

The Twentieth Colloquium on High-Resolution Molecular Spectroscopy

The Twentieth Colloquium on High-Resolution Molecular Spectroscopy was held from the 3rd to 7th of September, 2007 in Dijon (France). It was organized by the Institute Carnot de Bourgogne (CNRS), Physical Society of France, and Administration of Bourgogne and Dijon city.

This Colloquium is traditionally extremely representative; the majority of European groups present here new theoretical, experimental, and different application results.

In 2007, the following events took place within the Colloquium:

- Amat-Mills Award contest among young scientists;
- Mini-Symposium "Spectroscopy and Fundamental Physics;"
- presentation of spectroscopic application products of a number of well-known laser and optics enterprises and scientific publishing houses.

More than 350 specialists from Europe, Asia, North and South America, and Africa participated in the Colloquium.

The presented reports were grouped into the following topics:

- theoretical study of molecule, radical, ion, and molecular complex spectra and spectral-line profile shape (76 reports);
- electronic spectra (32);
- infrared and Raman spectroscopy (104);
- microwave spectroscopy (43);
- spectroscopy in molecular flows and beams (16);
- spectroscopy of condensed media and matrix isolation (5);
- radicals and ions spectroscopy (12);
- spectroscopy of molecules of astrophysical interest (47);
- atmospheric spectroscopy (57);
- spectroscopy of biomolecules (10);
- spectroscopy of molecular complexes, clusters, and drop molecules (18);
- molecular dynamics (15);
- ultracold atoms and molecules (9);
- spectroscopy for fundamental physics (20);
- new experimental equipment (20).

In total, the Colloquium program included 17 plenary reports, covering almost all the above subjects. Authors or coauthors of 48 posters were 64 Russian scientists, working in Russian scientific institutions.

The lecture of M.-C. Gazeau et al. (Y. Benilan, T. Ferradaz, N. Fray, A. Jolly, M. Schwell, F. Raulin) opened the Colloquium. It was devoted to

study of IR and UV spectra of a number of molecular compounds, required for Cassini's spacecraft data analysis on Titan atmosphere composition. To understand the processes responsible for Titan atmosphere evolution, photochemical models were proposed, required the following: 1) known photodissociation rates and corresponding values of detected molecule absorption coefficients; 2) reconstruction of organic compounds from the observed vertical profiles from upper to lower thermosphere. These vertical profiles are obtainable from Cassini's spacecraft observations, in particular, from the analysis of limb sensing data and on-board spectrometer-measured IR and UV spectra of Titan atmosphere.

To validate the models and interpret observation data, the authors determined unknown spectroscopic parameters of compounds, probable in the Titan atmosphere, such as HCN, $C_{2n}H_2$, and $HC_{(2n+1)}N$, as well as IR and UV spectra of HCN, C_4H_2 , HC_3N , and HC_5N . Difficulties were noted in studying such unstable compounds as C_6H_2 and HC_5N , which are unattractive for commercial use. For further understanding of composition and evolution of the Titan atmosphere, the authors investigated spectra of organic compounds within the 80–190 nm and 7–17 μm ranges when varying the temperature within the 80–200 K range. The given experimental results pointed out to a weak temperature dependence of HC_3N , HC_5N , and C_4H_2 spectra within the 100–300 K range.

The authors considered the following problems:

- analysis of hot bands contribution, e.g. the 664 cm^{-1} band, for HC_3N ;
- more precise spectral list definition for C_2HD and some others.

The measurement results, presented by the authors, are available on the site www.lisa.univ-paris12.fr.

The study results of diffusion absorption bands and interstellar substance radiation, characterized by a width of 2–100 cm^{-1} , were discussed in the plenary report by P.J. Sarre. The author formulated a number of assumptions for developing laboratory experiments on interpreting the fine structure of these diffusion bands, such as:

- carbon chain and carbocycles spectroscopy;
- electronic spectra of large polycyclic hydrogen-carbon aromatic compounds (PAH_s) and $(PAH_s)^+$;
- C_{60} fullerene band near 9600 Å;
- molecular spectra in matrixes and helium nanodrops with the use of modern spectroscopic techniques.

The problems of the effect of molecular vibrational excitation on molecular dynamics, in particular, biomolecular chemical reactions, or molecular dissociation were considered in the report by F.F. Crim. A higher reactivity of symmetric valence vibrations in comparison with the asymmetric ones was ascertained by the example of chlorine atom reaction with the vibrationally excited CH₃D molecule. Excitation of symmetric vibrations for NH₃ similarly results in more effective dissociation of the molecule as compared with asymmetric ones.

The report by H. Kato was devoted to Zeeman effect on benzole and naphthalene S₁ ← S₀ transitions and use of these data in analysis of the nonradiative relaxation processes in these molecules.

The efficiency of new satellite spectral devices was a subject matter of M. Lopez-Puertas report on new investigations of local thermodynamic equilibrium violation processes with MIPAS (Michelson Interferometer for Passive Atmospheric Sounding), providing for limb ENVISAT-onboard measurements of atmospheric transmission spectra with the 0.05–0.1 cm⁻¹ resolution within the 4.15–14.6 μm range.

The author analyzed the quality of MIPAS data on local thermodynamic equilibrium (LTE) violation, including IR emission of the majority of atmospheric molecules, active in IR radiation, i.e., CO₂, O₃, H₂O, CH₄, CO, NO₂, N₂O, NO, and NO⁺. He showed that the accounting for the “hot” O₃ band, e.g., 4.8 μm, resulted in difference with the old model from a height of 30 km.

Study of the NO+O₃ system behavior during a solar storm, accounting for the NO⁺(v₃) vibrational band, and elimination of the variation between CO contribution into the LTE violation model and MIPAS measurements results (5%), are issues of the day. An essential LTE violation model refinement at heights of ≥ 50 km is to be possible after MIPAS measurement data accumulation.

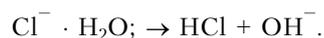
R.W. Field in its plenary report discussed the acetylene spectra study with the use of laser induced IR–UV fluorescence technique. As a result, a high-resolution spectrum was obtained for the S₁ state within the 0–4000 cm⁻¹ range (40 vibrational bands with K = 0, 1, 2).

A new KDTL (Kapitza–Dirac–Talbot–Lau) conception of interferometer, combining material and wave 3D gratings, was developed in the report by M. Arndt. Use of such interferometer for acknowledgement of wave-corpuscle duality for large molecules and qualitative definition of scalar polarizability of fullerenes and porphyrin derivatives was discussed. Another field of the technique application is nanomodulation of free propagating three-dimensional light beams.

M. Johnson in his report considered intracuster proton-transfer reactions in two types of systems:



An example is the reaction

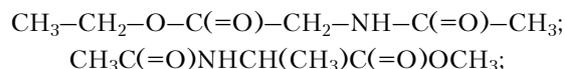


Red shift of spectral bands in such complexes is caused by both electric forces and discharge transfer. This was shown when studying the spectral complexes SO₂⁻ · H₂O, SO₂⁻ · HDO, and SO₂⁻ · D₂O.

Two plenary reports were devoted to biomolecules spectroscopy.

Thus, T.R. Rizzo reported on definition of biomolecule structure and dynamics in gas phase at ultra-low temperatures. A spectrometer, cooled to 6 K, was used in the experiments to record photofragmented ions. One of the subjects of investigation was tryptophan, for which the smooth molecule absorption band, centered at 35100 cm⁻¹, became strained in the complex with one H₂O molecule and transformed into a specific spectrum with several characteristic peaks in the complex with two H₂O molecules. Using the IR–UV double resonance technique, IR spectra of peptides, including up to 12 aminoacids, were studied. It was shown that ¹⁴N-to-¹⁵N isotope substitution in different places of the complicated molecule structure results in essential spectrum change. A number of problems were outlined on dynamics of complex biomolecules, concerned with the dissociation time and possibility to retrieve the information on biomolecule structure from an observed spectrum.

I. Kleiner in his report gave recommendations on efficiency of the optical spectroscopy methods for biomolecule study. The author considered biomimetic molecules – relatively small molecules, forming elementary blocks of biomolecules. Among such molecules are small peptides, aminoacids, and sugar. Spectroscopic methods are suitable for molecular systems, containing up to 5 aminoacids, measurements of dipole moment or diffusion rate in gas are better for systems with 5 to 30 aminoacids, and mass-spectrometers are preferable for large molecules (> 30 aminoacids). Study results were shown for different molecules which can be considered as prototypes of the peptide bonding, namely



and



J. Gauss and C. Puzzarini showed how quantum-chemical calculations can be used in study of molecule rotational spectra, especially in detection of new molecules. Theoretical predictions for the hyperfine parameters (quadrupole-coupling constants, spin-rotation tensors, spin-spin couplings, etc.) are often essential for a detailed analysis of the hyperfine structure of the measured rotational spectra. The authors gave many examples of successful interplay of the quantum-chemical theory and experiment in the field of rotational spectroscopy and possibilities to detect a number of molecules, e.g., HSOH, by their rotational spectra.

The plenary report by the group of co-authors (P. Cacciani, J. Cosleou, M. Guinet, M. Khelkhal, and M. Tudorie) discussed spectroscopic effects, concerned with the nuclear spin conversion, in particular, problems of spectroscopy of *ortho* and *para*-molecules H_2 , H_2O , NH_3 , and CH_3F . The nuclear spin of symmetric atoms is important, though magnetic interactions (spin-spin and spin rotation) are weak in a number of effects, such as light-induced molecule drift, selective photodissociation (e.g., H_2CO), reactions with H_3^+ ions, fast cooling of H_2O in the rare gas matrix.

Questions of spin conversion dynamics were considered, explained by intramolecular magnetic interactions (model of quantum relaxation). The hypothesis on *ortho*-isomer-to-*para*-isomer transformation inhibition in gas phase was considered.

The last in the spectroscopic block was the report by W. Lafferty devoted to the study of high-resolution spectra of small molecules in presence of strong anharmonic resonances by the example of IR spectra of N_2O , H_2CO , and H_2CS molecules.

Design of new radiation sources for high-resolution spectroscopy was the subject of M. Bellini's report. Ways of high-order laser harmonic generation were considered in interacting of short and intensive laser pulses with rare gas atoms as well as their state-of-the-practice. As a result, an extreme UV radiation source was designed.

Classification of the spectroscopic data and their representation in the form of user-friendly databases or knowledgebases are very important for many applications, related to the study of radiation processes in atmosphere, development of ground, airborne and satellite remote sensing techniques of molecular compounds. State-of-the-art and prospects for the development of the most popular spectroscopic databases HITRAN and GEISA were discussed in a number of posters, as well as new approaches to management of large bulks of spectroscopic data.

L.S. Rothman and I.E. Gordon presented the new version of HITRAN-2008. It is to be essentially improved with accounting for requirements of experts working out new techniques and instruments for remote satellite sensing of atmospheric composition. As compared with HITRAN-2004, the new version is to include nitric acid spectra within the 600–1790 cm^{-1} range; improved data on air widening and adding H_2O isotopes in the visible range; present data on OCS and PH_3 spectra, recalculated parameters of NO^+ lines, adjusted data for Schumann–Runge bands, additional data for the Herzberg band of O_2 in the UV range, and data on additional acetylene bands. Along with new absorption bands of new molecules, data were included allowing “line by line” calculations of IR and UV absorption cross-sections, induced by absorption band collisions, and parameters of spectral line profiles.

N. Jacquinet-Husson, R. Armante, N.A. Scott, and A. Chedin considered the state-of-the-art of

GEISA database. It also develops in the interest of more accurate radiation atmospheric models and provides for “line by line” calculations for multilayer atmosphere. GEISA-03 includes three independent databases with transition parameters and absorption lines; IT, visible, and UV absorption cross-sections; microphysical and optical parameters of atmospheric aerosol. At present, GEISA is actively used in IASI (Infrared Atmospheric Sounding Interferometer) data processing, which is mounted on-board the European satellite METOP. GEISA documentation is available on the site <http://ara.lmd.polytechnique.fr>.

A variant of information system for water molecules and its isotopes was suggested by A.G. Czarzar, A.Z. Fazliev, and J. Tennison. This system is constructed as a knowledgebase consists of three parts: energy levels, transitions, and line profiles. Data on $H_2^{16}O$, $H_2^{17}O$, and $H_2^{18}O$ are the fullest.

Further development of the HITEMP database (a part of HITRAN), containing data on molecule spectra at high temperatures, was discussed in the report by large authors group (I.E. Gordon, L.S. Rothman, V.I. Perevalov, S.A. Tashkun, R.R. Gamache, R.J. Barber, J. Tennyson, P.F. Bernath, A. Goldman). Here the list of lines for CO, H_2O , CO_2 , NO, OH, CH_4 , etc. molecules was renewed in comparison with the previous version.

The detailed review of all the presented posters is impossible in this information message. Dwell upon the results interesting for atmospheric spectroscopy.

Progress is evident in study of H_2O and its isotopes spectra, corresponding to transitions into very high vibrational states with the energy compared with the dissociation one. H_2O spectra were double- and triple resonance spectroscopy recorded by M. Grechko, P. Maksytenko, T.R. Rizzo, and O.V. Boyarkin up to 41450 cm^{-1} energies, i.e., higher than the dissociation threshold. A new HDO absorption list up to 25000 cm^{-1} was presented in the report by B.A. Voronin, R.N. Tolchenov, J. Tennyson, S.V. Shirin, N.F. Zobov, and O.L. Polyansky. Spectra of $H_2^{17}O$ and $H_2^{18}O$ radiation in the 1654–2500 cm^{-1} range at a temperature of 1950 K were studied by S. Mikhailenko, G.Ch. Mellau, I.V. Kishkina, and V.I.G. Tyuterev. More than 770 new $H_2^{17}O$ and $H_2^{18}O$ lines were recorded and identified.

The detailed study and analysis of ethylene absorption spectrum in the 6035–6210 cm^{-1} range which is of practical importance for applications (laser gas analysis) were presented in the report by V.A. Kapitanov, Y.N. Ponomarev, V. Boudon, M. Rotger, N. Zvereva-Loete, and M. Loete.

H.M. Niederer, S. Albert, M. Quack, V. Boudon, J.P. Champion, S. Bauerecker presented the global analysis results for high-resolution spectrum of $^{13}CH_4$ in the 0–3200 cm^{-1} range; the absorption lines centers were determined with an accuracy of 0.0009 cm^{-1} .

A number of posters presented new data on absorption spectra of CO₂, H₂S and its isotopes, O₃, NH₃ and the isotopes, N₂O (weak transitions within the 4100–4350 cm⁻¹ range), and other atmospheric molecules.

In general, a very high scientific level of the Colloquium should be noted as well as impressive spectroscopic results, presented there.

An up-to-date level of the intermolecular spectra theory, combining integrated use of *ab initio* techniques for potential energy surface modeling, effective Hamiltonian methods, global approach to rovibrational spectra analysis, provides for a mass calculation error of line centers, comparative with the modern experimental error.

A great progress was shown in experimental study of molecular absorption spectra near the dissociation threshold and the effect of selective vibration excitation of molecules on their chemical activity, dissociation processes, and complex formation.

A modern spectroscopy technique allows study of very fine intra- and intermolecular interactions and determination of a number of basic physical parameters. An example is the first direct measurements of the Boltzmann's constant in the experiment on precise measurement of Doppler absorption line profile at a fixed temperature of thermostat with absorbing low-pressure gas (K. Djerroud, C. Daussy, A. Amy-Klein, C.J. Borde, C. Chardonnet, S. Briaudeau, and Y. Hermier).

Another tendency is integrated use of laser and Fourier spectroscopy techniques and mass spectroscopy

in experiments; polyatomic resonance technique. A broadband intracavity laser-induced spectrometer and a time-resolved Fourier one were used together in the experiment by D. Boudjaadar, G. Guelachvili, and N. Picqué on studying very weak NO₂ transitions. An applicable length of 110 m absorbing path provided for a detection threshold of $6 \cdot 10^{-11} \text{ cm}^{-1} \cdot \text{Hz}^{-1/2}$.

The results of many reports, presented in the Colloquium, can be directly applicable in solving many urgent atmospheric optics problems:

- development of calculation methods for atmospheric radiation fluxes in climatic models;
- working out of techniques and instrumentation for local and remote analysis of molecular composition of the atmosphere;
- spectroscopy of atmospheric nanostructures from molecular clusters to particles with complicated molecules, e.g., biomolecules;
- selective effect on gas-phase reactions, including directed photodissociation of complicated molecules for their detection by fragments, and a number of other applications.

The Program and abstracts of the reports, presented at the Twentieth Colloquium on High-Resolution Molecular Spectroscopy, are available on the site <http://vesta.u-bourgogne.fr/hrms/Program/AbsBook.pdf>.

***Doctor of physical-mathematical sciences,
professor Yu.N. Ponomarev***