Department of Molecular Theory and Spectroscopy

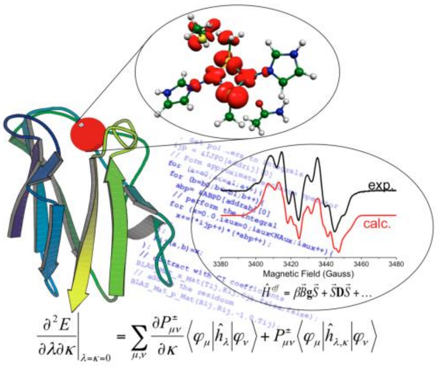

Fig. 1: In our department, theory development, application and advanced spectroscopy are combined.

Our department is interested in fundamental science related to the activation of small molecules by transition metals in a broad sense as well as in the development and application of quantum chemical methods. The activities of the group span the three major, interrelated areas:

I. Development of new quantum chemical methods
II. Computational chemistry
III. Molecular spectroscopy

The leading overall motivation is to unravel reaction mechanisms of complex, transition metal catalyzed reactions at the electronic structure level. As the experimental means of addressing electronic structure involves various forms of spectroscopy, a thorough understanding of structure/spectra relationships is of paramount importance (and clearly branches into the area of material science). Furthermore, the characterization of reaction intermediates can in almost all cases only proceed through a thorough interpretation of spectra taken under transient or quench conditions.

The activation of small molecules by transition metals is of paramount importance in the active sites of metalloproteins, in homogenous and in heterogeneous catalysis. In fact, the chemistry of sustainable energy, the coming focus of the future institute involves a number of elementary reactions (for a review see ref [1]):

$$2\,H^+ + 2\,e^- \rightarrow H_2 \qquad (1)$$

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4e^- \qquad (2)$$

$$O_2 + 4\,H^+ + 4e^- \rightarrow 2\,H_2O \qquad (3)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH \qquad (4)$$

$$CH_4 + 1/2\,O_2 \rightarrow H_3COH \qquad (5)$$

$$N_2 + 6H^+ + 6e^- \rightarrow 2\,NH_3 \qquad (6)$$

While all of these reactions are catalyzed in a highly efficient manner by metalloproteins, the search for suitable low molecular weight catalysts represents an active area of research in all cases. In our department, we are interested in all of these reactions, the associated enzymes (in cooperation with the department of Prof. Wolfgang Lubitz), low-molecular weight catalysts with potential for large scale applications, as well as heterogeneous processes (in cooperation with the department of Prof. Robert Schlögl).

The group and project leaders who are assigned specific projects in the department are shown in Figure 2.

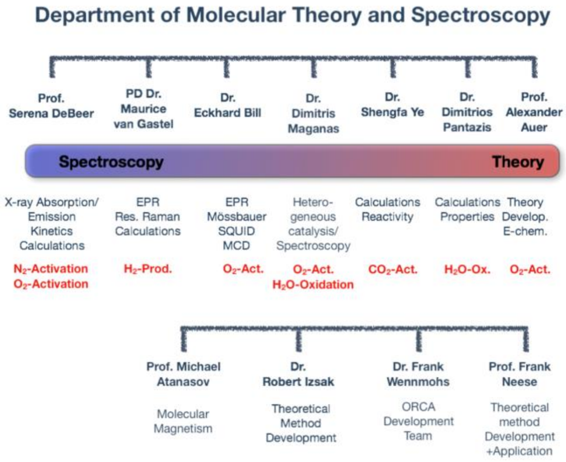

Fig. 2: Group and project leaders in the department for molecular theory and spectroscopy.

The overall strategy of the work involves a careful combination of theoretical and experimental techniques. Where necessary, theoretical or experimental methods will be developed in house. Furthermore, the department is involved in a large number of coordinated research programs and collaborations with scientists worldwide.

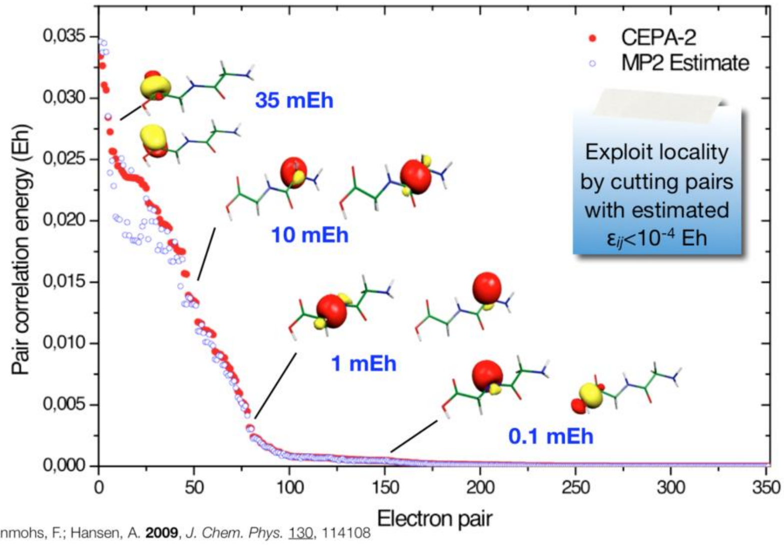

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Figure 4

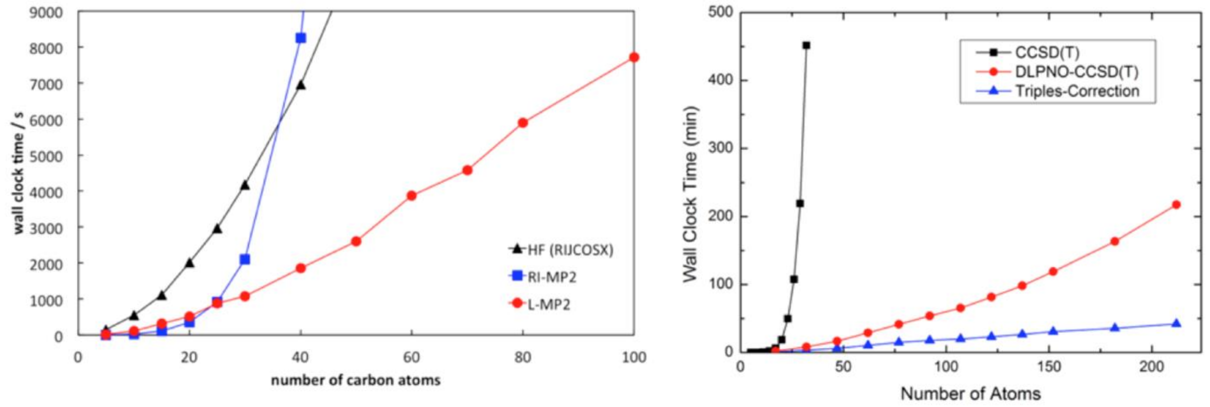

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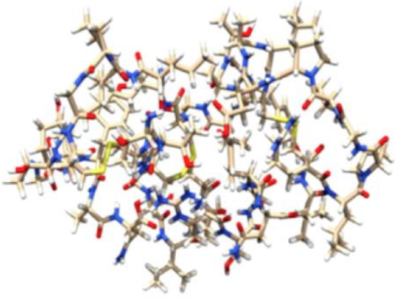
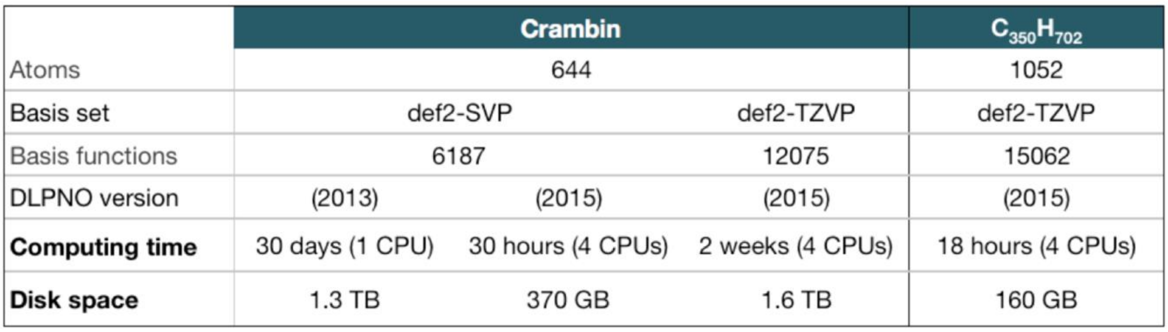
Figure 5





	Crambin			$C_{350}H_{702}$
Atoms	644			1052
Basis set	def2-SVP		def2-TZVP	def2-TZVP
Basis functions	6187		12075	15062
DLPNO version	(2013)	(2015)	(2015)	(2015)
Computing time	30 days (1 CPU)	30 hours (4 CPUs)	2 weeks (4 CPUs)	18 hours (4 CPUs)
Disk space	1.3 TB	370 GB	1.6 TB	160 GB

C. Riplinger, P. Pinski, U. Becker, E.F. Valeev, FN, **2016**, 144, 024109

Fig. 4,5,6: Low order scaling local coupled cluster methods based on the pair natural orbital concept allow application to real life molecules in reasonable turnaround times. The physical basis of these calculation is the fast decay of the electron pair correlation energies with interelectronic distance. Gigantic calculations are possible with this formalism with at very small loss in accuracy. For example, the first CCSD(T) level calculation of an entire protein (Crambin) in 2013.

(1) Quantum chemical method development

In our group, the large-scale quantum chemistry program ORCA is developed. ORCA is a highly-efficient, flexible and user friendly quantum chemistry program that is intensely used by a quickly growing user community of about 15,000 researchers worldwide. Its features are fully described elsewhere[2].

ORCA features all common standard functionality involving density functional theory (DFT), correlated single- (CCSD(T)) and multireference (MR-CI, SORCI, NEVPT2) ab initio wavefunction methods, as well as semi-empirical methods. ORCA is particularly well suited for the calculation of molecular spectra and is widely used by spectroscopists in various areas of research ranging from solid state chemistry to pharmacology.

One obvious goal of the theoretical method development is to enhance the efficiency and accuracy of theoretical methods and thereby push the boundaries of what is possible with computational chemistry. In recent years, a particular focus has been the development and application of low-order scaling electron correlation methods. This has led to the domain-based local pair natural orbital (DLPNO) family of methods that we regard as ‘breakthrough’ technology in the application of ab initio quantum mechanics to chemistry.[3] In a nutshell, DLPNO methods recover about 99.9% of the canonical correlation energy but the computational effort scales linearly with system size and with a sufficiently low prefactor to treat molecules with hundreds of atoms on standard hardware.

The DLPNO family presently spans DLPNO-MP2[3f] and DLPNO-CCSD(T)[3a, 3h, 3i] in the single-reference case as well as DLPNO-NEVPT2 and DLPNO-Mk-MRCC in the multireference case. DLPNO is based on the powerful concept of *SparseMaps* that we have developed in order to simplify the complex task of implementing high-level, linear scaling quantum chemical methods.[3f] Methods have been developed for closed-[3a, 3h, 3i] and open-[4] shell systems, molecular properties,[3e] excited states[3d] and explicit correlation.[3b]

While the single-reference problem appears to be well under control based on the DLPNO concepts, much more work remains to be done in the multi-reference case. The latter methods are instrumental to treat complicated multiplet problems, bond breaking phenomena and magnetic properties. We have intensely worked on several aspects of this very challenging problem. First of all, DLPNO concepts have been used to achieve a linear scaling DLPNO-NEVPT2 method that provides 99.9% of the correlation energy reliably. Starting from there, several new developments are: a) the ability to treat much larger reference spaces with fifty and more orbitals using the new iterative configuration expansion (ICE-CI) algorithm (a variant of the CIPSI method[5]), b) a differential correlation dressed CAS (DCD-CAS) method to address the limitations of the internal contraction scheme, c) internally contracted multi-reference configuration interaction (FIC-MRCI)[6] and coupled cluster (FIC-MRCC) approaches to achieve higher accuracy than NEVPT2. d) a smoother approach to the one-particle basis set limit using explicit correlation and e) the incorporation of relativistic effects using quasi-degenerate perturbation theory.

These challenging developments are greatly aided by new technology to directly and automatically implement complex theories using an automatic code generator (ORCA-AGE) that reduces development times from years to days.[7]

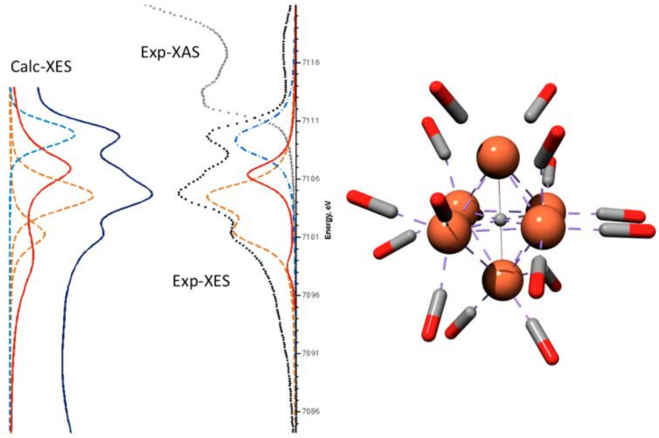


Fig. 7: Theoretical spectroscopy allows for the detailed assignment of complicated molecular spectra and thereby obtain deep insight into geometric and electronic structure. In this case the X-ray absorption and emission spectra of a six-iron carbide cluster.

Another major focus of method development is the design of suitable methods for the prediction of spectroscopic properties throughout all regions of the electromagnetic spectrum. An overview can be found in refs.[8] Being based on elementary to highly advanced theoretical concepts, methods to calculate Mössbauer parameters,[9] X-ray absorption and emission,[10] electron paramagnetic resonance (EPR[11]), resonance Raman (rR[8c, 12]) and magnetic circular dichroism (MCD[13]) spectra have found widespread application in various communities.

Finally, we are striving to provide a link between advanced computation and chemical intuition. In this realm, two important developments are the 'local energy decomposition' (LED) that allow to decompose the DLPNO coupled cluster energy into chemically meaningful parts.[14] For example, one can extract the dispersion component of the intermolecular interaction energy accurately from such calculations which can be used to give extended insights into the chemical origin of interaction energies.[15] Secondly, in the realm of inorganic chemistry, we have developed ab initio ligand field theory (AILFT) which provides a unique link between high-level multireference electronic structure theory and ligand field theory.[16] This can be used fruitfully to obtain insight into coordination complexes, for example magneto-structural correlations or periodic trends.[17]

The development efforts in Mülheim are coordinated jointly by *Prof. Neese* and *Dr. Frank Wennmohs*, who heads the ORCA development team. We are very grateful to our collaborators all over the world who contribute their expertise, energy and enthusiasm to the project.

The group of Prof. Alexander Auer is involved in theoretical method development. The focus is on accurate electronic structure methods based on tensor decomposition methods.[18]

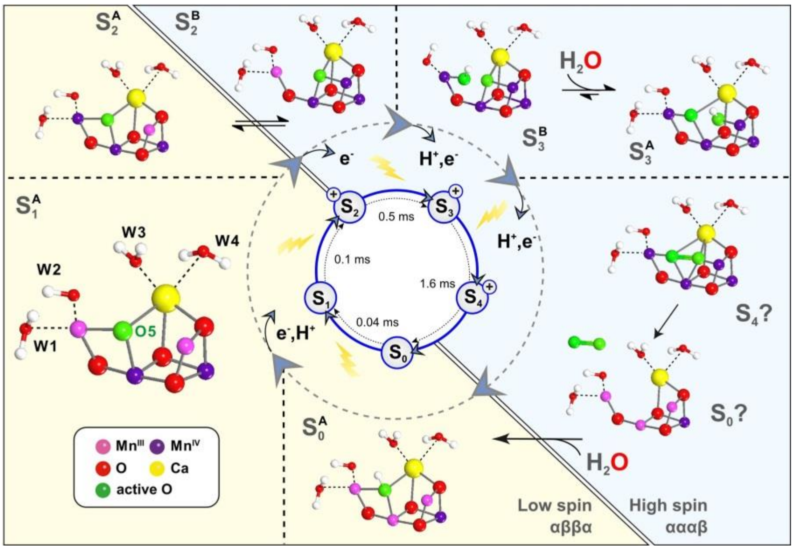


Fig. 8: Our present understanding of the mechanism of water oxidation in photosystem II as deduced from a combination of spectroscopy and quantum chemistry. The mechanism involves a very characteristic spin state change that is triggered by the conformational flexibility of an oxo bridge.

(2) Computational Chemistry

Our computational chemistry applications center around the reactions depicted above. Areas of recent interest are centered around:

(a) The ***oxidation of water*** by the oxygen evolving complex (OEC) of Photosystem II (PSII). This research area is led by Dr. Dimitrios Pantazis and is carried out in close collaboration with the department of Prof. Wolfgang Lubitz. The efforts that have led to the proposal of a refined structure for the OEC that is consistent with all crystallographic and spectroscopic data.[2, 19] Our desire to understand the reaction mechanism of the OEC on the basis of its spectroscopic properties[2, 19a, 19e] has led us to consider the properties of manganese complexes in greater detail and has led to a series of systematic investigations on manganese monomers, dimers and oligomers e.g.[10c, 11b, 20] Recent reviews summarize the state of affairs.[19c, 21]

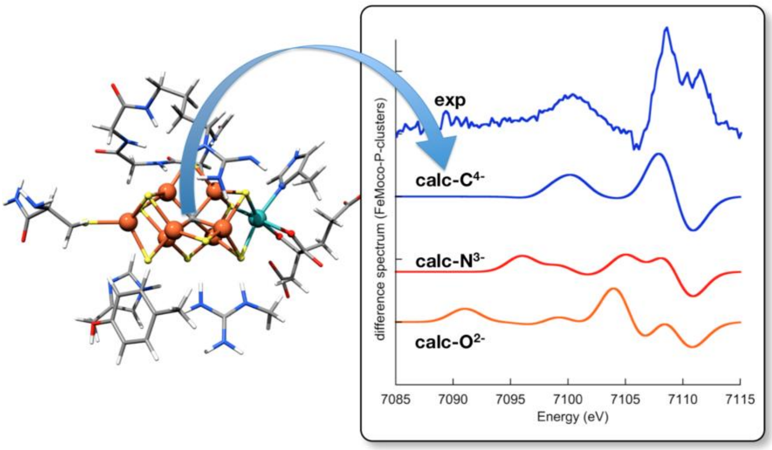


Fig. 9: A combination of X-ray emission and quantum chemistry reveals that the active site of nitrogenase contains a central carbide ion.

(b) The ***activation of dinitrogen***, one of the most inert molecules known in chemistry, by the enzyme nitrogenase is another focus of research in the group. This research area is headed by Prof. Serena

DeBeer.[22] Despite intense research efforts, even the structural basis for biological nitrogen fixation has been proven elusive. Highlights include the identification of the central atom in the active site of nitrogenase to be a carbide through the combination of X–ray emission spectroscopy with quantum chemistry,[22f] the assignment of the molybdenum oxidation state as Mo(III)[22e] as well as the characterization of a nitrogen activating trinuclear iron complex (in collaboration with the group of Prof. Patrick Holland, Rochester, USA).[23]

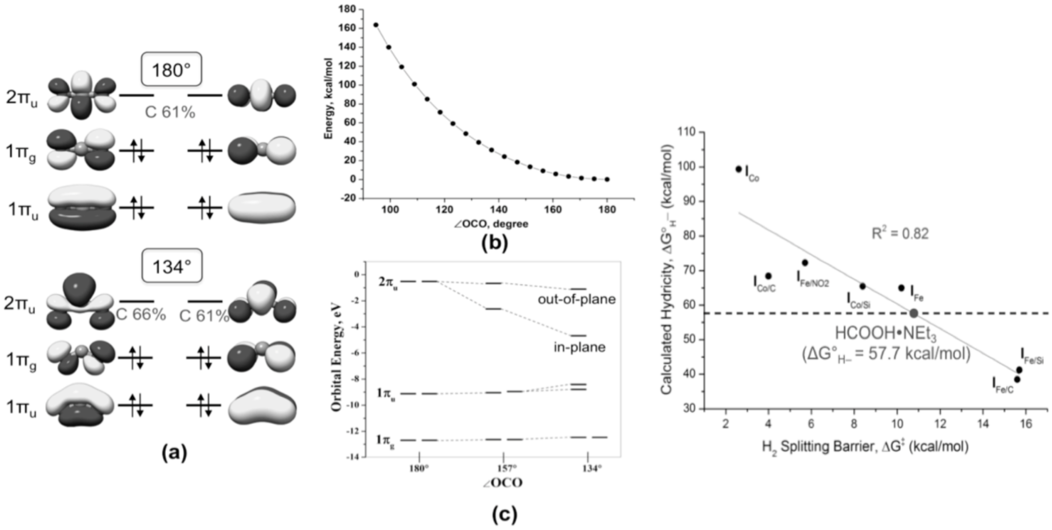


Fig. 10 Left: the molecular orbitals of CO_2 in linear and bent configurations. Middle: The total energy and the orbital energies of CO_2 along the bending mode showing that if CO_2 can be bent a low energy π* acceptor orbital becomes available as electron acceptor. Right: Correlation between the H_2 splitting barrier and the hydricity of coordinated CO_2 in CO_2 hydrogenation reactions.

(c) The ***activation of CO₂***, another extremely inert molecule is one of the most important reactions in energy research. Conversion of CO_2 to alcohols or other energy rich molecules could solve CO_2 pollution problems and provide liquid fuels at the same time. Our research in this area is headed by Dr. Shengfa Ye.[24]

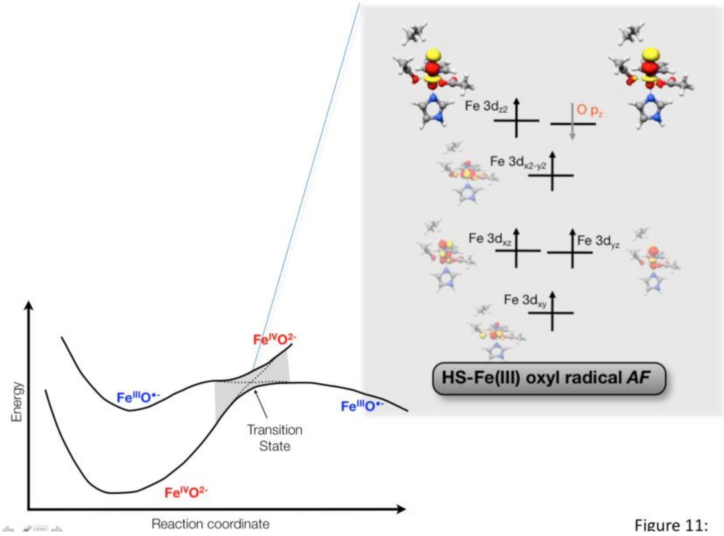


Fig. 11: The electronic structure analysis of the C-H bond activation catalyzed by high-valent iron(IV)-oxo species reveals that en route to the transition state an oxyl radical is formed that acts as a strong electrophile capable of attacking the C-H bond.

(d) The spectroscopy and reactivity of ***high-valent iron centers*** in iron enzymes and low-molecular weight catalysts. These research efforts are coordinated by Dr. Eckhard Bill (spectroscopy) and Dr. Shengfa Ye (theory).[25] A special focus of the DeBeer group is the study of the reaction mechanism of the important enzyme Methane Monooxygenase that features a dinuclear iron active site and catalyzes the chemically extremely complex transformation from methane to methanol. Highlights include the characterization of Fe(V)[26] and Fe(VI)[27] complexes (in collaboration with the former director, Prof. Karl Wieghardt), the detailed analysis of C-H bond activation reactions[28],[25a, 25e, 29] and the fascinatingly complex chemistry of iron-nitrosyls.[30]

(e) ***Molecular magnetism***, is a fascinating research field that has been a long term interest of the department. The ultimate goal is the design of molecules (SMMs) that show magnetic hysteresis at elevated temperatures (ideally room temperature). While this goal has been proven elusive so far, important progress has been made. Importantly, after it has been realized that big oligonuclear clusters are not necessary to design molecular magnets,[8a, 17, 20a, 25f, 31] focus has shifted towards systems with only one or two transition metal ion and fascinating progress has been made towards high-temperature SMMs.86-98 Our contributions to the field range from the development of electronic structure methods to high-level applications using multireference electronic structure theory. Importantly, we have developed the method of 'Ab initio ligand field theory'[8a, 16] that lets us deduce the classical ligand field parameters uniquely from multireference wavefunction calculations. This is invaluable for defining magnetostructural correlations and obtaining qualitative insights into the investigated systems (transition metals, lanthanides or actinides).[17, 31b, 31c, 31h, 31i]

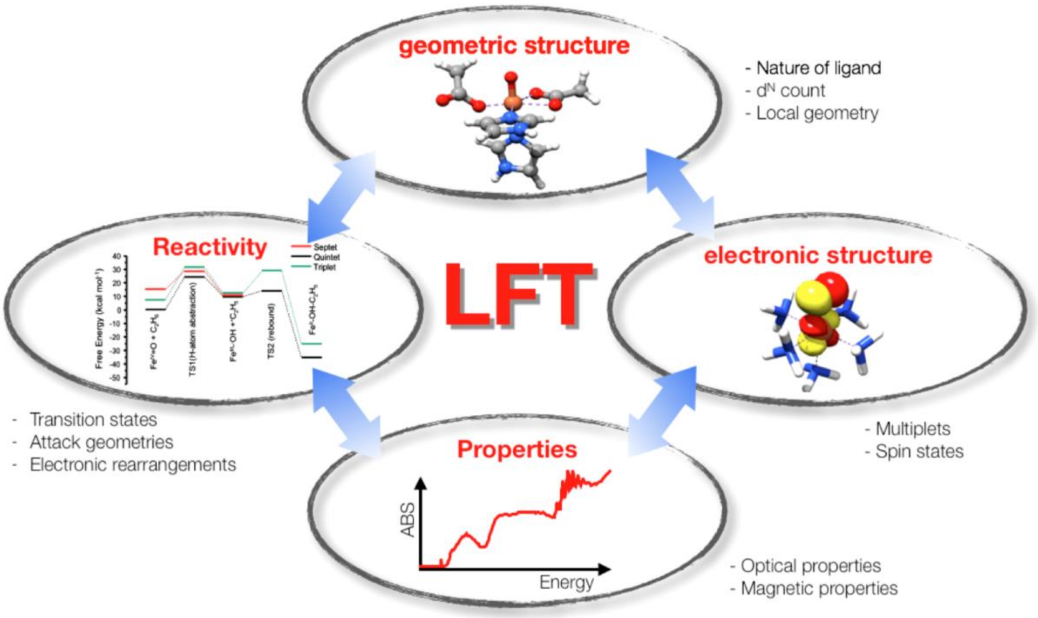


Fig. 12: Ligand field theory serves as the language that connects geometric structure, electronic structure, molecular properties and reactivity. Ab initio ligand field theory (AILFT) provides a unique link between modern high-accuracy multireference electroic structure theory and LFT, thus linking computations to chemical concepts).

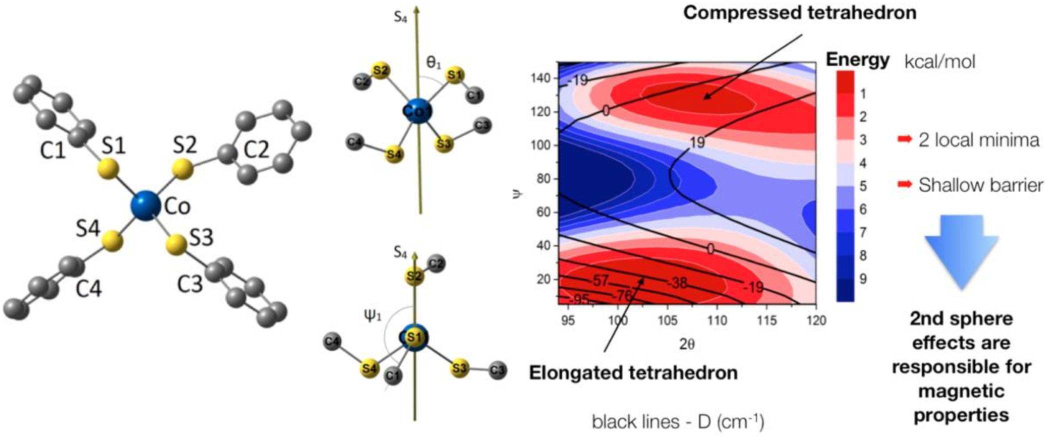


Fig. 13: Magneto-structural correlations for $[Co(S\text{-}Ph)_4]^{2-}$ the first mononuclear complex that was reported to posses single molecule magnet properties. Left: Structure of the complex. Middle definition of the two angles theta and psi that describe the distortion of the complex from perfect tetrahedral. Right: Variation of the total energy and the zero-field splitting as a function of these two angles demonstrating two equi-energetic minima separated by a low barrier. In one minimum the complex features a small positive ZFS, in the other a large negative ZFS thus showing that minor perturbations such as second sphere effects excerted by the counter ions can lock the system into one or the other minimum).

(f) ***Heterogeneous catalysis*** - We have shown that accurate wavefunction based methods can be applied to solids and surfaces without explicitly introducing periodic boundary conditions. While this approach is limited, it is also very powerful since with present day electronic structure know-how sufficiently large clusters can be treated such that cluster model is properly approaching the properties of the bulk system. This is demonstrated in Figure 14 by showing that a) cluster calculations at the DFT level approach the results of truly periodic cluster calculations and b) that DLPNO-CCSD(T) calculations converge with respect to cluster size.[32] Once carefully extrapolated to the basis set limit these DLPNO-CCSD(T) calculations were the first to predict binding energies to surfaces with an accuracy of 1 kcal/mol.[32] However, these studies are not limited to small molecule binding to surfaces. In collaboration with the department of Prof. Schlögl, we have shown that the same strategy of correlating calculations to spectroscopy and ultimately to reactivity that is so successful in the molecular realm, can be applied as well to heterogeneous catalysts thus opening fascinating avenues for future explorations in this important field.[33]

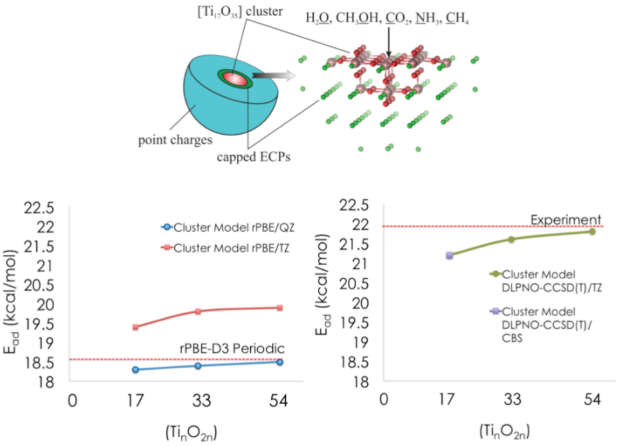


Fig. 14: Top: embedded cluster models for solid and surfaces. Bottom left: The binding energy of a water molecule to a TiO_2 surface as a function of cluster size in comparison to periodic DFT calculations. Right: Convergence of the binding energy at the DLPNO-CCSD(T) level using the same cluster models).

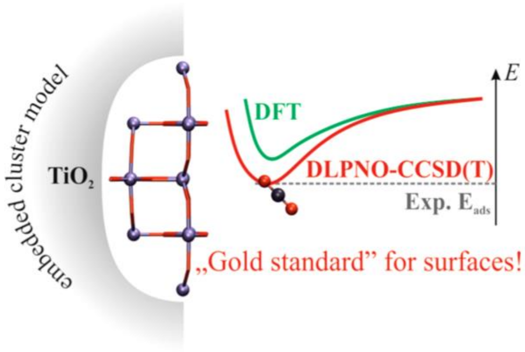


Fig. 15: Cluster calculations in combination with DLPNO technology has led to accurate binding energies for small molecules on TiO2 surfaces. For the first time results where obtained within 1 kcal/mol of experiment using careful cluster and basis set convergence studies. No DFT functional provides this type of accuracy over a range of substrates).

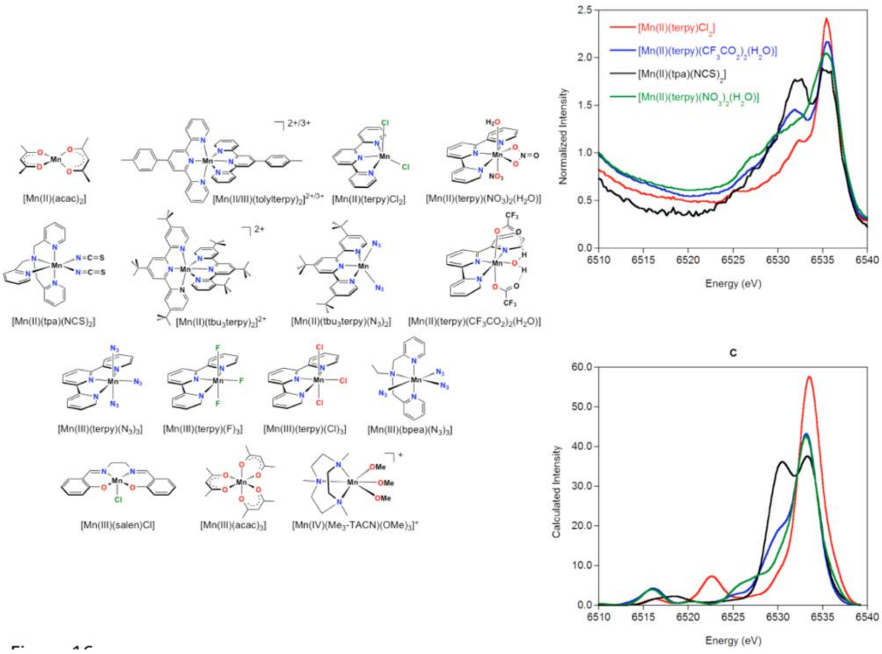


Fig. 16: A systematic study on a series of monomeric manganese complexes reveals that density functional theory is a powerful tool for the prediction of these spectra in the core-to-valence region

(3) Molecular spectroscopy

The department is involved in a wide range of advanced spectroscopic experiments that are aimed at obtaining geometric and electronic structure information on stable as well as transient open-shell transition metal species. Apart from standard laboratory equipment UV/vis, IR Raman, Fluorescence and NMR spectroscopy) the department focuses on the following techniques:

(a) ***X-ray Absorption and Emission spectroscopy***. Modern synchrotron based techniques allow for many exciting, element specific experiments to be performed. The group of Prof. DeBeer is actively involved in the development and application of new X-ray based techniques.[10a-d, 22b, 23a, 34]

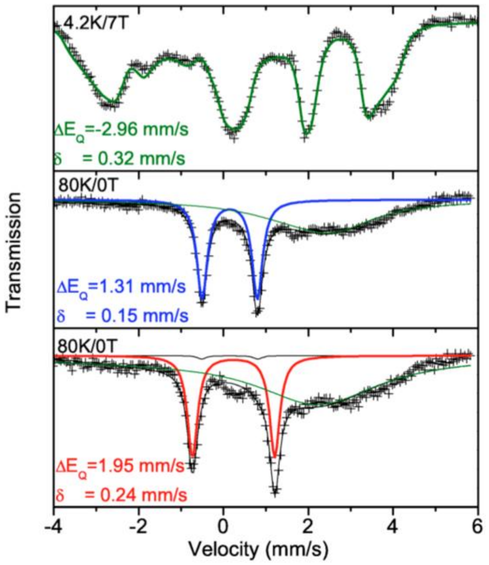


Fig. 17: Mößbauer spectroscopy can be used to investigate reaction intermediates. In this example three different intermediates have been observed in the course of an enzymatic reaction.

(b) ***Mößbauer spectroscopy*** is one of the most powerful tools for the investigation of iron containing enzymes, coordination complexes and materials. The group of Dr. Bill has a long term tradition on performing and analyzing Mößbauer spectra with and without an applied external magnetic field.[23b, 25a, 26-27, 35]

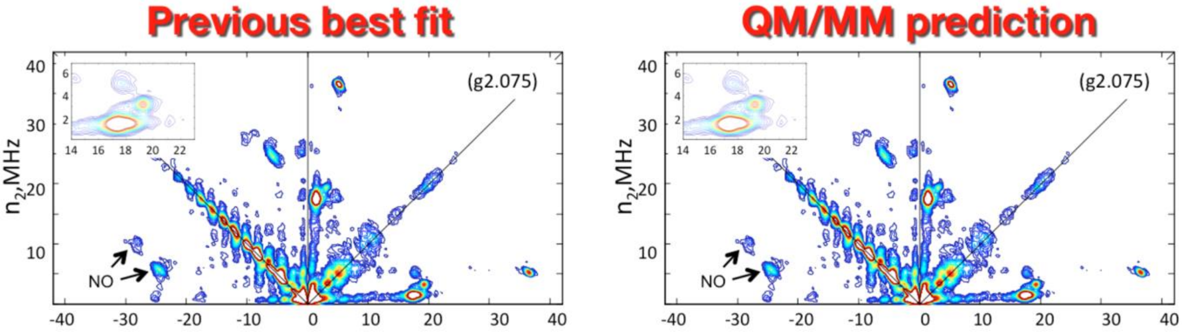


Fig. 18: High-resolution EPR combined with modern quantum chemistry provides extended insight into fine structural and electronic details. In this example, the HYSCORE spectra of nitrosyl-myoglobin have been successfully assigned on the basis of QM/MM calculations.

(c) ***High resolution electron paramagnetic resonance*** is the most powerful technique to investigate paramagnetic molecules. In addition to our collaboration with the department of Prof. Lubitz this technique is implemented in our department in the group of Dr. Maurice van Gastel who is exploring novel techniques as well as applications in the fields of bioinorganic chemistry and energy research.[36]

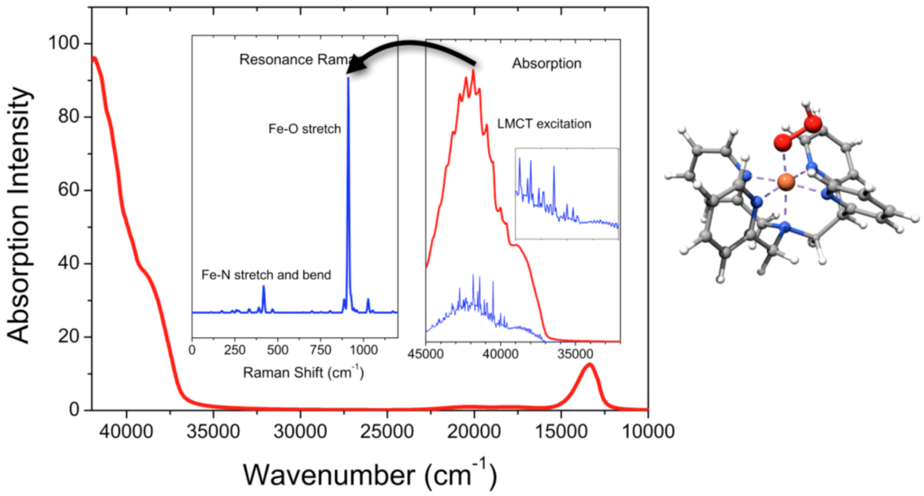


Fig. 19: Resonance Raman spectroscopy provides a detailed electronic structure picture of the excited state that is excited. The vibrational pattern is characteristic for the chromophore and type of excitation.

(d) ***Resonance Raman spectroscopy*** is a particularly powerful technique for the investigation of chromophores. This technique is represented in our department by Dr. Maurice van Gastel who is developing the instrumental as well as theoretical aspects of the technique.[8c, 12, 37] Using resonance Raman spectroscopy one obtains highly and selectively vibrationally resolved information about absorbing species. Besides carrying a wealth of electronic structure information, the enormous enhancement of the inelastic response of a system once excited in the area of an absorption band provides extremely powerful fingerprints that allow for the characterization of elusive species.[37a]

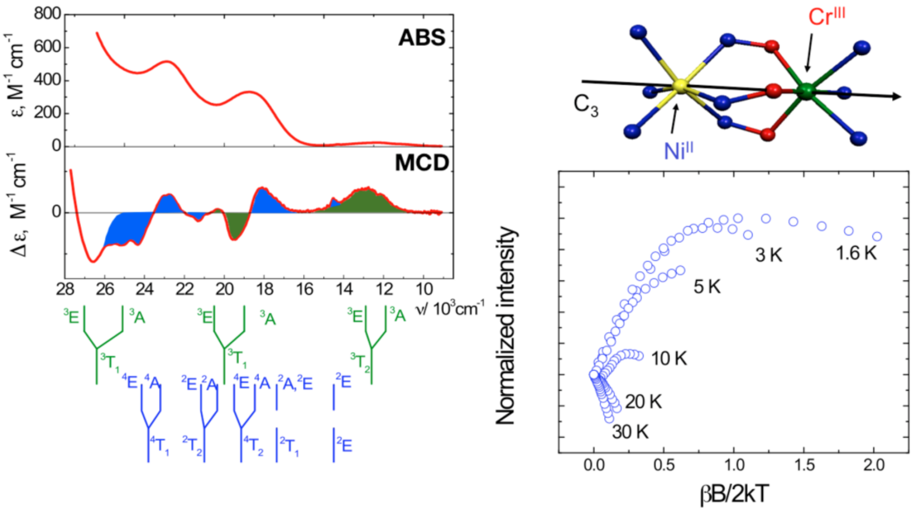


Fig. 20: MCD spectroscopy provides high-resolution electronic structure insight as well as an optical probe of the ground state magnetic properties. In this example the magnetism of an exchange coupled transition metal dimer has been revealed by MCD spectroscopy (right). The MCD spectra are superpositions of the individual ion spectra with the signs being characteristic of the magnetic coupling pattern.

(e) ***Magnetic Circular Dichroism spectroscopy*** is a powerful technique that bridges the fields of optical and magnetic spectroscopy. MCD, as applied to paramagnetic substances, provides a wealth of electronic structure information. In addition, variation of applied field and temperature allows for the optical measurement of the ground state magnetic susceptibility even in the presence of mixtures or impurities. The MCD laboratory is also headed by Dr. Bill using a home-designed setup that allows for spectra to be taken all the way from the deep UV to the near-IR regions.[13, 25a, 25e, 38]

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