

Report on the activities performed with the financial support of the European Marie Curie COFUND / Belspo programme (February 2011-January 2013)

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1 Report on the performed research

The work performed in the framework of my return fellowship, offered by the European Marie Curie COFUND programme and the Belgian Science Policy Office, was mainly focused on spectroscopy, on simulating excitation and two-photon absorption spectra, and on the investigation of biological lipid bilayers and DNA strands.

In one of the first studies done in Mons, the gas-phase photoelectron spectra of ethene, formaldehyde, formic acid and difluoromethane were simulated using the reflection principle and the unrestricted second-order algebraic diagrammatic construction [UADC(2)] scheme of the polarization propagator for the computation of the vertical-excited states of the cations at the equilibrium geometry of the parent neutral molecule. Comparison was made with experimental spectra and the established highly accurate ionization IP-ADC(3) theory to gain insight into the accuracy and applicability of recently developed excitation UADC schemes. Within UADC(2), we distinguished between the strict and extended schemes UADC(2)-s and UADC(2)-x. While the latter approach was found to slightly underestimate the experimental photoelectron spectra by 0.3 eV and can thus be regarded as a reliable scheme within the limits of the applied reflection principle and the underlying approximations, the UADC(2)-s scheme tended to overestimate the excitation energies by about 0.5 eV. Time-dependent density functional theory was also applied in combination with the standard B3LYP xc functional and turned out to be a useful computational tool for the simulation of the photoelectron spectra of the studied species. The work was done in collaboration with Prof. P. Slavíček from the Institute of Chemical Technology in Prague (Czech Republic).

In the area of two-photon absorption (TPA), three topics were brought up. In the first one, performed in collaboration with A. Trofimov (Irkutsk State University, Russia) and co-workers, an approach to molecular response functions based on the intermediate state representation (ISR) of polarization propagator and ADC approximations was for the first time employed for calculations of nonlinear response properties. The hierarchy of the first- and second-order ADC/ISR computational schemes, ADC(1), ADC(2), ADC(2)-x, and ADC(3/2), was tested in applications to H_2O , HF , and C_2H_4 (ethylene). The calculated TPA spectra were compared with the results of coupled cluster (CC) models and time dependent density-functional theory (TDDFT) calculations, using the results of the CC3 model as benchmarks. As a more realistic example the TPA spectrum of C_8H_{10} (octatetraene) was calculated using the ADC(2)-x and ADC(2) methods. The results were compared with the results of the TDDFT method and earlier calculations, as well as to available experimental data. A prominent feature of octatetraene and other polyene molecules is the existence of low-lying excited states with increased double excitation character. We demonstrated that the two-photon absorption involving such states can be adequately studied using the ADC(2)-x scheme, explicitly accounting for interaction of doubly excited configurations. Observed peaks in the experimental TPA spectrum of octatetraene were assigned based on our calculations.

In a second study in non-linear optics, the computational design of two-photon active caging compounds was investigated. Through a collaboration with experimentalists within the cluster of excellence "Macromolecular complexes" in Frankfurt (Germany), who looked forward to our results avoiding long

and tedious processes in performing synthesis of non-appropriate molecules, the nitrodibenzofuran chromophore was chosen as a reference and virtual chemical modifications were performed by introduction of substituents and by replacement of the central furan ring by pyrrole, thiophene and even borrole heterocycles.

In a close collaboration with the group of Prof. J.-L. Brédas in Atlanta, GA (United States of America), the excited state energies, and the excited state as well as the transition state dipole moments of cyanines with a backbone of three, five and seven carbon atoms were investigated. Our analysis was performed using the strict and extended second order ADC scheme, the Symmetry Adapted Cluster Configuration Interaction (SAC-CI) general R method with $R = 2$, and Zerner's theory of Intermediate Neglect of Differential Overlap (ZINDO). For the two latter methods, the three state model was used to calculate the Two Photon Absorption spectra, while for ADC also a closed form of the TPA strength was available through the use of response theory. The TPA cross sections obtained for the three molecules showed that the results in Göppert-Mayer for the closed form were very close to the ones for the three-state model, which enforced our confidence with respect to a Sum-Over-States expression. Because of its relevance to two-photon absorption and all optical switching of molecular devices, the ratio of the second and first excited state energies was calculated. For the cyanine with three carbons, the ratio was found to be 1.70 and 1.51 at the Zindo and SAC-CI/6-31G* level, while it was found to be higher for the one with five carbons (1.96 for Zindo and 1.70 for SAC-CI) and the one with seven carbons (2.11 for Zindo and 2.39 for SAC-CI). The ADC(2)-s and ADC(2)-x/6-31G* ratios, which agreed very well with each other, could be found in between, and increased slightly with increasing backbone. With enlarging basis set, however, the ratio was found to diminish. The second hyperpolarizability γ of these compounds was examined, too.

Together with Dr. B. Hajgató, who holds a post-doctoral position at the Vrije Universiteit Brussel, SAC-CI general-R calculations were performed on the cage compound norbornane and compared with results obtained by the IP-ADC(3) scheme. This work was put in line with recent studies of the electronic structure of this molecule [J. Chem. Phys. 121 (2004), 10525, and J. Phys. Chem. A 109 (2005), 4267] and a comparison was made with previously performed electron momentum spectroscopy (EMS) and ultraviolet photo-electron measurements. The region around ~ 25 eV (band 12), characterized by an elaborated band in the EMS spectrum which was missing in previous Green's function and ADC calculations, was investigated. This study was completed with outer-valence Green's function (OVGF) and SAC-CI/SD-R calculations, and results were obtained by employing (single and double) ionization extended second order ADC. Since IP-ADC(3) only included 2h-1p shake-up states, while SAC-CI general-R also included higher order states, the agreement between both methods assured that the higher order shake-up states did not play an important role in the ionization spectrum of norbornane. In relation with the band at 25 eV, a tentative description in terms of ultrafast nuclear dynamical effects and autoionization processes in doubly ionized norbornane had become more plausible.

In a second study upon this subject, results were reported of Born-Oppenheimer Molecular Dynamics calculations performed on the singlet dication of norbornane, starting from the neutral ground state geometry. Intramolecular rearrangements and charge dissociation processes, which probably took place in the innermost valence ionization spectrum, were discussed and an analysis by means of natural bond orders and Wiberg bond indices had been performed. The outcome of these simulations and the observed cage fragmentation might explain the tremendous rise of electron-impact (e, 2e) ionization cross sections of norbornane at electron binding energies around the double-ionization threshold.

Focussing on the excited-state dynamics of biomolecules, photochromism or, equivalently, the change of color upon irradiation, was investigated. To examine the subtle differences in the geometric structure which influenced its occurrence, the mechanism of photoenolization of the photochromic compounds 3-benzoyl-2-benzyl-1-methyl-1H-quinoline-4-one (1) and 3-benzoyl-1,2-dibenzyl-1H-1,8 naphthyridin-4-one (2) as well as of the structurally closely related but nonphotochromic 3-benzoyl-1-benzyl-2-methyl-1H-1,8-naphthyridin-4-one (3) had been investigated theoretically using state-of-the-art quantum chemical methods. Focusing on the difference between 2 and 3 and stressing the absence of a phenyl group in the latter, the excited state potential energy surfaces along the photoenolization coordinate were calculated for both. While the initial proton transfer, which triggered the photoenolization, was found to

be feasible in presence of the phenyl group in 1 and 2, it was suppressed in 3.

In an other collaboration with experimentalists from the Molecular Materials and Nanosystems unit of the Eindhoven University of Technology, we described the photophysical properties of a series of derivatives of pyrrolo[3,2-b]pyrrole-2,5(1H,4H)-dione-3,6-diyl (iDPP) linked to two oligothiophenes of variable length (nT). The iso-DPP-oligothiophenes (iDPP n Ts) differed from the common pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-3,6-diyl-oligothiophene analogues (DPP n Ts) by a different orientation of the two lactam rings in the bicyclic iDPP unit compared to DPP. In contrast to the highly fluorescent DPP n Ts, the new isomeric iDPP n Ts exhibit only very weak fluorescence. We demonstrated with the help of quantum-chemical calculations that this could be attributed to a different symmetry of the lowest excited state in iDPP n T (A in C_2 symmetry) compared to DPP n Ts (B) and the corresponding loss in oscillator strength of the lowest energy transition. Upon extending the oligothiophene moiety in the iDPP n Ts molecules, the charge transfer character of the lowest A excited state became more pronounced. This tended to preclude high fluorescence quantum yields even in extended iDPP n Ts systems.

A current project in linear spectroscopy is performed in collaboration with Prof. A. Dreuw (Interdisciplinary Center for Scientific Computing, University of Heidelberg). It concerns the absorption spectra of bisbodipy (bis-borondipyrromethene), which are simulated using approximate second order coupled cluster theory and various TD-DFT functionals. The angle between both bodipy core units is found to play an important role.

Together with partners from the IAP P7/05 network, a new BODIPY based fluorescent probe, excitable in the blue region of the spectra was investigated. Groups in Leuven synthesized it with the purpose of studying membrane domains. Both steady-state and time-resolved fluorescence techniques were used to investigate the photophysical properties, which were found to be unaffected by solvent polarity. Experimentally, the probe was seen to partition preferentially into the liquid disordered (Ld) phase for the mixtures containing Sphingomyelin (SM), but into the gel phase (So) for the binary mixtures. Molecular simulations performed on the probe inserted into a DOPC bilayer allowed us to describe the position and orientation of BNP in a lipid bilayer. The BNP equilibrated position was found in between the phospholipids; its core was located between the hydrophobic core and the polar surface of the lipid bilayer. Throughout the simulation, it was seen that the transition state dipole moment, which was oriented along the body of the Bodipy core, was not parallel oriented to the membrane surface; on the contrary, it described a small angle, which slightly decreased from 30 to 15° between a simulation time from 40 to 80 ns. For the near future and in collaboration with our Belgian partners as well as with the group of Dr. P. Trouillas in Limoges, possibilities are worked out to run calculations upon BNP in mixed membranes. For our simulations, a ternary mixture with DOPC, SM and Cholesterol seems to be interesting.

Research had been done on the self-assembly of cationic conjugated polymers - DNA hybrid structures in a collaboration with experimentalists of the BINDER project (Bio-Inspired organic Nanostructures: Design and Recognition) and with Dr. M. Surin, who is "Chercheur Qualifié" in our Laboratory of Novel Materials in Mons. Inspired by Ho *et al.* (see Acc. Chem. Res. 48 (2008) 168), single and double stranded DNA were used and the complexation with a specific polythiophene molecule had been studied. Indeed, many DNA binding molecules were themselves known as being achiral, but, after binding to DNA, they acquired an induced circular dichroism (CD) that was characteristic of their interaction. Using a modified GAFF forcefield, taking the necessary amount of counter-ions into account and reverting to an implicit solvent model, simulations up to 100 and 54 ns for the single and double stranded DNA, respectively, have been performed up to the current time of writing. A strategy to calculate the CD spectra using TDDFT and Zindo methods has been set up and further possibilities to simulate analogous DNA strands and other π conjugated polymers are proposed.

2 Accepted and submitted publications

1. S. Knippenberg, M. Kunitski, A. Dreuw, "Large amplitude motions in cyclopentene and 1-butene: quantum chemical insights into the ground- and excited state potential energy surfaces", *Z. Phys. Chem.* 225 (2011), 525.
2. S. Knippenberg, P. Eisenbrandt, L. Šišťík, P. Slavíček, A. Dreuw, "Simulation of photoelectron spectra using the reflection principle in combination with unrestricted excitation ADC(2) to assess the accuracy of excited state calculations", *Chem. Phys. Chem.* 12 (2011), 3180.
3. S. Knippenberg, B. Hajgató, "The band 12 issue of norbornane: a study of higher shake-up states", *Spectrochim. Acta A* 88 (2012), 102.
4. S. Knippenberg, D. R. Rehn, M. Wormit, J. H. Starcke, I. L. Rusakova, A. B. Trofimov, A. Dreuw, "Calculations of nonlinear response properties using intermediate state representation and algebraic diagrammatic construction polarization propagator approach: Two-photon absorption spectra", *J. Chem. Phys.* 136 (2012), 064107.
5. A. Dreuw, M. Polkehr, R. Binder, A. Heckel, S. Knippenberg, "Computational design of caging compounds based on nitrodibenzofuran with increased two-photon absorption", *J. Comp. Chem.* 33 (2012), 1797.
6. S. Knippenberg, M. Schneider, P. Mangal, A. Dreuw, "The Molecular Mechanism of Photochromism in Photo-Enolizable Quinoline and Naphthyridine Derivatives", *J. Phys. Chem. A* 116 (2012), 12321.
7. S. Knippenberg, B. Hajgató, "The cage fragmentation of doubly ionized norbornane: a Born-Oppenheimer molecular dynamics study", *Chem. Phys. Lett.*, submitted.
8. M. Kirkus, S. Knippenberg, D. Beljonne, J. Cornil, R. A. J. Janssen, S. C. J. Meskers, "Synthesis and optical properties of pyrrolo[3,2-b]pyrrole-2,5(1H,4H)-dione (iDPP) based molecules", *J. Phys. Chem. A.*, submitted.

3 Invited talks

- 13 November 2012: "Simulating absorption and ionization spectra using the Algebraic Diagrammatic Construction", Auburn University, Auburn, Alabama (United States of America).
- 12 November 2012: "A theoretical study into absorption and ionization spectra of small and medium sized molecules using the ADC scheme", Georgia Institute of Technology, Atlanta, Georgia (United States of America).
- 21 March 2012: "Spectroscopy of medium-sized closed and open-shell molecules", Faculté de Pharmacie, Limoges (France).
- 21 December 2011: "Calculating absorption spectra and nonlinear response properties using the polarization propagator approach", Université de Liège, Liège (Belgium)
- 17 November 2011: "Simulating one and two photon absorption spectra using the algebraic diagrammatic construction scheme", Pohang University of Science and Technology, Pohang (South Korea)
- 8 November 2011: "Ionization spectra of cage compounds and conformationally versatile molecules: an investigation using electron impact spectroscopies and Green's function calculations", Pohang University of Science and Technology, Pohang (South Korea)

- 12 October 2011: "A theoretical study into absorption and ionization spectra of small and medium-sized molecules using the ADC scheme", Korean Advanced Institute of Science and Technology, Daejeon (South Korea).

4 Contributing lectures

- 17 September 2011: "The band 12 issue of norbornane: a comparison between photo-electron and electron momentum spectroscopies", at the sixteenth International Workshop on Quantum Systems in Chemistry and Physics (QSCP XVI), Kanazawa (Japan)
- 3 September 2011: "A Study into the low-lying excited states of small and medium-sized molecules using the (unrestricted) ADC(2) scheme: A close comparison with experiment", at the seventh Congress of the International Society for Theoretical Chemical Physics (ISTCP VII), Waseda University, Tokyo (Japan)

5 Attended schools and conferences

- 6-7 December 2012: "Robert J. Silbey Memorial Symposium on Theory for Experimentalists", Atlanta, GA (United States of America).
- 21 September 2012: "The IAP P7/05 Kick-off meeting", Leuven (Belgium).
- 23-24 August 2012: "2nd International Symposium on Electron Momentum Spectroscopy", Brussels (Belgium).
Presentation of the poster: "The cage fragmentation of doubly ionized norbornane"
- 1-6 April 2012: "Challenges in Density Matrix and Density Functional Theory", Ghent (Belgium).
Presentation of the poster: "Calculations of nonlinear response properties using the intermediate state representation and the algebraic-diagrammatic construction scheme: two-photon absorption spectra"
- 2-4 February 2012: "3rd European symposium on computing π -conjugated systems", Mons (Belgium).
Presentation of the poster: "A study into the low-lying excited states of small and medium-sized molecules using the (unrestricted) ADC(2) scheme: a close comparison with experiment."
- 19 November 2011: "Symposium/workshop of computational sciences 2011, SWOCS III", Pohang (South Korea)
- 11-17 September 2011: "16th International Workshop on Quantum Systems in Chemistry and Physics, QSCP XVI", Kanazawa (Japan);
Presentation of the poster: "The band 12 issue of norbornane: comparison between SAC-CI general-R and ADC(3)."
- 2-8 September 2011: "7th congress of the international society for theoretical chemical physics, ISTCP-VII", Tokyo (Japan)
- 25-27 July 2011: "Watoc satellite meeting: 'Excited states and non-adiabatic processes in complex systems: theoretical approaches'", San Feliu (Spain);
Presentation of the poster: "Low-lying excited states using the (unrestricted) ADC(2) scheme: a comparison with experimental data."
- 3-6 May 2011: "Amber workshop on molecular dynamics simulations", Barcelona supercomputing center, Barcelona (Spain).

6 Scientific visits to foreign research groups

6.1 Atlanta, United States of America

From September to December 2012, I stayed in the group of Prof. J.-L. Brédas at the Georgia Institute of Technology in Atlanta, Georgia, United States of America. This group has a strong historical connection with our group in Mons, and I could discuss the topics of my work deeply and openly with my colleagues in Atlanta.

The main focus of my research during this time was the calculation of the second hyperpolarizability γ of three cyanines with a different length. The calculations were performed using the Algebraic Diagrammatic Construction scheme, the Symmetry Adapted Cluster Configuration Interaction and the semi-empirical ZINDO code, while the pragmatic sum-over-states expression was applied. Before being able to summarize the results in a scientific paper, a fourth molecule is investigated, and various details are verified. The finalization of this part of the project is foreseen in the coming two months.

6.2 Heidelberg, Germany

To maintain the collaboration between the theoretical and computational chemistry group of Prof. A. Dreuw (Interdisciplinary Center for Scientific Computing, University of Heidelberg), I went back to Germany in April 2012. We worked on the molecular mechanism of photochromism in photo-enolizable quinoline and naphthyridine derivatives, a side study which I started during my time as an Alexander-von-Humboldt (AvH) fellow in this group. The results have recently been published in J. Phys. Chem. A. 116 (2012), 12321. Also the investigation of the influence of excitonic coupling and charge transfer mechanisms in the absorption spectra of bisbodipy has been continued; more calculations are nonetheless necessary before final conclusions can be drawn.

In line with my previous postdoc centered around the implementation of two-photon absorption in the second order Algebraic Diagrammatic Construction (ADC) scheme, a project proposal to the AvH foundation (a so-called "Return Grant") has been submitted. Taking advantage of the positive quotation, I will stay in Heidelberg from February to the end of April this year to implement the first and second hyperpolarizabilities in a closed form in ADC. To check our implementation, comparison will be made with the results obtained using the sum-over-states expression, which was used during my visit to the group of Prof. J.-L. Brédas in Atlanta, USA.

6.3 Limoges, France

In March 2012 and in January 2013, the School of Pharmacy and more specifically the group of Dr. P. Trouillas was willing to work together with me on the determination of the location and the orientation of molecular probes in lipid bilayer membranes. Triggered by the groups around Prof. M. Ameloot (Biomedical Research Institute, UHasselt, Belgium), and Profs. N. Boens and W. Dehaen (Department of Chemistry, KULeuven, Belgium), a new Bodipy based probe had been extensively investigated. This work gives access to an interdisciplinary paper "A blue emitting Bodipy based lipid phase sensitive probe", which is being finalized at the moment of writing before a presumable submission to Langmuir.

6.4 Pohang, South Korea

From September to December 2011, I stayed as a visiting scientist in the research group of Prof. E. J. Baerends and Dr. O. Gritsenko at the Pohang University of Science and Technology, South Korea, and explored the possibilities to use the time-dependent density matrix functional theory (TD-DMFT) to simulate spectroscopy experiments. I especially focused on real time dynamics, non-linear optics and pump-probe spectroscopy, and pointed out the necessary working schemes.

The work in Pohang has given rise to a successful project application to the FRS-FNRS funding agency of the French speaking community of Belgium. Consequently, I am honored to start my work as a "Chargé de recherche" at the University of Liège in the course of this year 2013.