We present a study of dynamics and ultrafast observables in the frame of pump–probe negative-to-neutral-to-positive ion (NeNePo) spectroscopy illustrated by the examples of bimetallic trimers Ag2Au−/Ag2Au/Ag2Au+ and silver oxides Ag3O5−/Ag3O2/Ag3O2+ in the context of cluster reactivity. First principle multiscale adiabatic dynamics allows us to determine time scales of different ultrafast processes and conditions under which these processes can be experimentally observed. Furthermore, we present a strategy for optimal pump–dump control in complex systems based on the ab initio Wigner distribution approach and apply it to tailor laser fields for selective control of the isomerization process in Na3F2. The shapes of pulses can be assigned to underlying processes, and therefore control can be used as a tool for analysis.

ultrafast ab initio dynamics | NeNePo spectroscopy | optimal control

Investigation of femtosecond dynamical processes in elemental clusters and their control by tailored laser fields are of fundamental importance for learning how the interplay of size, structures, and laser fields can be used to manipulate optical properties and reactivity of these species (1). This research area involving combination of laser-selective femtochemistry (2–5) with the functionality of nanostructures opens new perspectives for basic research and numerous technical applications. In particular, exploration of clusters in the size regime in which each atom counts is attractive, because in this regime structures and the numbers of atoms directly determine size-selective properties (6–12). Another important aspect is that the study of ultrafast dynamics in clusters with finite densities of states allows for separation of time scales of nuclear motion (1). Therefore, the identification of different ultrafast processes such as geometric relaxation, internal vibrational relaxation (IVR), different photoionization pathways, fragmentation, etc. becomes attainable (13–19). Moreover, optimization of the laser fields permits one to manipulate these processes by favoring or suppressing some of the chosen channels. In both contexts, the role of theory is essential from conceptual as well as from predictive point of view.

Theory not only determines time scales of different processes and predicts ultrafast observables, but also finds conditions under which they can be experimentally realized (13). Moreover, the analysis of shaped laser pulses and the comparison with experimentally optimized laser fields allows us to identify the underlying processes and therefore to use optimal control (20–23) as the tool for analysis (1, 23).

In this contribution we address both aspects by showing what we can learn (i) from the pump–probe signals and (ii) from the optimized pulse shapes. We also wish to show that for accurate simulations of pump–probe signals and for developing new control strategies for complex systems, the semiclassical limit of the Liouville formulation of quantum mechanics offers a suitable theoretical approach (1, 14, 15, 23). This is based on the Wigner–Moyal representation of the vibronic density matrix combined directly with adiabatic and nonadiabatic molecular dynamics (MD) “on the fly” (without precalculation of the energy surfaces) developed in one of our laboratories (14, 15, 23). This approach describes approximately quantum phenomena such as optical transitions by means of the averaged ensemble of classical trajectories. Moreover, the systematic introduction of quantum effects is possible although computationally demanding and still in development (24). Our ab initio Wigner distribution approach is an appropriate choice to study ultrafast processes in elemental clusters with heavy atoms, for which in the first approximation the classical description of nuclear motion is acceptable and all degrees of freedom have to be considered because usually these clusters do not contain a “chromophore type” subunit and do not obey regular growth patterns.

At the same time, we wish to show the scope of our pump–probe negative-to-neutral-to-positive ion (NeNePo) spectroscopy, introduced by some of the authors (25), which is capable of resolving structural properties, geometry relaxation, IVR, and isomerization processes (13). This will be illustrated on the example of bimetallic trimers and trimer–oxygen complexes.

We wish also to present a strategy for control of ultrafast processes applicable to complex systems. Many control experiments are based on evolutionary algorithms in a feedback loop proposed by Judson and Rabitz (26). By using an iterative process, the method enables one to find an optimal pulse from which, under the given conditions, the target system can be reached. The aim of these experiments was to achieve maximal yields for a selected objective. However, the major goal of our theoretical approach is to attain information about the photo-induced process itself, which we wish to address here. In this context, a strategy for optimal control will be shown and applied to control the isomerization process in Na3F2 cluster.

Dynamics and Ultrafast Observables in the Framework of NeNePo Spectroscopy

The real-time investigation of intra- and intercluster and molecular electronic and nuclear dynamics by femtosecond spectroscopy during the geometric transformation along the reaction coordinate is based on two steps: first on the preparation of the transition state of the chemical reaction by the optical excitation of a stable species in a nonequilibrium nuclear configuration in the pump step, and second on probing its time evolution by laser-induced techniques such as fluorescence, resonant multiphoton ionization, or photoelectron spectroscopy (2, 4). A nonequilibrium or transition state can also be produced by vertical photodetachment of stable negative ions (27, 28). Vertical one-photon detachment techniques were advanced by introducing the NeNePo pump–probe experiments (25). They allowed for probing of structural relaxation and isomerization processes in neutral clusters as a function of the cluster size and...
the atomic composition (13, 16). Moreover, the NeNePo spectroscopy of clusters bridges ground-state dynamics of these species with real-time investigation of chemical reactions, which opens opportunities to study reactions of clusters toward inorganic and organic molecules and to control them by laser fields.

Methods

Experimental and Computational. The experimental setup for temperature-controlled ultrafast NeNePo spectroscopy is described in ref. 18, and here only the main features will be outlined. The charged clusters formed in a sputtering process are steered into a helium-filled quadrupole where clusters are thermalized. After mass selection, monodisperse clusters are then introduced into a helium-filled (~1 Pa) octupole ion trap. The radio frequency octupole ion trap allows trapping of ions for seconds without significant loss. To achieve the temperature control, the trap is attached to a closed-cycle helium cryostat, which allows variation of temperature in the range between 20 and 350 K.

The femtosecond laser pulses were generated by a home-built Ti:sapphire oscillator of the Kaptay–Murnane type that was continuously pumped by a 5-W Spectra-Physics Millenium Nd:YVO4 laser. Pulses were amplified with a Nd:YLF-laser-pumped Quantunix Odin multipass amplifier to yield 1-mJ, 40-fs, 812-nm pulses at a 1-KHz repetition rate. The typical time resolution obtained in the NeNePo measurements is 80 fs. After the electron is photodetached the dynamics is probed by a time-delayed pulse that induces a two-photon ionization process. Cations formed then are extracted by electrostatic field and mass-analyzed with the final quadrupole mass filter. The cationic ion current is recorded as a function of the pump–probe delay giving rise to a transient NeNePo signal.

The simulations of the time-resolved NeNePo spectra were carried out in the framework of our Wigner distribution approach based on the propagation of the ensemble of classical trajectories carried out “on the fly.” Because here the dynamics in the ground electronic states of neutral species is required, we employ the gradient corrected density functional theory with the atomic orbitals (Gaussian basis sets) as the method of choice. For details on electronic structure calculations, cf. refs. 18 and 29.

The simulations of the NeNePo pump–probe signals involve three steps. (i) First an ensemble of initial phase space points is generated by sampling the Wigner distribution function corresponding to the initial state. This is done for the canonical ensemble invoking the harmonic approximation. The Wigner distribution for each normal mode is given by

\[ P(q, p) = \frac{\alpha}{\pi \hbar} \exp \left\{ -\frac{2\alpha}{\hbar \omega} (p^2 + \omega^2 q^2) \right\}, \]

where \( \alpha = \tanh(\hbar \omega/2k_B T) \), and \( \omega \) is the normal mode frequency, corresponding to the full quantum mechanical density distribution. (ii) In the second step the initial phase space ensemble is propagated on the neutral electronic state by solving the classical equations of motion using forces calculated “on the fly.” Parallel to the propagation of the ensemble, the time-dependent energy gaps between the neutral and cationic states are calculated for each trajectory. (iii) The pump–probe signal is determined for each trajectory according to

\[ S[t_d] = \lim_{t \to \infty} P_{EE}^{\infty}(t) \]

\[ = \int dq_0 dp_0 \int_0^\infty d\tau_1 \exp \left\{ -\frac{1}{\sigma_{pu}^2 + \sigma_{pr}^2} \left( \tau_1 - t_d \right)^2 \right\} \]

\[ \times \exp \left\{ -\frac{\sigma_{pr}^2}{\hbar^2} (p_0 - V_{DPE}(q_0, p_0))^2 \right\} \]

\[ \times \exp \left\{ -\frac{\sigma_{pu}^2}{\hbar^2} (q_0 - V_{DPE}(q_0, p_0))^2 \right\} P_{00}(q_0, p_0). \]

In this expression \( \sigma_{pu} \) (\( \sigma_{pu} \)) and \( E_{pu} = \hbar \omega_{pu} \) (\( E_{pr} = \hbar \omega_{pr} \)) are the pulse durations and excitation energies for the pump and probe step with a time delay \( t_d \). \( V_{DPE}(q_0, p_0) \) labels the time-dependent energy gaps between the neutral and cationic ground states calculated at coordinates \( q_0 \) on the neutral ground state with initial coordinates and momenta \( q_0 \) and \( p_0 \) given by the anionic thermal Wigner distribution \( P_{00}(q_0, p_0) \) and \( V_{DPE}(q_0) \) are the vertical detachment energies of the initial ensemble. The signal is calculated by averaging over the whole ensemble. The time resolution of the signal is determined by the pump–probe correlation function with the probe window located around the time delay \( t_d \), which is represented by the first exponential in Eq. 2.

Results: NeNePo on Ag2Au+/Ag2Au/Ag2Au+ and AgO2−/AgO2/AgO2+. The ultrafast dynamics in the ground electronic state of neutral Ag2Au induced by the photodetachment of the anionic species offers an opportunity to study the geometric relaxation followed by the ultrafast vibrational energy redistribution (IVR). The energy intervals necessary for detection of these processes can be inferred from the scheme of the multistate femtosecond dynamics presented in Fig. 1. Because the simulations have been carried out for the initial ensemble at 20 K, it is justified to assume that only the linear isomer in the anionic state contributes because the second isomer is 0.36 eV higher in energy (cf. Fig. 1). Moreover, due to the low temperature the harmonic approximation is valid, and the initial conditions for the ensemble propagation were generated by sampling the canonical Wigner distribution function as defined in Eq. 1. For the detection, two scenarios can be distinguished. The first involves the NeNePo-ZEKE (zero kinetic energy electrons) process in which no kinetic energy is transferred to the photodetached electron. The second scenario corresponds to the classical NeNePo experiment in which the excess energy is accounted for by integrating over the populations of anionic and cationic states over the entire excess of energy range. Usually, integrated signals do not allow distinguishing different processes (cf. refs. 13 and 18).

The simulated and experimental signals are presented on the right side of Fig. 1. Because the probe pulse energy \( E_{pr} = 7.7 \) eV exceeds the highest ionization potential of the neutral Ag2Au species (7.49 eV; cf. Fig. 1), our NeNePo simulations predict that the signal corresponding to this energy will rise and become constant at later times due to the contribution of the continuum. This allows probing the system while it leaves the transition state region reached by the photodetachment. Comparison between the simulated and experimental signal presented in Fig. 1c shows the time scale for leaving the transition state region to be \( \approx 1 \) ps. Reducing the energy of the probe pulse to 7.1 eV reveals an intermediate structure on the way between the linear and triangular structure. The simulated NeNePo-ZEKE and experimental signal are in perfect agreement and allow detection of the geometrical relaxation with the onset at \( \approx 500 \) fs. The signal reaches the maximum at \( \approx 1 \) ps and has an offset at \( \approx 2 \) ps. If the energy of the probe pulse is further lowered to 6.1 eV, the appearance of the triangular structure and subsequent IVR process can be probed. This signal has its onset at \( \approx 2 \) ps, reaches
the maximum at $\approx 2.4$ ps, and then decays slightly due to the increasing delocalization of the phase space ensemble due to the IVR process. Good agreement between the simulated NeNePo and experimental signals (cf. Fig. 1a) indicates that in this case the IVR process induced by the internal collision between the terminal Ag and Au atoms has been observed (18). It should be pointed out that, for the probe pulse energy of 6.1 eV, the contribution of the continuum is negligible and therefore NeNePo-ZEKE and NeNePo simulated signals are very close to each other (cf. two full lines in Fig. 1a). In summary, our joint theoretical and experimental effort has shown that different dynamical processes can be identified in the NeNePo spectra and that their time scales can be determined, provided that the experiment is carried out close to the ZEKE conditions shown in Fig. 1a.

Next, we show that NeNePo spectroscopy provides valuable information about dynamical processes in neutral species in the context of the cluster reactivity. We investigated previously the electronic and structural aspects of adsorption of molecular oxygen on anionic silver clusters (9). Here the dynamics of the complex Ag$_3$–O$_2$ will be presented for the first time. The scheme of the multistate dynamics is presented in Fig. 2a. Anionic isomers (isomer AI with a linear Ag$_3$ subunit, and isomer AII with a triangular Ag$_3$ subunit) are very close in energy, and the exact energy sequence is difficult to predict theoretically, even with highly accurate methods. However, due to the pronounced differences in vertical detachment energies (VDEs) of both isomers, they can be selected by appropriate choice of the pump-pulse energy. We assume that only isomer AI is populated in the anionic ground state and use a canonical Wigner distribution function given in Eq. 1 at $T = 20$ K to generate the initial conditions. After the photodetachment with the pump-pulse energy of 2.75 eV, a transition state in neutral Ag$_3$O$_2$ is reached. Three isomers are present for Ag$_3$O$_2$ as shown in Fig. 2. In the structure of the global minimum (isomer I), the molecular oxygen bridges two silver atoms (cf. Fig. 2a). In the two higher-lying isomers, molecular oxygen is bound to one silver atom, forming one and two bonds, respectively. Therefore, after the photodetachment a dynamical process dominated by the Ag$_3$ relaxation from the linear to the triangular structure is induced. At later times the energy gained by the cluster isomerization is partially transferred to molecular oxygen leading mainly to the mixture of the two higher lying isomers (II and III). After 5 ps the global minimum (isomer I) is populated only by $\approx 10\%$. The snapshots of the dynamics in the neutral state are presented in the Fig. 2c, showing the onset of the geometric relaxation of the Ag$_3$ subunit at 500 fs, the arrival to the triangular Ag$_3$ subunit at 1 ps, and the final ensemble of isomers after 5 ps. The simulated NeNePo-ZEKE pump–probe signals for Ag$_3$O$_2$ are presented in Fig. 2b. The signal for the probe pulse energy of 7.6 eV exhibits a fast decay after $\approx 1$ ps due to the escape from the initial Franck–Condon region reached upon the photodetachment. However, this signal starts to rise again after 2 ps because the global minimum with the ionization potential of 7.62 eV is being populated at later times. This signal offers an opportunity to identify the isomerization process leading to the global minimum in the ground state and also to determine its time scale. If the energy of the probe pulse is lowered to 7.3 eV the onset of the isomerization of the Ag$_3$ subunit starting at $\approx 500$ fs can be selectively probed. Further lowering of energy to 6.8 eV allows us to probe the IVR process induced after the intracluster collision within the Ag$_3$ subunit. It should be pointed out that in contrast to the Ag$_2$Au, here the IVR process is extended also to the O$_2$ subunit and is responsible for the final populations of the isomers, because they mainly differ by the bonding of O$_2$ subunit.

In summary, we expect that the future studies of the dynamics of reactive complexes between metal clusters and small molecules may shed new light on the influence of the dynamics and particularly IVR on their reactive (catalytic) properties. Moreover, the population of the minimum with corresponding reactive centers can be controlled by tailored laser fields.

Fig. 1. Ag$_2$Au$^+$/Ag$_2$Au/Ag$_3$Au$^+$ NeNePo. (Left) Scheme of the multistate femtosecond dynamics for NeNePo pump–probe spectroscopy of Ag$_2$Au$^+$/Ag$_2$Au/Ag$_3$Au$^+$ with structures and energy intervals for pump and probe steps. (Right) Comparison between simulated (full line) and experimental (circles) pump–probe signals at different probe pulse energies.
Concepts for Control of Ultrafast Processes in Complex Systems

Exploration of coherence properties of laser radiation due to quantum mechanical interference effects led to the idea of controlling the selectivity of product formation in a chemical reaction by using ultrashort pulses with the proper choice of their phase or duration and the delay between the pump and probe (20, 21). This initiated the shaping of pulses in the framework of the many-parameter optimal control theory (OCT) (22, 30, 31). Technological progress due to femtosecond-pulse shapers allowed introducing closed loop learning by Judson and Rabitz (26), which opened a possibility to control more complex systems. The idea was to combine a femtosecond-laser system with a computer-controlled pulse shaper to produce tailored fields that initiate the photochemical process and to use the learning algorithm to optimize iteratively the field based on yield obtained from the experimental target. Such a black box is very useful but does not provide information about the nature of the underlying processes that are responsible for the outcome. This is true in particular for complex systems, due to the manifold of local solutions within the multiparameter optimization scheme that are reachable depending on the initial conditions.

Therefore, for complex systems such as clusters, biomolecules, and their complexes, the important task is first to develop theoretical methods that allow one to design optimal laser pulses and second to establish a connection between the underlying processes. For such systems, precalculation of energy surfaces is impractical, and therefore ab initio adiabatic and nonadiabatic MD “on the fly” methods are particularly suitable. The Liouville space formulation of the OCT developed by Yan, Wilson, Mukamel, and their colleagues (32, 33), in particular its semiclassical limit in the Wigner representation, is suitable for developing optimal control strategies for complex systems despite its limitations. Quantum effects, such as interference phenomena, tunneling, and zero-point vibrational energy, are not accounted for, and these limitations had to be respected by choosing appropriate systems. Such a strategy for optimal control (23) will be presented and applied for optimization of the laser field that drives the photoisomerization process in the Na3F2 cluster into the second isomer avoiding the conical intersection between the excited and electronic ground state.

Methods and Results

New Strategy for Optimal Control in Complex Systems. The application of OCT to optical control of the complex molecular and cluster species has been until now mainly prohibited by the difficulties in the precalculation of multidimensional potential surfaces and the inability to perform the exact quantum dynamics simulations in these systems. Ab initio adiabatic and nonadiabatic MD “on the fly” represents a viable approach that can bypass these obstacles, identify properties necessary for assuring the controllability of complex systems, and detect the mechanisms responsible for the obtained pulse shapes. For complex systems it is still an open, central issue to determine the conditions under which optimal control involving more than one electronic state can be achieved (e.g., pump–dump control of...
isomerization). The complicated potential-energy landscapes of the ground and excited electronic states can substantially differ from each other, and therefore the existence of a connecting pathway between the initial state over excited state and the desired objective in the ground state has to be insured. Moreover, the optimal path must be found, and the method for nuclear dynamics and pulse optimization should be computationally realistic. This calls for the development of new strategies for the optimal control. An attractive possibility offers the concept of the intermediate target (cf. ref. 23) in the excited state. It is defined as a localized ensemble (wavepacket) corresponding to the maximum overlap between the forward propagated ensemble on the electronic excited state (starting from the initial state) and the backwards propagated ensemble from the objective in the ground state at the optimal time delay between both pulses.

In the case of the pump–dump control involving two phase-unlocked ultrafast fields in the weak response regime, we have shown that the concept of the intermediate target leads to the separate (uncoupled) optimization of the pump and dump fields, which is very advantageous from the computational point of view. An appropriate formalism to implement this strategy is based on the density matrix formulation of the OCT. It combines the Wigner–Moyal representation of the vibronic density matrix with \textit{ab initio} MD “on the fly” in the electronic excited and ground states (cf. refs. 14 and 15). (For details, cf. refs. 1 and 23.) The envelopes of the optimal pump and dump pulses are obtained by solution of two coupled Fredholm-type integral equations, which require an iterative solution because the integral kernels are coupled by the dump and pump field, respectively. The decoupling of these equations is possible in the short pulse regime, as outlined in refs. 1 and 23. The pump-pulse optimization involves the propagation on the excited state from \( t_0 \) until \( t_d \), forming the intermediate target. For the dump-pulse optimization, the dynamics in the ground state has to be carried out by taking the intermediate target as an initial ensemble and propagating in the ground state. Subsequently, both pump and dump pulses are determined by solving the Fredholm-type integral equations.

We illustrate this strategy to optimize pump and dump pulses for driving the isomerization process in the Na\(_3\)F\(_2\) cluster, avoiding the conical intersection between the ground and the first excited state and maximizing the population of the second ground-state isomer (cf. Fig. 3. Lower Left). For this purpose, the initial ensemble corresponding to the 50-K canonical ensemble has been generated by sampling the canonical Wigner distribution function in the harmonic approximation (cf. Eq. 1). The ensemble has been propagated on the excited state for 300 fs. (For details of electronic structure and MD, cf. refs. 1 and 23.)
To determine the intermediate target and the optimal time delay at which the dump should occur, the system has been dumped to the ground state (in regular time steps of 25 fs) and propagated subsequently. The isomer II is optimally reached by the ensemble dumping at \( t_d = 250 \) fs, and therefore this ensemble (cf. scheme in Fig. 3 Lower Left) is chosen to construct the intermediate target. The optimal pump and dump pulses are presented in Fig. 3 Upper Left. The optimal pump pulse exhibits two portions with durations of 70 and 10 fs, respectively. The Fourier analysis of the optimal pump pulse and the comparison with the Franck–Condon profile reveals that the excitation of low-lying vibrational modes at \( \approx 1.2 \) eV of the isomer I is responsible for driving the dynamics to the intermediate target. The Wigner–Ville transform of the optimal pump pulse shows that this energetically sharp transition corresponds to the first temporal portion of \( \approx 70 \) fs of the pump pulse. In contrast, a very short second portion after 80–90 fs is energetically much wider and corresponds to the tails of the Fourier transform that are symmetric with respect to the 1.2 eV transition. The optimal dump pulse is very short (\( \approx 20 \) fs) leading to a short time window for the depopulation of the excited state. The dynamics after the dump pulse illustrating the efficiency of the optimized pulses is presented in Fig. 3 Lower Left. It can be clearly seen that the phase space density is localized in isomer II after \( \approx 450 \) fs. The achieved population is \( \approx 78\% \).

In summary, our strategy for optimal control based on the concept of the intermediate target allows us to design pump and dump pulses that are able to drive the isomerization process and to populate the desired ground-state isomer. This is particularly important in the context of the control of photochemistry and for design of molecular switches that can be driven by laser fields. Furthermore, the combination of OCT with the \textit{ab initio} MD “on the fly” allows one to gain insight into the mechanism governing the control of the dynamics in complex systems and to establish a connection between the spectral features of the optimal pulses and the underlying dynamical processes, which means the use of tailored laser fields as a tool for analysis. In the future, one other possible approach may be through kinetics, based on master equations (34).

**Summary and Outlook.** We have shown that by joint theoretical and experimental effort to analyze the ultrafast processes in atomic clusters in size regime in which “each atom counts,” different ultrafast processes can be monitored and their time scales can be determined. They include bond-breaking, geometric relaxation of different nature, IVR, isomerization, and reaction channels. Moreover, in the framework of our strategy for tailoring laser fields, the selected processes can be driven such as isomerization toward one of the isomers, or the chosen reaction channel for which particular bond breaking or new bond rearrangements promote the emanation of reaction products. We have also shown that the optimal control schemes can be used as analysis, which is an important conceptual issue with a promising perspective for applications in complex systems such as biomolecules and clusters, or even their complexes.

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