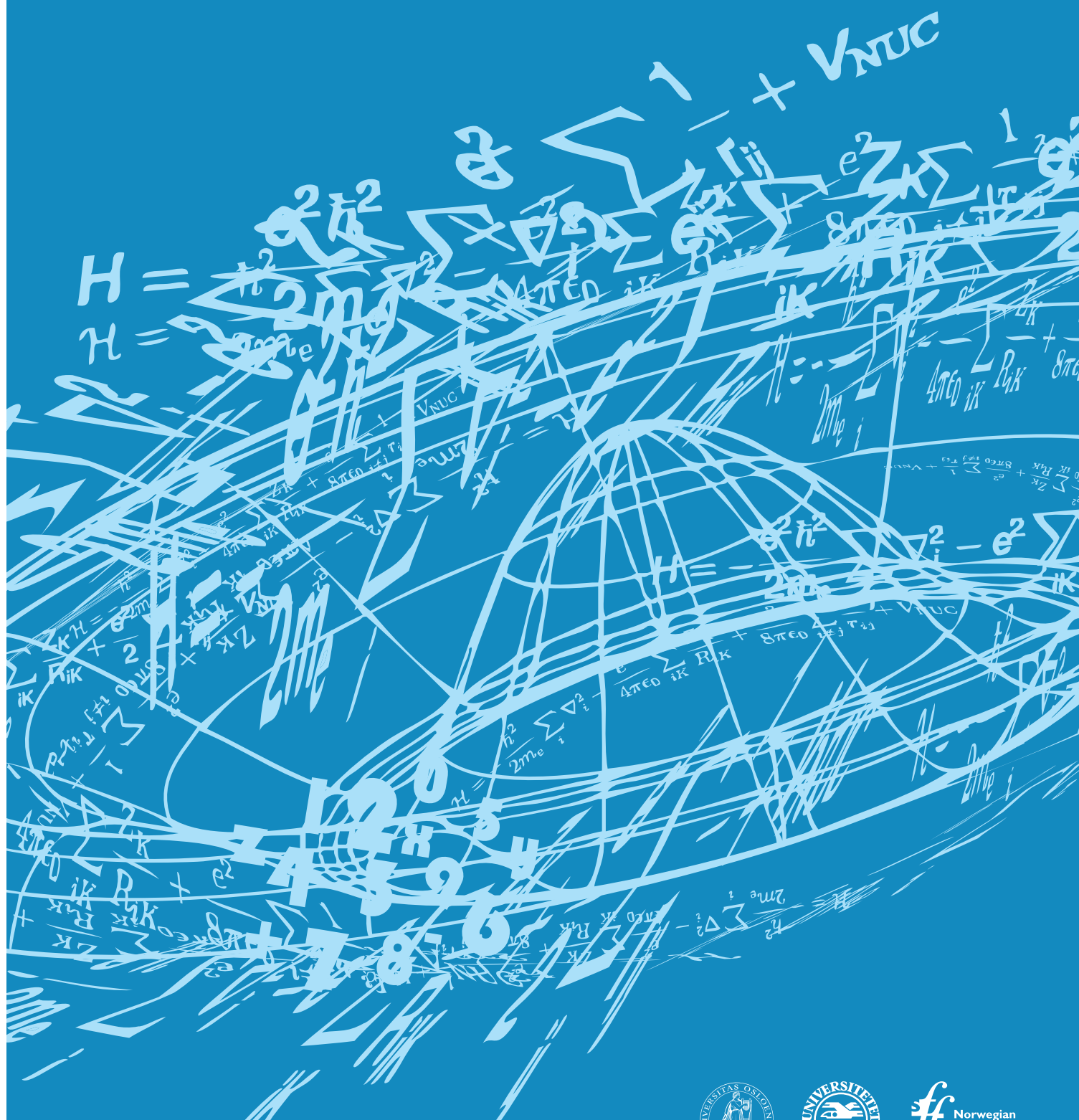
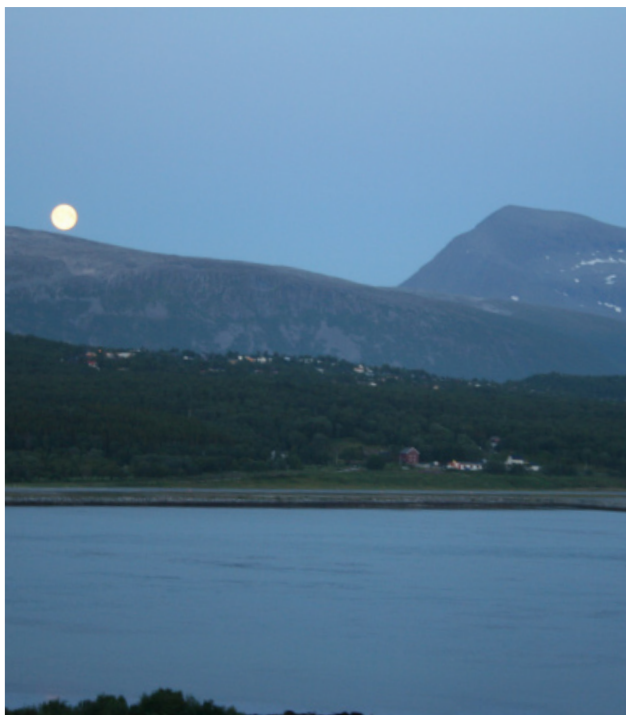


CTCC The Centre for Theoretical  
and Computational Chemistry

# annual report 2008



# The Centre for Theoretical and Computational Chemistry



The Centre for Theoretical and Computational Chemistry (CTCC) is a Norwegian Centre of Excellence (CoE) established by the Research Council of Norway in July 2007. The goal of the CoE program is to stimulate Norwegian research groups to establish larger units focusing on frontier research at a high international level, and contribute to raising the quality of Norwegian research.

The CTCC is one of 21 national centres of excellence in Norway and the only one in the field of chemistry. The centre has two nodes of equal size, hosted respectively by the University of Oslo and the University of Tromsø. The CTCC receives an annual funding from the Research Council of Norway of about 9.5 MNOK for the period July 2007 – June 2017, pending a successful mid-term evaluation. In addition, the centre receives substantial financial support from the respective host institutions.

The vision of the CTCC is to become a leading international contributor to computational chemistry by carrying out cutting-edge research in theoretical and computational chemistry at the highest international level.

The CTCC has established an extensive visitors program for world-leading scientists from around the world, as well as for PhD students and postdocs from other research groups who wish to benefit from the expertise available at the centre.

The CTCC is actively engaged in communicating the potentials offered by computational chemistry in all areas of chemistry, offering courses in the efficient utilization of modern quantum-chemistry programs on the computational infrastructure available in the Norwegian super-computing program.

More information about the CTCC and the day-to-day operations can be found at <http://www.ctcc.no>.



## A word from the directors

2008 was an important year for the CTCC, being the first full year of operation. During this year, the CTCC has grown to its full size, with the arrival of a large number of post docs and PhD students. The CTCC now comprises 46 members from 15 different countries and three continents. Likewise, the necessary refurbishments of office spaces and laboratories have been completed. As a result, we can now focus fully on the scientific problems at the heart of the CTCC activities.

To bolster these activities, the two CTCC nodes have established regular group meetings and set up seminars series open to visitors and members. In 2008, we organized two joint centre meetings, where all CTCC researchers met for scientific discussions and social gatherings. Importantly, one of these gatherings took place during the first annual autumn meeting of the newly established Division for Computational Science of the Norwegian Chemical Society, allowing for lively interactions between CTCC members and other computational chemists in Norway. Two workshops have been organized with research groups in organic and inorganic chemistry. These many gatherings and activities notwithstanding, a self-

evaluation of the CTCC at the end of 2008 indicates that we must work harder on integrating the activities of the two nodes by encouraging more CTCC-wide collaborations, producing better science by drawing on the complementary expertise of the two nodes.

The CTCC visitor program has turned out to be a great success. During this first year of full operation, more than 52 researchers from 23 countries have visited the CTCC. The good working conditions at the centre and its stimulating research atmosphere with a large number of excellent young researchers have earned us much praise from our visitors, and we believe the visitor program will further enhance the success of the CTCC.

We are happy that the Research Council of Norway endorsed our plan for improving the gender balance at the CTCC and look forward to appointing two new leading female researchers as adjunct professors at the CTCC during the next year.

As even a cursory perusal of this report will demonstrate, 2008 has been a very productive year for the CTCC, with many exciting new scientific results. We are confident this productivity will extend into 2009.



Kenneth Ruud



Trygve Helgaker

# From the board of directors

The board of directors is very pleased with the achievements of the CTCC in its first full year of operation. The board is in particular happy to note that the centre has been growing according to plan, and that the CTCC receives a large number of applications from highly qualified researchers in its announcements of open positions at the centre. We believe this is an important element in the future success of the CTCC.

Still, the hiring process is often a time consuming process, and the board believes a more aggressive long-term budgeting process is required in order to have a more equitable distribution of PhD students and postdocs, as well as of the budget, over the operational period of the centre.

The CTCC conducted an internal evaluation of its activities during the autumn of 2008. The purpose was to get additional feedback from the CTCC coworkers regarding their working conditions and the CTCC activities. The board was happy to see that the PhD students and postdocs are satisfied with having joined the CTCC and also

with the CTCC activities and scientific projects. However, the board noted a need to focus on integrating better the activities in Oslo and Tromsø, and particular attention has been given to this in the Action Plan for 2009.

The self-evaluation also revealed that the splitting of the CTCC members at the Tromsø node in several buildings is considered to have a negative influence on the working conditions at this node, an observation the board is concerned about.

The board believes that disseminating the advances made at the CTCC to the general public is an important element of the CTCC activities. However, with the CTCC still expanding, the board endorses the current stronger focus on science in the CTCC Action Plan for 2009. However, the board expects the CTCC to be a notable contributor to the International Year of Chemistry in 2011, proclaimed by the United Nations, using this general focus on chemistry to disseminate the findings and achievements of the CTCC to a wide audience.



**Professor Tore Vorren**  
(Dean of the Faculty of Science, University of Tromsø).  
Chairman of the board



**Professor Anne-Britt Kolstø**  
(University of Oslo)  
vice-chairman of the board



**Dr. Nina Aas**  
(Statoil-Hydro)



**Professor Knut J. Børve**  
(University of Bergen)



**Professor Aslak Tveito**  
(Simula Research Centre)





# The scientific activities at the CTCC

The scientific activities at the CTCC are concerned with the understanding of how the building blocks of the atoms, the nuclei and the electrons, interact with one another and create molecules. The focus of the CTCC is thus on the understanding of the fundamentals of chemistry.

To achieve this goal, a stimulating atmosphere for scientific discovery must be created. At the CTCC, this is achieved by taking an interdisciplinary approach to the underlying chemical challenges. The CTCC emphasizes the need for a close collaboration between theoreticians and experimentalists so as to provide the most fertile ground for making new advances in the understanding of the behavior of molecules. The principal scientists of the CTCC therefore comprise theoretical chemists devoted to the development and application of new computational methodology applicable to molecules of increasing size and accuracy, as well as computational chemists having a concurrent activity in experimental investigations of the reactions and properties of molecules. Added interdisciplinarity comes from the involvement of researchers in applied mathematics and in atomic and molecular physics.

A goal for the CTCC is to develop new computational chemistry methods, making these more applicable to real-life chemical problems. However, disseminating the knowledge about these methods, their use and range of applicability, is an integral part of the centre's activities. This is in part achieved by organizing training classes in the use of computational chemistry software, and through the establishment of nationally coordinated master and PhD programs. Regarding the former, the CTCC organized a workshop on the Schrödinger program packages in July 2008, gathering about 40 participants from most parts of Norway. The CTCC will continue this activity in 2009.

As part of its outreach activities, the CTCC organized joint seminars with the organic chemistry division at the University of Oslo, as well as with INGAP, a Norwegian Centre for Research-based Innovation focusing on the

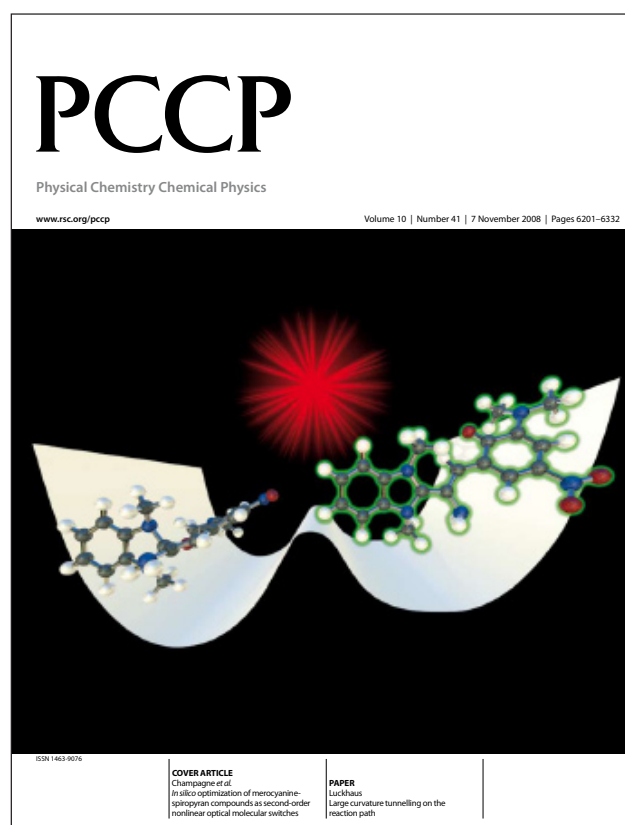


Figure: Work performed by one of the CTCC postdocs, Dr. Maxime Guillaume, was put on the front cover of PCCP in November 2008 [53].

development of new technologies for utilizing the natural gas resources of Norway. Through these seminars, valuable cross-fertilizations have been possible between these, at first sight, very different scientific disciplines. For early 2009, a similar joint workshop is being planned with the Centre of Mathematics for Applications (CMA), a Centre of Excellence at the University of Oslo.

An important ingredient of the scientific activities at the CTCC is the international visitors program. Through this program, the CTCC has the possibility to invite leading experts in the field, learning from these about new developments at an early stage. Furthermore, the visitors program allows international researchers to work at the



Figure: Professor Trygve Helgaker was awarded the 2008 Centenary Lectureship of the Royal Society of Chemistry



Figure: Professor Kenneth Ruud was awarded the Dirac medal of the World Association of Theoretical and Computational Chemists

two CTCC nodes, providing a very valuable channel for disseminating our scientific results and furthering the use of computational sciences to new research fields and research groups in chemistry worldwide.

Most of the research activities at the CTCC are concerned with the electronic many-body problem, whose approximate solution requires enormous computer resources for high accuracy and reliability of description. In 2008, the CTCC benefitted greatly from the investments in the Norwegian supercomputer program made at the end of 2007, enabling the CTCC members to pursue ambitious scientific goals because of the extensive computational resources made available through these investments. However, an integral part of supercomputing is also the development of improved algorithms and programming environments. The CTCC has been granted support from a Nordic initiative on grid computing, allowing us to get support for making chemistry applications run seamlessly on all the Nordic supercomputers through a common user interface.

The scientific activity of the CTCC is organized into eight thematic work packages, each package being managed by a principal scientist. Three of these work packages concern quantum-chemistry methods' development: (1) large periodic and non-periodic systems; (2) frag-

ment approaches for large systems, and (3) multiscale methods with wavelets. Two packages contain significant elements of both methods' development and applications: (4) properties and spectroscopy; and (5) dynamics and time development. Finally, three of our work packages are application oriented: (6) bioinorganic chemistry; (7) catalysis and organometallic chemistry; and (8) gas-phase reactions and photochemistry.

In 2008, two of the CTCC principal researchers received international recognitions for their scientific achievements. Professor Trygve Helgaker was awarded the 2008 Centenary Lectureship of the Royal Society of Chemistry, the first Norwegian since Nobel laureate Odd Hassel. Professor Kenneth Ruud was awarded the Dirac medal of the World Association of Theoretical and Computational Chemists, which is given annually to a computational chemist below the age of forty.

These scientific achievements are based on the research performed at the CTCC. In the next four pages, we give a few highlights from the achievements of the CTCC in 2008. Although this year we focus on the development of new computational methodology, we also highlight the importance of computational chemistry in rationalizing atmospheric processes that will result from CO<sub>2</sub> capture processes.

# Understanding molecules using lasers

We are all familiar with the interaction of molecules and materials with electromagnetic radiation (light) in our daily life. For instance, sunlight is scattered as it passes through the atmosphere, and the blue color is scattered the most and we therefore perceive the sky as being blue. The scattering occurs because a photon interacts with a molecule, leading to an instantaneous redistribution of the electron density, and when the energy is released again, its release can happen in all different directions. In a similar manner, the color of everyday objects is based on the absorption of photons in different energy regions.

However, one-photon processes are rather indiscriminate. They will occur along the entire path of the light, making it hard to have reactions happen at specific places only. However, we can obtain the desired *focality* by using processes in which multiple photons interact simultaneously with a molecule. For instance, by tuning two or more strong light sources to frequencies of high cross sections, interactions can be made to happen at only specific points in space, as illustrated in the figure.

The focality opportunities offered by multiphoton processes opens a wide range of new applications, from 3-dimensional storage of data to drug delivery and imaging processes inside the human body. In the latter cases, multiphoton processes have the additional advantage that the energy of the individual photons may be so low that they do not harm tissue through which they are passed, and only at a specific site in the body, e.g. a tumor cell, will the joint energy of two or more photons be large enough to cause chemical reactions to happen.

An important question in this field of science is: how we can design molecules that will be well suited for use in multiphoton processes? Synthesizing all possible molecules and testing their suitability for multiphoton processes would be a very time consuming and expensive approach. Computational chemistry here comes to our rescue, as we can calculate the multiphoton processes using quantum mechanics, finding the most promising

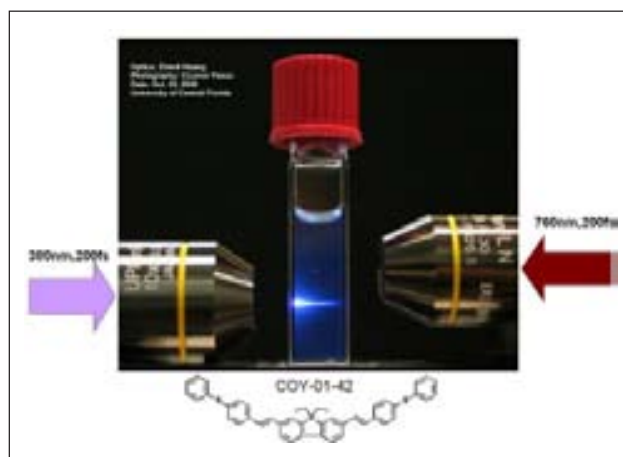


Figure: Illustration of one-photon (lower part) and two-photon interactions (small blue dot above the lower light source) with a molecule.

molecules for these processes, which then in turn can be synthesized in the laboratory.

In the recent PhD thesis by Andreas Thorvaldsen, defended at the CTCC in 2008, an important step towards developing tools to aid in finding new efficient multiphoton materials was presented. In the thesis, a unified theory for treating all possible perturbations to which a molecule can be exposed to was presented. The formalism and code is applicable to large molecules, utilizing the advances in linear-scaling technology being developed at the CTCC, and to any order in the interaction between the molecule and the applied perturbations. We can thus now calculate three-photon, four-photon and even higher-order processes using quantum-chemical methods.

In addition to the generality of the formalism in terms of the order and nature of the perturbation, it is also flexible with respect to the model used to describe the molecule, and we have thus been able to apply the methodology to all parts of the periodic table, using both nonrelativistic and relativistic models.

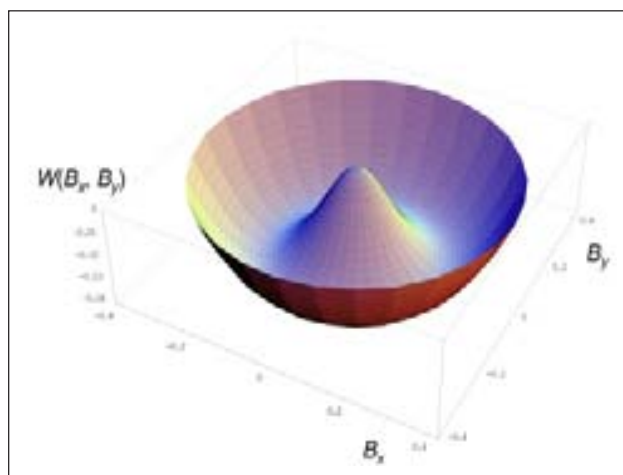
This work has been published in the *Journal of Chemical Physics* **129**, 214108 (2008).

# Molecular magnetic metamorphosis

Magnetism is an endlessly fascinating phenomenon. Most of us are familiar with permanent magnets in compasses and as decoration on refrigerator doors. Somewhat less familiar are perhaps the magnetic materials used for data storage in computer hard disks. Even things not usually thought of as magnetic objects, such as the Dutch frog that was levitated in an experiment at the High-Magnetic Field laboratories at the University of Nijmegen, interact with sufficiently strong magnetic fields. The frog was repelled by the magnet and is therefore *diamagnetic*. Objects like refrigerator doors that are attracted to magnets are *paramagnetic*. The same distinctions can be made at the microscopic level, where diamagnetic and paramagnetic molecules may be studied. Indeed, a frog's body contains roughly 70% water molecules, which are diamagnetic.

Manipulation of molecules using strong magnetic fields is an ambitious direction in the quest for molecule-based electronic devices that may overcome the limitations of silicon-based microelectronics. It is thus surprising that quantum-chemical computer modelling of molecules and materials in strong fields has remained largely unexplored in research. This at least was the situation until recently, when Dr. A. Soncini proposed and started a project aimed at filling this gap. The development of a quantum-chemical method its implementation in a new computer program, LONDON, was done in collaboration with the PhD student E. Tellgren and his supervisor Prof. T. Helgaker, codirector of the CTCC. Unlike most methods, which assume that the magnetic field is very weak, the method devised by these researchers enables a magnetic field of any strength to directly enter into the Schrödinger equation. On a technical note, their method makes use of so-called London orbitals; their use is crucial for the calculations, which would otherwise suffer problems related to gauge variance and low accuracy.

What happens to diamagnetic and paramagnetic molecules in strong magnetic fields? Calculations using



LONDON confirm that typical diamagnetic closed-shell molecules—for example,  $\text{H}_2\text{O}$  and benzene—boringly remain diamagnetic, just experiencing a more vigorous repulsion. By contrast, the computer modelling reveals a radically different situation for closed-shell paramagnetic molecules. Initially, as the magnetic field is turned on, such paramagnetic molecules are attracted by the magnetic field (thereby lowering their energy).

Surprisingly, however, at a critical field strength (characteristic of the molecule), all paramagnetic molecules undergo a veritable metamorphosis, becoming diamagnetic instead of paramagnetic. From now on, their energy is higher in the field than out of the field; consequently, these molecules are now repelled rather than attracted by the magnetic field. The figure shows the energy of two closed-shell paramagnets ( $\text{C}_{16}\text{H}_{10}^{2-}$  and  $\text{C}_{20}\text{H}_{20}^{2-}$ ). Although, for these molecules, the diamagnetic transition occurs at field strengths roughly ten times larger than what can be achieved in laboratory experiments, the critical field strength is expected to dramatically decrease for larger molecules. Many more developments are in progress, but already this finding of radical changes in the behaviour of electrons in response to external magnetic fields suggests that the new methodology and software are promising quantitative tools.





# Atmospheric chemistry from first principles



*The European Photochemical Reactor, EUPHORE, in Valencia (Spain). There are two Teflon domes in which photochemical experiments can be carried out under natural conditions. Each dome is equipped with state-of-the-art analytical instrumentation for on-line and *in situ* monitoring of chemical compounds.*

There is a comprehensive knowledge database of the chemistry of the atmosphere including mechanisms and rates and modes of photodecomposition. Evaluations are constantly carried out to allow an extrapolation of the existing kinetic and photochemical data to compounds that have not yet been studied in the laboratory: one of the main challenges in today's atmospheric chemistry research is: can we predict the fate of new compounds emitted into the atmosphere?

In the past year we have focused on developing a toolbox for describing chemical reactions. With this toolbox, we have now initiated a systematic theoretical study of aliphatic amines. This class of compounds is employed in new power-plant CO<sub>2</sub> capture technology. Their possible atmospheric degradation products include compounds of environmental concern such as *N*-nitrosamines, *N*-nitramines, and *N*-nitro amides.

Laboratory experiments are both time consuming and expensive. The rising power of computers at ever decreasing costs, the increasing reliability of quantum chemistry, and our growing understanding of the dynamical processes governing the rates of chemical reactions have led to the increasing acceptance of computational chemistry by the atmospheric chemistry community, to the point where IUPAC recommendations accept guidance from computational chemistry.

The amines present many difficulties to the experimentalist and meaningful experiments can only be carried out at a few places in the world. One such place is the European Photochemical Reactor, EUPHORE, in Valencia (Spain). We have carried out photo-oxidation experiments with simple amines and we expect that the combination of theoretical chemistry and experiment will allow us to predict the fate of the technologically important and more complex amines.

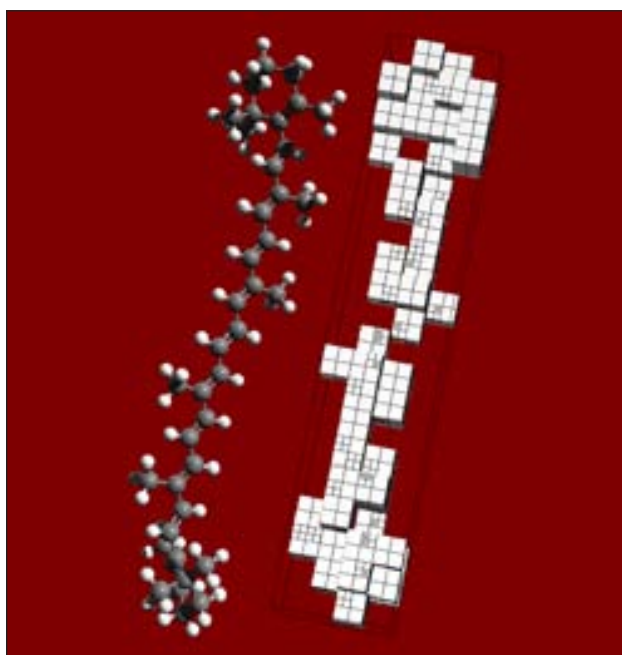
# Divide wisely and conquer accurately

Assume you have a huge cube filled with electrons and nuclei, the electrons constantly moving. How would you go about to measure the mean distance between all pairs of electrons in the room in the shortest possible time, yet being confident that you have measured the distances accurately? This is the challenge tackled by CTCC researchers when studying the electron density of molecules and the interactions between the electrons.

The naïve approach would be to divide the space into increasingly smaller boxes, counting all the electrons in each of the small boxes thus created, noting the distances between the different boxes. However, assume that we divide the box into eight smaller boxes (by splitting each side of the cube in two), counting the electrons in each of these boxes and then adding them up. The estimate of the number of electrons in each of the eight boxes will most likely not be accurate enough. We can then continue this process several times, for instance ten times. Each box is now very small, allowing us to count the electrons accurately, but we now have more than a billion boxes! This problem is often called the “curse of dimensionality”.

However, we know that the electrons prefer to be close to the nuclei. We can thus choose to only place a large number of small boxes close to the nuclei, and fewer and larger boxes further away from the nuclei. This will give us a lot less boxes to count, but how do we know that we have not lost any electrons by forgetting to add more boxes somewhere in space?

Modern tools of mathematics comes to our rescue at this point. Using mathematical functions called multiwavelets, we can ensure that our procedure for counting the electrons and measuring the mean distances between them fulfills: (1) Adaptivity: Division of boxes is only done where necessary; (2) Separability: Instead of performing the measurements of the distances in 3 dimensions, we rewrite the problem by performing 3 independent measurements along a single dimension; (3) Predefined accuracy: We can at the outset define how accurately we need to know the distance between the electrons (cm, mm,  $\mu\text{m}$ , nm), and then discard all the boxes we know



will contribute less than this threshold. The adaptive nature of this approach is shown for the carotene molecule in the figure.

Using multiwavelets, we thus get the best of two worlds: We reduce the number of measurements/counts that needs to be considered, but we still know how accurate the result is going to be, and we can even decide how accurate we want the result to be.

Since interactions between electrons and nuclei in a molecule have, in practice, a finite length, we know that the cost of evaluating interactions between electrons should grow linearly with the size of the molecule. However, traditional quantum-chemistry methods scale cubically, or worse, with system size, severely limiting the sizes of the systems that can be studied.

The adaptive nature of the multiwavelets, with the stringent tests on the magnitude of the interactions, ensures that the method indeed scales linearly with system size. The multiwavelets thus have the potential to be an innovative and powerful tool to investigate molecules and their properties.



# CTCC members

## Principal investigators at the CTCC



**Tor Flå**  
Professor  
UiT



**Trygve Helgaker**  
Professor  
UiO



**Kenneth Ruud**  
Professor  
UiT



**Mats Tilset**  
Professor  
UiO



**Luca Frediani**  
Associate Prof.  
UiT



**Claus Jørgen Nielsen**  
Professor  
UiO



**Inge Røeggen**  
Professor  
UiT



**Einar Uggerud**  
Professor  
UiO



**Abhik Ghosh**  
Professor  
UiT



**Knut Fægri jr.**  
Professor  
UiO

## Researchers



**Dan Jonsson**  
UiT



**Alessandro Soncini**  
UiO



**Clemens Woywod**  
UiT

## Postdocs



**Radovan Bast**  
UiT



**Emmanuel Gonzalez**  
UiT



**Jonas Juselius**  
UiT



**Ville Weijo**  
UiT



**Emmanuel Formager**  
UiT



**Maxime Guillaume**  
UiT



**Andreas Krapp**  
UiO



**Li-Ming Yang**  
UiO



**Bin Gao**  
UiT



**Kathrin Hopmann**  
UiT



**Michal Przybytek**  
UiO



**Mohammed Solimannejad**  
UiO



**Adam Chamberlin**  
UiT



**Francesca Maria Iozzi**  
UiO



**Andrew Teale**  
UiO



## PhD students



**Antoine Durdek**  
UiT



**Ola Berg Lutnaes**  
UiO



**Anton Simakov**  
UiO



**Erik Tellgren**  
UiO



**Lara Ferrighi**  
UiT



**Simen Sommerfelt Reine**  
UiO



**Harald Solheim**  
UiT



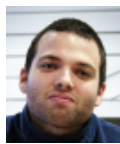
**Andreas Thorvaldsen**  
UiT



**Margret Gruber-Stadler**  
UiO



**Vladimir Rybkin**  
UiO



**Arnfinn Hykkerud Steindal**  
UiT



**Alexei Zatula**  
UiO



**Mihayo Musabila**  
UiO

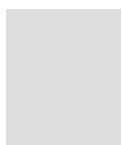


**Dmitry Shcherbin**  
UiT



**Espen Tangen**  
UiT

## Master students



**Hanne Bråthen**  
UiO



**Arne J. C. Bunkan**  
UiO



**Stig Rune Jensen**  
UiT



**Kai K. Lange**  
UiO

## Affiliates



**Bjørn Olav Brandsdal**  
Associate Professor  
UiT



**Harald Møllendal**  
Professor  
UiO



**Svein Samdal**  
Professor  
UiO

## Administrative staff



**Stig Eide**  
Head of Administration  
UiT



**John McNicol**  
Office Manager  
UiO



**Sonia Coriani**  
Associate Professor II  
UiO



**Magdalena Pecul**  
Associate Professor II  
UiT

## Adjunct Professors

## Board of directors

**Professor Tore Vorren**  
*(Dean of the Faculty of Science, University of Tromsø).*  
Chairman of the board

**Professor Anne-Britt Kolstø**  
*(University of Oslo)*  
vice-chairman of the board

**Dr. Nina Aas**  
*(Statoil-Hydro)*

**Professor Knut J.Børve**  
*(University of Bergen)*

**Professor Aslak Tveito**  
*(Simula Research Centre)*

## Scientific advisory board

**Prof.Emily A.Carter**  
*(Princeton University, USA)*

**Prof.Odile Eisenstein**  
*(University of Montpellier, France)*

**Prof.Kersti Hermansson**  
*(Uppsala University, Sweden)*

**Prof.Mike Robb**  
*(Imperial College London, UK)*

**Prof.Per-Olof Åstrand**  
*(Norwegian University of Science and Technology, Norway)*





## Other activities at the CTCC

Together with the Norwegian Chemical Society, the Royal Society of Chemistry, and the University of Oslo, the Centre for Theoretical and Computational Chemistry organized on May 5 2008, a symposium directed towards new horizons for computational chemistry research. The symposium was held at the University of Oslo and was opened by Vice Dean of the Faculty of Science, Professor Anders Elverhøi.

The speakers at the symposium were leading Norwegian and English prize winners in chemistry. Three of the speakers have during 2007 and 2008 been awarded by The Royal Society of Chemistry for their scientific work in the field of computer based chemical research. Among these was Professor Trygve Helgaker, co-director of the CTCC, as the recipient of the Centenary Lectureship of the Royal Society of Chemistry, the first Norwegian to receive this award since Nobel Laureate Odd Hassel. From the Norwegian research community, three additional speakers that have recently been recognized through national awards: for their scientific activity participated: was Professor Signe Kjelstrup from The Norwegian University of Science and Technology, Professor Unni Olsbye from The

University of Oslo and Professor Helmer Fjellvåg from The University of Oslo.

The symposium was attended by about 60 persons, including a number of participants from the CTCC at the University of Tromsø as well as members of the Center for Advanced Studies (CAS) at the Norwegian Academy of Science and Letters. The high quality and diversity in the topics presented clearly demonstrated the opportunities offered by computational chemistry in modern chemical research.

As part of the outreach activities, the CTCC organized the 10th Sostrup Summerschool on Quantum Chemistry and Molecular Properties together with the Lundbeck Foundation for Theoretical Chemistry, in the framework of the Nordic Network of Centers of Excellence in Computational Chemistry (NCOECC). In addition to the lecturers Trygve Helgaker (CTCC), Poul Jørgensen (LCTC) and Jeppe Olsen (LCTC), a number of PhD students and postdocs of the CTCC participated as tutors. Many of the CTCC PhD students and postdocs also participated as students at this very intensive summer school. Starting from 2010, the summer school will be organized in Norway.



## Almlöf-Gropen lecture 2008



From left to right: Prof. Björn Roos, Eva Gropen, CTCC director Kenneth Ruud, and chairman of the CTCC board, Prof. Tore Vorren.

The Centre for Theoretical and Computational organized in 2008 the first Almlöf-Gropen lecture. On May 19 the lecture was held at The University of Oslo and on May 20 the same lecture was held at The University of Tromsø. The first lecturer for this series of lectures was Professor Björn Roos from Lund University in Sweden. Professor Roos lecture was titled *Multiconfigurational Quantum Chemistry: The State of the Art*.

Professor Björn Roos is among the world's leading researchers in quantum chemical research. He has published more than 300 articles in international journals. The publications are mainly about the development of methods for the calculation of wave functions that includes electron correlation, in particular the multiconfigurational self-consistent field method (MCSCF). Professor Roos is also the architect of the popular quantum chemical software package MOLCAS. He was good friend and colleague of both Jan Almlöf and Odd Gropen.

Together with his significant scientific production, Prof. Roos has also shown a huge interest in disseminating his knowledge to new generations of quantum chemists. In his lecture, Prof. Roos gave an introduction to the MCSCF method with emphasis to the development of the method in recent years.

Approximately 40 persons attended the lecture in Oslo and approximately 25 persons attended the lecture in Tromsø this year. The CTCC was very glad to note that Elisabeth Almlöf and Eva Gropen, the widows of Jan Almlöf and Odd Gropen, had been able to attend the lectures in Oslo and Tromsø, respectively.

The Almlöf-Gropen lecture was established to honour the memory of two central scientists in quantum chemical research in Norway. Professor Almlöf (1945-1996) was educated at The University in Uppsala and worked at The University of Oslo from 1976 until 1986. He then received a chair at The University of Minnesota. He kept his connection to Norway as an adjunct professor at The University of Tromsø. Prof. Gropen (1941-2005) worked his whole career at The University of Tromsø after he graduated from The University of Oslo. He was one of the persons responsible for the establishment of theoretical chemistry as a research field in Tromsø. Prof. Gropen was also instrumental in the establishment of a Norwegian e-infrastructure for supercomputing, which is of central importance to the research currently conducted at the CTCC.



# Visiting scientists

The CTCC believes that the most significant scientific advances often arise from interactions between skilled scientists with diverse backgrounds and training, as well as in the challenging discussions between PhD students, postdocs and experts in their respective fields of science. Already from the start of the CTCC in July 2007, we have had a strong focus on quickly establishing an extensive visiting researcher program at the CTCC. During 2008,

we have had numerous researchers, from PhD students to full professors, visiting the centre for periods ranging from a few days up to almost three months. The CTCC is pleased to see that the centre has already become an attractive collaborative partner through this exchange program, attracting also visitors with no prior established scientific collaboration with the CTCC principal investigators.

Name	Sex	Country	Period (from - to)
Ondřej Julínek	M	Czech Republic	17.11.08-17.12.08
Adva Goaz	M	Israel	10.11.08-29.12.08
Patrick Andersson	M	Sweden	27.10.08-06.11.08
Mauritz Ryding	M	Sweden	27.10.08-06.11.08
Penny Brothers	F	New Zealand	19.10.08-25.10.08
Mounia Touil	F	France	19.10.08-26.10.08
Branislav Jansik	M	Denmark	19.10.08-26.10.08
Kestutis Aidas	M	Denmark	13.10.08-13.12.08
Filip Pawlowski	M	Poland	12.10.08-18.10.08
Andrej Antusek	M	Slovenia	10.10.08-30.10.08
Michael Palmer	M	Scotland	07.10.08-14.10.08
Joachim Friedrich	M	Germany	01.10.08-29.12.08
Jeanet Conradie	F	South Africa	26.09.08-16.11.08
Helmut Harbrecht	M	Germany	25.09.08-01.10.08
Pawel Kozolowski	M	Poland	20.09.08-05.10.08
Christian Brückner	M	USA	15.09.08-20.09.08
Mike Walter	M	USA	07.09.08-09.09.08
Pradip Mascharak	M	India	03.09.08-07.09.08
John Earles	M	New Zealand	26.08.08-29.08.08
Ville Weijo	M	Finland	25.08.08-26.08.08
Patrick Normann	M	Sweden	18.08.08-22.08.08
David J Tozer	M	England	18.08.08-22.08.08
Sebastien Lebegue	M	France	11.08.08-21.08.08
Janos Angyan	M	France	11.08.08-21.08.08
Trond Saue	M	France	11.08.08-22.08.08
Helene Bolvin	F	France	11.08.08-15.08.08
Jacob Kongsted	M	Sweden	10.08.08-16.08.08
Yizhen Tang	F	China	04.08.08-28.12.08

Name	Sex	Country	Period (from - to)
Malgorzata Olejniczak	F	Poland	01.08.08-29.08.08
Na Lin	F	Italy	26.07.08-08.08.08
Antonio Rizzo	M	Italy	26.07.08-08.08.08
Antonio Monari	M	Italy	11.07.08-30.07.08
Filip Pawlowski	M	Poland	16.06.08-20.06.08
Swapan Chakrabarti	M	India	12.06.08-12.09.08
Magnus Ringholm	M	Norway	02.06.08-10.08.08
Zilvinas Rinkevicius	M	Sweden	02.06.08-02.09.08
Antoine Durdek	M	France	30.05.08-06.06.08
Filip Pawlowski	M	Poland	26.05.08-30.05.08
Liviu Chibotaru	M	Belgium	26.05.08-06.06.08
Björn Roos	M	Sweden	19.05.08-21.05.08
Pawel Salek	M	Sweden	18.05.08-24.05.08
Pawel Salek	M	Sweden	02.05.08-10.05.08
Seyed Tabatabaei	M	Iran	19.04.08-26.04.08
Stefan Höfener	M	Germany	12.04.08-16.04.08
Filip Pawlowski	M	Poland	04.04.08-12.04.08
Mauritz Ryding	M	Sweden	10.03.08-20.03.08
Patrick Andersson	M	Sweden	10.03.08-20.03.08
Marianne Conradie	F	South Africa	15.02.08-30.06.08
Patrick Normann	M	Sweden	11.02.08-15.02.08
Trond Saue	M	France	09.02.08-16.02.08
Sebastian Höfner	M	Germany	08.02.08-18.05.08
Thomas Kjærgaard	M	Denmark	05.02.08-10.02.08
Pawel Salek	M	Sweden	28.01.08-15.03.08
Mauritz Ryding	M	Sweden	08.01.08-20.01.08
Patrick Andersson	M	Sweden	08.01.08-20.01.08
Bin Gao	M	Sweden	27.02.08-29.02.08



## Visiting scientist: Dr. Swapan Chakrabarti (Kolkata, India)



Figure: Three of the summer visitors to the CTCC in Tromsø on a trip to the island of Senja. From left to right: Antonio Monari (Bologna, Italy), Zilvinas Rinkevicius (Stockholm, Sweden) and Swapan Chakrabarti (Kolkata, India)

Dr. Chakrabarti left a sweltering Kolkata in early June to spend three months in the cool arctic summer of Tromsø as a visiting scientist at the CTCC.

– Unfortunately, I did not get chance to visit many places in Norway during my stay, but I must say that Tromsø is just absolutely wonderful and beyond my imagination, he says.

His main motivation for coming to Tromsø was, however, science:

– The focus of my research is on theoretical calculations of molecular response properties, which is also a central research activity at the CTCC. I had therefore decided to visit the CTCC if the opportunity would arise. Through the research work of Prof. Kenneth Ruud, I came to learn about the CTCC, and then found the information about the visitors program in the website of the CTCC, Dr. Chakrabarti elaborates.

During his stay in Tromsø, Dr. Chakrabarti got to experience local Tromsø traditions, such as a whale barbeque:

– I think the working conditions and social scientific environment at the CTCC are excellent. The environment is very friendly and cooperative as well. I will never forget the warm hospitality that I received from CTCC and always remember all of my friends at CTCC, he says.

Although now back in India, the visit to the CTCC has been very helpful to his own research:

– As far scientific activity is concerned I have benefited immensely from the CTCC. During my stay at CTCC, I had learned many things about response theory both in the relativistic and nonrelativistic domain.

Several scientific publications have also been completed as part of his visit. On his overall experience with the CTCC and visitors program, his conclusions are clear:

– I already told many in India that CTCC has world class expertise on parallel coding and method development of modern quantum chemistry. Moreover the working atmosphere is very friendly and highly commendable.



# Total revenue and expenditure figures

Finansiering (i tusen kroner)	Reell finans 2007	Reell finans 2008	Planlagt finans 2009	Planlagt finans 2010	Planlagt finans 2011	Planlagt finans 2012	Planlagt finans 2013-17	Total finans
<b>Direkte inntekter = Regnskapsførte inntekter på SFF ved vertsinstitusjonen</b>								
Vertsinstitusjonen								
Vertsinstitusjonen	2 200	5 355	5 982	4 700	4 800	5 100	20 100	48 237
Norges forskningsråd - SFF	3 900	6 400	10 100	10 400	10 600	10 600	34 800	86 800
Aktiv samarbeidspartner (navngis)	1 100	2 744	5 439	3 300	3 400	3 600	11 500	31 083
Internasjonale midler								0
Andre offentlige								0
NFR (likestillingstiltak)		75	1 037	532				1 644
NFR (prosjektnummer)								0
Andre private								0
<b>Sum</b>	<b>7 200</b>	<b>14 574</b>	<b>22 558</b>	<b>18 932</b>	<b>18 800</b>	<b>19 300</b>	<b>66 400</b>	<b>167 764</b>
<b>Indirekte inntekter = Ikke regnskapsførte midler på SFF ved vertsinstitusjonen</b>								
Aktiv samarbeidspartner A								0
Aktiv samarbeidspartner B								0
Vertsinstitusjonen								0
Andre								0
<b>Sum</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>
<b>Sum årets finansiering</b>	<b>7 200</b>	<b>14 574</b>	<b>22 558</b>	<b>18 932</b>	<b>18 800</b>	<b>19 300</b>	<b>66 400</b>	<b>167 764</b>
<b>Finansieringsplanens beløp</b>								<b>0</b>
Avvik fra finansieringsplanen	7 200	14 574	22 558	18 932	18 800	19 300	66 400	167 764
Overført (+/-)	0	2 916	2 133	819	19 751	19 751	38 551	
<b>Sum finansiering og overføring</b>	<b>7 200</b>	<b>17 490</b>	<b>24 691</b>	<b>19 751</b>	<b>38 551</b>	<b>39 051</b>	<b>104 951</b>	<b>251 685</b>

Utgifter (i tusen kroner)	Reelle utgifter 2007	Reelle utgifter 2008	Utgiftsbudsjett 2009	Utgiftsbudsjett 2010	Utgiftsbudsjett 2011	Utgiftsbudsjett 2012	Utgiftsbudsjett 2013-17	Totalt budsjett
<b>Direkte kostnader = Regnskapsførte utgifter på SFF ved vertsinstitusjonen</b>								
Personell og lokaler (Lønn og sosiale kostnader)	632	13 139	21 167	0	0	0	0	34 938
(Lokaler - husleie og drift)		300	300					600
Innkjøpte FoU tjenester								0
Vitenskapelig utstyr								0
Andre driftskostnader	1 562	2 218	2 705					6 485
<b>Sum</b>	<b>2 194</b>	<b>15 357</b>	<b>23 872</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>41 423</b>
<b>Indirekte kostnader = Ikke regnskapsførte utgifter på SFF ved vertsinstitusjonen</b>								
Personell og lokaler (Lønn og sosiale kostnader)	722		0	0	0	0	0	722
(Lokaler - husleie og drift)								0
Innkjøpte FoU tjenester								0
Vitenskapelig utstyr								0
Andre driftskostnader								0
<b>Sum</b>	<b>722</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>722</b>
<b>Sum utgifter</b>	<b>2 916</b>	<b>15 357</b>	<b>23 872</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>42 145</b>
Til overføring (+/-)	4 284	2 133	819	19 751	38 551	39 051	104 951	209 540

Personale/Stillinger	Årsverk 2007	Årsverk 2008	Årsverk 2009	Årsverk 2010	Årsverk 2011	Årsverk 2012	Årsverk 2013-17
Professorer, forskere o.l		7,2					
Doktorgradsstipendiater		1,0					
Postdoktorstipendiater		4,0					
Teknisk/adm.stillinger		1,6					
<b>Sum årsverk stillinger</b>	<b>-</b>	<b>13,8</b>	<b>-</b>	<b>-</b>	<b>-</b>	<b>-</b>	<b>-</b>
Gjesteforskere		3,3					
Utenlandsstipendiater							

## Appendix A: Publications 2008

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Inverse hydrogen bonds between  $\text{XeH}_2$  and hydride and fluoride derivatives of Li, Be, Na and Mg  
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# Appendix B: Activity reports

## WP1: Large periodic and nonperiodic systems

**Principal investigator Trygve Helgaker, UiO**

The work on this project has continued in several directions. With respect to large molecular systems, we have published two papers on the Augmented Roothaan–Hall (ARH) optimization method for the density-matrix based optimization of Hartree–Fock and Kohn–Sham energies [27,28]. This method, which may be viewed as a quasi-Newton optimization of the electronic energy of such systems, provides a hugely improved convergence over the standard two-step method with alternating Roothaan–Hall diagonalization and density-matrix averaging steps. At present, we continue the work on optimization by improving the density-matrix starting guess. Our scheme provides a hierarchical three-level approach to the energy optimization: first, individual atomic optimizations; second, a coarse-grained molecular optimization in a subset of the full basis; finally, a fine-grained molecular optimization in the full basis. The combination of this three-level energy optimization with the ARH method promises to be a particularly efficient approach for large molecular systems, whose electronic structure is typically more complicated than that of small systems. The work on energy optimization is carried out in collaboration with the group of Poul Jørgensen and Jeppe Olsen in Denmark through the NCOECC network [27,28].

As further work towards large systems, we have developed and published a new technique for the calculation of exact exchange with density fitting [54]. Particularly important is the fact this method enables the solution of the fitting equations in local metrics instead of the traditional Coulomb metric, as required for linear scaling, at little loss of accuracy. Currently, the proposed scheme provides excellent timings for small and medium-sized systems, with a speed-up by a factor of almost 30 relative to the old Dalton code. Current work on integral evaluations is towards the efficient evaluation of gradients with and without exact exchange. Moreover, the integral evaluation in Dalton is given a complete overhaul, being fully rewritten in Fortran 90. The new integral code is specifically designed with

large systems in mind, with a better control over memory usage than the old integral code in Dalton.

With respect to periodic systems, we have completed the development of a code for the calculation of gradients, allowing for the optimization of structures of periodic systems in one-, two- and three-dimensions. At the same time, we are working towards the development of an ARH code for periodic systems, to provide a more robust scheme for the optimization of the electronic structure of such systems.

Our current periodic code is based on the use of Gaussian basis functions. Future development for periodic systems may involve the use of a mixed one-electron basis, consisting of plane waves and Gaussians, so as to avoid the linear-dependency problems associated with large Gaussian basis sets for such electronic systems. Indeed, the integral evaluation necessary for such a development is already in place, having been implemented during the last year in our new code for the calculation electronic energies of molecular systems in finite magnetic fields, using London orbitals, whose phase factors are equivalent to the plane waves in mixed-basis calculations [71].

## WP2: Fragment approach for large systems

**Principal investigator Inge Røeggen, UiT**

In chemistry and physics a huge body of experimental results can be interpreted by the notion that matter consists of atoms. However, in standard quantum chemistry models, atomic states in a complex are not defined. The PATMOS (Perturbed AToms in MOlecules and Solids) model is a new conceptual and computational scheme where a complex can be considered as a collection of mutually interacting perturbed atoms. The model has favorable interpretative features. The decisive question is whether the computational code based on this model is feasible, i.e. if it can be applied to large systems.

The key element in the PATMOS model is the calculation of the occupied orbitals to be used in the basic



approximation. For the complex in question we are using one spatial orbital for each valence electron. The orbitals associated with core electrons are kept doubly occupied.

Four different approaches are considered for the valence electrons:

1. Unrestricted Hartree-Fock (UHF).
2. A Hartree model with orthogonality constraints.
3. An Antisymmetric Product of Strongly orthogonal Geminals (APSG).
4. A Hartree-GVB (Generalized Valence Bond) model.

Each of these approaches has their specific advantages and weaknesses. The UHF is computationally simple, but for metals, when the occupied orbitals are localized, it is not always possible to define “perturbed atoms” in a unique way. The Hartree model yields better localization, but is computationally more demanding. As for the UHF model, when applied to molecules with a nuclear geometry close to the equilibrium structure, alpha and beta orbitals coincide and accordingly it is not straightforward how to define the “perturbed atoms”. The APSG model is computationally demanding, but allows the definition of “perturbed atoms” when applied to molecules. However, when applied to metals, the APSG model yields some strange type of localization. Hence, the definition of “perturbed atoms” is not always possible. The model which has the best localization properties for all types of systems considered so far, is the Hartree-GVB model. In this model we add to the Hartree energy, corrections obtained by a singlet coupling of any alpha orbital to all beta orbitals, i.e. GVB corrections. However, the model is computationally very demanding. Defining new optimization algorithms for this model is therefore of paramount importance.

### WP 3 Multiwavelet

**Principal investigator Tor Flå, UiT**

The goal of the present work package is to develop a multiwavelet code for Kohn-Sham Density Functional Theory calculations. We aim at a code that scales linearly in the size of the system, is adaptive and can run in parallel on large clusters.

Presently, we have developed a toolbox for applying integral operators such as the Poisson and Helmholtz kernels in multiple dimensions. The code is based on a

formalism for a multiwavelet representation of functions and operators that is consistent with the tensor product structure of a multidimensional implementation.

The so-called Non-Standard (NS) representation of operators has been implemented to avoid direct interactions among different scales. The explicit calculation of all operator terms for a finite, but arbitrary number of dimensions has been developed.

Moreover, the developed notation, which is based on extensive use of a binary formalism to label operators and functions, proved to be an effective tool for developing efficient algorithms.

The implementation has been parallelized showing fairly good scaling performances up to several hundred processors. The preliminary linear scaling tests showed that the code is able to achieve a linear scaling computational cost with the system size.

The current developments focus on (1) the implementation of the iteration for the Kohn-Sham equation, (2) the calculation of the electrostatic potential for large systems through the direct resolution of the Poisson equation, (3) the extension of the adaptivity paradigm to the polynomial order employed.

### WP 4 Properties and spectroscopy

**Principal investigator Luca Frediani, UiT**

A prime focus has in the current project period been on the application of the new, atomic orbital-based linear response formalism, described in the highlight “Understanding Molecules Using Lasers”, to a wide number of different molecular properties. As such, we have in the project period applied the code to the calculation of the first quantum-mechanical calculations of Coherent Anti-Stokes Raman Scattering spectra, an important experimental method as a microscopic method for biological samples.

We have also applied the method to two nonlinear birefringences, that is, interactions between molecules and different external electric and magnetic fields, in which the refractive indices parallel and perpendicular to a given axis in the molecular sample differ. In particular, we have performed the first gauge-origin independent and frequency-dependent calculations of the so-called electric-field gradient induced (Buckingham) birefringence, and the Cotton-Mouton effect. However, both these sets of calculations were limited to the Hartree-Fock level of

theory, and we aim to extend this to the level of density-functional theory in the next project period.

We have also in the project period extended the general response theory framework to the relativistic domain. This has been possible to achieve because of the atomic-orbital based formulation, in which the nature of the wave function or density as having one, two or four components does not appear directly, allowing us to very easily adopt the response framework to use perturbed and unperturbed densities generated by the four-component relativistic program Dirac. However, all energy calculations and perturbed density matrices are in this set-up performed in the molecular orbital basis, and will therefore not be linearly scaling.

We have also initiated the necessary complementary work required to make the response theory framework general, by developing general, flexible and open-ended programs for the calculation of derivatives of arbitrary one-electron operators, derivatives of the conventional two-electron integrals, and an open-ended exchange-correlation kernel driver. We hope significant progress on these important components can be achieved in the next year.

Parallel to these developments, we have also been working on combining the polarizable continuum model as implemented in Dalton by our group with the polarizable quantum mechanics/molecular mechanics (QM/MM) model developed by Mikkelsen and coworkers at the University of Copenhagen, achieving in this way a truly multiscale approach for modeling large molecules such as biomolecular complexes.

This code is now fully parallelized, and has been extended to the quadratic level of response theory. We have initiated preliminary calculations using this code in order to elucidate the origin of the strong enhancement of two-photon absorption in a mutant of green fluorescent protein compared to the native protein, including the full protein structures in the simulations.

We have also in the project period, in collaboration with one of our long-term scientific visitors to the CTCC, Dr. Swapan Chakrabarti from the University of Kolkata (India), reported the highest two-photon absorption cross section to date in the literature for a molecular tweezer complex. This large two-photon absorption cross-section is obtained due to a highly efficient intermolecular charge-transfer effect taking place during the excitation process.

## WP 5 Dynamics and time development

**Principal investigator: Einar Uggerud, UiO**

Full insight into a chemical reaction can only be obtained by explicit consideration of the time development of the reaction system. The practical implementation of this idea involves the calculation of a large number of reaction trajectories to reflect the variation in the initial conditions corresponding to the actual experimental situation. Particular emphasis is put on understanding chemical reaction dynamics as the interplay between the initial conditions ( $\mathbf{p}_0, \mathbf{r}_0$ ) and the topography ( $v(\mathbf{r})$ ) of the potential energy surface. From the start of the CTCC, efforts have been concentrated on two topics, one related to biomolecular chemistry and physics, and one to water cluster chemistry. These will be discussed in turn. When developed to maturity, within a few years, we plan to compute the time development of large molecular systems, consisting of hundreds of atoms. The work package is based on close interactions between theory and experiment.

### Quantum chemical simulation of mechanochemical processes in biological molecules.

When a molecule is deformed from its equilibrium geometry by the application of external forces, its chemical and physical properties change, often dramatically. At one extreme limit, stretching a molecule has the consequence that it breaks. In other less dramatic situations, stretching a molecule to some extent brings it closer to the transition state of a reaction of that molecule. We may term the latter force-enhanced reactivity. Both these processes have been investigated experimentally for various proteins, applying the atomic force microscope (AFM), but are incompletely or poorly understood. We are convinced that only theoretical modelling coupled to reliable experimental data can provide the necessary insight into these processes [1]. It is hardly necessary to point out the intimate link between this topic and biology, for example for muscle contraction and expansion.

As the next phase of our ambitious project, we now simulate small molecular systems, essentially fragments of proteins, with the twofold purpose of understanding the molecular physics of the process and to determine which quantum chemical level of theory that can be used to describe the physical and chemical processes accurately and realistically, and at the same time be efficient





enough to allow for extension to larger and more relevant molecular systems.

Another branch of the biomolecular project is centered on small molecular models of DNA. The purpose of these studies is to uncover how alkali metal and alkali earth metal cations interact with the negatively charged backbone of DNA [7]. The work is conducted in close collaboration with Diethard Bohme, York University.

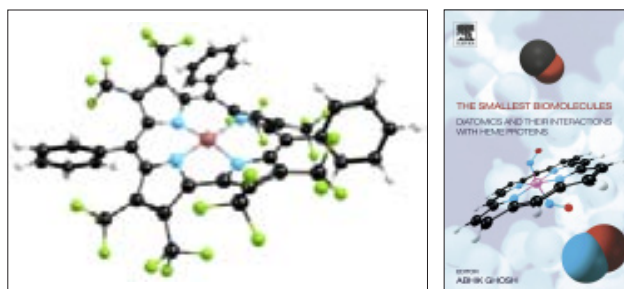
#### Dynamics of elementary reactions of water clusters.

Water clusters mimic water, and elementary processes occurring in water are best understood when conducted under the carefully controlled conditions one may obtain in isolated populations of small size-selected clusters. In the laboratory we study the chemical reactions and physical properties of water clusters containing inorganic or organic ions applying several techniques including FTICR and low energy collision experiments with beams of cluster ions. The reactions studied are water evaporation kinetics, ligand and isotope exchange, and red/ox reactions. Two Ph.D. students started their research during 2008 working in this field. In addition, we are involved in collaborations with international partners, including Patrik Andersson, Gothenburg University and Steen Brøndsted Nielsen, Aarhus University. By using existing software for ab initio direct dynamics calculations we are currently modeling two reactions, H/D-isotope exchange in protonated water clusters [6] and water exchange and elimination in reactions between water and protonated alcohols. The results of preliminary ab initio reaction dynamics studies of proton transfer and mobility are very promising. A third Ph.D. student will contribute to the work package through method development, programming and application of new software for reaction dynamics calculations.

## WP6 Bioinorganic chemistry

### Principal investigator Abhik Gosh, UiT

The synergy of theory and experiment continued to be the prime driver of theoretical research for the bioinorganic work package. Syntheses of new high-valent transition metal corroles, including octakis(trifluoromethyl) corrole derivatives (see figure, left), led to extensive DFT studies by postdoc Emmanuel Gonzalez, which established that the phenomenon of ligand noninnocence is far more pervasive in corrole chemistry, relative to por-



phyrin chemistry. High-valent metallocorroles serve as intriguing, if rather inexact, models of a variety of bioinorganic intermediates such as peroxidase compounds I and II and the ox1 state of methylcoenzyme M reductase (MCR-ox1), the enzyme responsible for the last (methane-evolving) step of biological methanogenesis. With respect to the iron species, an ongoing collaboration with Professor Björn Roos of Lund University, Sweden, established, by means of a detailed CASSCF/CASPT2 study, that chloroiron corrole does not contain Fe(IV), but is an Fe(III)-corrole<sup>•2-</sup> metalloradical, which ended a long-standing controversy on the subject. Similar studies of heme protein intermediates are now in progress. Dr. Gonzalez's work established that MCR-ox1 is best viewed as a Ni(III)-thiolate intermediate, a remarkable example of a high-valent metal center with a reducing thiolate ligand.

Over the last few years, the Ghosh group has conducted broad DFT surveys of two major classes of complexes: (a) transition metal NO complexes and (b) low-coordinate imido and oxo complexes. During 2008, both these projects were brought to a certain closure, thanks significantly to an ongoing collaboration with Dr. Jeanet Conradie of The University of the Free State, South Africa. A review on quantum chemical studies of transition metal nitrosyls was written for the upcoming computational chemistry volume of the Encyclopedia of Inorganic Chemistry (Wiley). Also published in 2008 was a major edited volume (Elsevier) on heme-diatom interactions titled "The Smallest Biomolecules: Diatomics and Their Interactions with Heme Proteins" (above, right). In a collaborative project between the Ghosh group and Louis Noodleman of The Scripps Research Institute, La Jolla, California, CTCC postdoc Kathrin Hopmann traveled to the Noodleman laboratory to carry out a DFT analysis of spin couplings in Roussin's black salt, an intriguing tetranuclear Fe/S/NO complex. Also being pursued, in collaboration with Professor Pradip Mascharak of the University of

California, Santa Cruz, are theoretical approaches to modeling the photochemistry of NO donor drugs.

Perhaps the most exciting development in 2008 was that the group's fundamental research on porphyrins and corroles has served as a jumping off point for a number of projects on functional materials, of which the most promising appears to be a collaborative project on dye-sensitized solar cells with Professor Carl Wamser of Portland State University, Oregon, USA. A long-standing collaborative project with Professor Penny Brothers of The University of Auckland, New Zealand, has been concerned with the unique coordination chemistry of boron corroles, where corrole (like porphyrins) may act as a binucleating ligand toward boron. Theory and experiment are strongly intertwined in both these projects.

## WP 7: Catalysis and organometallic chemistry

**Principal investigator Mats Tilset, UiO**

Catalysis is of paramount importance for the development of efficient, selective, and environmentally benign processes in the production of bulk and fine chemicals and materials. Any rational approach to catalyst design requires an in-depth understanding of the underlying reaction mechanisms and the influence of external (medium) and internal (metal, ligand, substituent electronic and steric effects) factors on it. Currently, the most fruitful way to gain this insight is the combination of experimental and computational approaches. In 2007, we started a collaborative work in the field of homogenous transition metal catalysis. Several coworkers are now involved in this activity. One (Li-Ming Yang, post.doc since Sept 2008) is funded by CTCC. Others (Marianne Lenes Rosenberg, PhD student; Mathivathani Kandiah, post.doc) are supplementing their experimental projects in organometallic chemistry with computational studies. Andreas Krapp, also a CTCC post.doc, has been instrumental in integrating the new computational activities with ongoing experimental efforts in the area.

Our current efforts in computational organometallic chemistry primarily utilize DFT methodologies and are focused on four activities, to be briefly described in the following.

One project comprises the crucial C-C coupling processes that are catalyzed by organometallic species in the oligomerization and polymerization of terminal alkenes. While these polymerization processes were long domi-

nated by early (most importantly, group 4) transition metal catalysts, group 8–10 based systems were established as efficient catalysts in the late 1990's. One focus of our past experimental work in this field has been on ethene dimerization with the cationic rhodium compound  $\text{Cp}^*\text{Rh}(\text{C}_2\text{H}_4)(\text{C}_2\text{H}_4-\mu\text{-H})^+$ . Solution-phase studies by Erik Fooladi (former experimental PhD student) raised a number of interesting mechanistic questions pertaining to isotope scrambling processes that might involve repeated C-H bond cleavage/bond forming reactions within the coordination sphere of the metal. These questions were attacked with gas phase experiments (Fourier transform ion cyclotron resonance mass spectrometry) in collaboration with Einar Uggerud, see also WP 5, and DFT calculations in collaboration with CTCC post.doc Andreas Krapp. The insight that has been gained from combined experimental gas phase and computational results will be described in a forthcoming manuscript.

A second project in which experiment and calculation work hand in hand deals with mechanistic studies of a highly cis-selective cyclopropanation reaction catalysed by a rh(I) system with a chelating N-heterocyclic iminocarbene ligand. Most catalysts that have been previously developed are selective for formation of the thermodynamically favoured trans-isomer. Therefore, the observed selectivities are of considerable interest for organic chemists. The experimental results of our efforts were recently published in *Org. Lett.* Computational efforts with DFT methods are under way with the hope that important mechanistic insight can be provided, which might in turn aid the tuning of the catalyst for improved productivity and selectivity. These studies are performed as a collaborative work between an experimental PhD student with separate NFR funding (Marianne Lenes Rosenberg) and CTCC post.doc Andreas Krapp. This collaboration comprises – in addition to the scientific activity – a training of the PhD student in computational chemistry. This serves one of the broader goals of CTCC, namely to propagate the possibilities of computational modelling to the scientific community; it is one ambition of the WP responsible that all future coworkers should be equipped with computational methodologies in their “toolbox” once their terms as PhD students or post.docs are over.

A third project which also benefits from the integration of experiment and computational work deals with structural features of platinum(II) and palladium(II) com-



plexes ( $\kappa^2\text{N,C}$ ) $\text{MX}_2$  and ( $\kappa^1\text{N,C}$ ) $\text{MX}_2$  ( $\text{N,C}$  = iminocarbene ligands;  $\text{x}$  = halide, alkyl). These species bear iminocarbene ligands that are related to those found in the  $\text{Rh(I)}$  complex discussed above. It has been observed that the preferred structures of these complexes (cis vs. trans coordination mode; mono- vs. bis-carbene; chelate vs. open structure) is strongly dependent on the substituent pattern at the iminocarbene moiety. Computational efforts are directed at providing insight into the nature of metal-iminocarbene bonding, which may lead to further catalyst development based on these ligand systems. These studies are performed as a collaborative work between an experimental post.doc student with separate NFR funding (Mathivathani Kandiah) and CTCC post.doc Andreas Krapp and again is an example of propagating computational methodologies to experimentalists.

The fourth project is focused on previously reported, experimentally observed, intramolecular H atom exchange processes between coordinated phenyl and benzene ligands in (diimine) $\text{Pt(phenyl)(}\eta^2\text{benzene)}^+$  complexes. Two fundamental questions arising from the experimental work need to be answered. First, does the H atom exchange occur via a  $\text{Pt(II)-Pt(IV)-Pt(II)}$  process that involves formal oxidative addition of a ligand CH bond or by a direct interligand H transfer without formal oxidation of  $\text{Pt(IV)}$ ? Second, is quantum mechanical tunneling involved in the H atom exchange? These studies are performed by Li-Ming Yang, CTCC post.doc since September 2008.

## WP 8: Clusters, surfaces and solids

### Principal investigator Claus Nielsen, UiO

We have continued our investigations of electronic ground-state potential surfaces of atmospherically relevant reactions in 2008. The quantum chemical calculations have in general been accompanied by experimental kinetic studies employing stable isotopes and by variational transition state calculations. Isotope effects are useful and sensitive benchmarks for quantum chemical calculations since they provide unique information about the bottlenecks of reactions. The motivation behind these studies of relatively simple systems is to build up expertise in calculating rates of chemical reactions from first principles. The ultimate goal is then to apply this knowledge to reactions which are currently difficult or even impossible to address in experiments.

Reaction	Status
$\text{CH}_3\text{OH} + \text{OH} / \text{CH}_3\text{OH} + \text{Cl}$	Published.
$\text{CH}_3\text{F} + \text{OH} / \text{CH}_3\text{F} + \text{Cl}$	Published.
$\text{CHCl}_3 + \text{OH} / \text{CHCl}_3 + \text{Cl}$	Manuscript accepted.
$\text{CH}_3\text{Br} + \text{OH} / \text{CH}_3\text{Br} + \text{Cl}$	Manuscript in preparation.
$\text{CH}_2\text{Cl}_2 + \text{OH} / \text{CH}_2\text{Cl}_2 + \text{Cl}$	Manuscript in preparation.
$\text{HCOCl} + \text{Cl}$	Manuscript is in preparation.
$\text{CH}_3\text{CH}_2\text{OH} + \text{OH} /$ $\text{CH}_2\text{FCH}_2\text{OH} + \text{OH} /$ $\text{CHF}_2\text{CH}_2\text{OH} + \text{OH} /$ $\text{CF}_3\text{CH}_2\text{OH} + \text{OH}$	Manuscript in preparation.
$\text{HCOOH} + \text{OH} /$ $\text{HCOOH} + \text{Cl}$	The reactions have been characterized in MP2 and CCSD(T)/aug-cc-pVTZ calculations.
$\text{HCN} + \text{OH} / \text{HCN} + \text{Cl} /$ $\text{HCN} + \text{F}$	The reactions have been characterized in MP2 and CCSD(T)/aug-cc-pVQZ calculations.
$\text{CH}_3\text{NH}_2 + \text{OH} /$ $(\text{CH}_3)_2\text{NH} + \text{OH} /$ $(\text{CH}_3)_3\text{N} + \text{OH}$	The reactions have been studied in MP2 and CCSD(T)/aug-cc-pVTZ calculations. The reactions are all characterized by being barrierless, and we have extended the study of the $\text{CH}_3\text{NH}_2 + \text{OH}$ system to include CASPT2 calculations.
$\text{NH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{OH}$	The reaction has been studied in MP2 and CCSD(T)/aug-cc-pVTZ calculations. Apparently the reaction proceeds without barrier.

On the experimental side we have carried out relative rate studies of the  $\text{CH}_3\text{NH}_2$ ,  $\text{CD}_2\text{NH}_2$ ,  $(\text{CH}_3)_2\text{NH}$ ,  $(\text{CD}_3)_2\text{NH}$ ,  $(\text{CH}_3)_3\text{N}$  and  $(\text{CD}_3)_3\text{N}$  reactions with OH radicals at the European Photoreactor Facility in Valencia, Spain (EUPHORE). We have further analyzed previously obtained data from photolysis experiments of formaldehyde and acetaldehyde carried out at EUPHORE. The average relative photolysis rates obtained are  $j_{\text{HCHO}} / j_{\text{DCDO}} = 3.15 \pm 0.08$  and  $j_{\text{CH}_3\text{CDO}} / j_{\text{CH}_3\text{CHO}} = 1.26 \pm 0.03$ . It is concluded that the large isotope effect in the acetaldehyde photolysis is related to the dynamics in the  $\text{s}_1 \leftrightarrow \text{T}_1$  intersystem crossing. The results for  $\text{CH}_3\text{CDO}$ ,  $\text{CH}_3\text{CHO}$ , and  $\text{HCHO}$  and  $\text{DCDO}$  were submitted for publication in The Journal of Physical Chemistry.

