Eur. Phys. J. D **16**, 151–155 (2001)

THE EUROPEAN PHYSICAL JOURNAL D
EDP Sciences

Theoretical investigation of the ultrafast NeNePo spectroscopy of Au_4 and Ag_4 Clusters

M. Hartmann, R. Mitrić, B. Stanca, and V. Bonačić-Koutecký[a]

Walther-Nernst-Institut für Physikalische und Theoretische Chemie, Humboldt-Universität Berlin, Bunsenstrasse 1, D-10117 Berlin, Germany

Received 22 December 2000

Abstract. Ultrafast ground state nuclear dynamics of Au_4 and Ag_4 is theoretically explored in the framework of negative ion - to neutral - to positive ion (NeNePo) pump-probe spectroscopy based on the *ab initio* Wigner distribution approach. This involves the preparation of a nonequilibrium neutral ensemble by pump induced photodetachment of a thermal anionic ground state distribution, gradient corrected DFT classical trajectory simulations "on the fly" on the neutral ground state, and detection of the relaxation process of the ensemble in the cationic ground state by a time-delayed probe pulse. In Au_4, the initially prepared linear structure is close to a local minimum of the neutral state giving rise to characteristic vibrations in the signals for probe wavelength near the initial Franck-Condon transition. A timescale of ~1 ps for the structural relaxation towards the stable rhombic D_{2h} neutral isomer was determined by the increase of the signal for probe wavelength in vicinity of the vertical ionization energy of the rhombic structure. In contrast, the relaxation dynamics in Ag_4 is characterized by normal mode vibrations since both the initially prepared anionic ground state and the neutral ground state have rhombic minimum geometries. Thus, time-resolved oscillations of pump-probe signals are fingerprints of structural behaviour which can be used experimentally for the identification of particular isomers in the framework of NeNePo spectroscopy.

PACS. 31.15.Qg Molecular dynamics and other numerical methods – 31.15.Ar Ab initio calculations

1 Introduction

Recent advances in femtosecond spectroscopy involve the development of NeNePo fs spectroscopy which was experimentally pioneered by Wöste and coworkers [1]. It has become a versatile tool for the investigation of ultrafast dynamical processes of mass selected, isolated neutral clusters and molecules in real time [1,2]. In principle it allows to address essential questions such as for the timescales of configurational changes including the forming or breaking of bonds and of IVR processes. However, due to the preparation process in NeNePo spectroscopy, a large region of phase space on the neutral ground state is involved and the separation of particular processes from the characteristic lineshapes of signals is not an easy task. Theoretical developments in the framework of Wigner distributions based on classical trajectory simulations [3] allowed to formulate conditions under which a clear separation of given processes will be possible.

In this contribution we present theoretical exploration of the ultrafast ground state dynamics in the framework of NeNePo spectroscopy of the $Au_4^-/Au_4/Au_4^+$ and $Ag_4^-/Ag_4/Ag_4^+$ systems. In Section 2 we briefly outline our *ab initio* Wigner distribution approach which has been established as powerful tool for the simulation of fs signals [3]. This method combines the Wigner-Moyal representation of the vibronic density matrix with the classical trajectory propagation performed by *ab initio* quantenchemical calculations "on the fly". In such a way it allows naturally to describe optical transitions by laser fields which is essential for the simulation of signals in the framework of fs spectroscopy. It was successfully applied for the investigation of ultrafast geometric relaxation and IVR processes in electronic ground [3,4] as well as excited states of clusters [5] including the passage through a conical intersection [6]. The application of this method to the exploration of processes involved in ultrafast ground state dynamics of Au_4 and Ag_4 is described in Section 3. Finally, Summary and outlook is given in Section 4.

2 Ab initio Wigner distribution approach

Equations of motion for the Wigner distributions are obtained from the Liouville equation for the density operator $i\hbar\dot{\hat{\varrho}} = [\hat{H}, \hat{\varrho}]$ by performing a Wigner-Moyal transformation and restricting to lowest order of $\hbar$. This approximation is well justified for thermal or nonequilibrium

---

[a] e-mail: `vbk@chemie.hu-berlin.de`

ensembles where quantum effects are washed out. For low laser intensities, only first order transition processes induced by the pump and the probe laser have to be taken into account. Assuming Gaussian pulse envelopes, an analytical expression for the signal were derived [3]. According to this method, the simulation of NeNePo-ZEKE pump-probe signals involves the following steps: (i) Generation of a Wigner phase space distribution on the anionic ground state for which we use a canonical thermal ensemble at temperature T. This is appropriate when the temperature is not too high so that anharmonic couplings between the normal vibrational modes can be neglected. The sampling of the anionic phase space spanned by coordinates $\mathbf{q}_0$ and momenta $\mathbf{p}_0$ yields an ensemble of initial conditions. (ii) This initial ensemble is photodetached to the neutral ground state with Franck-Condon transition probability determined by an exponential function comprising the vertical detachment energy $V_{VDE}(\mathbf{q}_0)$. (iii) The ensemble is propagated on the neutral ground state by classical trajectory simulations yielding coordinates $\mathbf{q}_1(\tau_1;\mathbf{q}_0,\mathbf{p}_0)$ on the neutral ground state with the initial values $\mathbf{q}_0,\mathbf{p}_0$. (iv) The probe step includes the time-dependent energy gaps $V_{ion}(\mathbf{q}_1(\tau_1;\mathbf{q}_0,\mathbf{p}_0))$ between the cationic and the neutral ground states which enter the exponential Franck-Condon transition probabilities to the cation. (v) The time resolution of the signal is given by the pump-probe correlation function with a probe pulse window located around the time delay t_d between the pump and the probe pulse. (vi) Finally, for the calculation of the signal a summation over the entire phase space has to be performed.

3 Results for ultrafast dynamics

In this section starting from structural properties we present an analysis of the ultrafast processes involved in the relaxation dynamics on the neutral ground states of Au_4 and Ag_4 as well as their signature in the NeNePo-ZEKE fs pump-probe signals.

3.1 Structural properties

The geometry optimization as well as MD "on the fly" have been carried out using gradient corrected density functional method with exchange and correlation functionals of Becke and Lee, Young and Parr (BLYP). We developed one-electron relativistic effective core potentials (1e-RECP) and the corresponding AO basis sets [7] for Ag and Au atoms based on DFT BLYP procedure which allow to calculate ensemble of trajectories necessary for the simulation of signals at low computational cost. The energy ordering of isomers as well as their energy differences are often very sensitive on methodological details. This is in particularly the case of Au_4^-. For example, the zig-zag structure of Au_4^- [8] can be almost degenerate with linear structure dependent on the choice of ECP or of correlation treatment. We compared results obtained with different effective core potentials (11e-RECP or 19-RECP) in combination with DFT-BLYP and coupled cluster (CCSD) approaches [7] and concluded that sampling of initial conditions in which a mixture of linear and zig-zag structures of Au_4^- are present will not influence dynamical processes on the ground state of the neutral Au_4. The situation is simpler for Ag_4^- and Ag_4 in which case the rhombic structures are global minima and the energy ordering of isomers is less sensitive on the details of the method employed.

Table 1. Harmonic frequencies in cm^{-1} for linear isomers of Au_4^- and Au_4, resp., and the rhombic isomer of Ag_4.

	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
Au_4^-	15	32	76	141	176	
Au_4	9	19	65	172	179	
Ag_4	36	81	90	114	165	196

3.2 Ultrafast ground state dynamics and NeNePo signals of Au_4

The investigation of the ground state dynamics of Au_4 within the $Au_4^-/Au_4/Au_4^+$ NeNePo spectroscopy is illustrated in Fig. 1 (LHS). For the preparation of a well defined anionic initial ensemble which is essential for NeNePo spectroscopy one has to assume low temperatures in order to exclude contributions from rhombic and Y-shape isomers. Then, the initial ensemble is characterized only by the linear geometry which is propagated on the neutral state after photodetachment by a 3.25 eV (381 nm) pump pulse by using DFT-BLYP classical trajectory calculations "on the fly". First a local minimum with linear geometry is reached from which the ensemble may escape towards the rhombic and Y-shape isomers on the neutral ground state. The dynamics is monitored by the probe pulse with excitation energies between 8.09 eV (153 nm) and 8.86 eV (140 nm).

The initial ensemble is represented by 250 phase space points which were obtained by sampling the canonical Wigner distribution (*cf.* Section 2) where normal mode frequencies of Au_4^- are given (*cf.* Table 1).

We have simulated NeNePo pump-probe signals for two excitation energies of the probe pulse (*cf.* RHS of Fig. 1). Wavelengths close to the initial Franck-Condon transition (E_{pr} = 8.86 eV (140 nm)) allow to investigate the geometrical change within the linear local minimum of Au_4. As can be seen from Fig. 1a, the signal exhibits oscillations during the first ps with a period of ~194 fs corresponding to vibrational relaxation along the antisymmetric Σ_u^+ (172 cm^{-1}, *cf.* Table 1) normal mode. This picture can also be confirmed from the analysis of the ensemble averaged kinetic energy (not shown) which yields that more than 80% of the energy is contained in the antisymmetric stretch mode and the remaining one in the symmetric stretch modes ω_3 and ω_5 (*cf.* Table 1). The contributions

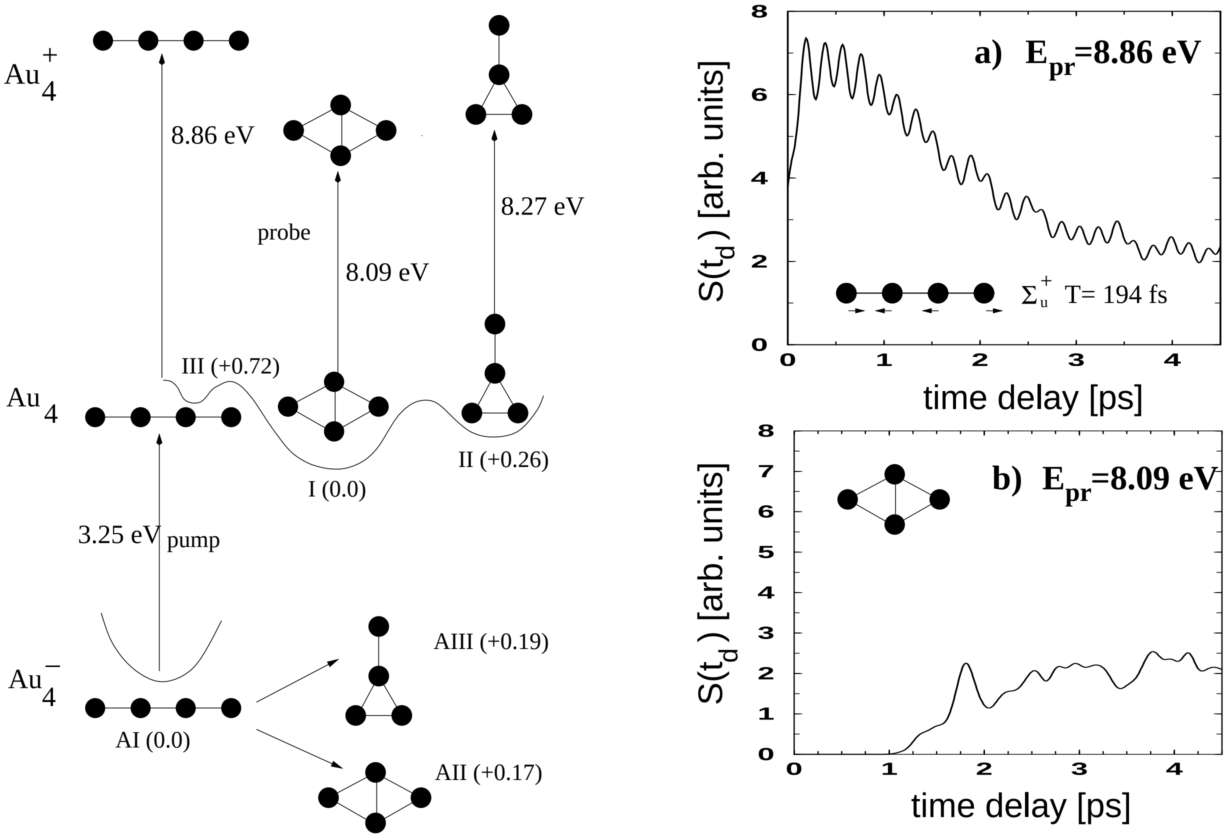

Fig. 1. LHS: Scheme of the NeNePo pump probe spectroscopy of the $Au_4^-/Au_4/Au_4^+$ system. The three isomers of Au_4^- are shown which were obtained by DFT-BLYP calculations with 1-electron RECP. Relative energies in eV of isomers with respect to the linear isomer are given in brackets. Transition energies for the pump step and for probe steps belonging to the three isomers I, II, III of the neutral Au_4 are indicated. Relative energies in eV of isomers with respect to the rhombic isomer I are given in brackets. RHS: Simulated NeNePo-ZEKE pump probe signals for a 50 K initial temperature ensemble of Au_4^- at two different excitation energies E_{pr} of the 100 fs probe pulse. a) Oscillations are attributed to the antisymmetric stretch mode Σ_u^+. b) The increase of the signal after 1 ps monitors the isomerization dynamics towards the rhombic geometry.

in the bending modes are negligible up to 1 ps. From the analysis of results conclusion has been drawn that only the stretching modes are significantly involved in the process of the geometric changes. The stronger contribution of the antisymmetric stretch mode is due to the difference of the normal mode frequencies of the anionic and the neutral linear structures, respectively (*cf.* ω_4 for Au_4^- and Au_4 of Table 1). Since ω_4 is larger for Au_4, also the gradient is larger resulting in a stronger relaxation dynamics along this mode.

After 1 ps the signal intensity is decreasing indicating isomerization processes towards the rhombic minimum structure. Consequently, the NeNePo signal tuned at probe wavelengths near the stable rhombic isomer (*cf.* Fig. 1b) is increasing after 1 ps. Since the excess energy of ∼0.72 eV corresponding to an equilibrium temperature of 2700 K is very high, this signal does not correspond uniquely to the rhombic geometry in particular for longer times (above 2 ps), since the contributions of other structures including from the second Y-shape isomer are present.

3.3 Ultrafast ground state dynamics and NeNePo signals of Ag_4

The LHS of Fig. 2 illustrates the excitation processes by pump and probe lasers as well as the relaxation dynamics of Ag_4 in the framework of NeNePo spectroscopy. Similar to the case of Au_4, there are three isomers in the anionic ground state but here the rhombic D_{2h} structure is the most stable. The energetically very close lying linear isomer (*cf.* LHS of Fig. 2) has a large transition barrier to the rhombic structure. Therefore, at relatively low temperatures one can assume a thermal distribution of the rhombic isomer. Photodetachment induced by an 1.52 eV (815 nm) pump pulse generates the nonequilibrium ensemble on the neutral ground state and the subsequent relaxation dynamics can be probed by the second time delayed pulse between 6.41 eV (194 nm) and 6.54 eV (189 nm). Since the global minimum of the neutral state corresponds also to a rhombic structure, the relaxation dynamics will be mainly characterized by vibrations determined by the eigenmodes of the minimum. Isomerization towards the

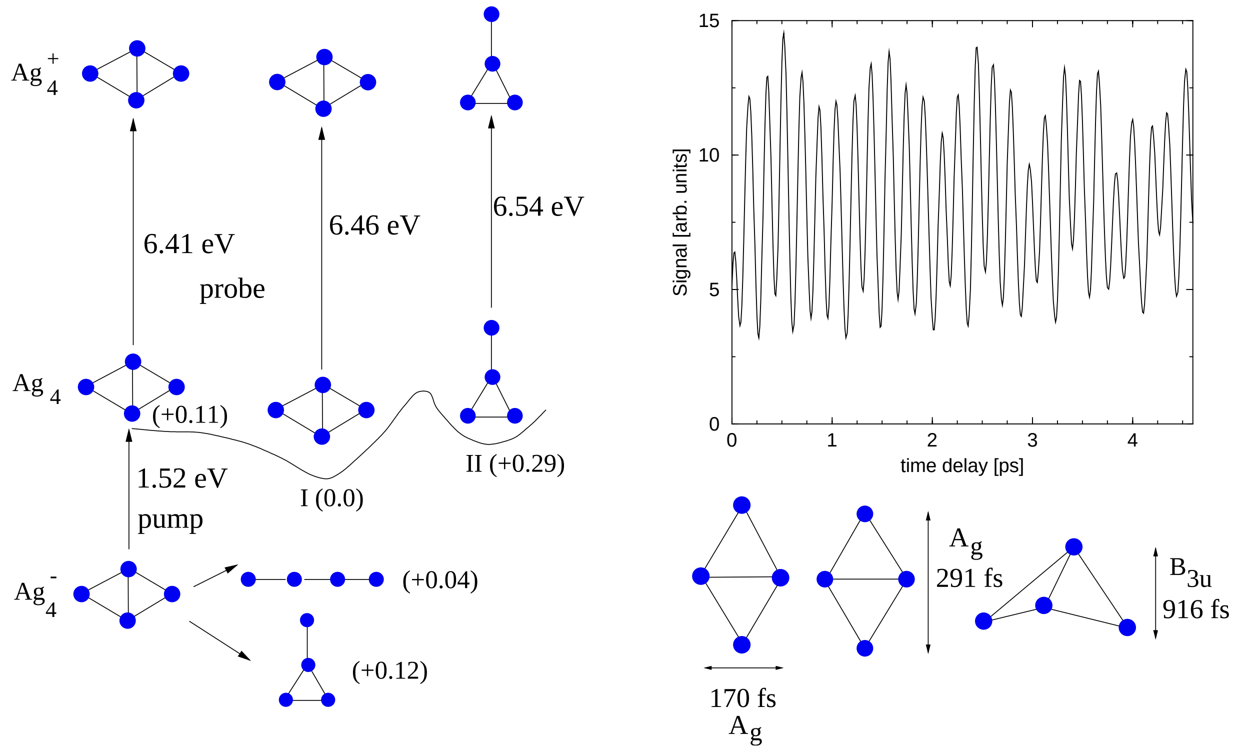

Fig. 2. LHS: Scheme of the NeNePo pump probe spectroscopy of the $Ag_4^-/Ag_4/Ag_4^+$ system. The three isomers of Ag_4^- are shown. Relative energies in eV of isomers with respect to the anionic rhombic isomer are given in brackets. Transition energies for the pump step and for probe steps belonging to the initial Franck-Condon region and the rhombic and Y-shape isomers of the neutral Ag_4, resp. are indicated. Relative energies in eV of isomers with respect to the rhombic isomer I are given in brackets. RHS: Simulated NeNePo-ZEKE pump probe signal for a 50 K initial temperature ensemble of Ag_4^- at excitation energy $E_{pr} = 6.41$ eV of a 100 fs probe pulse. Oscillations of the signal can be mainly attributed to the three normal mode vibrations shown below.

second Y-shape isomer required large initial temperatures of more than 700 K which, however, would result in isomerization processes already in the anionic ground state (*cf.* LHS of Fig. 2). Therefore, NeNePo spectroscopy of the $Ag_4^-/Ag_4/Ag_4^+$ system can be appropriately applied for temperatures lower than ~400 K in order to ensure an uniquely defined initial ensemble which is an essential condition for the clear separation of timescales of processes involved in the relaxation dynamics on the neutral ground state. For the simulations we used initial temperature of 50 K and generated 100 initial conditions for the classical trajectory propagation by sampling of the corresponding canonical Wigner distribution (*cf.* Section 2). The RHS of Fig. 2 shows the simulated NeNePo-ZEKE pump-probe signals for a 100 fs probe laser at 6.41 eV (193.5 nm). As it was expected, the signal shows pronounced oscillations. The Fourier analysis of the signal (not shown) revealed that these oscillatory behaviour up to the simulation time of 4.5 ps can be attributed to three normal modes of the rhombic minimum structure shown in the lower part of RHS of Fig. 2. The main contribution corresponds to vibrational relaxation with 170 fs along the short diagonal of rhombic Ag_4 which belongs to the total symmetric normal mode ω_6 (*cf.* Table 1). This relaxation dynamics is superimposed by vibrations along the long diagonal (291 fs) and the "butterfly mode" (916 fs) belonging to the normal modes ω_4 (A_g) and ω_1 (B_{3u}), respectively. Since the excitation of these modes are characteristic for the minimum rhombic structure, this opens the opportunity to identify given isomers in experimental NeNePo signals.

4 Summary and outlook

We have theoretically explored the ultrafast ground state dynamics of neutral Au_4 and Ag_4 clusters in the framework of the NeNePo-ZEKE spectroscopy based on Wigner distributions and *ab initio* DFT-BLYP classical trajectory calculations "on the fly".

The relaxation dynamics of Au_4 involves (i) vibrational relaxation towards the linear local minimum which is close to the initial Franck-Condon transition giving rise to characteristic oscillations in the signal, (ii) isomerization towards the rhombic global minimum structure for which a timescale of ~1 ps could be determined from the onset of the signal. In contrast, in Ag_4 isomerization does not occur since both the neutral and the anionic (initial ensemble) ground state have rhombic geometry. Therefore, the relaxation dynamics of Ag_4 is characterized by vibrational relaxation along the normal modes of the global minimum rhombic structure which can be identified in real time from the NeNePo signals. Since the oscillatory behaviour of the signals are clear fingerprints of the underlying structural properties of the systems, NeNePo spectroscopy can be used for the identification of particular isomers [9]. Future work concerns the formulation of conditions for the preparation of the initial ensemble in the framework of NeNePo spectroscopy which allows to restrict the occupied phase space in a minimum of a particular isomer and to control the vibrational relaxation as well as the isomerization dynamics including their timescales.

This work was supported by the "Sonderforschungsbereich 450, Analyse und Steuerung photoinduzierter ultraschneller Reaktionen" of the *Deutsche Forschungsgemeinschaft*. The calculations have been partly carried out at the *Konrad-Zuse-Zentrum für Informationstechnik* Berlin.

References

1. S. Wolf, G. Sommerer, S. Rutz, E. Schreiber, T. Leisner, L. Wöste, Phys. Rev. Lett. **74**, 4177 (1995).
2. D.W. Boo, Y. Ozaki, L.H. Anderson, W.C. Lineberger, J. Phys. Chem. **101**, 6688 (1997).
3. M. Hartmann, J. Pittner, V. Bonačić–Koutecký, A. Heidenreich, J. Jortner, J. Chem. Phys. **108**, 3096 (1998).
4. M. Hartmann, A. Heidenreich, J. Pittner, V. Bonačić–Koutecký, J. Jortner, J. Phys. Chem. A **102**, 4069 (1998).
5. M. Hartmann, J. Pittner, V. Bonačić–Koutecký, J. Chem. Phys. **114**, 2106 (2001).
6. M. Hartmann, J. Pittner, V. Bonačić–Koutecký, J. Chem. Phys. **114**, 2123 (2001).
7. R. Mitrić, M. Hartmann, B. Stanca, V. Bonačić–Koutecký (in press).
8. H. Haekkinen, U. Landman, Phys. Rev. B **62**, 2287 (2000).
9. H. Hess, K.R. Asmis, T. Leisner, L. Wöste, Eur. Phys. J. D **16**, 145 (2001).