



## 2018

- *Dipole moment and polarizability of tunable Intramolecular charge transfer states in heterocyclic  $\pi$ -conjugated molecular dyads determined by computational and Stark spectroscopic study*  
E. J. Rohwer, M. Akbarimosavi, S. E. Meckel, X. Liu, Y. Geng, L. M. Lawson Daku, A. Hauser, A. Cannizzo, S. Decurtins, R. J. Stanley, S.-X. Liu, T. Feurer  
Journal of Physical Chemistry C **122** (2018), p9346-9355 DOI:10.1021/acs.jpcc.8b02268

The annulation of two redox-active molecules into a compact and planar structure paves the way toward a new class of electronically versatile materials whose physical properties can be tuned via a substitution of one of the constituting moieties. Specifically, we present tetrathiafulvalene-benzothiadiazole donor-acceptor molecules. The critical role played by the dielectric properties of these molecules is evident by the large spectral shifts of the ground-state absorption spectra in a range of solvents. Stark spectroscopy is performed to determine experimentally dipole and polarizability change over transitions in the visible range with particular attention to the transition from the highest-occupied molecular orbital (HOMO) to the lowest-unoccupied molecular orbital (LUMO). The experimental results are compared to the results of time-dependent density functional theory calculations, and we reciprocally validate results from calculation and experiment. This allows us to filter out effective models and reveal important insights. The calculations are initially performed in the gas phase and subsequently a polarizable continuum model is adopted to probe the influence of the solvent on the molecular dielectric properties. The results show a large charge displacement from the HOMO to the LUMO and confirm the intramolecular charge transfer nature of the lowest-energy transition. Substitution of the acceptor moiety with electron-withdrawing groups results in changes to the experimentally determined molecular properties consistent with the effects predicted by computational results. The dominant contribution to the electroabsorption signal is due to the change in dipole moment, which is measured to be roughly 20 D for all samples and forms a small angle with the transition dipole moment in a toluene solvent environment.

- *Spin-state dependence of the structural and vibrational properties of solvated iron(II) polypyridyl complexes from AIMD simulations: aqueous  $[Fe(bpy)_3]Cl_2$ , a case study*  
Latévi M. Lawson Daku  
Physical Chemistry Chemical Physics **20** (9) (2018), p6236-6253 DOI:10.1039/C7CP07862E

The accurate description of transition metal complexes in liquid solutions is a challenging fundamental research problem, which must be tackled when it comes to understanding the role of the solvent in the photoinduced low-spin (LS)  $\rightarrow$  high-spin (HS) transition in solvated Fe(II) complexes. We report an in-depth ab initio molecular dynamics (AIMD) study of the spin-state dependence of the structural and vibrational properties of the prototypical  $[Fe(bpy)_3]^{2+}$  ( $bpy = 2,2'$ -bipyridine) LS complex in water. The description achieved for the LS and HS solution structures of aqueous  $[Fe(bpy)_3]^{2+}$  significantly improves on and actually supersedes the one from our previous AIMD study [Lawson Daku and Hauser, *J. Phys. Chem. Lett.*, 2010, 1, 1830], thanks to substantially longer simulation times and the use of the dispersion-corrected BLYP-D3 functional in place of the standard BLYP functional. The present results confirm the 0.19 Å... lengthening of the Fe-N bonds and the increased thermal fluctuation of the molecular edifice stemming from the weakening of the Fe-N bonds upon the LS  $\rightarrow$  HS change of states. Revisiting our previous finding on the solvation of  $[Fe(bpy)_3]^{2+}$ , they indicate that the number of water molecules in its first hydration shell actually increases from ~15 in the LS state to ~17 in the HS state. The vibration modes and associated vibrational density of states (VDOS) of  $[Fe(bpy)_3]^{2+}$  have been determined from a generalized normal coordinate analysis. The VDOS of the Fe-N stretching and bending modes are located in the far-IR region. For LS  $[Fe(bpy)_3]^{2+}$ , the peak positions of the VDOS of the Fe-N stretching modes agree very well with the experimental Fe-N stretching frequencies. For HS  $[Fe(bpy)_3]^{2+}$ , the spanned frequency range encompasses the Fe-N stretching frequency range reported for HS polypyridine Fe(II) complexes. The LS and HS IR spectra of the complex have also been calculated in the 0 - 2500  $cm^{-1}$  range from the dynamics of the Wannier function centers. The calculated LS IR spectrum matches available experimental data. The predicted HS-LS IR difference spectrum of aqueous  $[Fe(bpy)_3]^{2+}$  shows mostly an increase in intensity upon the LS  $\rightarrow$  HS change of states.

- *Correlating Boron-Hydrogen Stretching Frequencies with Boron-Hydrogen Bond Lengths in Closoboranes: An Approach Using DFT Calculations*  
Hans Hagemann, Manish Sharma, Daniel Sethio and Latévi Max Lawson Daku  
Helvetica Chimica Acta **101** (2) (2018) DOI:10.1002/hlca.201700239

## 2017

- *Probing the Impact of Solvation on Photoexcited Spin Crossover Complexes with High-Precision X-ray Transient Absorption Spectroscopy*  
Cunming Liu, Jianxin Zhang, Latévi M. Lawson Daku, David Gosztola, Sophie E. Canton and Xiaoyi Zhang  
Journal of the American Chemical Society **139** (48) (2017), p17518-17524 DOI:10.1021/jacs.7b09297

Investigating the photoinduced electronic and structural response of bistable molecular building blocks incorporating transition metals in solution phase constitutes a necessary stepping stone for steering their properties toward applications and performance optimizations. This work presents a detailed X-ray transient absorption (XTA) spectroscopy study of a prototypical spin crossover (SCO) complex  $[Fe^{II}(mbpy)_3]^{2+}$  (where  $mbpy = 4,4'$ -dimethyl-2,2'-bipyridine) with an  $[Fe^{II}N_6]$  first coordination shell in water ( $H_2O$ ) and acetonitrile ( $CH_3CN$ ). The unprecedented data quality of the XTA spectra together with the direct fitting of the difference spectra in  $k$  space using a large number of scattering paths enables resolving the subtle difference in the photoexcited structures of an  $Fe^{II}$  complex in two solvents for the first time. Compared to the low spin (LS)  $A_1$  state, the average Fe-N bond elongations for the photoinduced high spin (HS)  $T_2$  state are found to be  $0.181 \pm 0.003$  Å... in  $H_2O$  and  $0.199 \pm 0.003$  Å... in  $CH_3CN$ . This difference in structural response is attributed to ligand-solvent interactions that are stronger in  $H_2O$  than in  $CH_3CN$  for the HS excited state. Our studies demonstrate that, although the metal center of  $[Fe^{II}(mbpy)_3]^{2+}$  could have been expected to be rather shielded by the three bidentate ligands with quasi-octahedral coordination, the ligand field strength in the HS excited state is nevertheless indirectly affected by solvation effects that modifies the charge distribution within the Fe-N covalent bonds. More generally, this work highlights the importance of including solvation dynamics in order to develop a generalized understanding of the spin-state switching at the atomic level.

- *Computational study of the vibrational spectroscopy properties of boron-hydrogen compounds:  $Mg(B_3H_6)_2$ ,  $CB_9H_{10}^-$  and  $CB_{11}H_{12}^-$*   
Daniel Sethio, Latévi Max Lawson Daku and Hans Hagemann  
International Journal of Hydrogen Energy **42** (35) (2017), p22496-22501 DOI:10.1016/j.ijhydene.2017.03.044  
Keywords: boron-hydrogen species • IR • Raman • vibrational frequencies • anharmonicity • density functional theory

We report the DFT study of the vibrational spectroscopy properties of  $Mg(B_3H_6)_2$ , a potential intermediate in the decomposition of  $Mg(BH_4)_2$ , as well as those of  $CB_{11}H_{12}^{2-}$  and  $CB_9H_{10}^-$ , whose salts can exhibit high ionic conductivities. Because the inclusion of anharmonicity is key to the accurate description of the vibrational properties of BH species [D. Sethio, L. M. Lawson Daku, H. Hagemann, *Int. J. Hydrogen Energy*, 41 (2016) 6814], the calculations were performed both in the harmonic and in the anharmonic approximation. The IR and Raman spectra of  $Cs(CB_{11}H_{12})$  and  $Na_2(B_{10}H_{10})$  have also been measured. The calculated and experimental spectra are in good agreement. A comparative analysis of the vibrational spectroscopy properties is made for  $B_3H_6^{2-}$  and  $Mg(B_3H_6)_2$ ,  $B_{12}H_{12}^{2-}$  and  $CB_{11}H_{12}^{2-}$ , and for  $B_{10}H_{10}^{2-}$  and  $CB_9H_{10}^-$ .

- *A Simple Approach for Predicting the Spin State of Homoleptic Fe(II) Tris-diimine Complexes*  
Hoa Phan, Jeremy J. Hrudka, Dilyara Igimbayeva, Latévi M. Lawson Daku and Michael Shatruk  
Journal of the American Chemical Society **139** (18) (2017), p6437-6447 DOI:10.1021/jacs.7b02098

We propose a simple method for predicting the spin state of homoleptic complexes of the Fe(II)  $d^6$  ion with chelating diimine ligands. The approach is based on the analysis of a single metric parameter within a free (noncoordinated) ligand: the interatomic separation between the N-donor metal-binding sites. An extensive analysis of existing complexes allows the determination of critical N–A–N distances that dictate the regions of stability for the high-spin and low-spin complexes, as well as the intermediate range in which the magnetic bistability (spin crossover) can be observed. The prediction has been tested on several complexes that demonstrate the validity of our method.

- *Ultrafast transient IR spectroscopy and DFT calculations of ruthenium(II) polypyridyl complexes*  
Qinchao Sun, Bogdan Dereka, Eric Vauthey, Latevi Max Lawson Daku and Andreas Hauser  
Chemical Science **8** (1) (2017), p223-230 DOI:10.1039/C6SC01220E

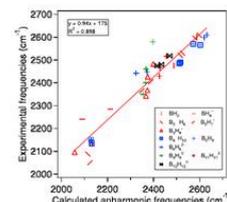
Ultrafast time-resolved infrared spectroscopy of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (bpy = 2,2'-bipyridine),  $[\text{Ru}(\text{mbpy})_3]^{2+}$  (mbpy = 6-methyl-2,2'-bipyridine), and  $[\text{Ru}(\text{mphen})_3]^{2+}$  (mphen = 2-methyl-1,10-phenanthroline) in deuterated acetonitrile serves to elucidate the evolution of the system following pulsed excitation into the  $^3\text{MLCT}$  band at 400 nm. Whereas for  $[\text{Ru}(\text{bpy})_3]^{2+}$  no intermediate state can be evidenced for the relaxation of the corresponding  $^3\text{MLCT}$  state back to the ground state, for  $[\text{Ru}(\text{mbpy})_3]^{2+}$  and  $[\text{Ru}(\text{mphen})_3]^{2+}$  an intermediate state with a lifetime of about 400 ps is observed. The species associated IR difference spectra of this state are in good agreement with the calculated difference spectra of the lowest energy  $^3\text{dd}$  state using DFT. The calculated potential energy curves for all the complexes in the triplet manifold along the metal-ligand distance show that for  $[\text{Ru}(\text{bpy})_3]^{2+}$  the  $^3\text{dd}$  state is at higher energy than the  $^3\text{MLCT}$  state and that there is a substantial barrier between the two minima. For  $[\text{Ru}(\text{mbpy})_3]^{2+}$  and  $[\text{Ru}(\text{mphen})_3]^{2+}$ , the  $^3\text{dd}$  state is at lower energy than the  $^3\text{MLCT}$  state.

## 2016

- *Halide Free  $M(\text{BH}_4)_2$  ( $M = \text{Sr}, \text{Ba}, \text{ and Eu}$ ) Synthesis, Structure, and Decomposition*  
Manish Sharma, Emilie Didelot, Alexandra Spyratou, Latévi Max Lawson Daku, Radovan Cerný and Hans Hagemann  
Inorganic Chemistry **55** (14) (2016), p7090-7097 DOI:10.1021/acs.inorgchem.6b00931

Borohydrides have attained high interest in the past few years due to their high volumetric and gravimetric hydrogen content. Synthesis of di/trimetallic borohydride is a way to alter the thermodynamics of hydrogen release from borohydrides. Previously reported preparations of  $M(\text{BH}_4)_2$  involved chloride containing species such as  $\text{SrCl}_2$ . The presence of residual chloride (or other halide) ions in borohydrides may change their thermodynamic behavior and their decomposition pathway. Pure monometallic borohydrides are needed to study decomposition products without interference from halide impurities. They can also be used as precursors for synthesizing di/trimetallic borohydrides. In this paper we present a way to synthesize halide free alkaline earth metal (Sr, Ba) and europium borohydrides starting with the respective hydrides as precursors. Two novel high temperature polymorphs of Sr and Eu borohydrides and four polymorphs of Ba borohydride have been characterized by synchrotron X-ray powder diffraction, thermal analysis, and Raman and infrared spectroscopy and supported by periodic DFT calculations. The decomposition routes of these borohydrides have also been investigated. In the case of the decomposition of strontium and europium borohydrides, the metal borohydride hydride ( $M(\text{BH}_4)\text{H}_3$ ,  $M = \text{Sr}, \text{Eu}$ ) is observed and characterized. Periodic DFT calculations performed on room temperature  $\text{Ba}(\text{BH}_4)_2$  revealed the presence of bidentate and tridentate borohydrides.

- *A theoretical study of the spectroscopic properties of  $B_2H_6$  and of a series of  $B_x$  species ( $x = 1-12, y = 3-14, z = 0-2$ ): From  $\text{BH}_3$  to  $\text{B}_{12}\text{H}_{12}^{2-}$*   
Daniel Sethio, Latévi Max Lawson Daku and Hans Hagemann  
International Journal of Hydrogen Energy **41** (16) (2016), p6814-6824  
DOI:10.1016/j.ijhydene.2016.02.121  
Keywords: boron-hydrogen species •  $^{11}\text{B}$  and  $^1\text{H}$  NMR chemical shifts • vibrational frequencies • anharmonicity • density functional theory

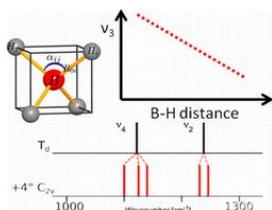


The characterization of boron-hydrogen compounds is an active research area which encompasses subjects as diverse as the chemistry and structures of closoboranes or the thermal decomposition mechanism of the borohydrides. Due to their high gravimetric hydrogen content, borohydrides are considered as potential hydrogen storage materials. Their thermal decompositions are multistep processes, for which the intermediate products are not easily identified. To help address this issue, we have extensively investigated the vibrational and NMR properties of 21 relevant  $B_m$  boron-hydrogen species ( $m = 1-12$ ) within density functional theory. We could thus show that the B3LYP-D2 dispersion-corrected hybrid can be used in combination with the large cc-pVTZ basis set for the reliable prediction of the  $^{11}\text{B}$  and  $^1\text{H}$  NMR spectra of the boron-hydrogen species, and also for the reliable prediction of their IR and Raman spectra while taking into account the anharmonicity of their molecular vibrations.

## 2015

- *$\text{Pd}_2\text{Au}_{36}(\text{SR})_{24}$  cluster: structure studies*  
Bei Zhang, Sameh Kaziz, Houhua Li, Dawid Wodka, Sami Malola, Olga V. Safonova, Maarten Nachtegaal, Clement Mazet, Igor Dolamic, Jordi Llorca, Elina Kalenius, Latevi Max Lawson Daku, Hannu Häkkinen, Thomas Buerger and Noelia Barrabes  
Nanoscale **7** (40) (2015), p17012-17019 DOI:10.1039/C5NR04324G

The location of the Pd atoms in  $\text{Pd}_2\text{Au}_{36}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ , is studied both experimentally and theoretically. X-ray photoelectron spectroscopy (XPS) indicates oxidized Pd atoms. Palladium K-edge extended X-ray absorption fine-structure (EXAFS) data clearly show Pd-S bonds, which is supported by far infrared spectroscopy. By comparing theoretical EXAFS spectra in R space and circular dichroism spectra of the staple, surface and core doped structures with experimental spectra.

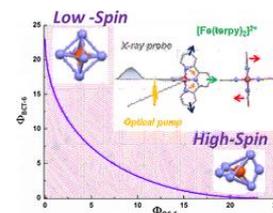


- *Quantitative Spectra-Structure Relations for Borohydrides*  
Vincenza D'Anna, Latévi Max Lawson Daku and Hans Hagemann  
The Journal of Physical Chemistry C **119** (38) (2015), p21868-21874 DOI:10.1021/acs.jpcc.5b06045

Among the different potential hydrogen storage materials, borohydrides have been largely investigated because of their high gravimetric

and volumetric hydrogen content. In the analysis of borohydrides, vibrational spectroscopy plays an important role since it gives information on the local structure of the  $\text{BH}_4^{\delta-}$  ion inside the solid. Here the GF method, developed by Wilson, is used in order to determine the local symmetry of  $\text{BH}_4^{\delta-}$  in solid borohydrides starting from their vibrational spectra. Two different cases of deformations of  $\text{BH}_4^{\delta-}$  are considered. In the first case, the effects of small angular variations on the vibrational spectra of borohydrides will be taken into account; starting from the splitting of the bands corresponding to the deformation modes, the angular deformations will be estimated. In the second one, the  $\text{BH}_4^{\delta-}$  under chemical pressure (in different cubic alkali halides) is considered; in this case, the symmetry of the  $\text{BH}_4^{\delta-}$  remains  $T_d$ , while the bond lengths change according to the pressure experienced. Different practical examples will be illustrated.

- **Mapping the Ultrafast Changes of Continuous Shape Measures in Photoexcited Spin Crossover Complexes without Long-Range Order**  
S. E. Canton, X. Zhang, L. M. Lawson Daku, Y. Liu, J. Zhang and S. Alvarez  
The Journal of Physical Chemistry C **119** (6) (2015), p3322-3330 DOI:10.1021/jp5117189



Establishing a tractable yet complete reaction coordinate for the spin-state interconversion in  $d^4\text{e}^-d^0$  transition metal complexes is an integral aspect of controlling the dynamics that govern their functionality. For spin crossover phenomena, the limitations of a single-mode approximation that solely accounts for an isotropic increase in the metal-ligand bond length have long been recognized for all but the simple octahedral monodentate  $\text{Fe}^{\text{II}}$  compounds. However, identifying the coupled deformations that also impact on the unimolecular rate constants remains experimentally and theoretically challenging, especially for samples that do not display long-range order or when crystallization profoundly alters the dynamics. Owing to the rapid progress in ultrafast X-ray absorption spectroscopy (XAS), it is now possible to obtain transient structural information in any physical phase with unprecedented details. Using picosecond XAS and DFT modeling, the structure adopted by the photoinduced high-spin state of solvated  $[\text{Fe}(\text{terpy})_2]^{2+}$  (terpy: 2,2',6'-terpyridine) has been recently established. Based on these results, the methodology of the continuous shape measure is applied to classify and quantify the short-lived distortion of the first coordination shell. The reaction coordinate of the spin-state interconversion is clearly identified as a double axial bending. This finding sets a benchmark for gauging the influence of first-sphere and second-sphere interactions in the family of  $\text{Fe}^{\text{II}}$  complexes that incorporate terpy derivatives. Some implications for the optimization of related photoactive  $\text{Fe}^{\text{II}}$  complexes are also outlined.

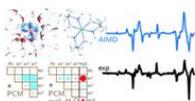
- **Dynamic Jahn-Teller Effect in the Metastable High-Spin State of Solvated  $[\text{Fe}(\text{terpy})_2]^{2+}$**   
X. Zhang, L. M. Lawson Daku, J. Zhang, K. Suarez-Alcantara, G. Jennings, C. A. Kurtz and S. E. Canton  
The Journal of Physical Chemistry C **119** (6) (2015), p3312-3321 DOI:10.1021/jp5117068

Characterizing structural distortions in the metastable spin states of  $d^4\text{e}^-d^0$  transition metal ion complexes is crucial to understand the nature of their bistability and eventually control their switching dynamics. In particular, the impact of the Jahn-Teller effect needs to be assessed for any electronic configuration that could be effectively degenerate, as in e.g. the high-spin (HS) manifold of highly symmetric homoleptic  $\text{Fe}^{\text{II}}$  complexes. However, capturing its manifestations remains challenging since crystallization generally alters the molecular conformations and their interconversion. With the rapid progress of ultrafast X-ray absorption spectroscopy, it is now possible to collect data with unprecedented signal-to-noise ratio, opening up for detailed structural characterization of transient species in the homogeneous solution phase. By combining the analysis of picosecond X-ray absorption spectra with DFT simulations, the structure of the photoinduced HS state is elucidated for solvated  $[\text{Fe}(\text{terpy})_2]^{2+}$  (terpy = 2,2',6'-terpyridine). This species can be viewed as the average  $D_2$  structure in  $A_2$  symmetry that originates from a dynamic Jahn-Teller effect in the HS manifold. These results evidence the active role played by this particular instance of vibronic coupling in the formation of the HS state for this benchmark molecule. Ultimately, correlating the interplay between intramolecular and intermolecular degrees of freedom to conformational strain and distortions in real time should contribute to the development of advanced functionalities in transition metal ion complexes.

- **On the Role of Ligand-Field States for the Photophysical Properties of Ruthenium(II) Polypyridyl Complexes**  
Qinchao Sun, Sandra Mosquera-Vazquez, Yan Suffren, Jihane Hankache, N. Amstutz, Latévi Max Lawson Daku, Eric Vauthey and Andreas Hauser  
Coordination Chemistry Reviews **282-283** (2015), p87-99 DOI:10.1016/j.ccr.2014.07.004  
Keywords: Ruthenium(II) polypyridyl complexes • ligand-field states • luminescence quenching • photophysical properties • high-pressure

The role of ligand-field states for the photophysical properties of  $d^6$  systems has been discussed in a large number of publications over the past decades. Since the seminal paper by Houten and Watts, for instance, the quenching of the  $^3\text{MLCT}$  luminescence in ruthenium(II) polypyridyl complexes is attributed to the presence of the first excited ligand-field state, namely a component of the  $^3T_1(t_2g^5e_g)$  state, at similar energies. If this state lies above the  $^3\text{MLCT}$  state, the luminescence is quenched via thermal population at elevated temperatures only. If it lies well below, then the luminescence is quenched down to cryogenic temperatures. In this contribution we present transient absorption spectra on non-luminescent ruthenium polypyridyl complexes such as  $[\text{Ru}(\text{m-bpy})_3]^{2+}$ , m-bpy = 6-methyl-2,2'-bipyridine, in acetonitrile at room temperature, which reveal an ultra-rapid depopulation of the  $^3\text{MLCT}$  state but a much slower ground state recovery. We propose that in this and related complexes the methyl groups force longer metal-ligand bond lengths, thus resulting in a lowering of the ligand-field strength such that the  $^3\text{dd}$  state drops to below the  $^3\text{MLCT}$  state, and that furthermore the population of this state from the  $^3\text{MLCT}$  state occurs faster than its decay to the ground state. In addition we demonstrate that in this complex the luminescence can be switched on by external pressure, which we attribute to a destabilisation of the ligand-field state by the pressure due to its larger molecular volume compared to the ground state as well as the  $^3\text{MLCT}$  state.

## 2014

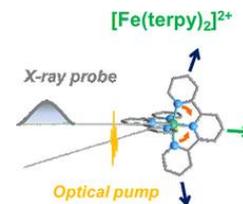


- **Where does the Raman optical activity of  $[\text{Rh}(\text{en})_3]^{3+}$  come from? Insight from a combined experimental and theoretical approach**  
Marie Humbert-Droz, Patric Oulevey, Latévi Max Lawson Daku, Sandra Luber and Hans Hagemann and Thomas Bürgi  
Phys. Chem. Chem. Phys. **16** (42) (2014), p23260-23273 DOI:10.1039/C4CP02145B

Backscattered Raman optical activity (ROA) spectra are measured for  $\text{[Rh(en)}_3\text{]}^{3+}$  and  $\text{[Rh(en)}_2\text{py)}_2\text{]}^{3+}$  tris-(ethylenediamine)rhodium(III) chloride in aqueous solution. In addition, the spectra of the four possible conformers in the  $\text{[Rh(en)}_3\text{]}^{3+}$  configuration are investigated *ab initio* calculations. The  $\text{[Rh(en)}_3\text{]}^{3+}$  conformer is in best agreement with experimental spectra and examined in more details. The two most stable conformers according to the calculations are not compatible with the experimental ROA spectrum. Insights into the origin of observed band intensities are obtained by means of group coupling matrices. The influence of the first solvation shell is explored *via* *ab initio* molecular dynamics simulation. Taking explicit solvent molecules into account further improves the agreement between calculation and experiment. Analysis of selected normal modes using group coupling matrices shows that solvent molecules lead to normal mode rotation and thus contribute to the ROA intensity, whereas the contribution of the Rh can be neglected.

- *Probing the Anisotropic Distortion of Photoexcited Spin Crossover Complexes with Picosecond X-ray Absorption Spectroscopy*

Sophie E. Canton, Xiaoyi Zhang, Latévi M. Lawson Daku, Amanda L. Smeigh, Jianxin Zhang, Yizhu Liu, Carl-Johan Wallentin, Klaus Attenkofer, Guy Jennings, Charles A. Kurtz, David Gosztola, Kenneth Wärnmark, Andreas Hauser and Villy Sundström  
Journal of Physical Chemistry C **118** (8) (2014), p4536-4545 DOI:10.1021/jp5003963



For numerous spin crossover complexes, the anisotropic distortion of the first coordination shell around the transition metal center governs the dynamics of the high-spin/lowspin interconversion. However, this structural parameter remains elusive for samples that cannot be investigated with crystallography. The present work demonstrates how picosecond X-ray absorption spectroscopy is able to capture this specific deformation in the photoinduced high-spin state of solvated [Fe(terpy)<sub>2</sub>]<sup>2+</sup>, a complex which belongs to the prominent family of spin crossover building blocks with nonequivalent metal-ligand bonds. The correlated changes in Fe-N<sub>axial</sub>, Fe-N<sub>distal</sub>, and bite angle N<sub>distal</sub>-Fe-N<sub>axial</sub> extracted from the measurements are in very good agreement with those predicted by DFT calculations in D<sub>2d</sub> symmetry. The outlined methodology is generally applicable to the characterization of ultrafast nuclear rearrangements around metal centers in photoactive molecular complexes and nanomaterials, including those that do not display long-range order.

## 2013

- *Modeling Transition Metal Complexes in the Framework of the Spin-Crossover Phenomenon: a DFT Perspective*

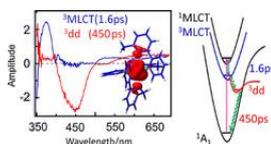
Latevi Max Lawson Daku  
Current Inorganic Chemistry **3** (3) (2013), p242-259 DOI:10.2174/1877944103666140110231029  
Keywords: density functional theory • spin crossover • transition metal complexes

Using the study of the low-spin complex [Fe(bpy)<sub>3</sub>]<sup>2+</sup> in the gas phase and in condensed phases as a guideline, we examine different aspects of the application of DFT to the study of transition metal complexes in the framework of spin crossover or related phenomena.

- *Crystal structure solution of an elusive polymorph of Dibenzylsquaramide*

Anna Portell, Xavier Alcobé, Latévi M. Lawson Daku and Radovan Cerny and Rafel Prohens  
Powder Diffraction **28** (S2) (2013), p470-480 DOI:10.1017/S0885715613000821  
Keywords: dibenzylsquaramide • crystal structure • X-ray powder diffraction

The crystal structure of the third polymorph of dibenzylsquaramide (Portell, A. *et al.*, 2009) (fig. 1) has been determined from laboratory X-ray powder diffraction data by means of direct space methods using the computing program FOX. (Favre-Nicolin and ACernA, 2002) The structure resolution has not been straightforward due to several difficulties on the indexing process and in the space group assignment. The asymmetric unit contains two different conformers, which has implied an additional difficulty during the Rietveld (Rietveld, 1969) refinement. All these issues together with particular structural features of disquaramides are discussed.



- *Experimental Evidence of Ultrafast Quenching of the <sup>3</sup>MLCT Luminescence in Ruthenium(II) Tris-bipyridyl Complexes via a <sup>3</sup>dd State*

Qinchoo Sun, Sandra Mosquera-Vazquez, Latevi Max Lawson Daku, Laure Guénée, Harold A. Goodwin, Eric Vauthey and Andreas Hauser  
Journal of the American Chemical Society **135** (37) (2013), p13660-13663 DOI:10.1021/ja407225t

Ultrafast transient absorption spectroscopy serves to identify the <sup>3</sup>dd state as intermediate quencher state of the <sup>3</sup>MLCT luminescence in the non-luminescent ruthenium complexes [Ru(m-bpy)<sub>3</sub>]<sup>2+</sup> (m-bpy = 6-methyl-2,2'-bipyridine) and [Ru(tm-bpy)<sub>3</sub>]<sup>2+</sup> (tm-bpy = 4,4'-dimethyl-6,6'-tetramethyl-2,2'-bipyridine). For [Ru(m-bpy)<sub>3</sub>]<sup>2+</sup>, the population of the <sup>3</sup>dd state from the <sup>3</sup>MLCT state occurs within 1.6 ps, while the return to the ground state takes 450 ps. For [Ru(tm-bpy)<sub>3</sub>]<sup>2+</sup>, the corresponding values are 0.16 and 7.5 ps, respectively. According to DFT calculations, methyl groups added in the 6 and 6' positions of bipyridine stabilize the <sup>3</sup>dd state by  $\sim 4000 \text{ cm}^{-1}$  each, compared to [Ru(bpy)<sub>3</sub>]<sup>2+</sup>.

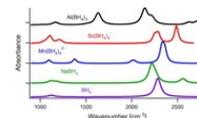
- *A modified cyclen azaxanthone ligand as a new fluorescent probe for Zn<sup>2+</sup>*

Hela Nouri, Cyril Cadiou, Latevi Max Lawson Daku, Andreas Hauser, Sylviane Chevreux, Isabelle Déchamps-Olivier, Fabien Lachaud, Riadh Ternane, Malika Trabelsi-Ayadi, Françoise Chuburu and Gilles Lemerrier  
Dalton Transactions **42** (2013), p12157-12164 DOI:10.1039/c3dt51216a

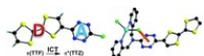
A new cyclen derivative, bearing a methyl-chromeno-pyridinylidene hydrazone moiety, was synthesized and studied in MeOH, as potential fluorescent OFF-on-ON sensors for Zn(II). Photophysical properties of this ligand being PET regulated, fluorescence was only weakly emissive in the absence of metal ions (OFF). Fluorescence was increased modestly upon addition of one equivalent of Zn(II), and further increased upon addition of a second equivalent. Therefore, ZnL behaved as a highly sensitive ON sensor for zinc. This efficiency was correlated to Zn(II) coordination via the hydrazone moiety of the fluorophore, producing an efficient Chelation-Enhanced Fluorescence (CHEF) effect. A complementary theoretical study carried out with DFT calculations further elucidated of the optical properties.

- *Vibrational spectra and structure of borohydrides*

Vincenza D'Anna and Latévi Max Lawson Daku and Hans Hagemann  
Journal of Alloys and Compounds **580** (S1) (2013) DOI:10.1016/j.jallcom.2013.01.112  
Keywords: hydrogen storage • vibrational spectra • borohydrides • FG method



A comparison of the vibrational spectra of many inorganic borohydrides allows us to distinguish compounds with isolated BH<sub>4</sub><sup>-</sup> ions and compounds containing complex ions such as Sc(BH<sub>4</sub>)<sub>4</sub><sup>-</sup>. The characteristic spectral features of both types of compounds are identified, showing that the B-H bonding is quite different in both cases. A detailed analysis of the vibrations of the isolated BH<sub>4</sub><sup>-</sup> ions provides new information about their local structure. Angular deformations of individual borohydride ion are analyzed quantitatively. It appears that the compounds containing isolated BH<sub>4</sub><sup>-</sup> ions belong to those with the most electropositive cations and the highest decomposition temperature, while the complex borohydrides show significantly lower decomposition temperatures and possible diborane formation.



- *Tetrathiafulvalene-s-tetrazine: versatile platform for donor-acceptor systems and multifunctional ligands*
- Flavia Pop, Jie Ding, Latévi Max Lawson Daku, Andreas Hauser and Narcis Avarvari  
RSC Advances **3** (2013), p3218-3221 DOI:10.1039/c3ra21702g

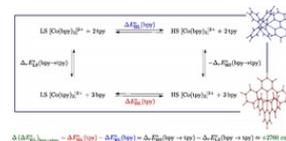
The structurally characterized tetrathiafulvalene-1,2,4,5-tetrazine donor-acceptor system shows redox tuneable intramolecular charge transfer, solvatochromic and electrochromic behaviour. Attachment of a dipicolyl-amine chelating unit affords a multifunctional ligand, which allows the preparation of the ZnCl<sub>2</sub> complex in which an anion-π interaction is seen.

- **Towards accurate estimates of the spin-state energetics of spin-crossover complexes within density functional theory: a comparative case study of cobalt(II) complexes**

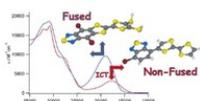
Alfredo Vargas, Itana Krivokapic, Andreas Hauser and Latévi Max Lawson Daku

Physical Chemistry Chemical Physics **15** (11) (2013), p3752-3763

DOI:10.1039/c3cp44336a



We report a detailed DFT study of the energetic and structural properties of the spin-crossover Co(II) complex  $[Co(tpy)_2]^{2+}$  ( $tpy = 2, 2\text{-}\epsilon\text{-}\text{6}\text{-}\epsilon\text{-}\text{2}\text{-}\text{2}\text{-}\epsilon\text{-}\text{2}\text{-}\text{terpyridine}$ ) in the low-spin (LS) and the high-spin (HS) states, using several generalized gradient approximation and hybrid functionals. In either spin-state, the results obtained with the functionals are consistent with one another and in good agreement with available experimental data. Although the different functionals correctly predict the LS state as the electronic ground state of  $[Co(tpy)_2]^{2+}$ , they give estimates of the HS $\leftrightarrow$ LS zero-point energy difference  $\hat{I}^{\text{E}}_{\text{HL}}$  (tpy)  $\text{\AA}$  which strongly depend on the functional used. This dependency on the functional was also reported for the DFT estimates of the zero-point energy difference  $\hat{I}^{\text{E}}_{\text{HL}}$  (bpy)  $\text{\AA}$  in the HS complex  $[Co(bpy)_3]^{2+}$  ( $bpy = 2, 2\text{-}\epsilon\text{-}\text{2}\text{-}\text{bipyridine}$ ) [A. Vargas, A. Hauser and L. M. Lawson Daku, *J. Chem. Theory Comput.*, 2009, **5**, 97]. The comparison of the  $\hat{I}^{\text{E}}_{\text{HL}}$  (tpy)  $\text{\AA}$  and  $\hat{I}^{\text{E}}_{\text{HL}}$  (bpy)  $\text{\AA}$  estimates showed that all functionals correctly predict an increase of the zero-point energy difference upon the bpy  $\hat{\rightarrow}$  tpy ligand substitution, which furthermore weakly depends on the functionals, amounting to  $(\hat{I}^{\text{E}}_{\text{HL}})_{\text{bpy}\rightarrow\text{tpy}} \hat{\approx} +2670 \text{ cm}^{-1} \text{\AA}$ . From these results and basic thermodynamic considerations, we establish that, despite their limitations, current DFT methods can be applied to the accurate determination of the spin-state energetics of complexes of a transition metal ion, or of these complexes in different environments, provided that the spin-state energetics is accurately known in one case. Thus, making use of the availability of a highly accurate *ab initio* estimate of the HS $\leftrightarrow$ LS energy difference in the complex  $[Co(NCH)_6]^{2+}$  [L. M. Lawson Daku, F. Aquilante, T. W. Robinson and A. Hauser, *J. Chem. Theory Comput.*, 2012, **8**, 4216], we obtain for  $[Co(tpy)_2]^{2+}$  and  $[Co(bpy)_3]^{2+}$  best estimates of  $\hat{I}^{\text{E}}_{\text{HL}}$  (bpy)  $\hat{\approx} -2800 \text{ cm}^{-1} \text{\AA}$  and  $\hat{I}^{\text{E}}_{\text{HL}}$  (tpy)  $\hat{\approx} 0 \text{ cm}^{-1} \text{\AA}$ , in good agreement with the known magnetic behaviour of the two complexes.



- **Tetrathiafulvalene-Benzothiadiazoles as Redox-Tunable Donor-Acceptor Systems: Synthesis and Photophysical Study**

Flavia Pop, Anneliese Amacher, Narcis Avarvari, Jie Ding, Latevi Max Lawson Daku, Andreas Hauser, Marius Koch, Jürg Hauser and Shi-Xia Liu and Silvio Decurtins

Chemistry - A European Journal **19** (7) (2013), p2504-2514

DOI:10.1002/chem.201202742

Keywords: charge transfer • donor-acceptor systems • fluorescence • photophysics • redox chemistry

Electrochemical and photophysical analysis of new donor $\leftrightarrow$ acceptor systems **2**  $\hat{\text{A}}$  and **3**, in which a benzothiadiazole (BTD) unit is covalently linked to a tetrathiafulvalene (TTF) core, have verified that the lowest excited state can be ascribed to an intramolecular-charge-transfer (ICT)  $\hat{I}^{\text{E}}(\text{TTF})\hat{\rightarrow}^{\text{BTD}}$  (benzothiadiazole) transition. Owing to better overlap of the HOMO and LUMO in the fused scaffold of compound **3**, the intensity of the  $\hat{I}^{\text{E}}$  ICT band is substantially higher compared to that in compound **2**. The corresponding CT fluorescence is also observed in both cases. The radical cation  $\text{TTF}^{\cdot+}$  is easily observed through chemical and electrochemical oxidation by performing steady-state absorption experiments. Interestingly, compound **2**  $\hat{\text{A}}$  is photo-oxidized under aerobic conditions.

## 2012

- **Accurate Spin-State Energetics of Transition Metal Complexes: I. CCSD(T), CASPT2 and DFT Study of  $[M(\text{NCH})_6]^{2+}$  ( $M = \text{Fe}, \text{Co}$ )**

Latevi Max Lawson Daku, Francesco Aquilante, Timothy William Robinson and Andreas Hauser

Journal of Chemical Theory and Computation **8** (11) (2012), p4216-4231

DOI:10.1021/ct300592w

Highly accurate estimates of the high-spin/low-spin energy difference  $\hat{I}^{\text{E}}_{\text{HL}}$  in the high-spin complexes  $[\text{Fe}(\text{NCH})_6]^{2+}$   $\hat{\text{A}}$  and  $[\text{Co}(\text{NCH})_6]^{2+}$   $\hat{\text{A}}$  have been obtained from the results of CCSD(T) calculations extrapolated to the complete basis set limit. These estimates are shown to be strongly influenced by scalar relativistic effects. They have been used to assess the performances of the CASPT2 method and of 30 density functionals of the GGA, meta-GGA, global hybrid, RSH and double-hybrid types. For the CASPT2 method, the results of the assessment support the proposal [Kepenekian, M.; Robert, V.; Le Guennic, B. *J. Chem. Phys.* 2009, **131**, 114702] that the ionization potential $\leftrightarrow$ electron affinity (IPEA) shift defining the zeroth-order Hamiltonian be raised from its standard value of 0.25 au to 0.50 $\hat{\approx}$ 0.70 au for the determination of  $\hat{I}^{\text{E}}_{\text{HL}}$  in Fe(II) complexes with a  $[\text{FeN}_6]$  core. At the DFT level, some of the assessed functionals proved to perform within chemical accuracy ( $\hat{\pm}350 \text{ cm}^{-1}$ ) for the spin-state energetics of  $[\text{Fe}(\text{NCH})_6]^{2+}$ , others for that of  $[\text{Co}(\text{NCH})_6]^{2+}$ , but none of them simultaneously for both complexes. As demonstrated through a reparametrization of the CAM-PBE0 range-separated hybrid, which led to a functional that performs within chemical accuracy for the spin-state energetics of both complexes, performing density functionals of broad applicability may be devised by including in their training sets highly accurate data like those reported here for  $[\text{Fe}(\text{NCH})_6]^{2+}$   $\hat{\text{A}}$  and  $[\text{Co}(\text{NCH})_6]^{2+}$ .

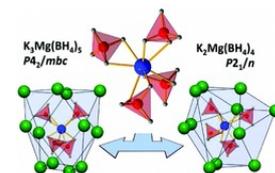
- **Bimetallic Borohydrides in the System  $M(\text{BH}_4)_2\text{-KBH}_4$  ( $M = \text{Mg}, \text{Mn}$ ): On the Structural Diversity**

Pascal Schouwink, Vincenza D'Anna, Morten Brix Ley, Latévi Max Lawson Daku, Bo Richter, Torben R.

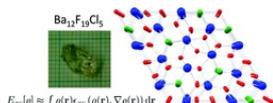
Jensen and Hans Hagemann and Radovan Cerný

The Journal of Physical Chemistry C **116** (20) (2012), p10829-10840

DOI:10.1021/jp212318s



Four novel bimetallic borohydrides have been discovered,  $K_2M(\text{BH}_4)_4$  ( $M = \text{Mg}$  or  $\text{Mn}$ ),  $K_3\text{Mg}(\text{BH}_4)_5$ , and  $\text{KMn}(\text{BH}_4)_3$ , and are carefully investigated structurally as well as regarding their decomposition reaction mechanism by means of in situ synchrotron radiation powder X-ray diffraction (SR-PXD), vibrational spectroscopies (Raman and IR), thermal analysis (TGA and DTA), and *ab initio* density functional theory (DFT) calculations. Mechano-chemical synthesis (ball-milling) using the reactants  $\text{KBH}_4$ ,  $\hat{\pm}\text{-Mg}(\text{BH}_4)_2$ , and  $\hat{\pm}\text{-Mn}(\text{BH}_4)_2$  ensures chlorine-free reaction products. A detailed structural analysis reveals significant similarities as well as surprising differences among the two isomorphs  $K_2M(\text{BH}_4)_4$ , most importantly concerning the extent to which the complex anion  $[M(\text{BH}_4)_4]^{2-}$  is isolated in the structure. Anisotropic thermal expansion and an increase in symmetry at high temperatures in  $K_3\text{Mg}(\text{BH}_4)_5$  is ascribed to the motion of  $\text{BH}_4$   $\hat{\text{A}}$  groups inducing hydrogen repulsive effects, and the dynamics of  $K_3\text{Mg}(\text{BH}_4)_5$  are investigated. Decomposition in the manganese system proceeds via the formation of  $\text{KMn}(\text{BH}_4)_3$ , the first perovskite type borohydride reported to date.



- **Crystal chemistry in the barium fluoride chloride system**

Hans Hagemann, Vincenza D'Anna and Latevi Max Lawson Daku and Frank Kubel

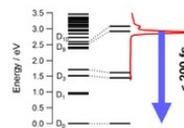
Crystal Growth & Design **12** (3) (2012), p1124-1131

DOI:10.1021/cg201588s

The crystal chemistry of the barium fluoride chloride system is studied both experimentally and theoretically. Different synthetic approaches yield nanocrystalline materials as well as large single crystals. The crystalline phases identified so far are  $\text{BaFCl}$ ,  $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$  and  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$  (in two modifications) and compared with analogous compounds. It is demonstrated that the compound  $\text{Ba}_2\text{F}_3\text{Cl}$  reported by Fessenden and Lewin 50 years ago corresponds to  $\text{Ba}_7\text{F}_{12}\text{Cl}_2$ . The phase diagram of the  $\text{BaCl}_2$   $\hat{\text{A}}$   $\text{BaF}_2$  system is reinvestigated for fluoride mole fractions between 0.5 and 1. The peritectic formation of  $\text{Ba}_{12}\text{F}_{19}\text{Cl}_5$  is observed. Periodic DFT calculations are performed for all structures in this system, including a hypothetical structure for  $\text{Ba}_2\text{F}_3\text{Cl}$ , based on the experimental structure of  $\text{Ba}_2\text{H}_3\text{Cl}$ . The energy of formation of the different barium fluoride chloride compounds from  $\text{BaCl}_2$  and  $\text{BaF}_2$  (normalized for one barium atom per formula unit), as calculated by DFT at 0K, is within only about  $\hat{\pm} 15 \text{ kJ/mol}$ . Comparison with recent experimental results on calcium and strontium hydride chloride (bromide) compounds, suggest the possibility of a mutual exclusion between the  $\text{M}_2\text{X}_3\text{Y}$  and  $\text{M}_7\text{X}_{12}\text{Y}_2$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}, \text{X} = \text{H}, \text{F}, \text{Y} = \text{Cl}, \text{Br}$ ) structures. The single crystal structure of  $\text{PbFBr}$  is also reported.

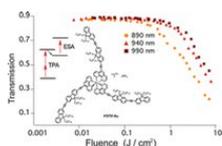
• *Photophysics of Galvinoxyl Free Radical Revisited*

Jakob Grilj, Cedric Zonca and Latevi Max Lawson Daku and Eric Vauthey  
 Physical Chemistry Chemical Physics **14** (2012), p6351-6358 DOI:10.1039/c2cp23577c



The photophysical properties of the free neutral radical galvinoxyl were studied by a combination of femtosecond time-resolved spectroscopy and quantum chemical calculations. The electronic absorption spectrum is dominated by an intense band at 430 nm that is ascribed to the D<sub>9,10</sub>†•D<sub>0</sub> transitions. Upon photoexcitation at 400 nm, the population of the D<sub>9,10</sub> states decays within less than 200 fs to the electronic ground state. This ultrafast internal conversion does not involve intramolecular modes with large amplitude motion as the measured dynamics does not show any significant dependence on the environment, but is most probably facilitated by a high density of electronic states of different character. Depending on the solvent, a weak transient band due to the galvinoxylate anion is also observed. This closed-shell species, which is fluorescent although its deactivation is also dominated by non-radiative decay, is generated upon biphotonic ionization of the solvent and electron capture. The ultrashort excited-state lifetime of the galvinoxyl radical precludes photoinduced disproportionation previously claimed to be at the origin of the formation of both anion and cation.

2011

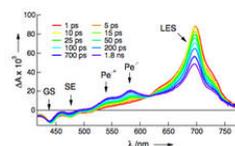


- *A novel ruthenium(ii) complex for two-photon absorption-based optical power limiting in the near-IR range*  
 Mickaël Four, Didier Riehl, Olivier Mongin, Mireille Blanchard-Desce, Latévi Max Lawson Daku, Juliette Moreau, Jérôme Chauvin and Jacques A. Delaire and Gilles Lemerrier  
 Physical Chemistry Chemical Physics **13** (38) (2011), p17304-17312 DOI:10.1039/c1cp21661a

In this article, the synthesis of a novel high-conjugated ligand and its corresponding Ru(II) complex PTTF:Ru is reported, along with the linear and nonlinear optical characterizations. Two-photon absorption based optical power limiting properties (OPL), especially in the near infrared, are described and compared to those of the analogous complexes previously published. Combined with a preliminary theoretical approach, this allows us to highlight several key parameters for OPL optimization in such molecular systems and more particularly the spectral overlap between TPA and excited-state absorption.

• *Photoinduced Symmetry-Breaking Charge Separation: The Direction of the Charge Transfer*

Vesna Markovic, Diego Villamaina, Igor Barabanov, Latevi Max Lawson Daku, and Eric Vauthey  
 Angewandte Chemie International Edition **50** (33) (2011), p7596-7598 DOI:10.1002/anie.201102601



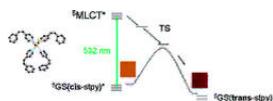
Even flow: Photoinduced symmetry-breaking charge separation takes place in a few picoseconds in a 1,3-bis(perylene)propane dyad in polar solvents. Polarized transient absorption measurements show that the direction of the charge flow is random and entirely governed by the fluctuations of the solvent orientation around the dyad.

• *Structural and vibrational properties of Ca<sub>2</sub>FeH<sub>6</sub> and Sr<sub>2</sub>RuH<sub>6</sub>*

H. Hagemann, V. D'Anna, L.M. Lawson Daku, S. Gomes, G. Renaudin, and K. Yvon  
 Journal of Physics and Chemistry of Solids **72** (2011), p286-289 DOI:10.1016/j.jpcs.2011.01.001  
 Keywords: hydrogen storage materials • DFT calculations • lattice vibrations

The structural and vibrational properties of the isostructural compounds Ca<sub>2</sub>FeH<sub>6</sub> and Sr<sub>2</sub>RuH<sub>6</sub> are determined by periodic DFT calculations and compared with their previously published experimental crystal structures as well as new experimental vibrational data. The analysis of the vibrational data is extended to the whole series of alkaline-earth iron and ruthenium hydrides A<sub>2</sub>TH<sub>6</sub> (A = Mg, Ca, Sr; T = Fe, Ru) in order to identify correlations between selected frequencies and the T-H bond length. The bulk moduli of Ca<sub>2</sub>FeH<sub>6</sub> and Sr<sub>2</sub>RuH<sub>6</sub> have also been determined within DFT. Their calculated values prove to compare well with the experimental values reported for Mg<sub>2</sub>FeH<sub>6</sub> and several other compounds of this structure.

2010

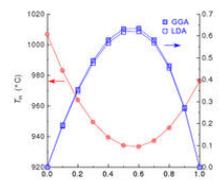


- *Unidirectional Photoisomerization of Styrylpyridine for Switching the Magnetic Behavior of an Iron(II) Complex: A MLCT Pathway in Crystalline Solids*  
 Antoine Tissot, Marie-Laure Boillot, Sébastien Pillet, Epiphane Codjovi, Kamel Boukheddaden, and Latévi Max Lawson Daku  
 Journal of Physical Chemistry C **114** (49) (2010), p21715-21722 DOI:10.1021/jp106583f

The photoreactivity of two iron(II) styrylpyridine frameworks Fe(stpy)<sub>4</sub>(NCSe)<sub>2</sub> (stpy = 4-styrylpyridine) has been investigated for the very first time in a crystalline solid. A quantitative cis-to-trans isomerization of stilbenoids is shown to occur in the confined environment of the inorganic solid. The photochromic reaction was driven by a visible excitation into the metal-to-ligand charge transfer absorption of the high-spin all-cis complex. The solid-state transformation is accompanied by a unit-cell volume increase and an amorphization. Interestingly, the photoproduct formed by irradiating the high-spin all-cis reactant undergoes a spin conversion when the temperature is decreased. This observation is related to the ligand-driven light-induced spin change effect in a constrained environment.

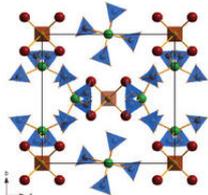
• *Ionic layered BaFCl and Ba<sub>1-x</sub>Sr<sub>x</sub>FCl compounds: Physical- and chemical-pressure effects*

Vincenza D'Anna, Latévi Max Lawson Daku, Hans Hagemann and Frank Kubel  
 Physical Review B **82** (2) (2010), p24108 DOI:10.1103/PhysRevB.82.024108



The effect on crystal structure and vibrational frequencies of physical pressure in BaFCl and chemical pressure in Ba<sub>1-x</sub>Sr<sub>x</sub>FCl solid solutions is studied using periodic density-functional theory (DFT) calculations performed within the local-density approximation (LDA) and the generalized gradient approximation (GGA). These results are compared with previously published experimental data for BaFCl in conjunction with new experimental data for Ba<sub>1-x</sub>Sr<sub>x</sub>FCl and show overall a good agreement with experiment. The GGA method outperforms the LDA method for the description of BaFCl under pressure. However, the two DFT methods perform equally well for the description of the solid solutions, which have been studied within the virtual-crystal approximation. They also give consistent values of the energy of formation of Ba<sub>1-x</sub>Sr<sub>x</sub>FCl, which can be correlated with the experimentally observed melting points. The comparison of the calculated mode Grüneisen parameters shows that, for the investigated systems, the effect of the chemical pressure and that of the

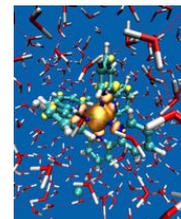
physical pressure are not identical.



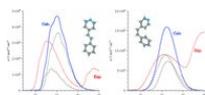
- *Al<sub>3</sub>Li<sub>4</sub>(BH<sub>4</sub>)<sub>13</sub>: A Complex Double-Cation Borohydride with a New Structure*  
Inge Lindemann, Roger Domènech Ferrer, Lothar Dunsch, Yaroslav Filinchuk, Radovan Cerný, Hans Hagemann, Vincenza D'Anna, Latévi Max Lawson Daku, Ludwig Schultz, Oliver Gutfleisch  
Chemistry - A European Journal **16** (2010), p8707-8712 DOI:10.1002/chem.201000831  
Keywords: borohydrides • density functional calculations • hydrogen storage • metathesis • X-ray diffraction

The new double-cation Al-Li-borohydride is an attractive candidate material for hydrogen storage due to a very low hydrogen desorption temperature (~70 Å°C) combined with a high hydrogen density (17.2Å wtÅ %). It was synthesised by high-energy ball milling of AlCl<sub>3</sub> and LiBH<sub>4</sub>. The structure of the compound was determined from image-plate synchrotron powder diffraction supported by DFT calculations. The material shows a unique 3D framework structure within the borohydrides (space group=*P*-43*n*, *a* =11.3640(3)Å...). The unexpected composition Al<sub>3</sub>Li<sub>4</sub>(BH<sub>4</sub>)<sub>13</sub> can be rationalized on the basis of a complex cation [(BH<sub>4</sub>)Li<sub>4</sub>]<sup>3+</sup> and a complex anion [Al(BH<sub>4</sub>)<sub>4</sub>]<sup>-</sup>. The refinements from synchrotron powder diffraction of different samples revealed the presence of limited amounts of chloride ions replacing the borohydride on one site. In situ Raman spectroscopy, differential scanning calorimetry (DSC), thermogravimetry (TG) and thermal desorption measurements were used to study the decomposition pathway of the compound. Al-Li-borohydride decomposes at ~70Å Å°C, forming LiBH<sub>4</sub>. The high mass loss of about 20Å % during the decomposition indicates the release of not only hydrogen but also diborane.

- *Ab Initio Molecular Dynamics Study of an Aqueous Solution of [Fe(bpy)<sub>3</sub>](Cl)<sub>2</sub> in the Low-Spin and in the High-Spin States*  
Latévi Max Lawson Daku and Andreas Hauser  
Journal of Physical Chemistry Letters **1** (2010), p1830-1835 DOI:10.1021/jz100548m



The mechanism of the photoinduced low-spin<sup>+</sup> high-spin spin crossover is actively being investigated in Fe(II) complexes in solution using ultrafast spectroscopies. These studies accurately inform on the reaction coordinate of the Fe(II) chromophore upon photoexcitation. However, they leave open questions regarding the role of the solvent. Here, we report the description from a fully ab initio molecular dynamics study of the structure of [Fe(bpy)<sub>3</sub>]<sup>2+</sup> in water and of the organization of its solvation shell in the low-spin and the high-spin states. In particular, the low-spin<sup>+</sup> high-spin change of states is shown to be accompanied (i) by a 0.191 Å... lengthening of the Fe<sup>+</sup>N bond, in agreement with experiment, and (ii) by an increased thermal fluctuation of the molecular edifice, which both result from the weakening of the Fe<sup>+</sup>N bond. Furthermore, our results suggest that about two water molecules are expelled from the first solvation shell of [Fe(bpy)<sub>3</sub>]<sup>2+</sup>, which consists of water molecules intercalated between the bpy ligands.

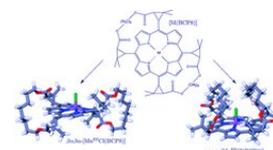


- *Ab initio static and molecular dynamics study of the absorption spectra of the 4-styrylpyridine photoswitch in its cis and trans forms*  
Latévi Max Lawson Daku, Jorge Linares and Marie-Laure Boillot  
Physical Chemistry Chemical Physics **12** (2010), p6107-6123 DOI:10.1039/b920850j

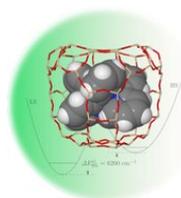
We report a thorough investigation of the absorption spectra of the *cis* and *trans* isomers of the 4-styrylpyridine photoswitch based on TDDFT calculations. The spectra of both isomers were analysed first from the results of excitation calculations performed on their optimised geometries. The main absorption band of the *cis* isomer is thus predicted to be due to the S<sup>+</sup><sub>1</sub> S<sub>1</sub> and S<sup>+</sup><sub>2</sub> S<sub>2</sub> transitions, while the main absorption band of the *trans* isomer is predicted to originate exclusively from the S<sup>+</sup><sub>1</sub> S<sub>1</sub> transition. The convolution of the calculated oscillator strengths with Gaussians helped mimic the broadening of the electronic transitions. However, it proved necessary to use Gaussians with a large full width at half maximum of 5000 cm<sup>-1</sup>; and, compared to experiment, the calculated main absorption bands of the two isomers are significantly red-shifted and far too symmetric. Consequently, as required for the detailed analysis of the finite-temperature absorption spectrum of a molecule as flexible as 4-styrylpyridine, the influence of the thermal fluctuations has been taken into account by calculating the spectra as time averages over Car<sup>+</sup>Parrinello molecular dynamics trajectories. For both isomers, this led to a noticeable improvement in the relative positions of the calculated and experimental main absorption bands, and the asymmetry of the calculated bands brings them in better agreement with the experimental ones. Furthermore, these last results show that, actually, the S<sup>+</sup><sub>1</sub> S<sub>1</sub> and S<sup>+</sup><sub>2</sub> S<sub>2</sub> transitions both contribute significantly to the finite-temperature main absorption bands of the two isomers. Finally, in order to also take the vibrational broadening into account, the Franck-Condon factors of the relevant vibrations were calculated within the displaced harmonic oscillator approximation. By thus taking both the thermal and the vibrational broadening into account for the calculation of the absorption bands, the agreement between experiment and theory could be further improved.

## 2009

- *Density-Functional Theory Study of the Stereochemistry of Chloroiron(III) and Chloromanganese(III) Complexes of a Bridled Chirophyrin*  
Latévi Max Lawson Daku, Anna Castaings and Jean-Claude Marchon  
Inorganic Chemistry **48** (12) (2009), p5164-5176 DOI:10.1021/ic900031c

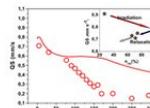


Transition metal complexes of chirophyrins, in which two adjacent meso substituents are linked by a strap of eightmethylene groups, [M(BCP8)], can exist as either an  $\pm 1 \pm 1 \pm 1 \pm 1$  or  $\pm 1^2 \pm 1^2$  atropisomer depending on the nature of the coordinated metal cation. This remarkable conformational versatility was investigated by density-functional theory calculations for the d<sup>6</sup> chloroiron(III) complex in the low-spin and high-spin states and for the d<sup>5</sup> high-spinchloromanganese(III) complex. The lowest-lying electronic state of all of the conformers of the chloroiron(III) bridledchirophyrin is found to be the high-spin state. For the chloroiron(III) complex in the low-spin or the high-spin state and for the high-spin chloromanganese(III) complex, the most stable form is predicted to be the  $\pm 1 \pm 1 \pm 1 \pm 1$  conformer in which the chloride axial ligand is located within the cavity provided by the bridles. The predicted stereochemistries are compared with those similarly obtained (i) for the chloroiron(III) and chloromanganese(III) complexes of the tetramethylchirophyrin, which is devoid of straps, and (ii) for the d<sup>10</sup> zinc(II) and low-spin d<sup>8</sup> nickel(II) BCP8 complexes, on the basis of the effects tied to the occupancy of the stereochemically active d<sub>x<sup>2</sup>-y<sup>2</sup></sub>-type antibondingorbital level, to the restraints imposed by the straps, and to the presence of the axial chloride ligand.



- *Influence of Guest-Host Interactions on the Structural, Energetic, and M<sup>+</sup>ssbauer Spectroscopy Properties of Iron(II)tris(2,2'-bipyridine) in the Low-Spin and High-Spin States: A Density-Functional Theory Study of the Zeolite-Y Embedded Complex*  
Alfredo Vargas, Andreas Hauser and Latévi Max Lawson Daku  
Journal of Chemical Theory and Computation **5** (1) (2009), p97-115 DOI:10.1021/ct800284g

Density functional theory is applied within a supramolecular approach to the study of the guest-host interactions in  $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Y}$  and their influence on the structural, energetic, and  $^{57}\text{Fe}$  Mössbauer spectroscopy properties of the encapsulated  $[\text{Fe}(\text{bpy})_3]^{2+}$  complex in the low- and high-spin states. The structures of the isolated complex and the supramolecular model used for  $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Y}$  were optimized in both spin-states using different generalized gradient approximation (PBE, HCTH, OLYP) and hybrid (B3LYP\*, O3LYP) functionals. The results obtained are consistent with one another and show that, in either spin-state, the structure of  $[\text{Fe}(\text{bpy})_3]^{2+}$  shrinks and distorts upon encapsulation. Still, the structural changes experienced by the complex in a given spin-state remain limited, especially in that they do not lead to a substantial variation of the  $^{57}\text{Fe}$  quadrupole splitting, whose calculated values are in very good agreement with available experimental data. The decomposition of the guest-host interaction energy into its electrostatic, Pauli and orbital contributions shows that the bonding between the complex and the supercage is more electrostatic than covalent. The ability of modern functionals to accurately describe the interactions explains the remarkable consistency of the results obtained with the various functionals. In particular, although the functionals perform very differently for the determination of the high-spin/low-spin energy difference  ${}^1E_{\text{HL}}^{\text{el}}$  in  $[\text{Fe}(\text{bpy})_3]^{2+}$  and  $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Y}$ , they consistently predict that the encapsulation entails a destabilization of the high-spin state with regard to the low-spin state of  ${}^1E_{\text{HL}}^{\text{el}} = 2500 \text{ cm}^{-1}$ . Using for  $[\text{Fe}(\text{bpy})_3]^{2+}$  the CASPT2 value of  ${}^1E_{\text{HL}}^{\text{el}} = 3700 \text{ cm}^{-1}$  [Pierloot, K.; Vancoillie, S.J. Chem. Phys. 2006, 125, 124303; Pierloot, K.; Vancoillie, S.J. Chem. Phys. 2008, 128, 034104], we obtain for the high-spin/low-spin energy difference in  $[\text{Fe}(\text{bpy})_3]^{2+}@\text{Y}$ , a best ab initio estimate of  ${}^1E_{\text{HL}}^{\text{el}} = 6200 \text{ cm}^{-1}$ .



• *Spin-transition in nearly cubic site in  $[\text{Fe}^{\text{II}}(\text{L})_3][\text{PF}_6]_2$*

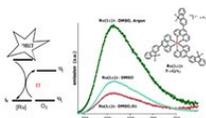
Vibha Mishra, Rabindranath Mukherjee, Jorge Linares, Epiphane Codjovi, François Varret and Latévi Max Lawson Daku

Hyperfine Interactions **188** (1-3) (2009), p71-78 DOI:10.1007/s10751-008-9891-6

Keywords: spin-transition •  $^{57}\text{Fe}$  Mössbauer spectroscopy • iron(II) complex • ligand-field • density functional theory

The spin-transition ( ${}^1A_1 \rightarrow {}^5T_2$ ) behaviour of a new mononuclear iron(II) compound  $[\text{Fe}^{\text{II}}(\text{L})_3][\text{PF}_6]_2$  [ $\text{L} = 2\text{-[3-(2\text{-}\pi\text{-pyridyl)pyrazole-1-ylmethyl]pyridine}$ ] has been investigated by  $^{57}\text{Fe}$  Mössbauer spectroscopy. Analysis of the Mössbauer spectra revealed low value of the quadrupole splitting of the high-spin state which reflects iron(II) to be in nearly cubic lattice site. Mössbauer spectra under light show the light-induced excited spin state trapping effect and the observed quadrupole splitting of the metastable high-spin state is found little sensitive to the high-spin fraction value. DFT calculations are in progress to document the almost cubic nature of the ligand-field acting on the iron atom.

## 2008



•  *${}^3\text{MLCT}$  excited states in Ru(II) complexes: Reactivity and related two-photon absorption applications in the near-infrared spectral range*

Gilles Lemerrier, Adeline Bonne, Mickaël Four and Latévi M. Lawson Daku

Comptes Rendus Chimie **11** (6-7) (2008), p709-715 DOI:10.1016/j.crci.2007.11.012

Keywords: Ruthenium(II) complexes • Polypyridyl ligands • Two-photon absorption •  ${}^3\text{MLCT}$  • Dioxygen sensors • Photodynamic therapy

The synthesis and characterization of new 1,10-phenanthroline-based chromophores LT1, LT2 and LD1 featuring fluorene unit(s) are reported. Their absorption and emission as well as their two-photon absorption properties in the  $450\text{--}650 \text{ nm}$  spectral range are discussed in comparison with the parent 1,10-phenanthroline and already described ligands L1 and L2.

## 2007

• *First-principles study of the pressure dependence of the structural and vibrational properties of the ternary metal hydride  $\text{Ca}_2\text{RuH}_6$*

Latévi Max Lawson Daku and Hans Hagemann

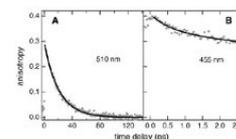
Physical Review B **76** (1) (2007), p14118 DOI:10.1103/PhysRevB.76.014118

The influence of pressure on the structural and vibrational properties of  $\text{Ca}_2\text{RuH}_6$  has been investigated using periodic density functional theory calculations performed at the local density approximation (LDA) and generalized gradient approximation (GGA) levels. At ambient pressure, the calculated structure and vibrational frequencies are in satisfactory agreement with experimental data. The calculated  $\text{em} > \text{P}$  curves could be fitted with the Vinet equation of state, yielding  $\text{em} > \text{B} = 67.6 \text{ and } 58.5 \text{ \AA GPa}$  at the LDA and GGA levels, respectively, and  $\text{em} > \text{B}^{\text{GGA}} = 4.0 \text{ \AA}$  at both theoretical levels. The unit cell parameter is found to decrease faster with increasing pressure than the  $\text{Ru}\text{--}\text{H}$  bond length. The calculated pressure dependence of the vibrational frequencies agrees well with experiment for  $\text{em} > 1/2g(A_{1g})$  but not for  $\text{em} > 1/2g(A_{1g})$ .

• *Investigation of the Influence of Solute-Solvent Interactions on the Vibrational Energy Relaxation Dynamics of Large Molecules in Liquids*

Anatolio Pigliucci, Guillaume Duvanel, Latévi Max Lawson Daku, Eric Vauthey

Journal of Physical Chemistry A **111** (28) (2007), p6135-6145 DOI:10.1021/jp069010y



The influence of solute-solvent interactions on the vibrational energy relaxation dynamics of perylene and substituted perylenes in the first singlet excited-state upon excitation with moderate ( $<0.4 \text{ eV}$ ) excess energy has been investigated by monitoring the early narrowing of their fluorescence spectrum. This narrowing was found to occur on timescales ranging from a few hundreds of femtoseconds to a few picoseconds. Other processes, such as a partial decay of the fluorescence anisotropy and the damping of a low-frequency oscillation due to the propagation of a vibrational wavepacket, were found to take place on a very similar time scale. No significant relationship between the strength of nonspecific solute-solvent interactions and the vibrational energy relaxation dynamics of the solutes could be evidenced. On the other hand, in alcohols the spectral narrowing is faster with a solute having H-bonding sites, indicating that this specific interaction tends to favor vibrational energy relaxation. No relationship between the dynamics of spectral narrowing and macroscopic solvent properties, such as the thermal diffusivity, could be found. On the other hand, a correlation between this narrowing dynamics and the number of low-frequency modes of the solvent molecules was evidenced. All these observations cannot be discussed with a model where vibrational energy relaxation occurs via two consecutive and dynamically well-separated steps, namely ultrafast intramolecular vibrational redistribution followed by slower vibrational cooling. On the contrary, the results indicate that both intra- and intermolecular vibrational energy redistribution processes are closely entangled and occur, at least partially, on similar timescales.

• *Ab initio static and molecular dynamics study of 4-styrylpyridine: Structure, energy and reactivity of the cis and trans isomers in the ground state*

Latévi Max Lawson Daku, Jorge Linares, Marie-Laure Boillot

ChemPhysChem **8** (9) (2007), p1402-1416 DOI:10.1002/cphc.200700117

Keywords: ab initio calculations • density functional calculations • isomerization • molecular dynamics • transition states

We report an in-depth theoretical study of 4-styrylpyridine in its singlet S ground state. The geometries and the relative stabilities of the *trans* and *cis* isomers were investigated within density functional theory (DFT) as well as within Hartree-Fock (HF), second-order Møller-Plesset (MP2), and coupled cluster (CC) theories. The DFT calculations were performed using the B3LYP and PBE functionals, with

basis sets of different qualities, and gave results that are very consistent with each other. The molecular structure is thus predicted to be planar at the energy minimum, which is associated with the *trans* conformation, and to become markedly twisted at the minimum of higher energy, which is associated with the *cis* conformation. The results of the calculations performed with the post-HF methods approach those obtained with the DFT methods, provided that the level of treatment of the electronic correlation is high enough and that sufficiently flexible basis sets are used. Calculations carried out within DFT also allowed the determination of the geometry and the energy of the molecule at the biradicaloid transition state associated with the thermal *cis*  $\rightarrow$  *trans* isomerization and at the transition states associated with the enantiomerization of the *cis* isomer and with the rotations of the pyridinyl and phenyl groups in the *trans* and *cis* isomers. Car-Parrinello molecular dynamics simulations were also performed at 50, 150, and 300 K using the PBE functional. The studies allowed us to evidence the highly flexible nature of the molecule in both conformations. In particular, the *trans* isomer was found to exist mainly in a nonplanar form at finite temperatures, while the rotation of the pyridinyl ring in the *cis* isomer was incidentally observed to take place within  $\sim 1$  ps during the simulation carried out at 150 Å K on this isomer.

- *Spin-crossover in cobalt(II) imine complexes*

Itana Krivokapic, Mohamed Zerara, Latévi Max Lawson Daku, Alfredo Vargas, Cristian Enachescu, Christina Ambrus, Philip Tregenna-Piggott, Nahid Amstutz, Elmars Krausz and Andreas Hauser  
 Coordination Chemistry Reviews **251** (2007), p364-378 DOI:10.1016/j.ccr.2006.05.006

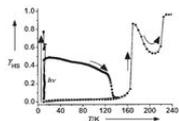
Whereas there are hundreds of known iron(II) spin-crossover compounds, only a handful of cobalt(II) spin-crossover compounds have been discovered to date, and hardly an in depth study on any of them exists. This review begins with an introduction into the theoretical aspects to be considered when discussing spin-crossover compounds in general and cobalt(II) systems in particular. It is followed by case studies on  $[\text{Co}(\text{bpy})_3]^{2+}$  and  $[\text{Co}(\text{terpy})_2]^{2+}$  (bpy = 2,2'-bipyridine, terpy = 2,2':6,6':2,2'-terpyridine) presenting and discussing results from magnetic susceptibility measurements, X-ray crystallography, optical spectroscopy, and EPR spectroscopy.

## 2006

- *Chiroptical and Computational Studies of a Bridled Chirophorphyrin and of Its Nickel(II), Copper(II), and Zinc(II) Complexes*

Géraldine Maheut, Anna Castaing, Jacques Pécaut, Latévi Max Lawson Daku, Gennaro Pescitelli, Lorenzo Di Bari, and Jean-Claude Marchon  
 Journal of the American Chemical Society **128** (19) (2006), p6347-6356 DOI:10.1021/ja054926o

Circular dichroism (CD) spectra and density functional theory (DFT) calculations are reported for a series of conformationally bistable chirophorphyrins with 8-methylene bridles MBCP-8, which can display either an  $l_1l_2l_3l_4$  or an  $l_1l_2l_3l_4'$  orientation of their meso substituents. From DFT geometry optimizations, the most stable form of ZnBCP-8 is found to be the  $l_1l_2l_3l_4$  conformer. By passing to NiBCP-8, there is a strong stabilization of the  $l_1l_2l_3l_4'$  conformation with respect to the  $l_1l_2l_3l_4$  conformation, consistent with the X-ray structures of  $l_1l_2l_3l_4$ -ZnBCP-8 and  $l_1l_2l_3l_4'$ -NiBCP-8. A correlation between the sign of the CD signal in the Soret region and the conformation of the BCP-8 compounds is reported: the  $l_1l_2l_3l_4$  conformers H<sub>2</sub>BCP-8 and ZnBCP-8 show a positive CD signal, whereas the  $l_1l_2l_3l_4'$  conformers NiBCP-8 and CuBCP-8 exhibit a negative signal. The possible contributions to the rotational strengths of  $l_1l_2l_3l_4$  and  $l_1l_2l_3l_4'$ -ZnBCP-8, calculated on the basis of their crystal structures, have been analyzed. The CD signals are found to result from a combination of both the inherent chirality of the porphyrin and of extrinsic contributions due to the chiral bridges. These results may have a broad significance for understanding the chiroptical properties of chiral porphyrins and hemoproteins and for monitoring stimuli-responsive, conformationally bistable chirophorphyrin compounds.



- *Photoswitching of the Dielectric Constant of the Spin-Crossover Complex  $[\text{Fe}(\text{L})(\text{CN})_2]\cdot\text{H}_2\text{O}$*

Sébastien Bonhommeau, Thomas Guillon, Latévi Max Lawson Daku, Philippe Demont, José Sanchez Costa, Jean-François Létard, Gábor Molnár, Azzedine Bousseksou  
 Angewandte Chemie International Edition **45** (10) (2006), p1625-1629 DOI:10.1002/anie.200503252

Photoswitching of the dielectric constant has been observed for the first time in the spin-crossover complex  $[\text{Fe}(\text{L})(\text{CN})_2]\cdot\text{H}_2\text{O}$  (L=2,13-dimethyl-6,9-dioxo-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene, see picture). The electrical detection of a photoinduced change in spin state could allow the use of such complexes in optical information-storage devices.

- *Ab initio calculations of external-field shifts of the 661-nm quadrupole clock transition in neutral Ag atoms*

Suat Topcu, Jamil Nasser, Latévi Max Lawson Daku, and Stephan Fritzsche  
 Physical Review A **73** (4) (2006), p42503 DOI:10.1103/PhysRevA.73.042503

Frequency shifts of the  $\text{Ag } 4d^{10}5s \rightarrow 4d^95s^2 (F=0, M_F=0) \rightarrow 4d^95s^2 (F^{\circ}=2, M_F^{\circ}=0)$  electric-quadrupole transition at 330.6 Å nm due to external fields are calculated using multiconfigurational self-consistent field methods. As this forbidden transition is free from first order Doppler and Zeeman effects, it is under investigation for the realization of an atomic optical clock. The calculated perturbations are the light shift, the blackbody frequency shift, and the quadratic Zeeman shift. Results show that a total uncertainty of  $10^{-18}$  could be reached without confining the atoms in a Lamb-Dicke regime in an optical lattice.

- *Density-functional theory investigation of the geometric, energetic and optical properties of the cobalt(II)tris(2,2'-bipyridine) complex in the high-spin and in the Jahn-Teller active low-spin state*

Alfredo Vargas, Mohamed Zerara, Elmars Krausz, Andreas Hauser, and Latévi Max Lawson Daku  
 Journal of Chemical Theory and Computation **2** (2006), p1342-1359 DOI:10.1021/ct6001384



State-of-the-art generalized gradient approximation (GGA) (PBE, OPBE, RPBE, OLYP, and HCTH), meta-GGA (VSXC and TPSS), and hybrid (B3LYP, B3LYP\*, O3LYP, and PBE0) functionals are compared for the determination of the structure and the energetics of the  $D_3$   $[\text{Co}(\text{bpy})_3]^{2+}$  complex in the  $^4A_2$  and  $^4E$  trigonal components of the high-spin  $^4T_{1g}$  ( $t_{2g}^5 e_g^3$ ) state and in the low-spin  $^2E_g$  ( $t_{2g}^6 e_g^1$ ) parentage. Their comparison extends also to the investigation of the Jahn-Teller instability of the  $^2E_g$  state through the characterization of the extrema of  $C_2$  symmetry of this spin state's potential energy surface. The results obtained for  $[\text{Co}(\text{bpy})_3]^{2+}$  in either spin manifold are very consistent among the functionals used and are in good agreement with available experimental data. The functionals, however, perform very differently with respect to the spin-state energetics because the calculated values of the high-spin/low-spin energy difference  $^1E_{\text{H-L}}$  vary between  $\sim 3212$  and  $3919 \text{ cm}^{-1}$ . Semilocal functionals tend to give too large  $^1E_{\text{H-L}}$  values and thus fail to correctly predict the high-spin state as the ground state of the isolated complex, while hybrid functionals tend to overestimate the stability of the high-spin state with respect to the low-spin state. Reliable results are, however, obtained with the OLYP, HCTH, B3LYP\*, and O3LYP functionals which perform best for the description of the isolated complex. The optical properties of  $[\text{Co}(\text{bpy})_3]^{2+}$  in the two spin states are also analyzed on the basis of electronic excitation calculations performed within time-dependent density functional response theory. The calculated absorption and circular dichroism spectra agree well with experimental results.

- *Low-temperature lifetimes of metastable high-spin states in spin-crossover and in low-spin iron(II) compounds: The rule and exceptions to the rule*

Andreas Hauser, Cristian Enachescu, Latévi Max Lawson Daku, Alfredo Vargas and Nahid Amstutz  
 Coordination Chemistry Reviews **250** (13-14) (2006), p1642-1652 DOI:10.1016/j.ccr.2005.12.006

The high-spin  $\rightarrow$  low-spin relaxation in spin-crossover compounds can be described as non-adiabatic multi-phonon process in the strong coupling limit, in which the low-temperature tunnelling rate increases exponentially with the zero-point energy difference between the two states. Based on the hypothesis that the experimental bond length difference between the high-spin and the low-spin state of  $\sim 0.2 \text{ \AA}$  is also valid for low-spin iron(II) complexes, extrapolation of the single configurational coordinate model allows an estimate of the zero-point energy difference for low-spin complexes from kinetic data. DFT calculations on low-spin  $[\text{Fe}(\text{bpy})_3]^{2+}$  support the structural assumption. However, for low-spin  $[\text{Fe}(\text{terpy})_2]^{2+}$  the relaxation rate constant shows an anomalous behaviour in so far as it is more in line with spin-crossover systems. This is attributed to very anisotropic bond length changes associated with the spin state change, and the subsequent breakdown of the single mode model.

## 2005

- **Reactivity of Copper(I) Complexes with Tripodal Ligands towards  $\text{O}_2$ : Structures of a Precursor  $[\text{L}^3\text{Cu}^{\text{I}}(\text{NCCH}_3)](\text{BF}_4)$ ,  $\text{L}^3 = \text{Tris}(3\text{-isopropyl-4,5-trimethylenepyrzoly})\text{methane}$  and of its Oxidation Product  $[\text{L}^3\text{Cu}^{\text{II}}(-\text{OH})_2\text{Cu}^{\text{I}}\text{L}^3](\text{BF}_4)_2$  with Strong Antiferromagnetic Spin-Spin Coupling**

Wolfgang Kaim, Christoph Titze, Thilo Schurr, Monika Sieger, Latévi Max Lawson Daku, Jeanne Jordanov, Darío Rojas, Ana M. García, Jorge Manzur

Zeitschrift für anorganische und allgemeine Chemie **631** (13-14) (2005), p2568-2574

DOI:10.1002/zaac.200500053

The molecular structure of the highly oxygen-sensitive complex  $[\text{L}^3\text{Cu}^{\text{I}}(\text{NCCH}_3)](\text{BF}_4)$  (**1**) reveals approximately symmetrical coordination by the *fac*-tridentate (tripodal) ligand  $\text{L}^3 = \text{tris}(3\text{-isopropyl-4,5-trimethylenepyrzoly})\text{methane}$  and a rather short  $\text{Cu}^{\text{I}} - \text{N}(\text{acetonitrile})$  distance of  $1.865(5) \text{ \AA}$ . In  $\text{CH}_2\text{Cl}_2$  at  $-78 \text{ }^\circ\text{C}$  the colourless compound reacts with  $\text{O}_2$  to yield a labile purple intermediate ( $\lambda_{\text{max}} = 517 \text{ nm}$ ) - presumably a peroxodicopper(II) complex - which decomposes at  $-30 \text{ }^\circ\text{C}$ . No such intermediate was observed on reaction of the  $\text{Cu}^{\text{I}}$  complex of bis(2-pyridylmethyl)benzylamine with  $\text{O}_2$  at  $-80 \text{ }^\circ\text{C}$ . However, an EPR spectrum with  $g^{\parallel} = 2.17$  and  $g^{\perp} = 2.03$  without  $^3\text{Cu}$  hyperfine splitting was observed at low temperatures. Exposure of the precursor **1** to air under ambient conditions yields dinuclear  $[\text{L}^3\text{Cu}^{\text{II}}(\frac{1}{2}\text{-OH})_2\text{Cu}^{\text{I}}\text{L}^3](\text{BF}_4)_2$  (**2**) which exhibits an EPR detectable dissociation into monomers in  $\text{CH}_2\text{Cl}_2$  solution. The structure of the hexakis(dichloromethane) solvate of **2** with Cu-Cu and Cu-O distances of  $3.055$  and  $1.94 \text{ \AA}$ , respectively, is typical for dihydroxo-bridged dicopper compounds with square-pyramidal  $\text{Cu}^{\text{II}}$  configuration ( $\tau = 0.03$ ), adopting an *anti* arrangement. In agreement with the relatively wide Cu-O-Cu angles of  $103.5^\circ$  an analysis of the temperature dependence of the magnetic susceptibility revealed a rather strong ( $J = -633 \text{ cm}^{-1}$ ) antiparallel spin-spin coupling. The effect is ascribed to the steric bulk of the ligand  $\text{L}^3$ .

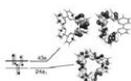
- **Comparison of density functionals for energy and structural differences between the high-  $[\text{ }^5\text{T}_{2g}; (t_{2g})^4(e_g)^2]$  and low-  $[\text{ }^1\text{A}_{1g}; (t_{2g})^6(e_g)]$  spin states of iron(II) coordination compounds. II. More functionals and the hexaminoferrous cation,  $[\text{Fe}(\text{NH}_3)_6]^{2+}$**

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The ability of different density functionals to describe the structural and energy differences between the high-  $[\text{ }^5\text{T}_{2g}; (t_{2g})^4(e_g)^2]$  and low-  $[\text{ }^1\text{A}_{1g}; (t_{2g})^6(e_g)]$  spin states of small octahedral ferrous compounds is studied. This work is an extension of our previous study of the hexaquoferrous cation,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ , [J. Chem. Phys. **120**, 9473 (2004)] to include a second compound - namely, the hexaminoferrous cation,  $[\text{Fe}(\text{NH}_3)_6]^{2+}$  and several additional functionals. In particular, the present study includes the highly parametrized generalized gradient approximations (GGAs) known as HCTH and the meta-GGA VSXC [which together we refer to as highly parametrized density functionals (HPDFs)], now readily available in the GAUSSIAN03 program, as well as the hybrid functional PBE0. Since there are very few experimental results for these molecules with which to compare, comparison is made with best estimates obtained from second-order perturbation theory-corrected complete active space self-consistent field (CASPT2) calculations, with spectroscopy oriented configuration interaction (SORCI) calculations, and with ligand field theory (LFT) estimations. While CASPT2 and SORCI are among the most reliable *ab initio* methods available for this type of problem, LFT embodies many decades of empirical experience. These three methods are found to give coherent results and provide best estimates of the adiabatic low-spin  $\rightarrow$  high-spin energy difference,  ${}^1\text{E}_{\text{HL}}^{\text{adia}}$ , of  $12200 \text{ cm}^{-1}$  for  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $9400 \text{ cm}^{-1}$  for  $[\text{Fe}(\text{NH}_3)_6]^{2+}$ . All functionals beyond the purely local approximation produce reasonably good geometries, so long as adequate basis sets are used. In contrast, the energy splitting,  ${}^1\text{E}_{\text{HL}}^{\text{adia}}$ , is much more sensitive to the choice of functional. The local density approximation severely over stabilizes the low-spin state with respect to the high-spin state. This  $\rightarrow$  density functional theory (DFT) spin pairing-energy problem  $\rightarrow$  persists, but is reduced, for traditional GGAs. In contrast the hybrid functional B3LYP underestimates  ${}^1\text{E}_{\text{HL}}^{\text{adia}}$  by a few thousands of wave numbers. The RPBE GGA of Hammer, Hansen, and Nørskov gives good results for  ${}^1\text{E}_{\text{HL}}^{\text{adia}}$  as do the HPDFs, especially the VSXC functional. Surprisingly the HCTH functionals actually over correct the DFT spin pairing-energy problem, destabilizing the low-spin state relative to the high-spin state. Best agreement is found for the hybrid functional PBE0.



- **Assessment of Density Functionals for the High-Spin/Low-Spin Energy Difference in the Low-Spin Iron(II)  $\text{Tris}(2,2'\text{-bipyridine})$  Complex**

Latévi Max Lawson Daku, Alfredo Vargas, Andreas Hauser, Antony Fouqueau, Mark Earl Casida

ChemPhysChem **6** (7) (2005), p1393-1410

DOI:10.1002/cphc.200400584

Keywords: density functional calculations • iron(II) complexes • time-resolved spectroscopy • high-spin  $\rightarrow$  low-spin relaxation • spin crossover

In the iron(II) low-spin complex  $[\text{Fe}(\text{bpy})_3]^{2+}$ , the zero-point energy difference between the  ${}^5\text{T}_{2g}(t_{2g}^4e_g^2)$  high-spin and the  ${}^1\text{A}_{1g}(t_{2g}^6)$  low-spin states,  ${}^1\text{E}_{\text{HL}}$ , is estimated to lie in the range of  $2500\text{-}5000 \text{ cm}^{-1}$ . This estimate is based on the low-temperature dynamics of the high-spin  $\rightarrow$  low-spin relaxation following the light-induced population of the high-spin state and on the assumption that the bond-length difference between the two states  ${}^1\text{r}_{\text{HL}}$  is equal to the average value of  $\sim 0.2 \text{ \AA}$ , as found experimentally for the spin-crossover system. Calculations based on density functional theory (DFT) validate the structural assumption insofar as the low-spin-state optimized geometries are found to be in very good agreement with the experimental X-ray structure of the complex and the predicted high-spin geometries are all very close to one another for a whole series of common GGA (PB86, PW91, PBE, RPBE) and hybrid (B3LYP, B3LYP\*, PBE1PBE) functionals. This confirmation of the structural assumption underlying the estimation of  ${}^1\text{E}_{\text{HL}}$  from experimental relaxation rate constants permits us to use this value to assess the ability of the density functionals for the calculation of the energy difference between the HS and LS states. Since the different functionals give values from  $-1000$  to  $12000 \text{ cm}^{-1}$ , the comparison of the calculated values with the experimental estimate thus provides a stringent criterion for the performance of a given functional. Based on this comparison the RPBE and B3LYP\* functionals give the best agreement with experiment.

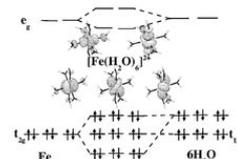
## 2004

- **Comparison of density functionals for energy and structural differences between the high-  $[\text{ }^5\text{T}_{2g}; (t_{2g})^4(e_g)^2]$  and low-  $[\text{ }^1\text{A}_{1g}; (t_{2g})^6(e_g)]$  spin states of the hexaquoferrous cation  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$**

Antony Fouqueau, Sébastien Mer, Mark E. Casida, Latevi Max Lawson Daku, Andreas Hauser, Tsonka Mineva, and Frank Neese

Journal of Chemical Physics **120** (20) (2004), p9473-9486

DOI:10.1063/1.1710046



A comparison of density functionals is made for the calculation of energy and geometry differences for the high-  $[\text{ }^5\text{T}_{2g}; (t_{2g})^4(e_g)^2]$  and low-  $[\text{ }^1\text{A}_{1g}; (t_{2g})^6(e_g)]$  spin states of the hexaquoferrous cation  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ . Since very little experimental results are available (except for crystal structures involving the cation in its high-spin state), the primary comparison is with our own complete active-space self-consistent field (CASSCF), second-order perturbation theory-corrected complete active-space self-consistent field (CASPT2), and



We present a theoretical analysis of the temperature dependence of the vanadyl pyrophosphate  $\text{VO}_2\text{P}_2\text{O}_7$   $^{31}\text{P}$  NMR spectra. Four distinct phosphorus sites responsible for four signals are identified in the crystal structure. The magnetic states of the crystal are described by two alternative models: the spin ladder and the dimer chain. Within both models, finite clusters with and without periodic conditions are considered. The fit of the experimental NMR data allows us to define combinations of hyperfine coupling parameters which are found to be similar in both spin models.

## 1999

- *Unusual Contact Shifts and Magnetic Tensor Orientation in Rhodobacter capsulatus Ferrocyclochrome c': NMR, Magnetic Susceptibility, and EPR Studies*

Pascale Tsan, Michael Caffrey, Latévi Max Lawson Daku, Michael Cusanovich, Dominique Marion, and Pierre Gans

Journal of the American Chemical Society **121** (9) (1999), p1795-1805 DOI:10.1021/ja9820745

In contrast to high-spin ferrous paramagnetic heme proteins, the chemical shifts of the heme protons are very unusual in the ferrocyclochromes  $\text{c}'$ . Magnetic susceptibility studies of *Rhodobacter capsulatus* ferrocyclochrome  $\text{c}'$  in frozen solutions have been performed and indicate an  $S = 2$  spin state and a large negative axial ( $D$ ) zero-field splitting parameter ( $\hat{a} \sim 18.3 \text{ cm}^{-1}$ ) as well as a significant rhombic ( $E$ ) value ( $\hat{a} \sim 4.9 \text{ cm}^{-1}$ ). The  $^1\text{H}$  and  $^{15}\text{N}$  resonances have been extensively assigned by TOCSY $\rightarrow$ HSQC, NOESY $\rightarrow$ HSQC, and HSQC $\rightarrow$ NOESY $\rightarrow$ HSQC 3-D heteronuclear experiments performed on a 8 mM sample labeled with  $^{15}\text{N}$ . Based on short-range and medium-range NOEs and  $\text{H}^{\text{N}}$ A exchange rates, the secondary structure consists of four helices: helix-1 ( $3\text{a} \sim 30$ ), helix-2 ( $34\text{a} \sim 49$ ), helix-3 ( $78\text{a} \sim 97$ ), and helix-4 ( $103\text{a} \sim 117$ ). The  $^{15}\text{N}$ ,  $\text{H}^{\text{N}}$ , and  $\text{H}^{\text{a}}$  chemical shifts of the reduced (or ferro) state are compared to those previously assigned for the diamagnetic carbon monoxide complex form. From the chemical shift differences between these redox states, the orientation and the anisotropy of the paramagnetic susceptibility tensor have been determined using the crystallographic coordinates of the ferric state. Values of  $\hat{a} \sim 23$  and  $\hat{a} \sim 3 \text{ cm}^{-1}$  have been inferred for  $D$  and  $E$ , and the  $z$ -axis of the tensor is tilted approximately  $30^\circ$  from the normal to the heme. The paramagnetic chemical shifts of the heme protons have been determined and split up into Fermi shift and the dipolar shift contributions. The pattern of the contact shifts is very unusual, exhibiting a 2-fold symmetry, and is discussed in terms of molecular orbital interactions between the porphyrin macrocycle and the imidazole ring.

## 1997

- *Paramagnetism of Tetranuclear Complexes between TCNX Ligands (TCNE, TCNQ, TCNB) and Four Pentaammineruthenium or Dicarbonyl(pentamethylcyclopentadienyl)manganese Fragments*

Eberhard Waldhör, Wolfgang Kaim, Latévi Max Lawson Daku, and Jeanne Jordanov

Inorganic Chemistry **32** (15) (1997), p3248-3252 DOI:10.1021/ic960998s

The tetranuclear complexes  $\{(\text{TCNX})_2[\text{Ru}(\text{NH}_3)_5]_2(\text{A})_2\}$  and  $\{(\text{TCNX})_2[\text{Mn}(\text{CO})_2(\text{C}_5\text{Me}_5)]_2[\text{A} = \text{PF}_6 \text{ or } \text{CF}_3\text{SO}_3^-; \text{TCNX} = \text{TCNE (tetracyanoethene), TCNQ (7,7,8,8-tetracyano-}p\text{-quinodimethane), or TCNB (1,2,4,5-tetracyanobenzene)}]\}$  were studied by variable-temperature ( $2\text{a} \sim 300 \text{ K}$ ) SQUID susceptometry. Mono- and dinuclear species  $\{(\text{PhCN})\text{Ru}(\text{NH}_3)_5(\text{PF}_6)_2\}$  ( $\text{PhCN} = \text{benzonitrile}$ ) and  $\{(\text{L})[\text{Ru}(\text{NH}_3)_5]_2(\text{PF}_6)_4\}$  ( $\text{L} = 1,4\text{-dicyanobenzene (terephthalodinitrile) or pyrazine}$ ) were also investigated for comparison and were found to be essentially diamagnetic. Despite the even electron count, both the ruthenium and manganese tetranuclear complexes are paramagnetic, albeit with different spin $\rightarrow$ spin exchange coupling patterns. The manganese systems are characterized by exchange-coupled  $S = 1$  states at the individual metal centers, whereas the magnetic behavior of the tetranuclear ruthenium compounds results from an exchange-coupling interaction between two  $S = 1/2$  sites, identified as  $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$  mixed-valence pairs.

## 1994

- *Redox behavior of the iron-sulfur cluster  $[\text{Fe}_4\text{Cp}_4\text{S}_5][\text{PF}_6]_2$  in protic organic solvents and aqueous micellar solutions*

Latévi Max Lawson Daku and Jeanne Jordanov

Inorganica Chimica Acta **226** (1-2) (1994), p341-344 DOI:10.1016/0020-1693(94)04065-6