

# The high-resolution CRDS absorption spectrum of the $^{16}\text{O}/^{18}\text{O}$ ozone isotopologues close to the dissociation energy (5850-7920 $\text{cm}^{-1}$ )

**D. Mondelain, A. Campargue, S. Kassi, R. Jost**

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 towards the dissociation limit in the electronic ground state ( $D_0 \sim 8480 \text{ cm}^{-1}$ ). This is needed to shed light onto the dynamics behind the lab kinetic data of unusual isotope dependence of ozone formation. As a consequence of the weakness of the considered bands, Cavity Ring Down Spectroscopy (CRDS) is used for the spectra recordings. The two homogeneous isotopologues ( $^{16}\text{O}_3$  and  $^{18}\text{O}_3$ ) were first investigated in the 5850-7920  $\text{cm}^{-1}$  spectral range. More recently, the symmetric and asymmetric isotopomers of  $^{18}\text{O}$ -enriched ozone were also studied in the 5850-6900  $\text{cm}^{-1}$  spectral range using two partial pressures of  $^{16}\text{O}_2/^{18}\text{O}_2$  mixtures for ozone generation. 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 for the different species.

In this talk, we will focus on the experimental work, particularly on the CRDS set-up and on the procedure followed to separate the spectra of the  $^{16}\text{O}^{16}\text{O}^{18}\text{O}/^{16}\text{O}^{18}\text{O}^{16}\text{O}$  and  $^{18}\text{O}^{18}\text{O}^{16}\text{O}/^{18}\text{O}^{16}\text{O}^{18}\text{O}$  isotopomers. An overview of the observations will be presented together with some examples of agreement between the CRDS spectra and the spectra modelled by using the effective Hamiltonian and the dipole transition moment parameters obtained by the GSMA group.

Finally, as a result of the extreme sensitivity of the CW-CRDS recordings, unexpected broad features due to the  $^3\text{A}_2(000)$ -  $\text{X}^1\text{A}_1(110)$  hot band were also detected between 7700 and 7920  $\text{cm}^{-1}$  for the  $^{18}\text{O}_3$  species permitting to investigate the spectroscopy and predissociation of the  $^3\text{A}_2(000)$  state.

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## FTIR Experiments in Reims: Past and Future

Maud Rotger, Xavier Thomas, Marie-Renée De Backer, Alain Barbe

Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences, BP 1039, 51687 Reims Cedex 2, France, tel. : +33 326918777, Fax : +33 326913147, E-mail : [maud.rotger@univ-reims.fr](mailto:maud.rotger@univ-reims.fr)

The home-made FTIR spectrometer in Reims coupled with different absorption cells is devoted to atmospheric studies and more particularly on the spectroscopy of molecules like water, methane and its isotopologues and of course to ozone.

We present here the recent experiences on ozone in the 5 microns region with our home-made FTIR spectrometer and with a 1m long multireflection cell at room temperature. These measurements help to confirm in intensity previous measurements already performed in Reims. It enables also comparisons between our intensity measurements and those of other groups.

We also plan to perform absolute intensities measurements on the 668 isotopologue of ozone in the 10 microns region. We will present here the new set-up and experimental conditions.

**Analyses of high-resolution infrared spectra of ozone recorded by FTS and CRDS,  
including all  $^{18}\text{O}$  isotopologues. Review of the recent results.**

Alain Barbe<sup>a</sup>, Marie-Renée De Backer<sup>a</sup>, Evgeniya N. Starikova<sup>a,b</sup>

<sup>a</sup> Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR CNRS 7331, UFR Sciences, BP 1039, 51687 Reims Cedex 2, France, tel. : +33 326918777, Fax : +33 326913147, E-mail : [alain.barbe@univ-reims.fr](mailto:alain.barbe@univ-reims.fr) [mr.debacker@univ-reims.fr](mailto:mr.debacker@univ-reims.fr)

<sup>b</sup> 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](mailto:starikova_e@iao.ru)

This work is a continuation of our systematic studies of high resolution near infrared spectra of ozone in the electronic ground state. A recent review of all the data has recently been published [1] concerned with the band analyses of all  $^{16}\text{O}$  and  $^{18}\text{O}$  enriched isotopologues. We present here most of the results for the six isotopologues derived from CRDS [2] and FTS [3] spectra: spectroscopic band parameters, dipole transition moment operator parameters, as well as many examples of mixing coefficients and agreements between observed and calculated spectra. A particular attention is paid for the  $3500\text{ cm}^{-1}$  region [3], where analysis of the triad of strongly interacting (220), (121), (022) states is performed using resonance coupling parameters derived from the molecular potential energy surface via high-order Contact Transformation method [4, 5]. We also will discuss the comparisons between band centres and rotational constants derived from analyses of experimental spectra with those derived from new theoretical predictions [6]. Recent unpublished analyses and works in progress will also be presented.

[1] A. Barbe, S. Mikhailenko, E. Starikova, M.-R. De Backer, Vl.G. Tyuterev, D. Mondelain, S. Kassi, A. Campargue, C. Janssen, S. Tashkun, R. Kochanov, R. Gamache, J. Orphal, *J. Quant. Spectrosc. Radiat. Transfer* **2013**, <http://dx.doi.org/10.1016/j.jqsrt.2013.06.007>

[2] D. Mondelain, A. Campargue, S. Kassi, A. Barbe, E. Starikova, M.-R. De Backer, Vl. G. Tyuterev, *J. Quant. Spectrosc. Radiat. Transfer* **2013**, 16, 49-66.

[3] A. Barbe, M.-R. De Backer, E. Starikova, S. A. Tashkun, X. Thomas, Vl. G. Tyuterev, *J. Quant. Spectrosc. Radiat. Transfer* **2012**, 113, 829-839.

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[6] Vl. G. Tyuterev, R. Kochanov, S. Taskhun, *Proceedings of the XVII International Symposium HighRus-2012*, <http://symp;iao;ru/en/hrms/17/proceedings>.

**Updates on ozone absorption cross sections and intensities:  
From UV (253.65 nm) to IR (10  $\mu\text{m}$ ) spectral regions**

*(C. Janssen, D. Simone, M. Guinet, H. Elandaloussi, C. Camy-Peyret,  
D. Mondelain, P. Jeseck and Y.V. Té)*

The ozone absorption cross section at 253.65 nm is at the heart of the recommended reference method—the photometric method—for the determination of ozone concentrations. The currently recommended value dates back to a measurement in 1961. In this paper, we will present new absolute absorption cross section measurements at the reference wavelength, UV-IR intercomparison measurements using a diode laser operating at  $1133\text{ cm}^{-1}$  and atmospheric column density measurements by ground-based FTIR for quasi direct intercomparison between 5 and 10  $\mu\text{m}$ .

## Terahertz rotational spectroscopy of atmospheric molecules

Roman A. Motiyenko, Laurent Margulès, Olena Zakharenko & Thérèse Huet

*Laboratoire PhLAM, UMR 8523 CNRS - Université Lille 1, 59655 Villeneuve d'Ascq Cedex,  
France*

We present recent activities of the Lille spectroscopic group concerning the development and implementation of the absorption spectrometers of the terahertz range. We have built a spectrometer, using as a source, solid-state devices technique. This is a multiplication chain based on a microwave synthesizer as a primary source and combination of different Schottky diode elements. The frequency range of the spectrometer has been constantly improved in the last few years and now it covers the frequency range 0.05 – 1.5 THz. We have also built a spectrometer capable of fast scanning over wide frequency range, preserving high frequency measurement accuracy. The spectrometer is based on electronic tubes and it uses a direct digital synthesizer as a fast scanning element. Several applications of the spectrometers to the studies of molecules of atmospheric interest will be discussed.

# Accurate description of potential energy surfaces by ab initio methods: A review and application to ozone

Péter G. Szalay<sup>1</sup>, Thomas Müller<sup>2</sup>, Vladimir G. Tyuterev<sup>3</sup>

<sup>1</sup> Laboratory of Theoretical Chemistry, Institute of Chemistry, Eötvös Loránd University, Budapest, Hungary <sup>2</sup> Institute of Advanced Simulation, Jülich Supercomputer Centre, Research Centre Jülich, Jülich, Germany

<sup>3</sup> Groupe de Spectrométrie Moléculaire et Atmosphérique, Reims University, Reims Cedex 2, France

szalay@chem.elte.hu

Ab initio methods became an important tool in hands of chemists and physicists: the increased accuracy of the calculations makes this theoretical information valuable and inevitable when interpreting experimental results. It becomes in particular useful in problematic cases when usual models break down or the large amount of experimental data makes interpretation tedious.

Ozone is one of these complicated systems; a reason why this workshop has been organized.

In this presentation we review the ab initio quantum chemical methods used to study ozone and will give a systematic account of various contributions considered in the calculation but also those which inclusion seems to be unavoidable in the near future. The goal is to give a guide for all working on this field and help them to judge the accuracy and reliability of various calculations.

After the methodological overview we also summarize the most important ab initio results on the potential energy surface of ozone, show the development in terms of accuracy. Finally, the newest results will be discussed which represent a promising advance in solving some of the long-standing problems of the field.

## New potential energy surface for the ozone electronic ground state and accurate vibration predictions for spectroscopy at high energy range

Vladimir G. Tyuterev<sup>(a,#)</sup>, Roman V. Kochanov<sup>(a,b)</sup>, Sergey A. Tashkun<sup>(b)</sup>

and Peter Szalay<sup>(c)</sup>

(a) *Groupe de Spectrométrie Moléculaire et Atmosphérique UMR CNRS 7331, UFR Sciences BP 1039, 51687 Reims Cedex 2, France, E-mail: vladimir.tyuterev@univ-reims.fr,*

(b) *Laboratory of Theoretical Spectroscopy, V.E. Zuev Institute of Atmospheric Optics SB RAS 1, Akademician Zuev square, 634021 Tomsk, Russia*

(c) *Institute of Chemistry, Eötvös University, H-1117 Budapest, Pázmány sétány 1/A, Hungary*

An accurate description of the complicated shape of the potential energy surface (PES) and that of the highly excited vibration states is of crucial importance for various unsolved issues in the spectroscopy and dynamics of ozone and remains a challenge for the theory. In this work new analytical representation is proposed for the PES of the ground electronic state of the ozone molecule in the range covering the main potential well and the transition state towards the dissociation [1]. This model accounts for particular features specific to the ozone PES for large variations of nuclear displacements along the minimum energy path. The impact of the shape of the PES near the transition state (existence of the “reef structure” [2]) on vibration energy levels was studied for the first time. The major purpose of this work was to provide accurate theoretical predictions for ozone vibrational band centres at the energy range near the dissociation threshold, which would be helpful for understanding the very complicated high-resolution spectra and its analyses currently in progress. Extended *ab initio* electronic structure calculations were carried out enabling the determination of the parameters of our minimum energy path PES model resulting to a new set of theoretical vibrational levels of ozone [1]. A comparison with all available high-resolution spectroscopic data on the vibrational levels gives the root-mean-square deviations below  $1\text{ cm}^{-1}$ , that represents an unprecedented *ab initio* accuracy for ozone band centres up to 90% of the dissociation energy and a significant improvement with respect to all previously available calculations. Assignment of recently analysed bands [3, 4] observed in CRDS spectra [5] are discussed.

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- [3] A. Barbe, M.-R. De Backer, E.N. Starikova, Analyses of High-resolution infrared spectra of ozone recorded by FTS and CRDS, including all  $^{18}\text{O}$  enriched isotopologues. Review of the recent results, talk at this Workshop (2013)
- [4] A. Barbe, S. Mikhailenko, E. Starikova, M.-R. De Backer, V.I. G. Tyuterev, D. Mondelain, S. Kassi, A. Campargue, C. Janssen, S. Tashkun, R. Kochanov, R. Gamache, and J. Orphal, *JQSRT*, in press, 2013.
- [5] D. Mondelain, A. Campargue, S. Kassi, R. Jost, High-Resolution CRDS absorption spectrum of the  $^{16}\text{O}/^{18}\text{O}$  ozone isotopologues close to the dissociation energy ( $5850\text{-}7920\text{ cm}^{-1}$ ), talk at this Workshop (2013)

# Long-range interactions in the ozone molecule: spectroscopic and dynamic points of view

Maxence Lepers<sup>1</sup>, Béatrice Bussery-Honvault<sup>2</sup> and Olivier Dulieu<sup>1</sup>

<sup>1</sup> *Laboratoire Aimé Cotton, CNRS/Univ. Paris-Sud/ENS-Cachan, Orsay, France*

<sup>2</sup> *Laboratoire Interdisciplinaire Carnot de Bourgogne, CNRS—Université de Bourgogne, Dijon, France*

Using the multipolar expansion of the electrostatic energy, we have characterized the asymptotic interactions between an oxygen atom  $O(^3P)$  and an oxygen molecule  $O_2(^3\Sigma_g^-)$ , both in their electronic ground state. We have calculated the interaction energy induced by the permanent electric quadrupoles of O and  $O_2$  and the van der Waals energy. On one hand we determined the 27 electronic potential energy surfaces including spin-orbit connected to the  $O(^3P) + O_2(^3\Sigma_g^-)$  dissociation limit of the O- $O_2$  complex. On the other hand we computed the potential energy curves characterizing the interaction between  $O(^3P)$  and a rotating  $O_2(^3\Sigma_g^-)$  molecule in its lowest vibrational level. Such curves are found adiabatic to a good approximation, namely they are only weakly coupled to each other. These results represent a first step for modeling the spectroscopy of ozone bound levels close to the dissociation limit, as well as the low energy collisions between O and  $O_2$  thus complementing the knowledge relevant for the ozone formation mechanism.



# A new global potential energy surface for the ground state of ozone based on explicitly-correlated MRCI-F12 *ab initio* data

Richard Dawes

*Missouri University of Science and Technology, Rolla, USA*

A new global potential energy surface for the ground state of ozone is presented. I will discuss the development of a high-level *ab initio* method (GDW-MRCI) designed to allow the electronic wavefunction to smoothly evolve across the PES and provide an accurate and balanced description of the various regions. For the new ozone PES, a total of 20 states were included in the calculations using dynamic weighting. A parallel scheme based on interpolating moving least squares (IMLS) was used to construct the *ab initio* PES automatically.

The new PES includes a spin-orbit correction and tends asymptotically to the recently developed long-range electrostatic model of Lepers *et al.* (JCP **137**, 234305, 2012). Features include 1) excellent equilibrium structural parameters, 2) good agreement with experimental vibrational levels, 3) accurate dissociation energy, and 4) most-notably, a transition region without a spurious reef. The origin of the spurious reef is understood from an electronic structure standpoint. Implications for kinetics and the results of quantum scattering calculations will be discussed. Time permitting, mention will be made of further applications of the developed methods, such as the transfer of ozone's isotope signature into other systems such as CO and CO<sub>2</sub>.

The Multi-Configuration Time-Dependent Hartree (MCTDH) method. Possible applications to Ozone

Fabien Gatti, *CTMM Institut Charles Gerhardt UMR-CNRS 5253 University of Montpellier, France*;  
Hans-Dieter Meyer, *Institute for Physical Chemistry  
University of Heidelberg, Germany*.

We present the Multi-Configuration Time-Dependent Hartree (MCTDH) approach [1]. MCTDH is a general algorithm to solve the time-dependent Schrödinger equation for multidimensional dynamical systems consisting of distinguishable particles. MCTDH can thus determine the quantal motion of the nuclei of a molecular system evolving on one or several coupled electronic potential energy surfaces.

The possibilities offered by the Heidelberg MCTDH package [2] are also presented: calculation of photoabsorption spectra, cross sections, eigenstates and quantum resonances, dynamics around conical intersections, etc. Some illustrations are given in the context of the spectroscopy of ozone.

[1] H.-D. Meyer, F. Gatti, and G. Worth, *Multidimensional Quantum Dynamics: MCTDH Theory and Applications* Wiley-VCH, 2009.

[2] See <http://www.pci.uni-heidelberg.de/tc/usr/mctdh/>

## OZONE PHOTOLYSIS: STRONG ISOTOPOLOGUE/ISOTOPOMER SELECTIVITY IN THE STRATOSPHERE

Fabien Gatti, *CTMM Institut Charles Gerhardt UMR-CNRS 5253 University of Montpellier, France*;  
Steve ndengué, Rémy Jost, *Univ. Grenoble 1 / CNRS, LIPhy UMR 5588, Grenoble, F-38041, France*.

Using the visible-UV absorption cross section (Abs. XS) of five ozone isotopologues and an averaged actinic flux, we have calculated the contribution of the atmospheric ozone photolysis to the oxygen isotope and ozone isotopologue/isotopomer enrichment. Five ozone isotopologues/isotopomers are considered among which three are symmetric,  $O^{16}O_2$  (noted 666),  $O^{16}O^{17}O^{16}$  (676) and  $O^{16}O^{18}O^{16}$  (686), and two are asymmetric,  $O^{17}O_2^{16}$  (667) and  $O^{18}O_2^{16}$  (668). The photolysis rates of the five ozone isotopologues have been calculated as a function of altitude. The Multi Configuration Time Dependent Hartree (MCTDH) method and the potential energy surfaces calculated by R. Schinke and *coworkers* have been used. We have used experimental actinic fluxes, averaged for latitude and season, for altitudes varying by step of 4km up to 80km. Below 35km, the contribution of the Hartley band to the photolysis rates is restricted to its low energy range, named the Huggins band, which has strong isotopologue/isotopomer selectivity and then induces strong enrichment. Consequently, the isotopologue enrichment's due to ozone photolysis are strongly dependent of the altitude, with pronounced enrichment peaks around 35 km, the altitude corresponding to the maximum relative contribution of the Huggins band.

**Experimental and Modelling Studies of Anomalous Oxygen Isotope Effects in the Formation of Carbon Dioxide from Irradiated Mixtures of Carbon Monoxide and Ozone or Oxygen – evidence for the spin-forbidden process  $O_3 + h\nu \rightarrow O(^1D) + O_2$  at wavelengths larger than 380 nm.**

*(D. Simone, C. Janssen, LMT Joellsson and MS Johnson)*

The ozone isotope anomaly due to the three body association  $O + O_2 + M \rightarrow$  is one of the few examples of a chemical reaction, that produces large mass independent isotope fractionations. Investigations of other systems are sparse, but mass independent fractionation in the spin-forbidden  $O + CO + M \rightarrow CO_2 + M$  reaction has been reported. Here we present kinetic studies that provide indirect evidence for  $O(^1D)$  production in the photolysis of  $O_3/O_2$  mixtures at  $\lambda > 380$  nm through the spin forbidden dissociation  $O_3 + h\nu \rightarrow O(^1D) + O_2$ . Including this channel in the isotope kinetic analysis, sheds new light on earlier experiments, indicating that the  $O + CO$  reaction likely is no source of mass independent fractionation.

# **"Ozone: challenges for the next century"**

Johannes Orphal  
KIT, Karlsruhe, Germany

Atmospheric ozone was discovered in the late 19th century and has been measured routinely for nearly 100 years. In this talk, I will try to review the current status of knowledge, to discuss important open issues, and to propose new challenges for the next century.

## Infrared radiation of ozone in the mesosphere and lower thermosphere: energetic effects and remote sensing

A.G. Feofilov (1), A.A. Kutepov (2,3), and L. Rezac (4)

1 - Dynamic Meteorology Laboratory, Ecole Polytechnique, Paris, France

2 – The Catholic University of America, Washington, DC, USA

3 – NASA Goddard Space Flight Center, Greenbelt, MD, USA

4 – Max-Planck Institute for Solar System Research, Katlenburg-Lindau,  
Germany

The translational degrees of freedom of atmospheric molecular and atomic gaseous compounds represent a heat reservoir. This reservoir obtains or loses energy due to a number of sources and sinks, among them heating and cooling related to various types of mass motions, redistribution of energy released in the course of various photochemical reactions (the translational energy, the chemical energy and the nascent electronic, vibration and rotational energy of the reaction products), and absorption and emission of the infrared (IR) radiation. In the latter case, one deals with interaction between matter and the IR radiative field, which, for the case of the mesosphere/lower thermosphere (MLT), includes the atmospheric radiation formed in these layers, the upwelling radiation from the ground and lower atmosphere, and, during daytime, the solar radiation.

In this talk, we address the energetic effects and remote sensing of ozone, for which the abovementioned interaction in the MLT is strongly affected by the situation when vibrational excitation does not obey Boltzmann's law with the local kinetic temperature. As a result, the IR radiation emitted in these layers does not reflect the thermal state of matter. This situation is referred to as the breakdown of local thermodynamic equilibrium (LTE) for the vibrational degree of freedom. Detailed treatment of non-LTE plays a crucial role for estimating thermal effects of the IR radiation as well as for the diagnostics of space-based IR observations.

We discuss the peculiarities of the non-LTE radiation forming in the IR bands of ozone, estimate radiative cooling/heating rates for typical atmospheric scenarios, and analyze sensitivity of the retrieved ozone concentration to the parameters of the non-LTE model.

# Ozone vertical columns over Paris (Creteil-France): diurnal and seasonal variations and comparison with correlative satellite and in situ observations

P. CHELIN<sup>1</sup>, C. Viatte<sup>1a</sup>, M. Eremenko<sup>1</sup>, M. Ray<sup>1</sup>, J. Cuesta<sup>1</sup>, F. Hase<sup>2</sup>, J. Orphal<sup>2</sup>,  
J.-M. Flaud<sup>1</sup>  
[chelin@lisa.u-pec.fr](mailto:chelin@lisa.u-pec.fr)

<sup>1</sup>Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), CNRS UMR 7583, Université Paris-Est Créteil et Université Paris Diderot, Institut Pierre Simon Laplace, 94010 Créteil, France

<sup>2</sup>Institute for Meteorology and Climate Research (IMK), Karlsruhe Institute of Technology (KIT), Karlsruhe, GERMANY

Ground-based Fourier-transform infrared (FTIR) solar absorption spectroscopy is a powerful remote sensing technique providing some information on the concentration and vertical distribution of various atmospheric constituents. This study reports measurements of total ozone and tropospheric ozone columns, made by a mid-resolution ( $0.06\text{ cm}^{-1}$ ) ground-based FTIR (named OASIS for “Observations of the Atmosphere by Solar absorption Infrared Spectroscopy”), installed in Paris suburbs, at Créteil (France). The information provided by OASIS ozone retrievals is clearly relevant to monitor both tropospheric (from the surface up to 8 km) and stratospheric ozone amounts [1].

Total ozone concentrations shown here are derived from 200 clear-sky days, from February 2009 to July 2013 at Créteil (France). It was shown the existence of seasonal variability of the total column ozone content with respective minimum values observed in autumn, and maximum values observed in spring due to the Brewer-Dobson circulation at mid-latitude. OASIS total columns are in very good agreement with correlative satellite data (IASI, OMI, and GOME-2) and the ground-based measurements in the visible (SAOZ). A very good agreement was found also with the chemical-transport model REPROBUS.

A daily comparison of OASIS measurements with tropospheric ozone columns derived from the spaceborne Infrared Atmospheric Sounding Interferometer (IASI) over the Paris area from February 2009 to July 2013 has shown a good agreement, especially during summer months. Also, a qualitative comparison between *in-situ* surface ozone measurements and OASIS data clearly shows OASIS’s capacity to observe diurnal tropospheric ozone variations, as well as ozone pollution episodes in the Paris area.

**Keywords:** ground-based Fourier-transform infrared (FTIR) spectroscopy – tropospheric ozone – solar occultation – ozone pollution

## References

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<sup>a</sup>New address: Department of Physics, University of Toronto, Toronto, ON, Canada

# On the origin of mass-independent fractionation of oxygen isotopes in the ozone forming recombination reaction

Mikhail V. IVANOV<sup>1,2</sup> and Dmitri BABIKOV<sup>1</sup>  
[mikhail.ivanov@marquette.edu](mailto:mikhail.ivanov@marquette.edu)

<sup>1</sup>Marquette University, Milwaukee, Wisconsin, USA

<sup>2</sup>Institute of Precambrian geology and geochronology RAS, St. Petersburg, Russia

## Abstract

We developed the mixed quantum/classical theory for collisional energy transfer and rovibrational energy flow [1]. This theory was applied for treating the recombination reaction that forms symmetric and asymmetric isotopomers of ozone. We focused on formation of singly substituted  $^{16}\text{O}^{16}\text{O}^{18}\text{O}$  and  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$  [2]. Formation and stabilization steps of the energy transfer mechanism are both studied. As expected, our calculations showed a large isotope effect for formation of an asymmetric isotopomer of ozone through two different channels, due to difference of associated vibrational zero-point energies—the  $\Delta\text{ZPE}$  effect. We also reproduced the experimental observation that the symmetric isotopomer of ozone is formed at a rate lower, compared with the asymmetric isotopomer—the so-called  $\eta$ -effect. Here, the  $\eta$ -effect was obtained by the first-principle calculations, without being postulated and adjusted to fit experiment. Most importantly, we identified the molecular level origin of the  $\eta$ -effect. Interestingly, it is not caused by the absence of some state-to-state transitions due to quantum symmetry selection rules, and does not occur during the stabilization step of the ozone forming process. The largest source of  $\eta$ -effect is in lifetimes of the metastable  $\text{O}_3^*$  states, more precisely, in differences of tunneling rates in/out of the reaction channels for symmetric and asymmetric isotopomers due to distortion of vibrational wave functions by isotopic substitutions. Our calculations, performed within the dimensionally reduced model of ozone, are in semiquantitative agreement with experiment.

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# Spectroscopy and Molecular Properties of Ozone (S&MPO) information system: state of art and critical issues

S.N. MIKHAILENKO<sup>1</sup>, A. Barbe<sup>2</sup>, Yu.L. Babikov<sup>1</sup>, and Vl.G. Tyuterev<sup>2</sup>

[semen@iao.ru](mailto:semen@iao.ru) [Alain.Barbe@univ-reims.fr](mailto:Alain.Barbe@univ-reims.fr) [ylob@iao.ru](mailto:ylob@iao.ru)  
[Vladimir.Tyuterev@univ-reims.fr](mailto:Vladimir.Tyuterev@univ-reims.fr)

<sup>1</sup> V.E. Zuev Institute of Atmospheric Optics, SB RAS, 1 Academician Zuev square, 634021 Tomsk, Russia

<sup>2</sup> Groupe de Spectrométrie Moléculaire et Atmosphérique, UMR 7331 CNRS, Université de Reims Champagne-Ardenne, B.P. 1039, 51687 Reims Cedex 2, France

Recent updates of the S&MPO information system (<http://smpo.iao.ru> and <http://smpo.univ-reims.fr>) and the corresponding database on ozone transitions will be presented.

During last two years the S&MPO databank has been completed by more than 20 vibration-rotation bands based on the analysis of the Fourier transform ozone spectra covering the spectral region between 1140 and 5700  $\text{cm}^{-1}$ . Several critical issues concerning the available ozone line list and comparisons with the HITRAN [1] and GEISA [2] databases will be discussed.

[1] L.S. Rothman et al., The HITRAN 2012 molecular spectroscopic database // JQSRT (2013) doi:10.1016/j.jqsrt.2013.07.002.

[2] N. Jacquinet-Husson et al., The 2009 edition of the GEISA spectroscopic database // JQSRT, **112**, 2395-2445 (2011) doi:10/1016/j.jqsrt.2011.06.004.

**Keywords:** ozone molecule, infrared spectroscopy, S&MPO

# GEISA 2013 Ozone and related atmospheric species contents description and assessment

N. JACQUINET-HUSSON<sup>1</sup>, C. Boutamine<sup>1</sup>, R. Armante<sup>1</sup>, L. Crépeau<sup>1</sup>, A. Chédin<sup>1</sup>,  
N. Scott<sup>1</sup>, C. Crevoisier<sup>1</sup>, V. Capelle<sup>1</sup>

[nicole.jacquinet@lmd.polytechnique.fr](mailto:nicole.jacquinet@lmd.polytechnique.fr)

<sup>1</sup> Laboratoire de Météorologie Dynamique (LMD), Ecole Polytechnique, 91128 Palaiseau, France

The ARA/ABC(t) group at LMD (<http://ara.abct.lmd.polytechnique.fr>) develops and maintains, for over three decades, [GEISA](#)<sup>1</sup> (Gestion et Etude des Informations Spectroscopiques Atmosphériques: Management and Study of Atmospheric Spectroscopic Information), a computer accessible database system.

GEISA comprises three independent sub-databases devoted respectively to: -1) line parameters, in the spectral range from  $10^{-6}$  to  $35,877.031 \text{ cm}^{-1}$ ; -2) infrared and ultraviolet absorption cross-sections; -3) microphysical and optical properties of atmospheric aerosols.

For ozone and related atmospheric species, the contents of each of the three sections of the GEISA 2013 edition<sup>2</sup> will be presented. A critical assessment of the current spectroscopic parameters archive will be made. Special emphasis of this assessment has been given in the frame of the scientific exploitation of operational missions. Example will be presented for the IASI and GOME-2 instruments on-board the European polar satellite Metop series since 2006 (<http://www.eumetsat.int/website/home/Satellites/CurrentSatellites/Metop/index.html?lang=EN>).

Since the launch of Metop-A, GEISA is the reference basis for the validation of the level-1 IASI data, using the 4A radiative transfer model<sup>3</sup> (4A/LMD; 4A/OP co-developed by LMD and Noveltis- <http://www.noveltis.fr/>, with the support of CNES).

GEISA is implemented on the CNES/CNRS/IPSL “Ether” Atmospheric Chemistry Data Centre WEB site (<http://www.pole-ether.fr>), where all the archived spectroscopic data and related information can be handled through general and user friendly associated management software facilities. More than 350 researchers, working in the domains of atmospheric physics, astronomy and astrophysics, and planetology, are registered for on line use of GEISA

## Refs:

<sup>1</sup>Jacquinet-Husson N., L. Crepeau, R. Armante, C. Boutamine, A. Chédin, N.A. Scott, C. Crevoisier, V. Capelle, C. Boone, N. Poulet-Crovisier, *et al.* The 2009 edition of the GEISA spectroscopic database. JQSRT, 112 (2011) 2395-2445.

<sup>2</sup>Jacquinet-Husson N., C. Boutamine, , R. Armante, L. Crepeau, A. Chédin, N.A. Scott, C. Crevoisier, V. Capelle, C. Boone, N. Poulet-Crovisier, *et al.* The 2013 edition of the GEISA spectroscopic database. *In preparation.*

<sup>3</sup>Scott, N.A. and A. Chedin, 1981: A fast line-by-line method for atmospheric absorption computations: The Automatized Atmospheric Absorption Atlas. J. Appl. Meteor., 20,556-564.

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