption cross-sections of ozone – Status report 2015", Journal of Molecular Spectroscopy special issue "New visions of spectroscopic databases" 2016 (submitted).

Temporal patterns of surface ozone levels and its relation with radon (^{222}Rn) and air quality

M. Zoran[1], D. Savastru[1], A. Dida[2]

[1]*National Institute of R&D for Optoelectronics, Bucharest -Magurele, Romania*

[2]*University Transylvania of Brasov*

This paper aims to explore trends of surface ozone levels in relation with radon (^{222}Rn), particle matter (PM2.5, PM10), nitrogen dioxide (NO_2), and sulphur dioxide (SO_2) over year 2012 at a periurban monitoring station of Bucharest metropolitan region in Romania. Specifically, daily mean monitoring concentrations of particle matter (PM2.5, PM10), ozone (O_3), nitrogen dioxide (NO_2), and sulphur dioxide (SO_2) have been analyzed in relation with recorded radon (^{222}Rn) concentrations in the air near the ground and global air quality indices (AQI) during 2012 year. The frequency distribution patterns of each target compound were evaluated for entire year using the relevant daily mean values (Fig.1). Figure 2 shows an anticorelation between the temporal variation of daily mean ground level ozone concentrations and daily mean particle matter PM10 for the year 2012 for Bucharest periurban test site. The changes recorded in the particulate matter PM2.5 and PM10 content are expected to affect considerably the photolysis of ozone and the rates of heterogeneous losses of ozone and its precursors. Also, increased temperatures during summer time may lead to increased biogenic isoprene emissions, strengthening the regional-scale ozone contribution.

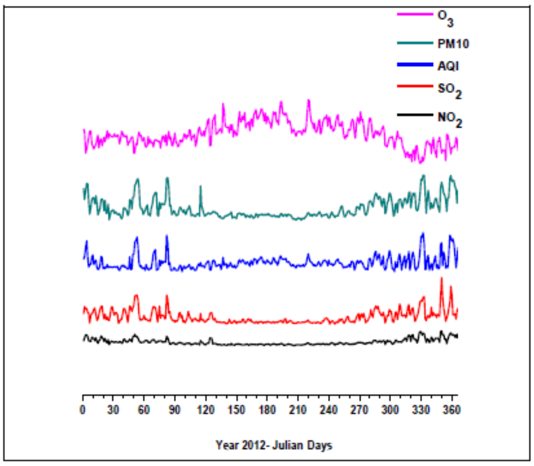

Figure 1

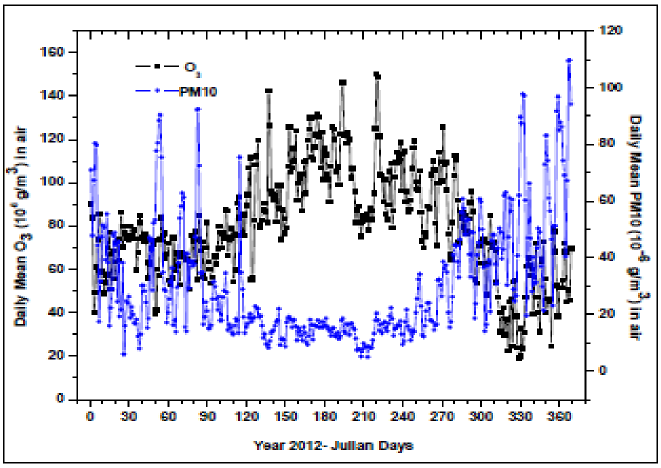

Figure 2

The ozone episodes in Bucharest metropolitan area are dominated by regular summertime pressure patterns and of ozone formation under urban heat island (UHI) phenomenon. Ozone formation is mainly controlled by chemistry, dry deposition, vertical transport, and horizontal transport processes. The ground level ozone concentrations are enhanced mainly by the vertical mixing of ozone-rich air from aloft, whereas dry deposition process mainly depletes ozone. Horizontal transport and chemistry processes play opposite roles in the net change of ozone concentration between central urban and periurban areas. The high ozone was first observed in central urban area and then was transported to the periurban area by local winds. Correlation analysis and principal component analysis (PCA) explained association of NO_2 with traffic related pollutants (PM, and SO_2) at a statistically significant level while O_3 exhibited patterns correlated with meteorological parameters. However, because of the prominent contribution of traffic sources in urban area of Bucharest, NO_x (NO + NO_2) is often used as a tracer of road traffic emissions, contributing to the formation of secondary airborne pollutants like O_3 and PM2.5, while ^{222}Rn is used as a tracer for atmospheric stability or turbulence analysis.

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Gas phase reaction of ozone with C5 and C6 unsaturated aldehydes and alcohols

C. Kalalian, E. Roth, A. Chakir

Carmen.kalalian@univ-reims.fr

Groupe de Spectrométrie Moléculaire et Atmosphérique GSMA, UMR CNRS 7331, Université de Reims, Moulin de la Housse B.P. 1039, 51687 Reims Cedex 2.

Emissions of biogenic volatile organic compounds (VOCs) are higher than those from anthropogenic sources. They are therefore likely to have a great influence on atmospheric chemistry both locally and regionally, through their impact on the HO_x balance ($HOx = HO + HO_2$), ozone production and ability to form secondary organic aerosols (SOA). Among the volatile organic compounds of biogenic origin are the family of C_5 and C_6 unsaturated aldehydes and alcohols. Few information exist regarding the fate of these compounds in the atmosphere especially there reaction with ozone.

In this work, we studied the kinetics and the mechanisms of the reaction of three unsaturated aldehydes (trans-2-pentenal, trans-2-hexenal and 2-methyl-2-pentenal) and three unsaturated alcohols (1-penten-3-ol, cis-2-penten-1-ol and trans-3-hexen-1-ol) with ozone O_3 in a rigid atmospheric simulation chamber coupled to an FTIR spectrometer and to an SPME-GC/MS at four different temperatures (273, 298, 333 and 353 K) and at atmospheric pressure. The rate constants of the ozonolysis reaction of the unsaturated aldehydes and unsaturated alcohols studied were determined and yielding the Arrhenius expressions (cm^3 molecule $^{-1}$ s^{-1}):

k (Trans -2-pentenal)= $1.38 \pm 0.73) \times 10^{-16}$ exp $(-(1406 \pm 163)) / T$

k (Trans-2-hexenal)= $(1.79 \pm 0.54) \times 10^{-16}$ exp $(-(1457 \pm 90)) / T$

k(2-Methyl-2-pentenal)= $(1.42 \pm 0.56) \times 10^{-17}$ exp $(-(664 \pm 124)) / T$

k(1-penten-3-ol) = $(1.44 \pm 1.12) \times 10^{-16}$ exp $(-(650 \pm 224)) / T$

k(Cis-2-penten-1-ol)= $(1.76 \pm 0.24) \times 10^{-15}$ exp $(-(891 \pm 41)) / T$

k(Trans-3-hexen-1-ol)= $(7.24 \pm 3.44) \times 10^{-16}$ exp $(-(726 \pm 139)) / T$

This work is the first temperature dependence study for the reaction of ozone with above-mentioned alcohols and aldehydes. Carbonyl product Formation yields were also measured. On the basis of the product measurement and kinetic results a reaction mechanisms are outlined and the atmospheric persistence of the compounds studied is discussed.

Friday October 6, 2017 Program		
Databases **Chair : A. Barbe**	**9:05 – 9:35**	F1 - V. Gorshelev
	9:40 – 10:10	F2 - R. Armante
	10:15	End of session
	10:15 – 10:45	Coffee break
Databases	**10:45 – 11:15**	F3 - I. Gordon
	11:20 – 11:40	F4 - V. Boudon
	11:45 – 12:05	F5 - M. Rey
	12:10	End of session
	12:15 – 13:45	Lunch
Other molecules **Chair : M. Rotger**	**14:15 – 14:35**	F6 - A. Perrin
	14:40 – 15:00	F7 - E. Neeman
	15:05 – 15:20	F8 - M. Mattoussi
	15:25 – 15:40	F9 - A. Boughdiri
	15:45 – 16:00	F10 - O. Ferchichi
	16:05	End of session
	16:15	Coffee break
		Departure

Updated ozone absorption cross-sections in the Huggins band

V. Gorshelev, M. Weber, J. P. Burrows

gorshelev@iup.physik.uni-bremen.de
Institute for Environmental Physics, Bremen University

The requirement to measure small changes in stratospheric and tropospheric ozone places strong demands on the accuracy of the ozone absorption cross-sections used in retrievals of spectra measured by remote sensing spectrometers. Use of the different absorption coefficients results in the retrieved ozone amounts differing by up to 3 %.

New and improved measurements of the ozone absorption cross-sections are currently being performed in the Molecular Spectroscopy Laboratory of the Institute of Environmental Physics (Bremen University). The region of interest is in the Huggins band (300 nm to 350 nm) with targeted uncertainties of 1–2 %. The new data will allow for further reduction of the uncertainties in the derived total ozone column for both ground- and satellite-based retrievals.

From GEISA-2015 to GEISA-2018: ozone content and validation

R. Armante, N. Jacquinet, A. Perrin, N. Scott, A. Chédin, L. Crépeau

Laboratoire de Météorologie Dynamique (LMD), Ecole Polytechnique, 91128 Palaiseau, France, armante@lmd.polytechnique.fr

The ARA/ABC(t) group at LMD (http://ara.abct.lmd.polytechnique.fr) develops and maintains, for over four decades, GEISA (Gestion et Etude des Informations Spectroscopiques Atmosphériques: Management and Study of Atmospheric Spectroscopic Information), a computer accessible database system available on the AERIS/ESPRI data center (http://cds-espri.ipsl.fr/etherTypo/?id=950).
For the latest version available (GEISA-2015, Jacquinet et al, 2016 [1]), an important effort was done to validate its content before delivering it to the community. Based on a strong experience in CAL/VAL activities at LMD, a quasi-automatic chain, called SPARTE (Armante et al, 2016 [2]) has been developed. Based on the direct comparison of model simulations (radiative transfer algorithm 4AOP developed and validated at LMD) and many thousands of observation like IASI and TCCON (covering Thermal and Short Wave spectral range), the chain permits to identify signature relative to spectroscopic features.

In the frame of GEISA-2015, SPARTE has been successfully applied to the validation of H_2O, CO_2 and CH_4.

Today, we will present the status of the 2015 ozone database as well as its validation made in the last months, thus preparing the validation of the next 2018 release.

[1] N. Jacquinet-Husson, R. Armante, N.A. Scott, A. Chédin, L. Crépeau, et al. *JMS* **327**, 31 (2016)
[2] R. Armante, N. Scott, C. Crevoisier, V.Capelle, L. Crepeau, N. Jacquinet, A. Chédin *JMS* **327**, 180 (2016)

HITRAN 2016 database: Reference atmospheric spectroscopy boosted by data science

I. E. Gordon (1), L. S. Rothman (1), R.V. Kochanov (1,2), Y. Tan (1), C. Hill (1,3),
and HITRAN contributors worldwide

(1) Harvard-Smithsonian Center for Astrophysics, MA, USA
(2) Tomsk State University, QUAMER, Tomsk, Russia
(3) University College London, UK

The HITRAN2016 database is now officially released. The line-by-line lists for almost all of the HITRAN molecules (including ozone and gases participating in ozone chemistry) were updated in comparison with the previous compilation HITRAN2012 [1]. The extent of the updates ranges from updating a few lines of certain molecules to complete replacements of the lists and introduction of additional isotopologues. Many more vibrational bands were added to the database, extending the spectral coverage and completeness of the datasets. The amount of parameters has also been significantly increased, now incorporating, for instance, non-Voigt line profiles [2]; broadening by gases other than air and "self" [3]; and other phenomena, including line mixing.

In addition, the amount of cross-sectional sets in the database has increased dramatically from about 50 to over 300 molecules. This update includes many recent experiments as well as existing databases that were not in HITRAN previously (for instance the PNNL database [4]). Many gases represented in cross-section part of the database are important for the terrestrial ozone chemistry.

The HITRAN2016 edition takes full advantage of the new structure and interface available at www.hitran.org [5] and the HITRAN Application Programming Interface [6].

This talk will provide a summary of the updates, emphasizing details of some of the most important or dramatic improvements.

This work is supported by the NASA AURA (NNX17AI78G) and PDART (NNX16AG51G) programs.

References

[1] L.S. Rothman *et al*, JQSRT **130**, 4 (2013).
[2] P. Wcisło *et al.*, JQSRT **177,** 75 (2016).
[3] J. S. Wilzewski *et al.*, JQSRT **168,** 193 (2016).
[4] S.W. Sharpe et al, Appl Spectrosc **58**, 1452 (2004).
[5] C. Hill *et al*, JQSRT **177**, 4 (2016).
[6] R.V. Kochanov *et al*, JQSRT **177**, 15 (2016).

Molecular Spectroscopy Databases in the Framework of the VAMDC and DAT@OSU Projects

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

[1] Laboratoire Interdisciplinaire Carnot de Bourgogne, UMR 6303 CNRS/Université Bourgogne Franche-Comté, 9 av. A. Savary, BP 47870, F-21078 Dijon Cedex, France
[2] GSMA, UMR CNRS 7331, Université de Reims Champagne-Ardenne, Moulin de la Housse B.P. 1039, F-51687 Reims Cedex, France

Using the latest results of the modeling of high-resolution infrared absorption and Raman scattering spectra performed in our two groups, we have set-up databases of calculated spectroscopic lines for several molecules of atmospheric and planetary science interest. These databases contain line positions, line intensities and collisional broadening coefficients, when available. They are complimentary to the well-known public databases like HITRAN or GEISA in the sense that, containing only calculated lines they may be, on the one hand, less accurate for some spectral regions which are not yet fully characterized, but, on the other hand, more complete so that they contain all possible lines (above a given intensity threshold).

Another particularity of these databases is that they allow to retrieve the full decomposition of molecular eigenstates on the initial basis set.

At present, we have six “CaSDa”, *i.e.* Calculated Spectroscopic Databases:

- MeCaSDa for the methane molecule ($^{12}CH_4$ and $^{13}CH_4$).
- TFMeCaSDa for the tetrafluoromethane molecule ($^{12}CF_4$).
- SHeCaSDa for the sulfur hexafluoride molecule ($^{32}SF_6$, $^{33}SF_6$, $^{34}SF_6$).
- ECaSDa for the ethylene/ethene molecule ($^{12}C_2H_4$).
- RuCaSDa for the ruthenium tetroxide molecule (RuO_4 for nine Ru isotopes).
- GeCaSDa for the germane molecule (GeH_4 for five Ge isotopes).

These databases have been set-up within the framework of the VAMDC (*Virtual Atomic and Molecular Data Centre*) [1,2,3] and are accessible through the portal of this project (http://portal.vamdc.org).

They are also referenced by the DAT@OSU project, which aims to gather research databases in the Bourgogne Franche-Comté Region (http://dataosu.obs-besancon.fr).

References

[1] M. L. Dubernet *et al.*, *J. Quant. Spectrosc. Radiat. Transfer* **111**, 2265–2278 (2010).
[2] M. L. Dubernet *et al.*, *J. Phys. B* **49**, 074003 (2016).
[3] Y. A. Ba *et al.*, *J. Quant. Spectrosc. Radiat. Transfer* **130**, 62–68 (2013).

TheoReTS: *ab initio*-based Reims-Tomsk database for atmospheric, planetological and astrophysical applications

M. Rey[1], A.Nikitin[2], Y. Babikov[2], I. Chizhmakova[3], A. Rodina[3], E. Starikova[2,3], D. Viglaska[1], Vl.G.Tyuterev [1]

[1] *GSMA, UMR CNRS 7331, Université de Reims Champagne Ardenne, Moulin de la Housse,BP 1039-51687 REIMS Cedex 2, France : michael.rey@univ-reims.fr*
[2]*Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, SB RAS, 634055 TOMSK, Russia*

[3]*Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia*

Knowledge of accurate line positions and line intensities of various molecules and theirs isotopic species in wide spectral and temperature ranges is essential for the modeling of optical properties of planetary atmospheres, brown dwarfs and for other astrophysical applications. This demonstrates the necessity of having adequate and reliable molecular line lists. The TheoReTS (Theoretical Reims Tomsk Spectra) project [1] aims at providing complete and comprehensive lists of transitions based on accurate and extensive *ab initio* variational calculations for a large variety of highly symmetric molecular species as CH_4, PH_3, C_2H_4, SiH_4, CH_3F, GeH_4 including all isotopologues. Predicted hot methane and ethylene line lists are also included. In case of very large high-temperature line lists, a data compression is implemented for fast interactive spectra. Upcoming updates will be available soon for other molecular systems as CF_4, CH_3Br, CH_3I, CH_3Cl, C_2H_2, H_2CO, CHF_3, NF_3, SF_6, etc and all their isotopologues.
The system is freely accessible *via* internet on the two mirror sites: in Reims, France (http://theorets.univ-reims.fr) and in Tomsk, Russia (http://theorets.tsu.ru).

References
[1] M. Rey, A. Nikitin, Y. Babikov, V. Tyuterev, *JMS* **327**, 138 (2016)

Investigation of the ν_8 and ν_{21} bands of propane $CH_3CH_2CH_3$ at 870.348 and 921.382 cm^{-1}: evidence of large amplitude tunnelling effects.

A.Perrin[1], Jean-Marie Flaud, F.Kwabia-Tchana[2], L.Manceron[3], P.Groner[4]

[1]Laboratoire de Météorologie Dynamique/IPSL, UMR CNRS 8539,
Ecole Polytechnique, Université Paris-Saclay, RD36, 91128 PALAISEAU Cedex, France.
[2]Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR7583 CNRS Univ. Paris Est Créteil and Univ. Paris 7 Denis Diderot, Institut Paul Simon Laplace (IPSL), 94010 Créteil, France
[3]Synchrotron SOLEIL,Beamline AILES, L'Orme des Merisiers, BP 48, 91192 Saint-Aubin, France, and MONARIS, UMR 8233 CNRS- Univ. Pierre et Marie Curie, 4 place Jussieu, 75252 Paris Cedex, France;
[4]Department of Chemistry, University of Missouri-Kansas City, MO64113, USA

We present the first investigation of the ν_8 band (B-type, C-C stretch, at 870.348 cm^{-1}), together with an extended analysis of the ν_{21} band (A-type, CH_3 rock, at 921.382 cm^{-1}) of propane, (C_3H_8). Our previous investigation of the ν_{21} band [1,2] has revealed that the rotational energy levels of 21^1 are split by interactions with the internal rotations of the methyl groups, leading to the identification of AA, EE and AE+EA components. During this new investigation a similar behaviour was observed for the B-type ν_8 band [3], and the analysis of the ν_{21} band was pursued in more details. One of the goals of the present study is an attempt to explain the behaviour of these torsional splittings through the understanding of anharmonic and Coriolis resonances couplings the 21^1 and 8^1 states with nearby highly excited internal rotation states. For this, an effective Hamiltonian model was built which accounts both for the observed "classical" vibration resonances together with the torsional splittings. In parallel, a code computing the line intensities was developed to help somehow assigning unambiguously torsional components. As during our first investigation, the line assignments were performed using a high resolution (0.0015 cm^{-1}) IR spectrum of propane, recorded with a Bruker IFS-125 Fourier transform spectrometer coupled to the synchrotron radiation at the French light source facility at SOLEIL The final goal of this work is to prepare a linelist of positions and intensities which can be used for the detection of propane in the Earth and outer planets atmospheres.

References

[1] A.Perrin, F. Kwabia-Tchana, J.M.Flaud, L.Manceron, P.Groner, W.J.Laferty. *J. Mol. Spectrosc.*, **315**, 55-62, 2015

[2] A.Perrin, F.Kwabia-Tchana, J.M.Flaud, L.Manceron, J.Demaison, N.Vogt, P.Groner, TG04, ISMS Illinois, (2015)

[3] P.Groner, A.Perrin, F.Kwabia-Tchana, L.Manceron, TA04, ISMS Illinois, (2016)

The quasi-unchanged structure of monoterpenes and their oxidation products

E. M. Neeman, M. Chrayteh, P. Drean and T. R. Huet

Univ. Lille, CNRS, UMR 8523 – PhLAM – Physique des Lasers Atomes et Molécules F-59000 Lille, France.

Biogenic volatile organic compounds (BVOCs) are emitted in abundance into the atmosphere. Their tropospheric oxidation with ozone, nitrogen oxides and hydroxyl radical is contributing to the formation of aerosols which are a major environmental issue considering the Earth's radiation budget and the associated effects on health and ecosystems. Monoterpenes are unsaturated hydrocarbons with molecular formula $C_{10}H_{16}$ belonging to the BVOCs, and constitute a major non methane emission after the isoprene. Among these monoterpene family, α-pinene,[1] β-pinene[2] and camphene[3] are emitted in high proportion mainly by pine forest and also from other plants. They are characterized by a short lifetime in the atmosphere, since they undergo several reactions, especially with ozone, leading to low volatility species involved in the formation of secondary organic aerosols. Microwave spectroscopy combined to theoretical calculation are powerful tools to study the molecular structure of these molecules as well as their ozonolysis products. In the present contribution, we report the analysis of the molecular structure of α-pinene and β-pinene and we compare them with the structure of their oxidation product myrtenal[4] and nopinone[2] respectively. The structural striking features between the reagents and the products are discussed.

References

1. E. M. Neeman, J.R. Avilés Moreno and T. R. Huet, Submitted for publication (2017)
2. E. M. Neeman, J.R. Avilés Moreno and T. R. Huet, Phys. Chem. Chem. Phys. 19, 13819-13827 (2017).
3. E. M. Neeman, P. Dréan and T. R. Huet, J. Mol. Spectrosc. 322, 50-54 (2016).
4. M. Chrayteh, P. Dréan and T. R. Huet, J. Mol. Spectrosc. 336, 22-28 (2017).

Analysis of the (ν_2+2ν_4, ν_2+ν_3, 4ν_2, ν_1+2ν_2, 2ν_1) pentad of CF_4

M. Mattoussi[1,4], M. Rey[1], A.V. Nikitin[2], I. Chizhmakova[3], M. Rotger[1],

H. Aroui[4], S. Tashkun[2], Vl.G. Tyuterev[1]

[1]*GSMA, UMR CNRS 7331, Université de Reims Champagne Ardenne, Moulin de la Housse B.P.1039, F-51687 Reims Cedex 2, France*
[2]*Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 634055 Tomsk, Russia*
[3] *Laboratory of Quantum Mechanics of Molecules and Radiative Processes, Tomsk State University, 36 Lenin Avenue, 634050 Tomsk, Russia*
[4]*LDMMP, Université de Tunis, Ecole Nationale Supérieure d'Ingénieurs de Tunis, 5 Av. Taha Hussein, 1008 Tunis, Tunisie*

The spectroscopic knowledge of Tetrafluoromethane CF_4 is essential for atmospheric measurements. This study involves the analysis of the vibrational levels and consequently the spectroscopy of diversified fundamental, harmonic and combined bands. This work is a further contribution on this subject, concerning the system of interacting bands (ν_2+2ν_4, ν_2+ν_3, 4ν_2, ν_1+2ν_2, 2ν_1). The CF_4 spectrum of this region was recorded at room temperature in the range of 1600-1800 cm^{-1}, with a spectral resolution of 0.003cm^{-1} in the GSMA Laboratory of the University of Reims Champagne-Ardenne using a Fourier transform Spectrometer of Connes type.

The data have been analyzed using the MIRS software [1] developed for XY4 tetrahedral molecules. Analysis has been performed in the O (3) $\supset$ Td group chain using the tensorial formalism, group theory and vibrational extrapolation method. Furthermore, based on full *ab initio* ro-vibrational normal mode predictions [2] and non-empirical contact transformation Hamiltonians [3], direct predictions have been occurred.

One thousand eight hundred forty-five lines were be assigned up to J max= 70, and the standard deviation is 1.458×10^{-3} cm^{-1} while line intensities were watched directly to those predicted by the *ab initio* variational calculation..

References

[1] A. V. Nikitin, M. Rey, J-P. Champion, Vl.G. Tyuterev, *J. Quant. Spectrosc. Radiat.* **113**, 1034 (2012).
[2] M. Rey, A. V. Nikitin, V. Tyuterev, *J. Mol. Spectr.* **327**, 138 (2016).
[3] V. Tyuterev *et al.*, *SPIE Proc.* **5311**, 165 (2004); J. Phys. Chem A. **117**, 13779 (2013).

Frequency analysis of the (υ2/υ3+υ6/υ5/3υ3) tetrad of CH3I

A.Boughdiri[1, 2*], M.Rey[2], A. Nikitin[3], M. Rotger[2], L. Manceron[4] and H. Aroui[1]

[1]*Laboratoire de Dynamique Moléculaire et Matériaux Photoniques, Université de Tunis, Ecole Nationale Supérieure d'Ingénieurs de Tunis, 5 Av Taha Hussein, 1008 Tunis, Tunisia*
[2]*GSMA, UMR CNRS 7331, Université de Reims Champagne Ardenne, Moulin de la Housse B.P. 1039, F-51687 Reims Cedex 2, France*
[3]*Laboratory of Theoretical Spectroscopy, Institute of Atmospheric Optics, Russian Academy of Sciences, 634055 Tomsk, Russia*
[4]*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*

Methyl iodide CH3I plays an important role in the natural iodine cycle and participates in atmospheric ozone destruction [1]. It is produced by the oceans and mainly removed from the atmosphere by solar ultraviolet radiation. It has been found to be the dominant gaseous organic iodine species in the earth's lower atmosphere. That is why, modeling the absorption spectrum of this molecule is essential for atmospheric concentration measurements.

A new high-resolution infrared spectrum of the (υ2/υ3+υ6/υ5/3υ3) bending tetrad ofCH3I in the region 1200-1600 cm^{-1} has been recorded at 296 K usingthe Bruker IFS125HR Fourier Transform Spectrometer (FTS) at the AILES beamline of SOLEIL.

The analysis of the tetrad has been performed thanks to the MIRS package [2] based on the effective Hamiltonian tensorial. This approach proved to be efficient to generate line positions and line intensities through the analysis of complex interacting band systems (so-called polyads).

In this work, we present the first results of our analysis for the (υ2/υ3+υ6/υ5/3υ3) tetrad. At present, a total of 3000 lines have been assigned and fitted in frequency with a root-mean square (RMS) about0.0009 cm-1.

References

[1] N. Bell, L. Hsu, D. J. Jacob, M. G. Schultz, D. R. Blake, J. H. Butler, D. B. King, J. M. Lobert, and E. Maier-Reimer, *Journal of Geophysical Research*,**107**, (2002).
[2] A. V. Nikitin, J. P Champion, Vl. G. Tyuterev. *J. Quant. Spectrosc. Radiat. Transf*, **82**:239–49 (2003).

Ab initio structural analysis of peroxide molecules: CH_3OOCH_3 and ClOOCl

O. Ferchichi[1,2,*], N. Derbel[1], N. Jaidane[1], T. Cours[2], A. Alijah[2]

[1] Laboratoire de Spectroscopie Atomique, Moléculaire et Applications (LSAMA), Faculté des Sciences de Tunis, Tunisie
[2] Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA), Université de Reims Champagne Ardenne, France

*Ferchich.olfa91@gmail.com

Peroxides are present in the Earth's atmosphere as pollutants [1,2] due to human activities. To monitor their chemical activities, it is important to study their structure properties.
In the present work, we are particularly interested in the study of dimethyl peroxide and chlorine peroxide, for which a discrepancy between theoretical and experimental results has persisted for more than thirty years, highlighted in a recent review article by Oberhammer titled “Gas phase structures of peroxides: experiments and computational problems [3]”.
We have analyzed the equilibrium and dynamical structures of these molecules using high-levels of theory MP2/AVTZ, MRCI/AVTZ and CCSD(T)/AVTZ in order to reconcile the theoretical and experimental results [4].

References

[1] Jackson, A. V.; Hewitt, C. N.; Crit. Rev. Environ. Sci. Technol. **29**, 175–228 (1999).
[2] Guo, J.; Tilgner, A.; Yeung, C.; Wang, Z.; Louie, P. K. K.; Luk, C. W. Y.; Xu, Z.; Yuan, C.; Gao, Y.; Poon, S.; Herrmann, H.; Lee, S.; Lam, K. S.; Wang, T. Environ. Sci. Technol **48**. 1443–1450 (2014).
[3] Oberhammer, H. ChemPhysChem **16**, 282–290 (2015).
[4] Ferchichi, O.; Derbel, N.; Jaidane, N.; Cours, T.; Alijah, A.; Phys. Chem. Chem. Phys. **19**, 21500-21506 (2017).