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Tailoring the Chemical Reactivity and Optical Properties of Nanoclusters by Size, Structures and Lasers

The reduction of dimensionality of solid materials imposes extraordinary novel features. Discovery and understanding of the chemical and physical properties of nanostructures (–10^{-9} m) and other low-dimensional systems have led to numerous technological applications. Prominent examples are new light sources, lasers, information storage and information processing technologies, etc. Agglomerates of atoms – clusters in the size regime in which the structure and the number of atoms control their properties, that means each atom counts, belong to such nanoscale materials. Our research on pure and doped metal clusters focuses on fundamentals as well as on novel applications in the following areas: I. Chemical reaction control or laser selective chemistry of nanoclusters with tailored light fields (ultrashort laser pulse shaping); II. Structure-reactivity relationships of metal oxide clusters as foundations for the development and design of nanoscale catalytic materials and III. Photophysical and photochemical size selective properties of metallic clusters and their potential for optical storage elements and for emitters in optical devices. We bridge the nano with bio science by investigating the metal binding site in the octarepeat domain of the prion protein which might induce transition from the native to the pathological form of PrP being responsible for mad cow disease and Creutzfeld-Jacob disease (CJD) in humans. Investigation of above topics requires development of theoretical concepts and methods combining ab initio quantum chemistry with molecular dynamics as well as close cooperation with experimentalists.

New strategy for optimal control of ultrafast processes in complex systems

Chemical bonds break and form extremely rapidly involving motions of electrons and atomic nuclei. In order to record or to observe atomic-scale dynamics over the distance of 1Å (10^{-8} cm) the time of ~100 fs (10^{-15} s) is required. Exploration of these processes in the field of femtochemistry became reality due to ultrafast pulsed laser techniques. With femtosecond time resolution one can »freeze« structures far from equilibrium and follow their time evolution recording particular snapshots [1]. The basic idea involves the preparation of a transition state of the chemical reaction by optical excitation of a stable species with the pump pulse in a nonequilibrium nuclear configuration and probing its time evolution by laser induced techniques using the time delayed probe or dump pulses. This involves multi state dynamics on three or two electronic states, respectively [2–5].

Furthermore the controlled or selective femtochemistry became an attractive field due to developments of pulse-shaping techniques and optimal control theory [6]. They allow to generate laser fields which control the molecular processes on fs-scale by suppressing one reaction pathway and by favouring the other one leading to the desired chemical product via optimal pathway and with the maximal yield. However the optimal control of complex multidimensional systems such as nanostructures or biological systems requires new concepts for establishing and finding the connective pathway between the initial state and the objective (target) involving two electronic states having usually very different features.

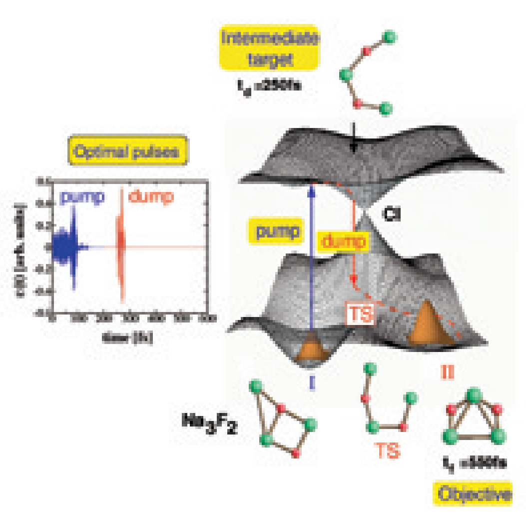

Fig. 1
New strategy for the pump-dump optimal control based on the intermediate target in the Na_3F_2 cluster. The optimised pulses are shown on the left side which drive the system to the objective (isomer II) with the maximal yield avoiding conical intersection (CI). Isomer I and transition state structure (TS) are also shown. Na atoms (green), F atoms (red).

We developed a new strategy for optimal pump-dump control in complex systems by introducing the concept of the intermediate target in the excited state [7,8]. Its role is to sample the appropriate parts of the energy surfaces at a given time delay between the two pulses, ensuring the connective pathway between the initial state and the objective as well as the optimal yield. Our theoretical approach involves density matrix formulation based on ab initio Wigner distribution approach which has been recently developed in the group [2,3]. This method involves ab initio adiabatic and nonadiabatic molecular dynamics (MD) »on the fly« in the excited and ground electronic state without precalculation of both energy surfaces and is therefore suitable for systems with a considerable number of degrees of freedom. The analysis of the resulting classical trajectories allows to identify intermediate target which is defined as a localized ensemble corresponding to the maximum overlap between the forward propagated density on the electronic excited state (started from the initial state) and the backward propagated density from the objective, at the optimal time delay between the two pulses. We illustrate the scope of this general concept by optimizing and analyzing the pump and dump pulses for driving the isomerization process in Na_3F_2 cluster to the isomer II by suppressing radiationless transition through the conical intersection as shown on Fig. 1. The pathway through the conical intersection is energetically most favourable but due to a large excess of energy both isomers are comparably populated. In contrast, with our new strategy for optimal control the maximal residence time in the second isomer was achieved for the ensemble corresponding to the dump time of t_d = 250 fs (cf. Fig. 1). This ensemble is used as the intermediate target and is related to the transition state (TS) separating two isomers in the ground state. Optimisation of the pump pulse outlined in the ref. [7] lead to 82 % efficiency of localizing the ensemble in the intermediate target. The optimal pump pulse is shown as the first pulse in the left panel of

Fig. 1. The analysis shows that the excitations of low lying vibrational modes involved in breaking of Na-Na bond and one of Na-F bonds in the first isomer, corresponding to the first temporal portion of the pulse, are responsible for reaching the intermediate target. The optimized dump pulse is very short (second pulse on the left panel of Fig. 1) providing evidence that the time window for the depopulation of excited state around t_d is very short. The optimized dump pulse localizes the density in the second isomer with 80 % efficiency achieving our aim. Control of population of such bimodal system might provide the basis to construct the bimolecular »flip-flop« switch which can be used for information storage.

The above analysis of the MD and of the tailored pulses allows us to identify mechanisms based on the selection of appropriate vibrational modes responsible for optimal control of chemical reaction. This opens the possibility for application of bond selective femtochemistry to complex nano or biological systems, provided that the intermediate target can be found.

Structure-reactivity relationships of metal oxide clusters

Development of effective catalysts with the ability to selectively oxidize hydrocarbons is important to many industrial processes [9]. For this purpose transition metal oxides are most widely used. In contrary, it is known that for the air purification supported gold catalysts in humid environment function well. However, the mechanisms which govern catalysts reactions are still not completely understood. Elucidating the structure-reactivity relationship of surfaces plays a key role in understanding catalytic activity and selectivity. The study of gas phase clusters serves as recognized approach to model active sites on catalytic surfaces, since the influence of composition, stoichiometry, charge and oxidation states, size and coordinative saturation on their reactivity can be determined. The influence of interface can be also included. Our research in this area focuses on both classes of materials, transition metals and nobel metals (pure and alloys). For example, we investigated the reactions of $V_xO_y^+$ clusters towards ethylene considering atomic and molecular oxygen loss, oxygen transfer and association reaction [10,11]. The experiments showed significant and highly cluster size specific reaction pathways, which prompted us to unravel the mechanism responsible for the observed phenomenon. We found a radical cation mechanism based on structure-reactivity relation of $(V_2O_5)_n^+$ n=1,2 clusters which explains oxygen transfer channel and confirms that this reaction is size selective. Structures of both $V_2O_5^+$ and $V_4O_{10}^+$clusters contain an oxygen centered radical center with an elongated V-O bond and unpaired electron localized at the oxygen atom. The energetic profile for oxygen transfer reaction for $V_4O_{10}^+$and the general mechanism for this reaction are shown on the left and right side of Fig. 2, respectively. The reaction is thermodynamicly favourable. The mechanism begins with the formation of a single bond between the first carbon atom of the ethylene and the oxygen atom of the cluster with the radical center. This radical is

Zusammenfassung

Die Dimensionsreduzierung in festen Stoffen bewirkt die Entstehung neuartiger Phänomene. So führten die Entdeckung und das Verständnis chemischer und physikalischer Eigenschaften von Nanostrukturen zu der Entwicklung von u.a. neuen Lichtquellen, Lasern und Technologien der Informationsverarbeitung und -speicherung. Agglomerate von Atomen, Cluster von einer Größe, in der die Eigenschaften durch die Zahl und Art der Atome bestimmt werden (Jedes Atom zählt!) gehören ebenfalls zu diesen Nanostrukturen. Unsere Forschung an reinen und gemischten Metall-Clustern konzentriert sich sowohl auf die Grundlagen als auch auf neuartige Anwendungen, wie unter anderem auch die I. Kontrolle chemischer Reaktionen und laser-selektive Chemie von Nanoclustern mit maßgeschneiderten Lichtfeldern (geformte ultrakurze Laserpulse); II. Analyse der Abhängigkeit zwischen Struktur und Reaktivität von Metalloxid-Clustern als Grundlage für die Entwicklung und das Design neuartiger Nanokatalysatoren; III. Untersuchung größenabhängiger photophysikalischer und -chemischer Eigenschaften metallischer Cluster und deren Potential, als optische Speicherelemente und Emittoren in der Optoelektronik zu dienen. Darüber hinaus kombinieren wir die Nano- mit der Biowissenschaft z.B. durch die Untersuchung der Bindungsmöglichkeiten von Metallen an die Oktarepeat-Domäne des Prion-Proteins (PrP). Diese Wechselwirkung kann Veränderungen von der natürlichen zur pathologischen Form des PrP induzieren und dadurch Rinderwahnsinn und die Creutzfeld-Jacob-Krankheit beim Menschen auslösen. Die Untersuchung dieser Forschungsthemen erfordert sowohl die Entwicklung von theoretischen Konzepten und Methoden, die ab initio-Quantenchemie mit Molekularer Dynamik verbinden, als auch eine enge Kooperation mit Experimentatoren.

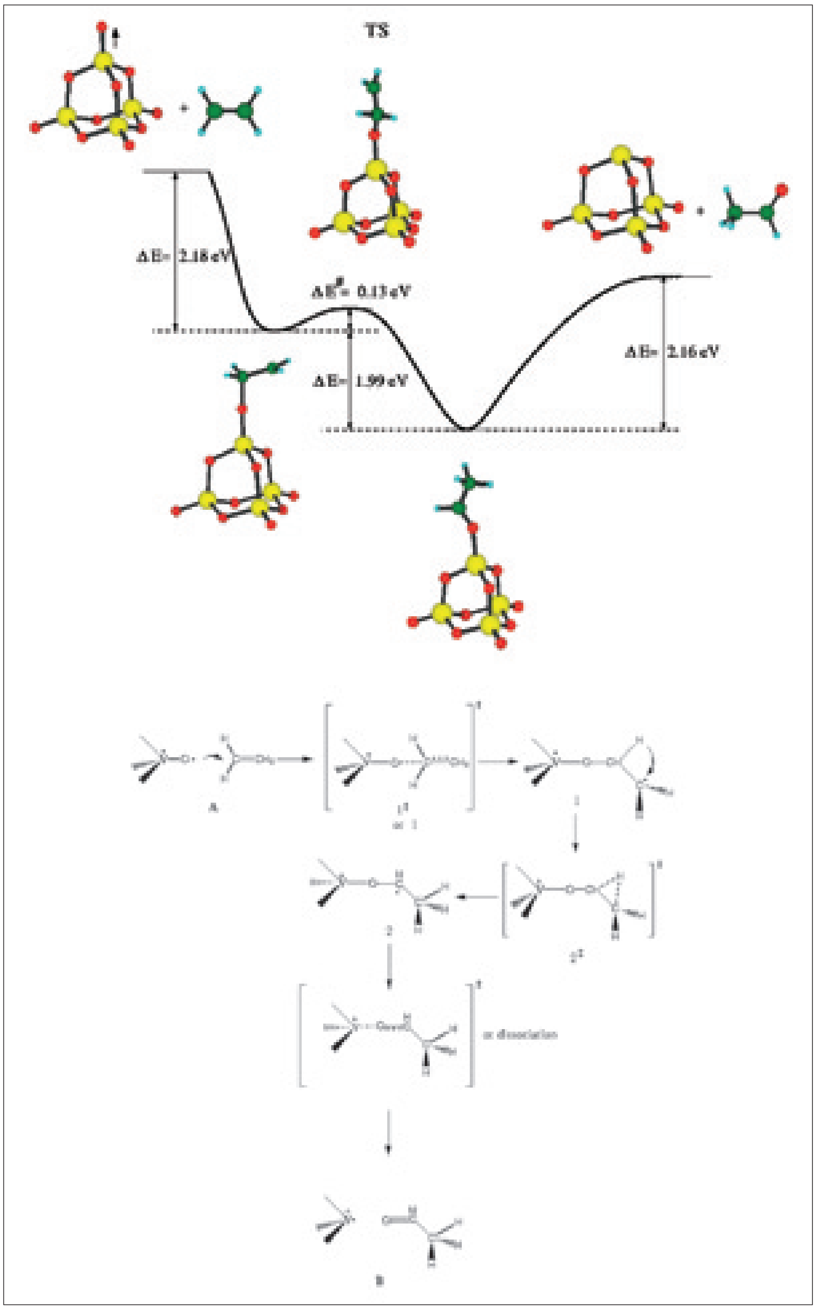

Fig. 2
Energetic profile for the reaction between $V_4O_{10}^+$ and C_2H_4 with a general mechanism.

shifted from the first to the second carbon atom and back after the hydrogen transfer occurs. Dissociation of the C_2H_4O product then takes place leaving the vanadium atom, which had been bound to oxygen atom with the radical center.

Our results together with the experimental findings provide evidence for the selectivity of the $V_xO_y^+$ clusters due to the charge as well as the capability of vanadium to assume different oxidation states for different cluster sizes. In the case of $(V_2O_5)_n^+$ n = 1,2, the oxygen atom can be reversibly bound and released promoting catalytic oxidation of hydrocarbons, providing evidence that gas phase clusters can serve as well suited prototypes for identification of reactive centers. In fact, the active sites identified as being responsible for oxidation are in agreement with indirect experimental findings of active sites on vanadia-titania surface, which were used to explain the formation of products such as acetaldehyde and formaldehyde. This illustrates that the study of reactions involving gas phase cationic vanadium oxide clusters and small hydrocarbons is suitable for identification of reactive centers responsible for selectivity in heterogeneous catalysis. Moreover, researchers were able to achieve a higher yield of acetaldehyde from the partial oxidation of ethane, which they attribute to an increased number of the active sites they believe are responsible for the reaction. This shows that a greater understanding of the active sites which facilitate certain catalytic processes can in fact lead to custom designed catalysts for specific purposes.

Structure and size dependent optical properties of nanoclusters and their application in optoelectronics
Photoactivated fluorescence has been recently produced upon visible illumination of silver oxide films due to photochemically generated silver nanoclusters [12]. Such newly identified properties of nanoparticles open the possibility to photochemically control their fluorescent spectral features. Ag_n photoproduction from silver oxide might be utilized in optical storage materials to write data. Observed strong size dependent fluorescence in small Ag clusters produced by silver oxide represents a potential for parallel readout and increased storage capacity due to the possibility of color mixing for different cluster sizes. We investigated absorption spectroscopic patterns of silver clusters using state of art accurate quantum chemical methods based on coupled cluster theory. They are strongly size and structure dependent (each atom counts) and are characterized by the dominant transition with extremely large absorption cross section, which is responsible for the ability of silver clusters to fluorescence [13] as shown on example of Ag_8 in the upper part of Fig. 3. Strong visible fluorescence has been also experimentally observed for Ag_8 in an argon matrix as shown in lower part of Fig. 3. The comparison with the experimental results in Fig. 3 illustrates accuracy and predictive power of our results. Only the stable T_d structure is responsible for observed excitation and fluorescence-spectra. The experimentalists were able to determine the amounts of different isomers of Ag_8 in their sample by fitting recorded absorption spectral profile to the calculated spectra for different isomers with T_d and D_{2d} structures as shown in Fig. 3. We are presently extending our studies on investigation of optical properties of silver clusters supported on silver oxides which serves as photoactivable material and at the same time stabilizes desired processes such as spontaneous or stimulated emission in Ag-clusters. We aim to identify and characterize supported silver clusters which are responsible for observed multicolour fluorescence as well as those one which are suitable for photostable emitters.

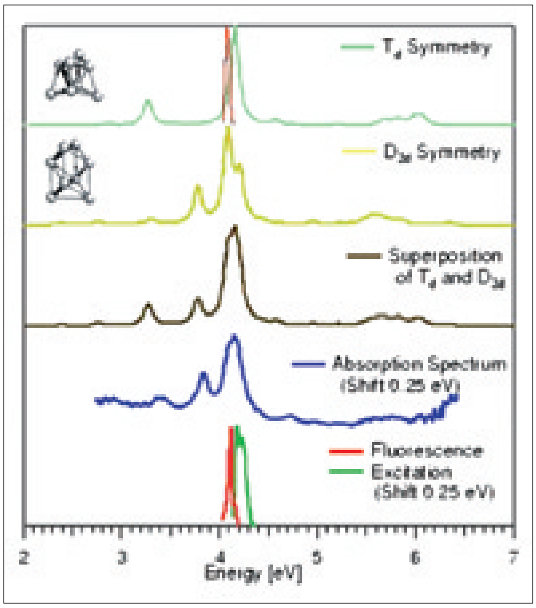

Fig. 3
Comparison of calculated absorption spectra for T_d (green) and D_{2d} structures (yellow), their superposition (brown) with experimental absorption spectra (blue). Observed fluorescence band in the bottom panel (red) and the calculated for the T_d structure (red) in the upper panel are in perfect agreement.

This is an ideal opportunity to obtain new functionality of the nanoparticles with tailored properties which are suitable for applications in optical devises.

Influence of metal ions on conformational changes in the octarepeat domain of the prion protein

Peptides are effective and specific ligands for a variety of metal ions and the formation of protein-metal complexes can have a decisive influence on the protein folding process. Recently, it has been shown that the prion protein binds Cu(II) ions, and might act as a regulator of the concentration of copper and reactive oxygen species. Moreover, copper coordination may affect the structure of the prion protein and induce the transition from the native to the pathological form of PrP [14]. Experimental data show that Cu^{2+} is bound by the N-terminal domain, which is composed of four or more octarepeats with eight-residue sequence PHGGGWGQ. In order to contribute to the characterization of structural and electronic properties of peptide-Cu complexes related to the octarepeat domain of the prion protein we have carried out DFT calculations on model complexes. We determined relative stabilities of four and five coordinated Cu-complexes and investigated the influence of different effects such as formation of hydrogen bonds and the peptide strain. Our results show that a modification in the coordination of Cu occurs by introducing additional stabilizing effects due to H-bonds [15]. This modification is of biological relevance for understanding transition from the native to the pathological form of the prion protein. In this context, further experimental and theoretical work is in progress.

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