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Transient Changes in Molecular Geometries and How to Model Them

Simulating Chemical Reactions of
Metal Complexes in Solution to Explore
Dynamics, Solvation, Coherence,
and the Link to Experiment

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Asmus Ougaard Dohn

Transient Changes in Molecular Geometries and How to Model Them

Simulating Chemical Reactions of Metal
Complexes in Solution to Explore Dynamics,
Solvation, Coherence, and the Link
to Experiment

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 Springer

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The articles listed below were partially or fully prepared during the period of the Ph.D. program. Parts of the content in this thesis are based upon publications IV, VI, VII, and I, while results from V and III are drawn upon when needed.

The articles are listed chronologically. I is still in preparation, while the rest are published.

- (I) Haldrup, M.K., Gawelda, W., Abela, R., Alonso-Mori, R., Bergmann, U., Bordage, A., Cammarata, M., Canton, S. Dohn, A.O., Brandt van Driel, T., Fritz, D., Gaffney, K., Galler, A., Glatzel, P., Harlang, T., Kjær, K., Lemke, H., Møller, K.B., Zoltan, N., Pápai, M., Sas, N., Uhlig, J., Zhu, D., Vankó, G., Sundström, V. & Nielsen, M.M. & Bressler, C., ‘Observing Solvation Dynamics with Simultaneous Femtosecond X-ray Emission Spectroscopy and X-ray Scattering’, *In preparation*.
- (II) Vankó, G., Bordage, A., Pápai, M., Haldrup, K., Glatzel, P., March, A.M., Doumy, G., Britz, A., Galler, A., Assefa, T., Cabaret D., Juhin, A., Brandt van Driel, T., Kjær, K., Dohn, A.O., Møller, K.B., Lemke, H.T., Gallo, E., Rovezzi, M., Németh, Z., Rosályi, E., Rozgonyi, T., Uhlig, J., Sundström, V., Nielsen, M.M., Young, L., Southworth, S.H., Bressler, C & Wojciech, G., (2015) ‘Detailed Characterization of a Nanosecond-Lived Excited State: X-ray and Theoretical Investigation of the Quintet State in Photoexcited $[\text{Fe}(\text{terpy})_2]^{2+}$ ’, *Journal of Physical Chemistry C*, just accepted, DOI: [10.1021/acs.jpcc.5b00557](https://doi.org/10.1021/acs.jpcc.5b00557)
- (III) Canton, S.E., Kjær, K.S., Vankó, G., Brandt van Driel, T., Adachi, S., Bordage, A., Bressler, C., Chabera, P., Christensen, M., Dohn, A.O., Galler, A., Gawelda, W., Gosztola, D., Haldrup, K., Harlang, T., Liu, Y., Møller, K.B., Németh, Z., Nozawa, S., Pápai, M., Sato, T., Sato, T., Suarez-Alcantara, K., Togashi, T., Tono, K., Uhlig, J., Vithanage, D.A., Wärnmark, K., Yabashi, M., Zhang, J., Sundström, V. & Nielsen, M.M., (2015) ‘Visualizing the Nonequilibrium Dynamics of Photoinduced Intramolecular Electron Transfer with Femtosecond X-ray Pulses’, *Nature Communications*, vol 6, 6359
- (IV) Dohn, A.O., Jónsson, E.Ö., Kjær, K.S., Brandt van Driel, T., Nielsen, M. M., Jacobsen, K.W., Henriksen, N.E. & Møller, K.B. (2014). ‘Direct Dynamics Studies of a Binuclear Metal Complex in Solution: The Interplay Between Vibrational Relaxation, Coherence, and Solvent Effects’ *Journal of Physical Chemistry Letters*, vol 5, pp. 2414–2418.
- (V) Canton, S.E., Zhang, J., Brandt van Driel, T., Kjær, K.S., Haldrup, M.K., Chabera, P., Harlang, T., Suarez-Alcantara, K., Liu, Y., Pérez, J., Bordage, A., Pápai, M., Vankó, G., Jennings, G., Kurtz, C.A., Rovezzi, M., Glatzel, P., Smolentsev, G., Uhlig, J., Dohn, A.O., Christensen, M., Galler, A., Gawelda, W., Bressler, C., Lemke, H.T., Møller, K.B., Nielsen, M.M., Lomoth, R., Wärnmark, K., & Sundström, V. (2013) ‘Toward Highlighting the Ultrafast Electron Transfer Dynamics at the Optically Dark Sites of

Photocatalysts' *Journal of Physical Chemistry Letters*, vol 4, pp. 1972–1976.

- (VI) Dohn, A.O., Møller, K.B., & Sauer, P.A. (2013), 'Optimizing the Structure of Tetracyanoplatinate (II): A Comparison of Relativistic Density Functional Theory Methods' *Current Inorganic Chemistry*, vol 3, pp. 213–219.
- (VII) Haldrup, M.K., Vankó, G., Gawelda, W., Galler, A., Doumy, G., March, A. M., Kanter, E.P., Bordage, A., Dohn, A.O., Brandt van Driel, T., Kjær, K. S., Lemke, H.T., Canton, S.E., Uhlig, J., Sundström, V., Young, L., Southworth, S.H., Nielsen, M.M. & Bressler, C. (2012), 'Guest-Host Interactions Investigated by Time-Resolved X-ray Spectroscopies and Scattering at MHz Rates: Solvation Dynamics and Photoinduced Spin Transition in Aqueous $\text{Fe}(\text{bipy})_3^{2+}$ ' *Journal of Physical Chemistry A*, vol. 116, pp. 9878–9887.

*Dedicated to the memory of Mogens Ougaard
—who sparked my interest in the wonders of
nature by sending me postcards addressed as
the marvellous bacteria living in my stomach.*

*For those who know
It's time to leave the house
And go back to the field
Find your strength in the sound
And make your transition*

—Mad Mike, Underground Resistance,
Detroit

Supervisors' Foreword

Structure and change are central concepts in chemistry. In recent years it has become possible to detect the latter at the molecular level where atoms move at very high speeds (equivalent to several km/s). Uncovering these dynamics is central for our understanding of chemical reactions at the fundamental level. This topic is at the heart of femtochemistry, where dynamical nonequilibrium structures are detected while chemical reactions take place. Most recently, large-scale international facilities—so-called X-ray free-electron lasers XFEL—are being built around the world. With these facilities it will become possible to record snapshots of chemical reactions—in the form of instantaneous X-ray scattering signals—at the femtosecond timescale. In parallel with this development of instrumentation, theory and modeling need to be developed in order to interpret all the new experimental data.

To that end, the thesis by Asmus O. Dohn *Transient Changes in Molecular Geometries and How to Model Them* describes the modeling of the dynamics of complex photochemical reactions in the solution phase. The thesis describes in particular the implementation of a highly efficient QMMM Direct Dynamics approach with application to the photochemistry of transition metal complexes in solution and analyzes various aspects of energy dissipation via dynamic changes in molecular structure, vibrational modes, and solvation. The agreement between theory and experiment is impressive and provides convincing validation of the method, while also providing significant new insight into the chemical dynamics and molecular determinants of the experimental data. Besides providing intriguing information about the solute–solvent dynamics, this type of modeling will also play an important role in the fast growing field of femtosecond X-ray science.

Kongens Lyngby, Denmark
March 2015

Prof. Klaus B. Møller
Prof. Niels E. Henriksen

Abstract

Light-induced chemical processes are accompanied by molecular motion on the femtosecond time scale. Uncovering this dynamical motion is central to understanding the chemical reaction on a fundamental level. This thesis focuses on the aspects of excess excitation energy dissipation via dynamic changes in molecular structure, vibrations and solvation.

In this thesis, we employ our recently developed Quantum-/Molecular-Mechanical Direct Dynamics method to do simulations of transition metal complexes in solution, to uncover their energy dissipation channels, and how they are affected by the solvent. The simulations have also served as benchmarks on this newly developed implementation.

First, we establish that the chosen model provides a trustworthy description of the systems; since transition metals are heavier than purely organic systems, we test a range of approximations to relativistic quantum mechanic descriptions, to ascertain the accuracy of the quantum model in the Direct Dynamics simulations. We then test—and improve—the framework for calculating the experimental X-ray Diffuse Scattering Difference signal from (any kind of) Molecular Dynamics (MD) simulations. Comparisons of purely classical MD simulations to literature Direct Dynamics simulations delineate the boundaries for the force-field approximation: Classical MD provides a solvent shell response sufficient for experimental fits, but fails to model specific solvent shell changes, such as intercalation.

The first Direct Dynamics project of this work focuses on a bi-metallic Ir complex, where the excited state bond formation results in a large Ir–Ir contraction with oscillatory behaviour. Forty simulated excited state trajectories of 3.5 ps each compare well with experimental results, and uncover a new vibrational mode. We observe how the wide distribution of ground state geometries is responsible for decoherence, and that the solvent cage actually facilitates coherent motion, by blocking the newly discovered vibrational mode. We furthermore observe a non-specific, rotational solvent response to the excitation.

The second Direct Dynamics project studies the effect of solvation on a bi-centred Ru-Co complex, and we observe how the intercalation solvation response which was lost in the study using only force-fields, is recovered in the Direct Dynamics description.

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As is customary, I would like to start out by thanking my supervisors. However, my appreciation for their supervision, insights, support, ambition, and trust is far from formality. In my days as a Master's student at the University of Copenhagen, Klaus B. Møller's reputation with the students as 'that scary censor from DTU who shouts a lot' preceded him, but I am glad that I still had the courage to convince him to take me on, and now I owe a major part of my academic (and probably also some of my personal) development to his influence.

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I have also had a bit of help on the sideline with Python and Fortran questions, since I was still wet behind my coding ears when this project started, so thank you very much Casper Steinmann, Simon Olsson, and ‘Ænders’ Jacobsen. I hope you won’t be afraid to turn on gchat anymore... Thanks also to my native-speaker-consultants Naoise MacNamara and Emma Blake, the latter with whom I’ve also enjoyed quite a few days at the library, reminding me, when it was most needed, that there is a life outside transient dynamics.

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