

# Physical Chemistry at the University of Geneva

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**Abstract:** A brief historical overview of physical chemistry at the University of Geneva as well as a description of the present research activities at the department of physical chemistry are presented.

**Keywords:** Department of Physical Chemistry · University of Geneva

## Introduction

The Department of Physical Chemistry (DPC) of the University of Geneva is presently composed of four professors (*Laura Gagliardi, Michel Geoffroy, Andreas Hauser and Eric Vauthey*), three *maîtres d'enseignement et de recherche* (*Theo Berclaz, Hans Hagemann and Tomasz Wesolowski*) (Figs 1 and 2), 26 PhD students and postdoctoral research associates and twelve permanent scientific, technical or administrative staff members who constitute four main research groups and one smaller associate group. The research activities of the DPC can be grouped in two main areas: spectroscopy and computational chemistry. There is a long tradition of research in these two fields in Geneva and thus before addressing the present activities in more detail, it is worthwhile to briefly consider the history of the DPC.



Fig. 1. Left to right: Theo Berclaz, Laura Gagliardi, Hans Hagemann and Andreas Hauser.

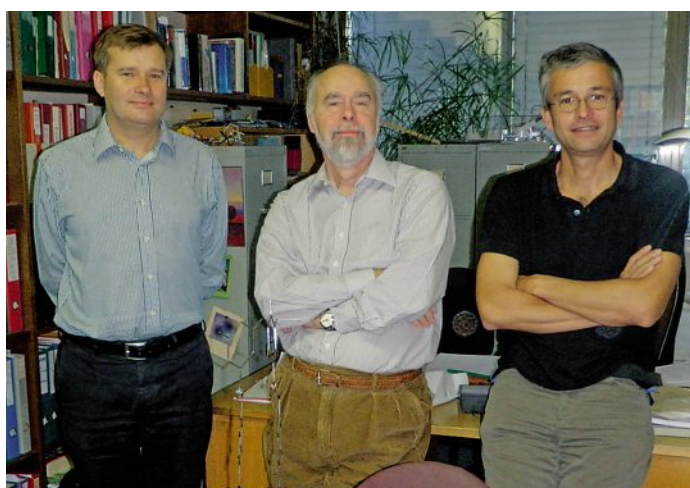


Fig. 2. Left to right: Tomasz Wesolowski, Michel Geoffroy and Eric Vauthey.

## History

The beginning of physical chemistry in Geneva can be traced back to 1892 when a chair in 'theoretical and technical chemistry' was offered to *Philippe Auguste Guye* (1862–1922). His laboratory was situated in the newly created (1879) *Ecole de Chimie* located on the *Boulevard des Philosophes*. P.-A. Guye was not only interested in industrial applications of

chemistry (nitrogen fixation on oxygen through electric discharges in air, applied electrochemistry) but he was also very active in more fundamental areas such as the precise determination of atomic weights (nitrogen, silver, sulphur, bromine and carbon) and the physical properties of gases (compressibility, density, critical point). Interestingly, one of his first research themes was the rotatory optical activity of molecular compounds, an area

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Fig. 3. One of the first Raman spectra recorded in Geneva.<sup>[1]</sup>

that is still highly topical, given the importance of chirality in modern chemistry. P.-A. Guye, the author of more than 200 articles, had always been a strong proponent of the use of rigorous theoretical concepts in any scientific reasoning. After his death, the chair was occupied by *Emile Briner* (1879–1965), well known for his studies of reactions between ozone and hydrocarbons as well as on chemical effects of electric discharges, which resulted in the development of a method for detecting ozone traces in air. E. Briner realised very early the strength of spectroscopy and, in collaboration with Susz (*vide infra*), he carried out many measurements using Raman spectroscopy (see Fig. 3), a very insensitive technique in this ‘pre-laser’ era, an experimental run requiring typically an exposure time of 3 to 24 hours to yield spectra of a useful signal to noise ratio. E. Briner, who retired in

1954, was very active as testified by his ~350 publications.

*Bernard-Pierre Susz* (1904–1975) who succeeded E. Briner was in fact the first professor of the University of Geneva to be appointed as a professor in physical chemistry. Most of his research was devoted to the study of the interactions between organic molecules and Lewis acids. In this context, he used infrared spectroscopy to investigate charge transfer complexes. B.-P. Susz retired in 1970 after having invested many efforts in the construction of a new building better adapted to modern research and chemistry teaching. This building, *Sciences II*, was destined to be an important element in the scientific campus on the Arve riverbank, bringing together the research activities in physics, chemistry, biology and pharmacy.

In fact, the DPC in its present form was born during this move in 1969–1970, when the old *Ecole de Chimie* became the *Section de Chimie*. From the beginning, the research activities at the DPC were related to spectroscopy and quantum chemistry, apart from those of Prof. *Desimir Janjic* (who studied charge transfer complexes using calorimetry as well as oscillating reactions) and of Prof. *Armand Buchs* who in 1965 initiated a research program in mass spectrometry with two main topics: chemistry of ions in the gas phase,<sup>[2]</sup> and U/Pb geochronology (see Fig. 4). At the same time, A. Buchs headed the mass spectrometry service for the whole Faculty of Sciences. After his retirement in 1997 and until 2008, this service remained associated with the DPC under the supervision of Prof. *Fazil Gülaçar*, a former collaborator of A. Buchs, who continued the research on the mass spectrometric fragmentation and identification of organic molecules, more particularly from geological and biological matrices.<sup>[3,4]</sup> Since the retirement of F. Gülaçar in 2008, the mass spectrometry service is no longer associated with the DPC.

## Spectroscopy at the DPC

The two main spectroscopic approaches developed and applied at the DPC are the resonance techniques such as EPR, ENDOR and NQR spectroscopies and high-resolution (spectral or temporal) optical spectroscopies.

## Magnetic Resonance Spectroscopy

The development of the various resonance spectroscopic techniques at the DPC dates from 1968 when *E.A.C. Lucken*, a group leader at the Cyanamid European Research Institute, was appointed as professor at the School of Chemistry. He used the Nuclear Quadrupole Resonance (NQR) technique to study the electronic structure of diamagnetic crystalline molecular solids.<sup>[5]</sup> He was thus able to provide a precise description of the chemical bonds by measuring the quadrupole coupling constant of the quadrupolar nuclei <sup>35/37</sup>Cl, <sup>79/81</sup>Br, <sup>63/65</sup>Cu, <sup>75</sup>As and <sup>121/123</sup>Sb. He considerably improved the performance of this technique through the construction of a pulsed spectrometer and the development of specific instrumentation for the study of large single crystals.<sup>[6]</sup>

The effects of molecular motion within crystalline matrices are of considerable importance in solid-state chemistry and E.A.C. Lucken significantly increased our knowledge in this field by using NQR to study the mobility of small chlorinated molecules trapped in the matrices of inclusion complexes.<sup>[7]</sup> He also used rotational spectroscopy to determine the precise geometry of molecules in the gaseous phase.

Dating also from that period, E.A.C. Lucken employed the technique of Electron Paramagnetic Resonance (EPR) for liquid phase investigations of the structure of organic radicals formed either by photolysis or chemical means. A more detailed description of the structure of organic radicals can be obtained by the study of radicals trapped in a crystalline matrix; under these conditions all the elements of the tensors appearing in the spin Hamiltonian are accessible and the localisation of the unpaired electron can be determined precisely. This technique was successfully employed by E.A.C. Lucken and *Michel Geoffroy* – who was at that time *chef de travaux*, and who had studied chemistry at the University of Strasbourg – for the study of radicals generated by radiolysis in monocrystalline organic compounds containing a heteroatom.<sup>[8]</sup> It was in this manner that, for example, the structures of the sulphonyl radical PhSO<sub>2</sub>, phosphinyl Ph<sub>2</sub>P, phosphoranyl Ph<sub>3</sub>PCl, arsinyl Ph<sub>2</sub>As and antimonyl Ph<sub>2</sub>Sb were established. In these examples, the exact determination of the magnetic hyperfine (<sup>31</sup>P, <sup>75</sup>As, <sup>35</sup>Cl, <sup>121/123</sup>Sb) and quadrupolar (<sup>75</sup>As, <sup>121/123</sup>Sb) interactions were crucial to



Fig. 4. The first high-resolution mass spectrometer (Varian MAT Atlas SM1) being installed in the *Science I* building in 1965.

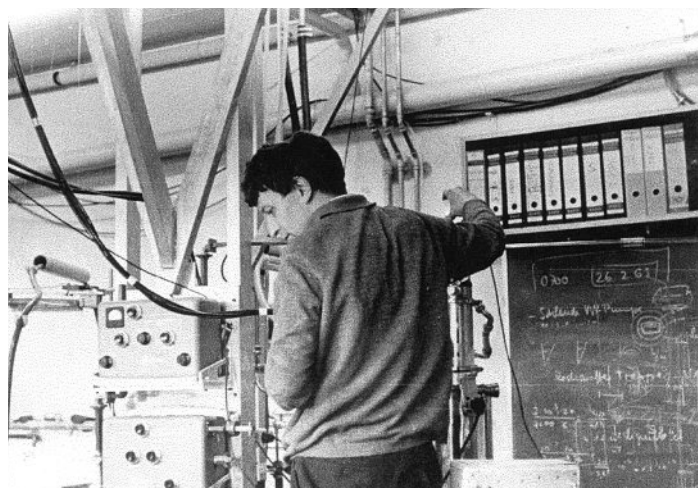


Fig. 5. Hans Bill adjusting a sample at He-temperature for an EPR/ENDOR measurement (26.2.1969).

the identification of the radical and to the determination of its geometry. E.A.C. Lucken retired in 1996.

Roger Lacroix (full professor) and Hans Bill (*chargé de recherche* from 1.11.1969) joined the DCP on January 1st 1969, with a program centred on inorganic crystalline solids – both, as the subject of research in their own right and as hosts and stabilizing agents for ionic and molecular systems in unusual valence states. Specifically, H. Bill's research program was centred on systems presenting specific aspects of electron-vibration coupling. H. Bill was appointed assistant professor in 1972 and full professor in 1979. His initial research activity included EPR and ENDOR investigations (Fig. 5) on the coloration of natural  $\text{CaF}_2$  crystals (fluorites). A paramagnetic  $\text{O}_3^{3-}$  molecular ion was identified in rose fluorine and shown to be at the origin of the coloration. With ENDOR, the coordination of the  $\text{F}^-$  neighbourhood was mapped out, and the presence of the associated  $\text{Y}^{3+}$  ion was demonstrated.<sup>[9]</sup> Further work on the green and yellow fluorites demonstrated that  $\text{Sm}^{2+}$  caused the green coloration and that an  $\text{O}_3^-$  molecular ion presenting local dynamics was at the origin of the coloration of the yellow fluorites.<sup>[10]</sup> Incidentally, this research gave rise to collaborations with jewellery companies: spectral characterization of natural blue turquoise and yellow/blue diamonds of jewel-grade, on aquamarines and emeralds. A systematic investigation of the orbitally non-degenerate  $^8\text{S}_{7/2}$  ground state of  $\text{Gd}^{3+}$  and  $\text{Eu}^{2+}$  introduced at low concentrations into  $\text{MeXY}$  compounds of the matlockite structure ( $\text{Me} = \text{Ca, Sr, Ba; X, Y} = \text{F, Cl, Br, I}$ ) gave insight into the action of the static and dynamic crystal fields on the electron spin multiplet. Remarkable host and temperature dependent signs and values of the ground state crystal field parameters were found in these systems and interpreted with superposition type models. A special research effort focused on the Jahn-Teller effect. The  $\text{O}^-$  ion in  $\text{CaF}_2$  and  $\text{SrF}_2$  was one

of the first well-defined anionic systems exhibiting a dynamic  $T_{1u} \times e_g$  Jahn-Teller situation with only partially quenched spin-orbit coupling. Here again the use of  $^{17}\text{O}$  and of EPR at 1.7 K (including uniaxial stress runs) was crucial. Subsequently, a number of cationic and anionic impurities in cubic and lower symmetry crystals were investigated.<sup>[11]</sup> In 1992, H. Bill organized the XIth Jahn-Teller Symposium (Ovronnaz, 30.8.–3.9.1992). Phase transitions in members of the  $\text{KLiSO}_4$  family and in fluoroperowskites were further investigated with the aid of paramagnetic impurities serving as probes. Another research activity dealt with the super-ionic conductivity of  $\text{Li}_2\text{S}$  and  $\text{Na}_2\text{S}$  single crystals at high temperatures, by using EPR, electrochemical methods and Raman spectroscopy.

With the nomination of Michel Geoffroy as assistant professor in 1976 and as full professor in 1982, then with the appointment of *Théo Berclaz as maître d'enseignement et de recherche*, the DPC fostered interdisciplinary applications of EPR. Thus the study of mineralized biological tissue with the Department of Morphology of the CMU (Prof. *Baud, Dr. H-J Tochon-Danguy*), the identification and conformational study of nitroxide reaction intermediates with the Section of Pharmacy (Prof. *Tronchet*), and the characterization of antioxidants with the Nestlé Research Center (Dr. *Lambelet*). In a similar context, the spin-labelling technique was used to obtain information about mitochondrial membranes (Department of Medical Biochemistry, Prof. *Favarger, Dr N. Fournier*) and fatty-acid-binding proteins (Department of Biochemistry, Prof. *Deshusses*), and T. Berclaz investigated phase transitions in artificial membranes.

In the field of organic and organometallic radicals, thanks to the spectacular improvements of quantum chemical methods (CNDO, INDO,  $X\alpha$ , *ab initio*) and to the many collaborations between the group of M. Geoffroy and the theoretical chemistry group headed by *J. Weber*, the interpreta-

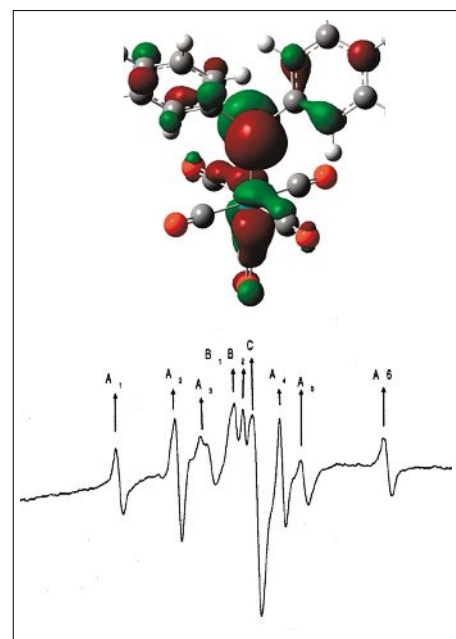


Fig. 6. EPR spectrum obtained at 300K with an X-irradiated single crystal of  $\text{Ph}_3\text{PMo}(\text{CO})_5$  and SOMO for  $\text{Ph}_2\text{P}\dots\text{M}(\text{CO})_5$ .

tion of the EPR measurements in oriented radicals became more and more easy and rich in information. Appropriate developments in instrumentation, for example the setup allowing radiolysis and EPR measurements at variable temperature, permitted the identification of the various reaction intermediates and, occasionally to discover changes in their conformation. This was the case with single crystals of  $\text{Ph}_3\text{M}(\text{CO})_5$  (with  $\text{M} = \text{Mo, W}$ ), which were shown to trap, after radiolysis, the electron excess species  $(\text{Ph}_3\text{M}(\text{CO})_4)^-$ , the electron deficient species  $\text{Ph}_3\text{M}(\text{CO})_5^+$  and the phosphinyl radical coordinated to the metal centre,  $\text{Ph}_2\text{P}\dots\text{M}(\text{CO})_5$  (Fig. 6).<sup>[12]</sup>

Stimulated by the recent developments in molecular electronics, the EPR group simultaneously intensified its efforts in three directions:

- i) The design of molecular systems capable of accepting or losing a single electron and delocalizing the resultant unpaired spin over a large part of the molecule. Most of these new compounds were based on phosphorus compounds with a low coordination number (Fig. 7) and their synthesis was either performed directly in M. Geoffroy's laboratory (e.g. diphosphaalkenes **1**, prepared by Dr *A. Jouaiti*)<sup>[13]</sup> or in collaboration with the group of Prof. *P. Le Floch* of the *Ecole Polytechnique de Paris* (e.g. macrocycle **2**).<sup>[14]</sup>
- ii) The development of instrumentation permitting the electrochemical oxidation or reduction of substances *in situ* in the EPR cell at variable temperature, an example of a spectrum being shown in Fig. 8.

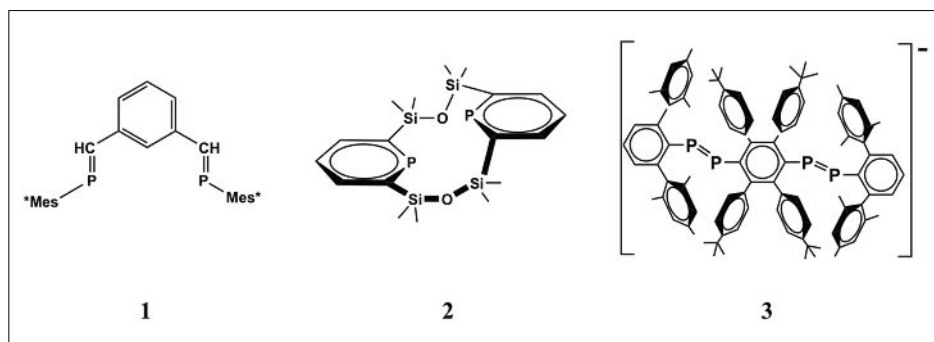


Fig. 7. Examples of phosphorus compounds investigated by M. Geoffroy and his group.

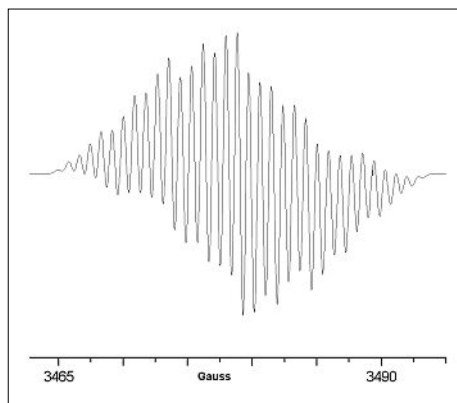


Fig. 8. EPR spectrum obtained after electrochemical oxidation of an iminophosphorane.

iii) The rationalization of the results with the aid of DFT calculations in collaboration with Prof. *Y. Ellinger* (University Pierre et Marie Curie, Paris), for instance spin delocalization on  $[\text{Ar-P}^{13}\text{C}^{13}\text{C-P-Ar}]^-$ . As shown with sterically encumbered diphosphaalkenes and bis(diphosphenes) **3**, synthesized in collaboration with Prof. *J. D. Protasiewicz* (University of Cleveland), some of these compounds can act as multiredox-active molecular switches. In addition, the electron-acceptor properties of these organophosphorous compounds can often be modulated by coordination with a transition metal (e.g. tetramethylbiphosphine and its Ni complex).

Recently one of the activities in the laboratory has been directed towards paramagnetic systems that present an interest for materials chemistry. Thus, in collaboration with Dr. *M. Fourmigué* (University of Rennes), the spin delocalisation in neutral radical complexes such as  $[(\text{CpNi}(\text{diselenolenes}))]$  has been determined from the measurement of the hyperfine coupling with  $^{77}\text{Se}$ . These results combined with those obtained from DFT studies of the dimer  $[(\text{CpNi}(\text{diselenolenes}))]_2$  led to the rationalisation of the antiferromagnetic proper-

ties measured in the crystalline state.<sup>[15]</sup> In a related context, in collaboration with the group of Dr. *N. Avarvari* of the University of Angers, the laboratory turned its attention to the electronic structure of molecules containing several tetrathiafulvalene (TTF) fragments. The aim was to demonstrate, with the aid of EPR/ENDOR measurements and cyclic voltammetry, the role of the bridging heteroatoms in the spin delocalisation.<sup>[16]</sup> An intramolecular mixed valence state passing through silicon or germanium could be detected.

After the retirement of M. Geoffroy in October 2009, the EPR/ENDOR technique will remain in active use at the DPC under the supervision of T. Berclaz.

### Optical Spectroscopy

High-resolution optical spectroscopy was introduced at the DPC by H. Bill who in 1974 built the first laser Raman spectrometer (Fig. 9). He used this setup in conjunction with EPR/ENDOR spectroscopy for his investigations of ionic Jahn-Teller centres in inorganic crystals – and organic phenobarbitals. During the 1960s, the Jahn-Teller effect ranked among the highlights in solid-state sciences. Ground-breaking papers by Longuet-Higgins *et al.*, Ham, Mary O'Brien, Bersuker and others proposed new theoretical concepts on the interaction between vibrations and a

degenerate electronic state. Basically, two situations with respect to this latter state occur: spatially localized ones and electronic band states. The former situation includes free molecules and ions or molecular structures stabilized in a host crystal. In this context H. Bill investigated with his students  $\text{N}_2^-$ ,  $\text{S}_2^-$ , ..., in  $\text{SrCl}_2$ ,  $\text{Sc}^{2+}$ ,  $\text{Y}^{2+}$ ,  $\text{La}^{2+}$  in several alkaline earth halides,  $nd^9$  ions in cubic fluoroperowskites and alkali halides. Later on, systematic Raman studies of structural phase transitions in crystals of bis-alkylammonium-metallo-tetrahalides (including thermochromic and antiferromagnetic effects), in fluoroperowskites and in some  $\text{K}_2\text{SO}_4$  family members were realized. From the mid-80s on the interest of H. Bill focused on the optical properties of  $\text{Sm}^{2+}$  in single crystals of perowskites and matlockites following the observation of Fano resonances in the absorption spectrum of  $\text{Sm}^{2+}$  in  $\text{SrFCl}$ ,<sup>[17]</sup> and the finding that some members of the  $\text{MeFX}:\text{Sm}^{2+}$  ( $\text{Me} = \text{Sr}, \text{Ba}$ ;  $\text{X} = \text{Cl}, \text{Br}$ ) family undergo reversible and stable bleaching at room temperature upon 488 nm laser light irradiation. These latter systems offer the possibility to perform optical spectral hole burning (OSHB). An OSHB setup was built 1991 enabling among others the first demonstration of reversible and stable OSHB at room temperature,<sup>[18]</sup> and the determination of the nuclear quadrupole coupling constant of  $\text{Sm}^{2+}$  in  $\text{SrFCl}$ . This opened interesting perspectives for applications such as high-density optical data storage.<sup>[19]</sup> Before his retirement H. Bill and his group identified new compounds ( $\text{Ba}_x\text{F}_{12}\text{Cl}_2$ , ...), which present strong white luminescence when doped with  $\text{Eu}^{2+}$ . As they absorb up to ca. 410 nm, these compounds were found to be potential candidates to act as emitters in UV LED and to substitute for the conventional phosphors in commercial fluorescence lamps. The latter require the 254 nm light produced by mercury vapour to be excited. This project led to a patent in 1998 by H. Bill and his coworkers *F. Kubel* and *H. Hagemann*. H. Bill and his group took

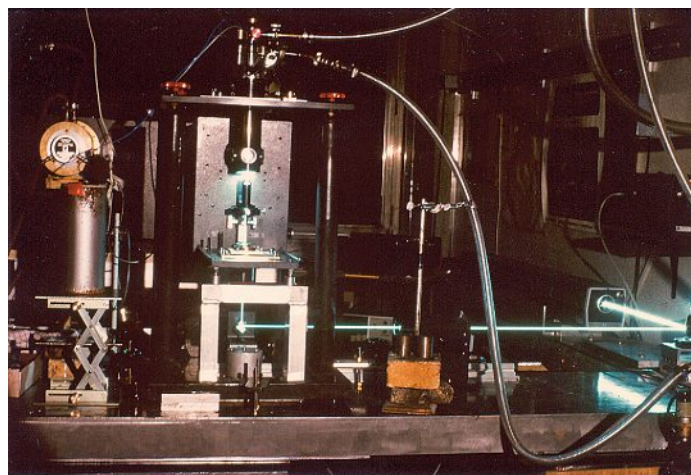


Fig. 9. The first laser Raman spectrometer at the DPC (4 Watt Ar laser, Spex double monochromator, photon counting detection with a cooled photomultiplier,  $0.2 \text{ cm}^{-1}$  effective resolution).

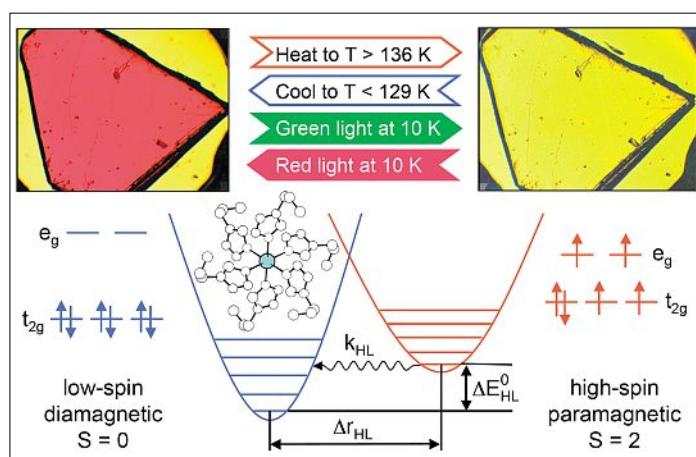


Fig. 10. The spin-crossover compound  $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$  ( $\text{ptz} = 1$ -propyl-tetrazole) dramatically changes its optical and magnetic properties as function of temperature and light-irradiation at low temperatures.<sup>[23,24]</sup>

part in the Swiss Optical Priority Programs PPO1 and PPO2 between 1993 and 2000.

Solid-state spectroscopy and the photophysics of transition metal compounds has since the work of H. Bill and *Christian Klixbüll Jørgensen*, professor at the DPC from 1970 to 1974, become something of a tradition at the DPC. Presently, research in these fields is pursued by H. Hagemann, a former collaborator of H. Bill, and A. *Hauser*, appointed as a full professor in 1996. Currently, high pressure experiments (up to 8 GPa) on  $\text{Sm}^{2+}$  and  $\text{Cr}^{3+}$  containing compounds are undertaken.<sup>[20]</sup> Over the past few years, H. Hagemann has developed an independent research program on the vibrational and structural properties of inorganic borohydrides, which are promising candidates for solid hydrogen storage. This work, in collaboration with the laboratory of crystallography of the University of Geneva and the Swiss-Norwegian beamline at the European synchrotron facility in Grenoble, aims to improve our fundamental understanding of bonding properties of these compounds. This research has led to the first structural characterization of several compounds such as the intensively studied magnesium borohydride ( $\text{Mg}(\text{BH}_4)_2$ ),<sup>[21]</sup> and the complex material  $\text{LiSc}(\text{BH}_4)_4$ .<sup>[22]</sup> The first experimental data of the elastic constants of  $\text{NaBH}_4$  have been obtained using inelastic X-ray scattering and the anharmonic behaviour has been studied using Raman spectroscopy. The current investigations of H. Hagemann and his co-workers aim at the development of isotopically labelled compounds as new structural probes of these materials.

After having studied chemistry at the University of Bern and following two post-doctoral research positions at the Research School of Chemistry, Australian National University, Canberra, and at the Johannes-Gutenberg-Universität in Mainz, respectively and four years as lecturer at

the University of Bern, *Andreas Hauser* started his own research group in the area of photophysics and photochemistry of transition metal compounds at the DPC in Geneva in 1996. His research is focused on the elucidation of photophysical processes using time-resolved spectroscopic methods. These include luminescence and transient absorption spectroscopy as well as fluorescence line narrowing and spectral hole burning relying on modern laser light sources and detection systems. The investigated processes include luminescence, intersystem crossing processes, and light-induced energy and electron transfer with the aim to arrive at a fundamental understanding of the underlying mechanisms. The following three examples may serve to illustrate the on-going research in this area.

A particularly illustrative example is given by so-called spin-crossover compounds, for instance of octahedral complexes of iron(II), which change their thermodynamically stable state from the diamagnetic low-spin state at low temperatures to the paramagnetic high-spin state at elevated temperatures (Fig. 10). These can also be switched back and forth between the two states at low temperatures by irradiation with light of different wavelengths. This light-induced spin transition involves a whole cascade of intersystem crossing steps, which occur on very different time-scales, going from minutes and hours for the extremely slow tunnelling process of the relaxation from the light-induced high-spin state back to the low-spin state<sup>[23,24]</sup> down to below picoseconds for the  $\Delta S = 2$  intersystem crossing process from the initially highly excited low-spin state to the high-spin state.<sup>[25,26]</sup>

With regard to excitation energy transfer, the three-dimensional oxalate networks first synthesised by *S. Decurtins et al.*<sup>[27]</sup> provide a model system for studying the process of excitation energy migration,

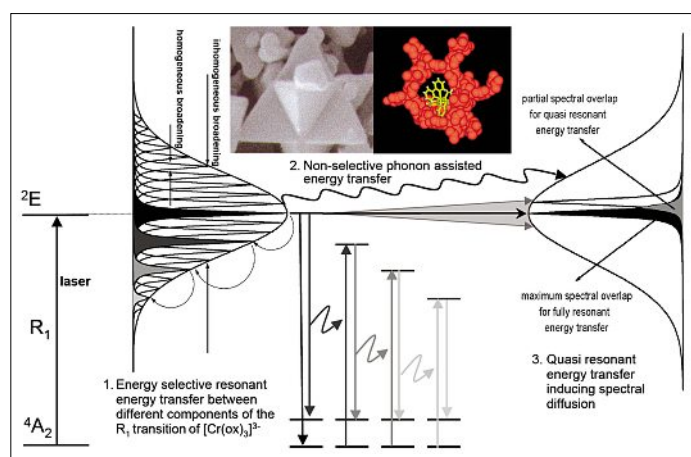


Fig. 11. The three mechanisms of energy migration within the  ${}^2E$  excited state of  $\text{Cr}^{3+}$  in the three-dimensional oxalate networks of compositions  $[\text{NaCr}(\text{ox})_3][\text{Rh}(\text{bpy})_3]\text{ClO}_4$  and  $[\text{NaCr}(\text{ox})_3][\text{Ru}(\text{bpy})_3]$ .

that is energy transfer between chemically identical chromophores in highly concentrated systems. Thus for instance in the systems  $[\text{NaCr}(\text{ox})_3][\text{Rh}(\text{bpy})_3]\text{ClO}_4$  and  $[\text{NaCr}(\text{ox})_3][\text{Ru}(\text{bpy})_3]$  three different mechanisms for such a migration within the famous  ${}^4A_2 \rightarrow {}^2E$  spin-flip transition of the  $\text{Cr}^{3+}$  ion could be identified (Fig. 11). In addition to the well-known phonon-assisted process at elevated temperatures, two types of resonant and thus energy selective processes lead to a multi-line pattern and fast spectral diffusion, respectively, at 1.4 K.<sup>[28,29]</sup>

In the complex  $[\text{Ru}(\text{bpy})_2\text{dppz-TTF}]^{2+}$  (Fig. 12) irradiation into the metal–ligand charge transfer (MLCT) bands results in both luminescence as well as the creation of a comparatively long-lived charge separated state ( $\tau = 2.4 \mu\text{s}$ ).<sup>[30,31]</sup> The charge-separated state results if in the excitation process the electron is first transferred to a bipyridine ligand creating formally a  $\text{Ru}^{3+}$  centre and subsequent electron transfer from the tetrathiafulvalene (TTF) unit acting as electron donor to restore the 2+ charge in the ruthenium ion. This effectively quenches the MLCT luminescence. If on the other hand in the excitation process the electron is transferred to the dppz unit of the dppz-TTF ligand, then the electron

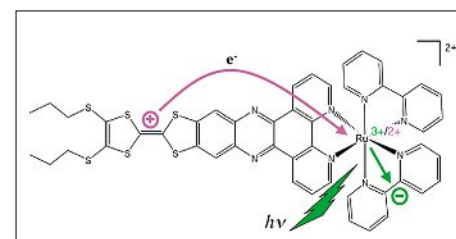


Fig. 12. In the complex  $[\text{Ru}(\text{bpy})_2\text{dppz-TTF}]^{2+}$ , synthesised in the group of *S. Decurtins* at the University of Bern, a long-lived charge separated state is created by irradiation into the MLCT band to the bpy ligands.

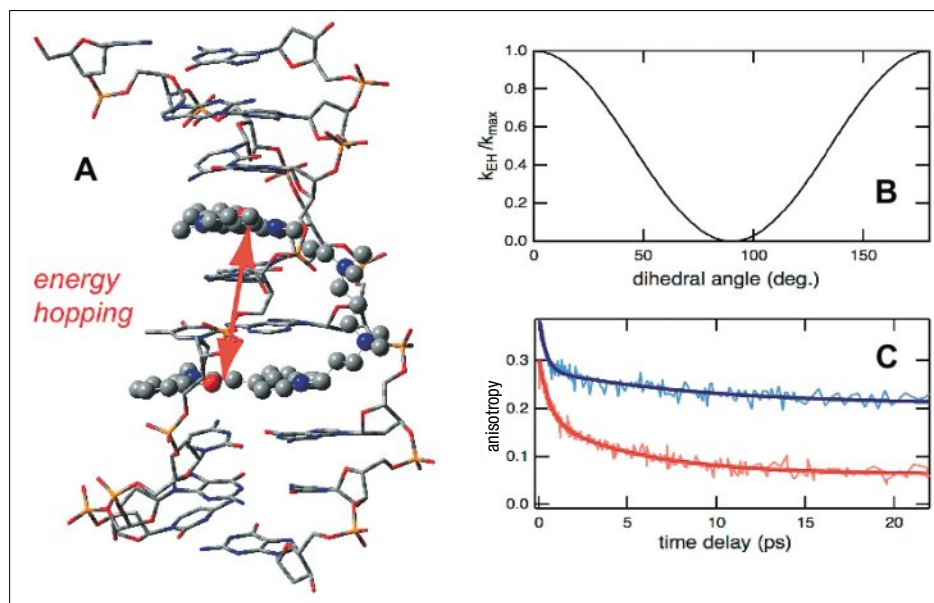


Fig. 13. A) Illustration of excitation energy hopping between the two chromophoric moieties of YOYO intercalated in DNA; B) dependence of the energy hopping rate constant on the dihedral angle between the two YO units and C) decay of the fluorescence anisotropy of YOYO in two different DNA helices.

transfer from TTF is blocked by the negative charge on dppz and MLCT luminescence is observed.

Research activity in the field of ultrafast spectroscopy started at the DPC in 2001 with the appointment of *Eric Vauthey* as full professor. E. Vauthey studied chemistry at the University of Fribourg and, after two postdoctoral stays, one at The Royal Institution and at the Imperial College in London, and the other at the ETH in Zurich, he returned to Fribourg in 1992, where he started an independent research on the development and the applications of nonlinear spectroscopy for the investigation of ultrafast photoinduced processes that he is still pursuing in Geneva. This research is presently concentrating along three main axes: photoinduced electron transfer reactions, excited-state dynamics in biological and organised environments, and photoinduced processes at liquid interfaces.

Although electron transfer reactions have been intensively investigated over the past decades, there are still several important unanswered questions. A major issue concerns the structure of the primary product of bimolecular charge separation reactions.<sup>[32]</sup> For example, to account for a well-known discrepancy between experiment and theory, it has been suggested that highly exergonic bimolecular charge separation reactions produce radical ions in an electronic excited state. This hypothesis proposed many years ago has neither been confirmed nor invalidated so far, mostly because the spectroscopy of excited open-shell ions in the condensed phase is almost unexplored. To solve this old problem, a

detailed study of the excited-state dynamics of these species is now being performed using various ultrafast spectroscopic methods. Beside this, the group is investigating ultrafast charge transfer reactions that take place on timescales similar to those of vibrational and solvent relaxations and whose dynamics depends on the excitation wavelength.<sup>[33]</sup> Such 'non-Kasha' photochemistry opens interesting perspective for a coherent control of chemical reactions in liquids.

The group is also exploring strategies to obtain structural information on biologically relevant molecules, such as nucleic acids and proteins, from the early excited-state dynamics of local probes.<sup>[34,35]</sup> As an example, Fig. 13 depicts the decay of the fluorescence anisotropy of the homodimeric chromophore YOYO intercalated into dsDNA helices of different form. This fast depolarisation of the fluorescence arises from the hopping of the excitation energy between both YO units and has been found to depend on the base content of the DNA double strand as well as on its form, A or B. Using energy transfer theory, the distribution of the dihedral angle between the YO units can be recovered from this decay and, as this angle is related to the helicity of the host molecule, rather direct structural information of the DNA strand can be deduced.

The properties of liquid interfaces differ considerably from those of bulk liquids because the asymmetry of forces leads to an anisotropy of molecular orientation. The determination of these features remains however a major problem, as a result of the difficulty to discriminate the

interfacial region from the bulk phases. Indeed, when performing conventional optical spectroscopy, the response from the interface, which consists of a few molecular layers only, is totally buried in that originating from the bulk. Two different methods to circumvent this problem are being developed in E. Vauthey's group. The first is the so-called transient evanescent grating technique, which is based on a four wave-mixing process where the pump and/or the probe waves are evanescent fields generated by total internal reflection at the interface (Fig. 14).<sup>[36]</sup> The second is transient surface second-harmonic generation where the material response that is probed is zero in the bulk and non-zero at the interface.<sup>[37]</sup> Both methods are complementary and are used to study the dynamics of photoinduced processes at liquid interfaces, two examples being illustrated in Fig. 14.

The group collaborates with several research groups for the investigation of new molecules with specific properties, as well as for the theoretical description of the various phenomena investigated.

### Computational Chemistry at the DPC

Computational chemistry (CC) is a comparatively young discipline, which started to be developed in the 1960s simultaneously with the advent of computers. At the University of Geneva, it may be traced back to the end of 1960s–early 1970s at the DPC. The main proponent of CC in Geneva was *Roger Lacroix*, appointed in 1971 as a full professor at the DPC and specialized in solid-state theory, namely the calculation of the magnetic properties of local impurities hosted by crystals. R. Lacroix wanted to use the LCAO-MO model to describe both the magnetic impurity and its first shell of neighbours. In order to achieve this, he used the basic tools of CC to calculate the SCF LCAO-MOs by diagonalizing Wolfsberg-Helmholtz Hamiltonians. Thus the first applications of CC in Geneva were born. Subsequently it was comparatively easy to transpose such models to molecules and to chemistry, and this was the work of *Jacques Weber*, a former PhD student of R. Lacroix, appointed in 1971 as *chef de travaux* in the Section of chemistry, in charge of developing so-called 'computer-assisted tools'. The first application of this kind was dedicated to the study of internal rotation barriers in small organic systems and published in 1973. The computers used then were very primitive with punched cards as input media and without time-sharing of the processor resources. CC applications were thus tedious to perform and it was not unusual to have to wait one week before having re-

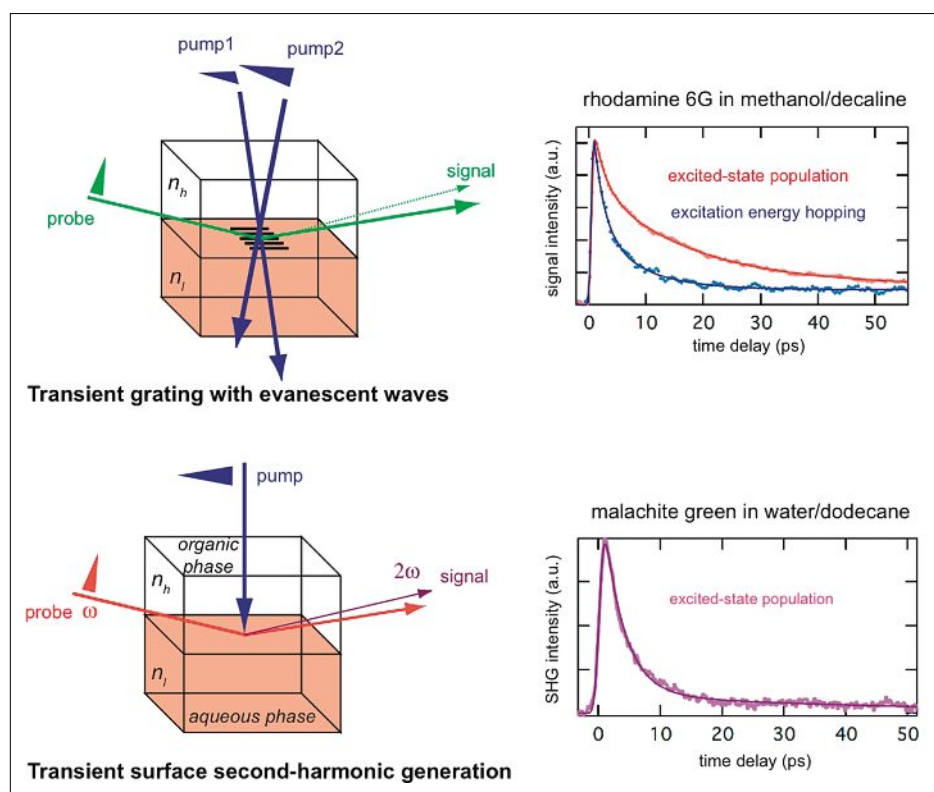


Fig. 14. (Left) Schematic illustration of the transient evanescent grating and of the transient surface SHG techniques, and (right) typical time profiles of the signal intensity associated with ultrafast population dynamics at liquid-liquid interfaces.

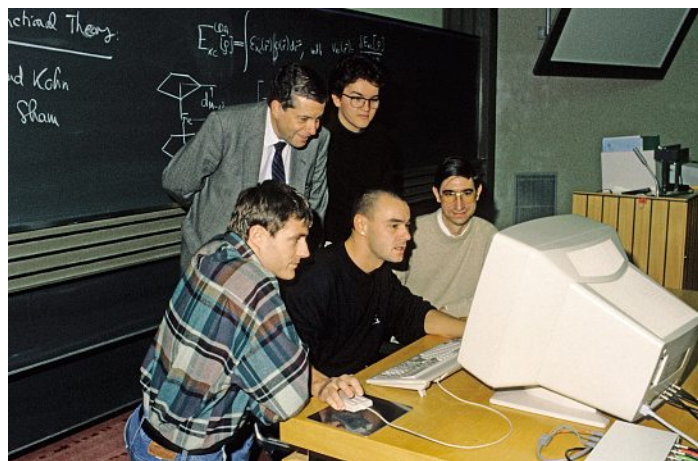


Fig. 15. Jacques Weber with some of his coworkers in 1992 looking at a molecular model displayed on a Silicon Graphics Iris workstation (from left to right: Dominique Stussi, Jacques Weber, François Savary (standing), Peter Flükiger and Pierre-Yves Morgantini).

results for systems consisting of about ten atoms. However, this situation changed very rapidly in 1970s due to the dissemination of powerful computers and efficient *ab initio* programs.

After two postdocs at the Quantum Theory Project Laboratory at the University of Florida and at the IBM Research Laboratory in Jan Jose (California), J. Weber came back to the DPC as *chargé de cours* and headed a small independent research group (Fig. 15). During the period 1976–1990, he specialized mostly in the so-called X-alpha method developed by the Florida laboratory, showing for example that the Density Functional Theory

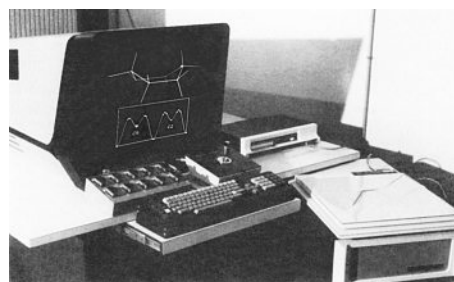


Fig. 16. The Vector General 3404 calligraphic system used by the DPC in 1978. The monitor displays the boat structure of cyclohexane whereas the cursor indicates its energy on the calculated minimum energy reaction path (from ref. [41]).

(DFT) calculated wavefunctions were of a very good quality, taking the example of the magnetic properties of cobaltocene.<sup>[38]</sup> This technique was the ancestor of the DFT-based methods used today on a large scale by CC specialists.

From 1976, J. Weber and his group developed several methodologies and improvements based on DFT, and performed many applications in collaboration with Swiss and international groups, mainly in the fields of inorganic chemistry, zeolites and catalysis (for typical examples, see refs [39,40]).

Some other applications of CC were simultaneously developed by the group of J. Weber in the field of molecular graphics (Figs 16 and 17). The contrast between these two figures illustrates well the tremendous progresses achieved in graphics hardware between 1980 and 1990. In 1989, J. Weber was promoted as a full professor of physical chemistry. He was attributed the chair of computational chemistry, the first of this type in Switzerland.

A key period for CC was the beginning of 1990s when important methodological progress was made by various groups to produce Kohn-Sham LCAO-DFT packages, which rapidly took over and replaced the old X-alpha technique. The Geneva group was involved in these developments and could benefit from the much more efficient DFT technique, which considerably enlarged its field of investigation. All these research activities performed in Geneva during 33 years in quantum CC contributed significantly to the popularity of the DFT technique, which has become a basic tool for interpreting and predicting molecular properties. Beside his research, J. Weber has been highly dedicated to the University of Geneva, being Dean of the Faculty of Sciences (1998–2004) and Rector (2006–2007).

Tomasz A. Wesolowski was appointed as *maître d'enseignement et de recherche* at the DPC in 2000 and started an inde-

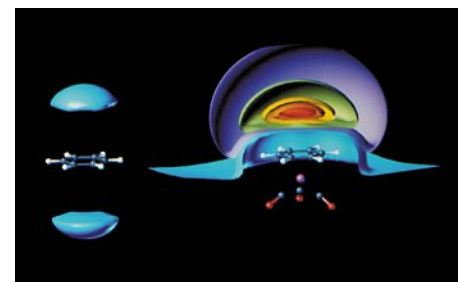


Fig. 17. Structural models of benzene (left) and (benzene)Cr(CO)<sub>3</sub> (right) represented on a Silicon Graphics Iris system, together with solid models of a semi-empirical reactivity index calculated for nucleophilic attack (from ref. [42]).

pendent research in the development and applications of his embedding theory.<sup>[43–45]</sup> The work on this theory started with the derivation of Eqns. (20) and (21) of ref. [43] (together with A. Warshel) when he was a visiting scientist at University of Southern California in Los Angeles on leave from his assistant professor position at the University of Warsaw. These equations provide a unique correspondence between the embedding potential and the pair of electron densities: that of the investigated quantum system and that of its environment. They can be used, therefore, as a basis for system-independent embedding methods for modelling electronic properties of chemical species in condensed phase. Between 1994 and 2000, working as a post-doctoral researcher at DPC in the group of J. Weber, he developed the first computer implementation of these equations of general applicability for intermolecular complexes. Since 2000, the work on the embedding theory and its numerical implementation intensified. Most of the current applications of the developed embedding formalism focus on electronic excitations of chemical species embedded in various environments such as solids, liquids, and biomolecules (see Fig. 18 and ref. [44] for a review). The combined analysis of the observed and calculated spectral features in such studies aim at obtaining detailed structural information about the local environment of the optically active species. Similar applications to NMR and EPR spectroscopy are currently in the test stage in T. Wesolowski's or other groups. His interests in many-body quantum theory focus on the density functional for the kinetic energy, which plays a crucial role in two types of computer modelling methods: those based on the embedding potential introduced by Wesolowski and Warshel in 1993 and the so-called orbital-free methods which recently attracted increasing attention.<sup>[47,48]</sup> He has organized four international meetings on this subject in France, Greece, Canada, and USA and is currently editing a volume over-viewing the current developments in this field.<sup>[48]</sup>

In 2005, Laura Gagliardi was appointed as the successor of J. Weber in charge of CC research in the Department. She obtained her PhD in computational chemistry from the University of Bologna in 1996. She then spent two years as postdoctoral associate in the group of Nicholas Handy in Cambridge. She had a position as lecturer at the University of Palermo until 2005, when she joined the University of Geneva as an associate professor. In 2004, she was awarded the Annual award of the International Academy of Quantum Molecular Science with citation: "...for her innovative contributions to prediction and understanding of new inorganic molecules using quantum chemical methods".

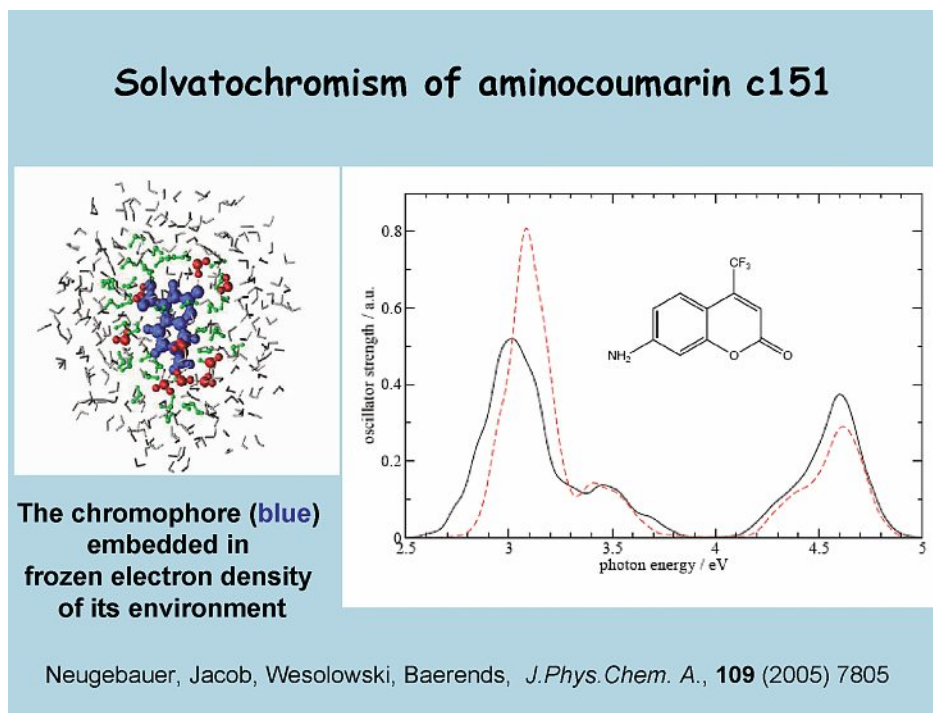


Fig. 18. Absorption spectra of aminocoumarin c151 in water (black) and n-hexane (red) obtained from multi-level simulations using orbital-free embedding potential to couple the solvent with the chromophore.<sup>[46]</sup>

L. Gagliardi's field of research is computational quantum chemistry with special focus on highly multiconfigurational chemical systems. She has expertise in treating ground and excited state properties of molecular species containing metals with many open shell electrons. These systems are difficult to handle with conventional DFT, especially in their excited states, and L. Gagliardi has pushed other methods, in particular the CASSCF/CASPT2 approach, to study such problematic cases. She has explored metal-metal multiple bonds along the entire periodic table, from first-row transition metals to actinides. One of her key contributions is the paper on the  $U_2$  molecule, which appeared in *Nature* in 2005.<sup>[49]</sup> Since then, the concept of metal-metal high-order multiple bonds has been explored extensively, both in isolated di-metal molecules ( $Mo_2$ ,  $W_2$  and the early diactinides) and in novel inorganic compounds containing di-metal units ( $PhCrCrPh$ ).<sup>[50–53]</sup>

L. Gagliardi's research has been predictive (see the work  $WH_4(H_2)_2$ , synthesized after her predictions) and at the same time explanatory of existing experiments (see in collaboration with spectroscopists). She believes that non-dynamical electron correlation is one of the big challenges of modern quantum chemistry. When she started working with the CASSCF/CASPT2 method, only organic molecules and conventional first row metal systems were studied. She has shown that the method can be used to study all atoms in the

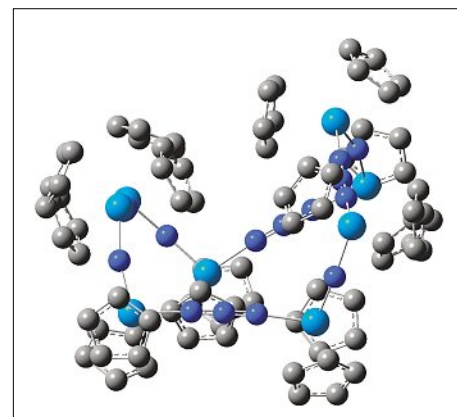


Fig. 19.  $[(C_5Me_5)_2U(\mu-N)(C_5Me_5)_2U(\mu-N)]_4$ , a compound dense in uranium and nitrogen, which can be used as a molecular precursor to high-purity UN, a potential nuclear fuel of the future.

periodic table. She has been aware of the fact that the bottleneck of the CASSCF/CASPT2 approach is the size of the active space, which can be at most about 15 electrons in 15 orbitals. Recently, she has worked on the extension of the method to the RASSCF/RASPT2 regime, which allows the study of systems with up to 30 electrons in 30 orbitals, with an accuracy comparable to the one of the CASSCF/CASPT2 method. Nowadays, in her group, systems with up to 200 atoms, several of which are heavy, are treated routinely with the RASSCF/RASPT2 approach (Fig. 19).



Many of the systems that she is studying, like metal ions, exist in solution in nature, and she has felt the need to combine quantum chemical methods with molecular dynamics simulation techniques in order to understand structural and dynamical properties of such systems. With this approach she has studied uranyl and Cm(III) in water and more recently lanthanide-chloride salts in solution. The difference between her treatment and what other groups do, is that she generates fully *ab initio* intermolecular potentials (usually with CASPT2) that will be used in the simulation. In such a way she can study also systems for which not enough experimental data are available, unlike when one uses semi-empirical force field.<sup>[54]</sup>

L. Gagliardi has proven that multiconfigurational quantum chemistry is a powerful and useful tool in chemistry that can tackle difficult problems and not just a nice formalism, relegated to model systems. She has shown that the CASSCF/CASPT2 approach is a competitive alternative to DFT and thus a modern tool in quantum chemistry.

## Concluding Remarks and Outlook

We hope that this non-exhaustive overview will give a flavour of the current research activities at the DPC and illustrate how two important pillars of physical chemistry, namely spectroscopy and quantum chemistry, have been developed and consolidated over the past decades. Given the relatively small size of the DPC, these two directions prevent too big a dispersion of the research and ensure good synergies between the different groups. On the other hand, these two areas are vast enough to warrant a large diversity of the research. This has stimulated strong and fruitful collaborations, not only with numerous groups worldwide, but also with several teams of other departments of the *Section de chimie et biochimie* of the University of Geneva. After the retirement of Michel Geoffroy in October 2009, the activities in EPR/ENDOR will be maintained by Theo Berclaz. On the other hand, a new research direction in spectroscopy will be initiated at the DPC with the arrival of a new professor in 2010.

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- [1] E. Briner, E. Perrottet, B. Susz, *Helv. Chim. Acta* **1936**, *19*, 558.
- [2] P. A. Blanc, O. F. Gülaçar, A. Buchs, *Org. Mass Spectrom.* **1980**, *15*, 198.
- [3] L. Verzeqnessi, C. Riffé-Chalard, W. Kloeti, F. O. Gülaçar, *Fresenius' J. Anal. Chem.* **1999**, *364*, 249.
- [4] Y. Finck, N. Aydin, C. Pellaton, G. Gorin, F. O. Gülaçar, *J. Chromatog. A* **2004**, *1049*, 227.
- [5] E. A. C. Lucken, 'Nuclear Quadrupole Coupling Constants', Academic Press, London, **1969**.
- [6] F. Zhenye, E. A. C. Lucken, J. Diolot, *Z. Naturforsch.* **1992**, *47a*, 395.
- [7] L. Pang, E. A. C. Lucken, G. Bernardelli, *J. Am. Chem. Soc.* **1990**, *112*, 8754.
- [8] M. Geoffroy, E. A. C. Lucken, C. Mazeline, *Mol. Phys.* **1974**, *28*, 839.
- [9] H. Bill, *Helv. Phys. Acta* **1969**, *42*, 771.
- [10] H. Bill, *J. Chem. Phys.* **1976**, *76*, 219.
- [11] H. Bill, in 'The Dynamical Jahn-Teller Effect in Localized Systems', Eds. Y. E. Perlin, M. Wagner, North Holland, Amsterdam, **1984**, chap. 13, pp 709.
- [12] B. Ndiaye, S. Bhat, A. Jouati, T. Berclaz, G. Bernardelli, M. Geoffroy, *J. Phys. Chem. A* **2006**, *110*, 9736.
- [13] A. Jouati, M. Geoffroy, G. Terron, G. Bernardelli, *J. Am. Chem. Soc.* **1995**, *117*, 2251.
- [14] L. Cataldo, S. Choua, T. Berclaz, M. Geoffroy, N. Mézailles, L. Ricard, F. Mathey, P. Le Floch, *J. Am. Chem. Soc.* **2001**, *123*, 6654.
- [15] P. Grosshans, H. Adkine, H. Sidorenkova, N. Nomura, M. Fourmigué, M. Geoffroy, *J. Phys. Chem. A* **2008**, *112*, 4067.
- [16] F. Biasco, M. Geoffroy, E. Canadell, P. Auban-Senzier, E. Levillain, M. Fourmigué, N. Avarvari, *Chem. Eur. J.* **2007**, *13*, 5394.
- [17] R. Jaaniso, H. Bill, *Phys. Rev. B* **1991**, *44*, 2389.
- [18] R. Jaaniso, H. Bill, *Europhys. Lett.* **1991**, *16*, 569.
- [19] H. Bill, R. Jaaniso, H. Hagemann, D. Lovy, A. Monnier, M. Schnieper, *Optical Engineering* **1995**, *34*, 2333.
- [20] T. Penhouet, H. Hagemann, *J. Alloys Compd* **2008**, *451*, 74.
- [21] R. Cerny, Y. Filinchuk, H. Hagemann, K. Yvon, *Angew. Chem., Int. Ed.* **2007**, *46*, 5765.
- [22] H. Hagemann, M. Longhini, J. W. Kaminski, T. A. Wesolowski, R. Czerny, N. Penin, M. H. Sørby, B. C. Hauback, G. Severa, C. M. Jensen, *J. Phys. Chem. A* **2008**, *112*, 7551.
- [23] P. Gütllich, A. Hauser, H. Spiering, *Angew. Chem., Int. Ed.* **1994**, *33*, 2024.
- [24] A. Hauser, *Topics in Current Chemistry* **2004**, *234*, 155.
- [25] A. L. Smeigh, J. K. McCusker, *Springer Series in Chemical Physics* **2007**, *88*, 273.
- [26] W. Gawelda, A. P. Cannizzo, V.-T. Pham, F. Van Mourik, C. Bressler, M. Chergui, *J. Am. Chem. Soc.* **2007**, *129*, 8199.
- [27] S. Decurtins, H. Schmalte, R. Pellaux, P. Schneuwly, A. Hauser, *Inorg. Chem.* **1996**, *35*, 1451.
- [28] M. Milos, S. Kairouani, S. Rabaste, A. Hauser, *Coord. Chem. Rev.* **2008**, *252*, 2540.
- [29] A. Hauser, M. E. von Arx, V. S. Langford, S. Kairouani, U. Oetliker, A. Pillonet, *Topics in Current Chemistry* **2004**, *241*, 65.
- [30] C. Goze, C. Leiggenger, S.-X. Liu, L. Sanguinet, E. Levillain, A. Hauser, S. Decurtins, *ChemPhysChem* **2007**, *8*, 1504.
- [31] C. Leiggenger, N. Dupont, S.-X. Liu, C. Goze, E. Beitler, S. Decurtins, A. Hauser, *Chimia* **2007**, *61*, 621.
- [32] O. F. Mohammed, K. Adamczyk, N. Banerji, J. Dreyer, B. Lang, E. T. J. Nibbering, E. Vauthey, *Angew. Chem.* **2008**, *47*, 9044.
- [33] O. Nicolet, N. Banerji, S. Pagès, E. Vauthey, *J. Phys. Chem. A* **2005**, *109*, 8236.
- [34] A. Fürstenberg, M. D. Julliard, T. G. Deligeorgiev, N. I. Gadjev, A. A. Vassilev, E. Vauthey, *J. Am. Chem. Soc.* **2006**, *128*, 7661.
- [35] A. Fürstenberg, O. Kel, J. Gradinaru, T. R. Ward, D. Emery, G. Bollot, J. Mareda, E. Vauthey, *ChemPhysChem* **2009**, *10*, 1517.
- [36] P. Brodard, E. Vauthey, *J. Phys. Chem. B* **2005**, *109*, 4668.
- [37] A. Punzi, G. Martin-Gassin, J. Grilj, E. Vauthey, *J. Phys. Chem. C* **2009**, *113*, 11822.
- [38] J. Weber, A. Goursot, E. Pénigault, J. H. Ammeter, J. Bachmann, *J. Am. Chem. Soc.* **1982**, *104*, 1491.
- [39] C. Daul, H. U. Güdel, J. Weber, *J. Chem. Phys.* **1993**, *98*, 4023.
- [40] F. Gilardoni, J. Weber, A. Baiker, *J. Phys. Chem. A* **1997**, *101*, 6069.
- [41] J. Weber, G. Bernardelli, J. J. Combremont, M. Roch, *Cahiers Fac. Sci. Univ. Geneva* **1980**, *2*, 15.
- [42] J. Weber, D. Stussi, P. Flükiger, P. Y. Morgantini, E. P. Kündig, *Comments Inorg. Chem.* **1992**, *14*, 27.
- [43] T. A. Wesolowski, A. Warshel, *J. Phys. Chem.* **1993**, *97*, 8050.
- [44] T. A. Wesolowski, in 'Computational Chemistry: Reviews of Current Trends', World Scientific, Singapore, **2006**, Vol. 10, p 1.
- [45] T. A. Wesolowski, *Phys. Rev. A* **2008**, *77*, 012504.
- [46] J. Neugebauer, C. R. Jacob, T. A. Wesolowski, E. J. Baerends, *J. Phys. Chem. A* **2005**, *109*, 7805.
- [47] Y. A. Wang, E. A. Carter, in 'Theoretical Methods in Condensed Phase Chemistry', Ed. S. D. Schwartz, Kluwer, Dordrecht, **2000**, p. 117.
- [48] Y. A. Wang, T. A. Wesolowski, 'Current Developments in Orbital-Free Methods', World Scientific, Singapore, to appear in **2010**.
- [49] L. Gagliardi, B. O. Roos, *Nature* **2005**, *433*, 848.
- [50] G. La Macchia, M. Brynda, L. Gagliardi, *Angew. Chem., Int. Ed.* **2006**, *45*, 6210.
- [51] G. La Macchia, L. Gagliardi, P. P. Power, M. Brynda, *J. Am. Chem. Soc.* **2008**, *130*, 5104.
- [52] M. Brynda, L. Gagliardi, B. O. Roos, *Chem. Phys. Lett.* **2009**, *471*, 1.
- [53] C. Jones, C. Schulten, R. P. Rose, A. Stasch, S. Aldridge, W. D. Woodul, K. S. Murray, B. Moubarak, M. Brynda, G. La Macchia, L. Gagliardi, *Angew. Chem., Int. Ed.* **2009**, *48*, 7406.
- [54] D. Hagberg, E. Bednarz, N. M. Edelstein, L. Gagliardi, *J. Am. Chem. Soc.* **2007**, *129*, 14136.