Chapter 3

NeNePo Spectroscopy of Metal Clusters

In this chapter, the principle of negative-to-neutral-to-positive (NeNePo) spectroscopy as a special femtosecond (fs) time-resolved, pump-probe technique for the investigation of the nuclei motion on the potential energy surface of neutral clusters will be presented. First, the general concepts of molecular dynamics will be outlined, where the Born-Oppenheimer approximation and Franck-Condon principle will be emphasized. Subsequently, the NeNePo method will be presented and its principle will be illustrated with the description of the fs-dynamics of Ag_3 clusters.

3.1   General Concepts of Molecular Dynamics

In order to obtain a quantum mechanical description of a molecular system, it is necessary to formulate and solve the Schrödinger equation for the system of interest. For a molecule which contains m nuclei and n electrons, the *time-dependent Schrödinger equation* is given by:

$$
i\hbar \, \frac{\partial}{\partial t} \Psi(\overrightarrow{r}_1, \overrightarrow{r}_2, \cdots, \overrightarrow{r}_n, \overrightarrow{R}_1, \overrightarrow{R}_2, \cdots, \overrightarrow{R}_m, t) \;\; =
$$
$$
= \hat{H} \; \Psi(\overrightarrow{r}_1, \overrightarrow{r}_2, \cdots, \overrightarrow{r}_n, \overrightarrow{R}_1, \; \overrightarrow{R}_2 \;, \cdots, \overrightarrow{R}_m, t) \qquad (3.1)
$$

where $\Psi(\overrightarrow{r}_1, \overrightarrow{r}_2, \cdots, \overrightarrow{r}_n, \overrightarrow{R}_1, \overrightarrow{R}_2, \cdots, \overrightarrow{R}_m, t)$ represents the molecular wavefunction, which depends on the electronic coordinates $\overrightarrow{r}_i$, with $1 \leq i \leq n$, the coor-

dinates of the nuclei $\overrightarrow{R}_a$, with $1 \leq a \leq m$ and time t. For simplification, the set of the electronic coordinates will be denoted with $\overrightarrow{r} := \overrightarrow{r}_1, \overrightarrow{r}_2, \cdots, \overrightarrow{r}_n$ and the set of the nuclear coordinates will be denoted with $\overrightarrow{R} := \overrightarrow{R}_1, \overrightarrow{R}_2, \cdots, \overrightarrow{R}_m$ in the following. Thus, the molecular wavefunction can be written as:

$$\psi(\overrightarrow{r}_1, \overrightarrow{r}_2, \cdots, \overrightarrow{r}_n, \overrightarrow{R}_1, \overrightarrow{R}_2, \cdots, \overrightarrow{R}_m, t) = \psi(\overrightarrow{r}, \overrightarrow{R}, t) \tag{3.2}$$

In the Schrödinger equation given by expression 3.1, $\hat{H}$ represents the Hamilton operator (Hamiltonian) of the system, which can be written as the sum of the total kinetic energy of the electrons $\hat{T}_e$, total kinetic energy of the nuclei $\hat{T}_n$ and the potential energy resulting from electron-electron $\hat{V}_{ee}$, nuclei-nuclei $\hat{V}_{nn}$, and electron-nuclei $\hat{V}_{en}$ Coulomb interactions:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{ee} + \hat{V}_{en} + \hat{V}_{nn} \tag{3.3}$$

When the expressions for the operators of kinetic and potential energy are introduced in equation 3.3, the Hamiltonian can be written as:

$$\hat{H} = -\sum_{i=1}^{n} \frac{\hbar^2}{2m_e} \triangle_i - \sum_{a=1}^{m} \frac{\hbar^2}{2M_a} \triangle_a \quad + \quad \sum_{i=1}^{n} \sum_{j=1, j>i}^{n} \frac{e^2}{r_{ij}} - \tag{3.4}$$
$$- \sum_{i=1}^{n} \sum_{a=1}^{m} \frac{Z_a e^2}{r_{ai}} + \sum_{a=1}^{m} \sum_{b=1, b>a}^{m} \frac{Z_a Z_b e^2}{R_{ab}}$$

If the Hamiltonian does not contain an explicit time dependence, the separation of the variables according to time and space can be performed in equation 3.1 by substituting the total molecular wavefunction of the system with:

$$\Psi(\overrightarrow{r}, \overrightarrow{R}, t) = \psi(\overrightarrow{r}, \overrightarrow{R}) \cdot \varphi(t) \tag{3.5}$$

This allows expression 3.1 to be separated in two differential equations, giving the *time-independent Schrödinger equation* for the spatial coordinates:

$$\hat{H}\psi(\overrightarrow{r}, \overrightarrow{R}) = E\psi(\overrightarrow{r}, \overrightarrow{R}) \tag{3.6}$$

For the time-dependent differential equation, the following solution is obtained:

$$\varphi(t) = exp\left(\frac{-iEt}{\hbar}\right) \tag{3.7}$$

where E represents the eigenvalues of the Hamilton operator and $\hbar = h/2\pi$ is the Planck constant. One can consider all eigenvalues E_k and the corresponding wavefunctions $\psi_k(\overrightarrow{r}, \overrightarrow{R})$, $\varphi_k(t)$ of the molecular system and the total wavefunction of the system can be written as:

$$\Psi(\overrightarrow{r}, \overrightarrow{R}, t) = \sum_k c_k \; \psi_k(\overrightarrow{r}, \overrightarrow{R}) \; exp\left(\frac{-iE_k t}{\hbar}\right) \tag{3.8}$$

The exact solutions of the time-independent Schrödinger equation are difficult and sometimes impossible to obtain, especially for the case of a molecule which contains a large number of atoms. The *Born-Oppenheimer approximation* provides a solution for this problem, by separating the electronic and nuclear motion.[68] Due to the different mass of the electrons compared to those of the nuclei, the motion of the electrons occurs on a much faster time scale than the motion of the nuclei. Therefore, on the time scale of the electronic motion the nuclei can be considered to be stationary. On the other hand, the influence of the electronic motion on the nuclei can be represented by an averaged electronic potential. Thus, the wavefunction of the system can be written as:[69]

$$\psi(\overrightarrow{r}, \overrightarrow{R}) = \psi_{el}(\overrightarrow{r}, \overrightarrow{R})\phi_{nucl}(\overrightarrow{R}) \tag{3.9}$$

where $\psi_{el}(\overrightarrow{r}, \overrightarrow{R})$ represents the electronic wavefunction for a given configuration of the nuclei, which depends on the electronic $(\overrightarrow{r})$ and nuclear $(\overrightarrow{R})$ set of coordinates and $\phi_{nucl}(\overrightarrow{R})$ represents the nuclear wavefunction, which depends only on the set of nuclear coordinates $(\overrightarrow{R})$.

The Hamiltonian given by equation 3.3 can be written as a sum of the electronic Hamiltonian $\hat{H}_{el}$ and the nuclear Hamiltonian $\hat{H}_{nucl}$ which have the expressions:[70]

$$\hat{H}_{el} \quad = \hat{T}_e + \hat{V}_{ee} + \hat{V}_{en} \tag{3.10}$$

$$\hat{H}_{nucl} \quad = \hat{T}_n + \hat{V}_{nn} \tag{3.11}$$

Introducing expression 3.9 in equation 3.6, the separation of the electronic and nuclear problem can be performed. For the electronic problem one considers that $\hat{T}_n = 0$ and $\hat{V}_{nn} = $ const. and the electronic Schrödinger equation becomes:

$$\hat{H}_{el} \; \psi_{el}(\overrightarrow{r}, \overrightarrow{R}) = E_{el}(\overrightarrow{R}) \; \psi_{el}(\overrightarrow{r}, \overrightarrow{R}) \tag{3.12}$$

Equation 3.12 can be solved parametrically with respect to the nuclear set of coordinates $\overrightarrow{R}$. This yields the eigenvalues of the electronic Hamiltonian which represent the electronic energies $E_i(\overrightarrow{R})$ as a function of the nuclear displacement. The set of the electronic energies $E_i(\overrightarrow{R})$ defines an adiabatic potential energy surface (PES). In the adiabatic picture, the potential energy surfaces are isolated, *i.e.* there is no interaction between different electronic states. Knowing the adiabatic potential energy surfaces, the nuclear problem can be approached. For this purpose, one can write the time-independent Schrödinger equation as:

$$(\hat{H}_{nucl} + \hat{H}_{el})\ \psi_{el}(\overrightarrow{r}, \overrightarrow{R})\phi_{nucl}(\overrightarrow{R}) = E\ \psi_{el}(\overrightarrow{r}, \overrightarrow{R})\phi_{nucl}(\overrightarrow{R}) \tag{3.13}$$

Since the electronic wavefunctions depend on the nuclear set of coordinates $\overrightarrow{R}$, the nuclear Hamiltonian acts on $\psi_{el}(\overrightarrow{r}, \overrightarrow{R})$ as well. As a result, there are terms in equation 3.13 that contain the derivative of $\psi_{el}(\overrightarrow{r}, \overrightarrow{R})$ with respect to the nuclear coordinates $\overrightarrow{R}$. Due to this, the nuclear problem can not be separated and solved. As discussed above, the motion of the nuclei and electrons occur on different time scales and therefore, all terms showing a derivative of the $\psi_{el}(\overrightarrow{r}, \overrightarrow{R})$ with respect to $\overrightarrow{R}$ can be approximated to be zero. This represents the Born-Oppenheimer approximation. Thus, the nuclear problem can be isolated and written as:[70]

$$(\hat{H}_{nucl} + E_{el}(\overrightarrow{R}))\ \phi_{nucl}(\overrightarrow{R}) = E\ \phi_{nucl}(\overrightarrow{R}) \tag{3.14}$$

From this equation, one can obtain the nuclear wavefunctions and the corresponding eigenvalues. In this way, the Born-Oppenheimer approximation provides a possibility to obtain the adiabatic potential energy surfaces and the respective vibrational states of a molecular system.

Through the interaction of a molecular system with the electric field of a laser pulse, an electronic transition between two adiabatic potential energy surfaces can be achieved. The interaction of a molecule with a laser field can be described by introducing an additional term $\hat{V}_{int}$ in the Hamilton operator given by expression 3.3. In the dipole approximation, $\hat{V}_{int}$ can be written as:

$$\hat{V}_{int}(\overrightarrow{R}, t) = -\overrightarrow{\mu}(\overrightarrow{R}) \cdot \overrightarrow{\varepsilon}(t) \tag{3.15}$$

where $\overrightarrow{\mu}(\overrightarrow{R})$ represents the transition dipole moment of the molecule between the respective potential energy surfaces and $\overrightarrow{\varepsilon}(t)$ represents the time-dependent electric field of the laser pulse.

An electronic transition between two potential energy surfaces occurs according to the *Franck-Condon principle.* Due to the different time scales of the electronic and nuclear motion, the nuclear configuration does not change significantly during an electronic transition. Therefore, the electronic transitions between two potential energy surfaces are referred to as *vertical transitions.* The transition probability depends on the overlap of the nuclear wavefunction in the initial and final surfaces, which is described by the *Franck-Condon integral.* If one assumes an electronic transition from an initial state (E, v) characterized by the energy E and the vibrational state v, into a final state (E', v') with the energy E' and vibrational state v', the Franck-Condon integral $\mathcal{S}_{v', v}$ is given by the following expression:[56]

$$\mathcal{S}_{v', v} = \int \phi^*_{nucl,v'}(\overrightarrow{R})\phi_{nucl,v}(\overrightarrow{R}) \ d^3\overrightarrow{R} \tag{3.16}$$

where $\phi_{nucl,v}(\overrightarrow{R})$ and $\phi_{nucl,v'}(\overrightarrow{R})$ represent the nuclear wavefunctions of the initial and final state, respectively. The intensity of the electronic transition is proportional to the value $\mathcal{S}^2_{v', v}$, which is referred to as the *Franck-Condon factor* corresponding to the transition $(E', v') \longleftarrow (E, v)$. Thus, the Franck-Condon principle allows for the calculation of the intensities of electronic transitions between the respective vibrational states and subsequently, the interpretation of the molecular spectra.

A particular case of laser-molecule interaction is represented by the interaction of molecules with ultrashort laser pulses, on the femtosecond time scale. An ultrashort laser pulse has a broad spectral bandwidth and therefore, it is able to create a coherent superposition of molecular eigenstates, *i.e.* a wave packet on a specific potential energy surface. Monitoring the time evolution of the created wave packet by using a second time-delayed fs-laser pulse provides the possibility to investigate intrinsic molecular processes like bond breaking, bond formation, isomerization and intramolecular vibrational energy redistribution (IVR) in real time.[17] Understanding these elementary processes represents a significant step in the deciphering of chemical reactions.

The exact solutions of the Schrödinger equation for a molecular system are difficult to obtain, due to the large number of parameters which are involved. With the exception of a diatomic molecule, the potential energy surfaces are multidimensional, and each additional atom brings three more nuclear coordinates. Therefore, accurate theoretical calculations (*ab initio* calculations) of the potential energy surfaces for

large molecules represent a challenging task. In special cases, a reduction of the parameters is possible due to the symmetry of the molecules and the potential energy surfaces can be calculated as a function of the normal modes of the molecule. One example will be shown in the next subsection, where the application of the NeNePo spectroscopy to the case of Ag_3 clusters will be presented.

3.2   The Principle of NeNePo Spectroscopy

In the framework of mass-selected ion detection, femtosecond pump-probe techniques allow the investigation of the molecular dynamics in an electronically excited state. The first laser pulse (pump pulse) transfers the initially neutral system from the electronic ground state into an excited state, while the second laser pulse (probe pulse) ionizes the system after a given delay time and the cation signal is detected.[71] In this way, the evolution of the system in a specific excited state can be monitored in real time. However, chemical processes generally occur on the electronic ground state potential energy surface of a neutral molecular complex. In order to gain insights into the dynamics of these type of processes, the negative-to-neutral-to-positive (NeNePo) method can be applied. This method allows for the investigation of the evolution of a wave packet created on the electronic ground state potential energy surface of a neutral molecular system.[19]

The principle of NeNePo spectroscopy is schematically presented in Fig. 3.1. The experiment starts with the production of an anionic cluster ensemble. The first femtosecond laser pulse photodetaches the excess electron (negative → neutral) and creates a vibrational wave packet on the electronic ground state of the neutral particle. As a consequence of the Franck-Condon principle, the position of the nuclei does not change during the photodetachment process and the initial configuration of the neutral molecule is identical with the structure of the negatively charged cluster. This initial configuration of the neutral particle can correspond to a non-equilibrium structure along the coordinate of a chemical reaction. After a variable delay time, the second fs-laser pulse ionizes the neutral molecule (neutral → positive) and the signal of the cations is detected as a function of the delay time between the two laser pulses. The photoionization step can be a one-photon process (as depicted in Fig. 3.1) or a multi-photon process, where multiple photons contribute to the ion-
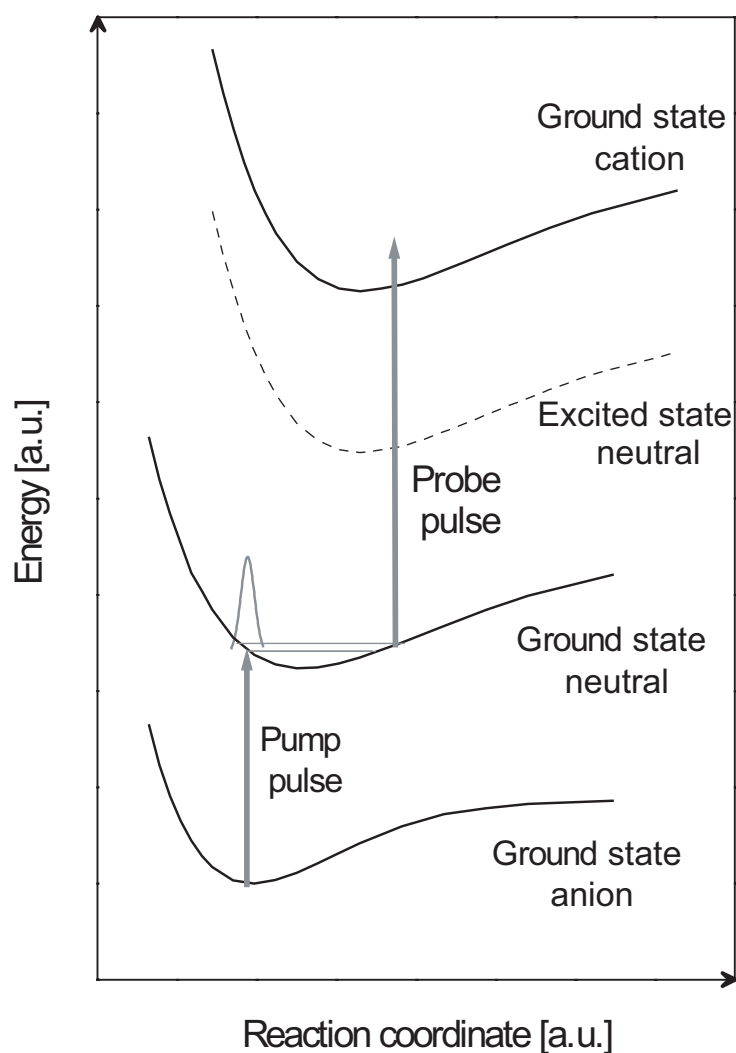
Figure 3.1: Schematic representation of the principle of NeNePo spectroscopy. The potential energy surfaces for the ground state of the anionic, neutral and cationic cluster are represented as solid lines. The dashed line represents an excited state of the neutral cluster. The pump and the probe laser pulse are depicted as grey arrows.

ization of the neutral particle. In the case of a multi-photon ionization process, an electronic excited state can be used for a resonant ionization step, which leads to a significant enhancement of the cation signal. The intensity of the NeNePo signal depends on the Franck-Condon factors for the neutralization and ionization processes of the investigated molecular system. Compared to standard pump-probe molecular

beam experiments, the NeNePo technique presents some significant advantages:

- Since the initial and final states of the molecular system are ionic states, the mass selection of the desired molecule prior to and after the interaction with the laser field can be performed. In this way, the signal carrier can be unambiguously identified, even when the experiments are performed on highly fragmentative molecular systems.

- The vertical transition from the negative to the neutral electronic ground state often allows the investigation of regions of the neutral ground state potential energy surface which are not accessible by photoabsorption spectroscopy of the neutral molecules.

- With an appropriate choice of the laser wavelength involved in the detachment process, all electronic states of the neutral molecule can be reached (including dark states) since the selection rules for optical transitions between electronic states of the neutral do not apply to photodetachment processes.

In the group of Prof. L. Wöste, the NeNePo method was successfully applied to the investigation of the neutral ground state dynamics of silver clusters.[19,72–76] The first molecular system explored with this method was the silver trimer Ag_3 and the results obtained from this system will be used in the following to illustrate the principle of NeNePo spectroscopy.

Theoretical calculations predict a linear geometry for the equilibrium structure of the Ag_3^- anion, an obtuse isosceles triangle for the neutral Ag_3 cluster and an equilateral triangular geometry for the Ag_3^+ cationic clusters.[77] By employing NeNePo spectroscopy, the isomerization reaction from the linear configuration of the neutral silver cluster, which is prepared through the photodetachment process, to its triangular equilibrium configuration was monitored in real time. Fig. 3.2 shows the measured NeNePo signal in the case of Ag_3 clusters as a function of the delay time (t_d) between the pump and the probe laser pulses, which possess a central wavelength of $\lambda_{Pump} = \lambda_{Probe} = 415\ nm$. From this graph, it can be seen that the cluster signal has a minimum at $t_d = 0\ fs$ delay time. The transient signal reaches a maximum after approximately $t_d = 700\ fs$, shows a slow decrease to about 80 % from the maximum intensity and converges to a constant value after a delay time of approximately $t_d = 2\ ps$.
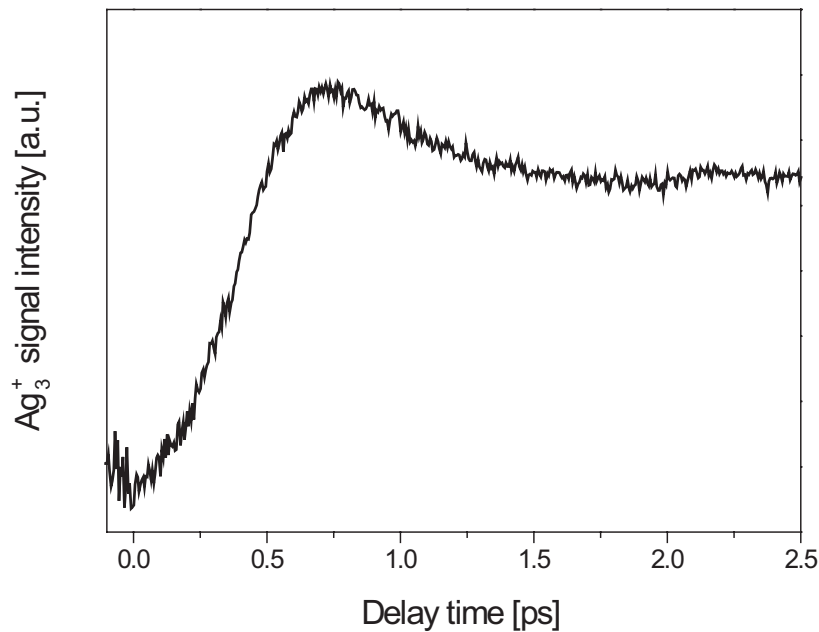
Figure 3.2: The experimental NeNePo signal for Ag_3 clusters measured for a wavelength of $\lambda_{Pump} = \lambda_{Probe} = 415 \ nm$, adapted from Heß.[75]

For the interpretation of the experimental data, it is necessary to have theoretical information about the potential energy surfaces of the silver trimer in the relevant electronic states. The potential energy surfaces for the anionic, neutral and cationic Ag_3 cluster were obtained by Hartmann *et al.* by using *ab initio* theoretical calculations.[77,78] Fig. 3.3 shows the potential energy surfaces as a function of the bending coordinate Q_x for the silver trimer and the three normal modes of this cluster (Q_s - the symmetric stretching mode, Q_x - the bending mode and Q_y - the antisymmetric stretching mode) are presented in Fig. 3.4. By combining the information obtained from experiment and theory, the NeNePo spectra can be interpreted as follows: the pump pulse neutralizes the linear anionic silver trimer (one-photon process) and prepares a vibrational wave packet on the potential energy surfaces of the neutral electronic ground state in a region which corresponds to a linear geometry configuration of Ag_3 cluster. After photodetachment, the bending mode of the linear neutral silver trimer is highly excited and the molecule starts to bend to the triangular geometry. Since the ionization potential changes on the potential energy surface, the probe pulse
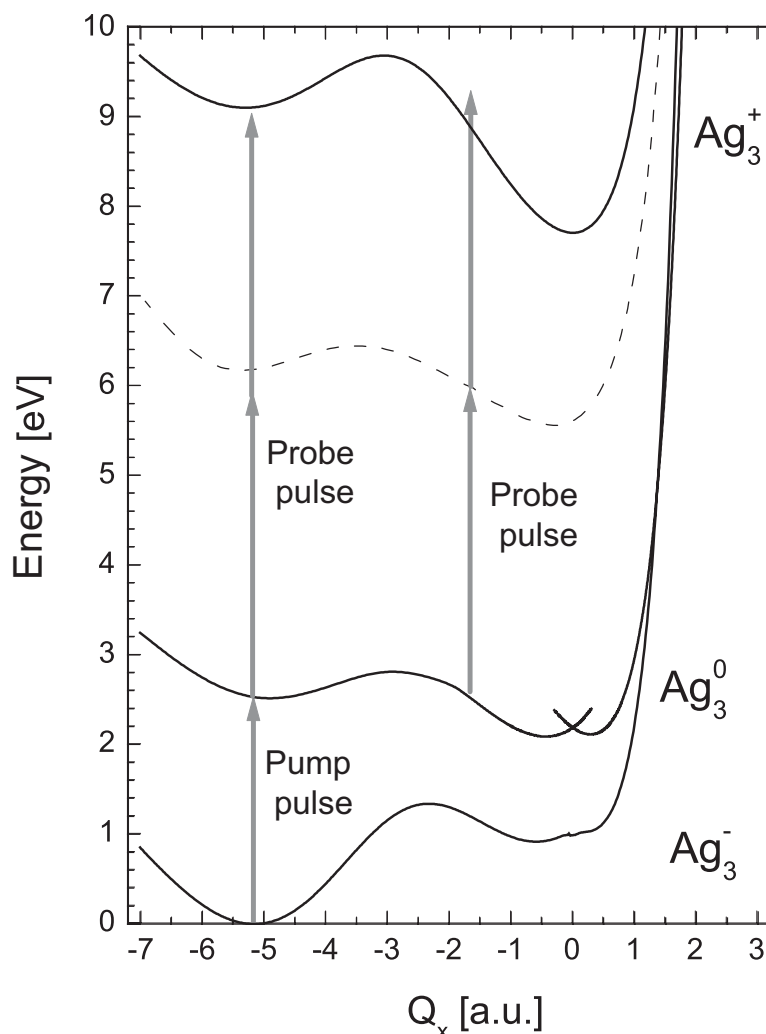
Figure 3.3: One dimensional cut along the bending mode coordinate Q_x of the potential energy surfaces for the silver trimer. The dotted line indicates an excited state of the Ag_3 cluster. The pump and the probe pulses are depicted as grey arrows, taken from Leisner *et al.*[72]

energy which has a value of 2.99 eV is not sufficient to ionize the linear structure *via* a two-photon process and the NeNePo signal presents a minimum at $t_d = 0\ fs$ delay time.[75] When the triangular geometry is attained, a favorable Franck-Condon window for ionization is reached and the NeNePo signal presents a maximum after about $t_d = 700\ fs$. Thus, the wave packet evolution along the potential energy surface of the neutral silver trimer can be monitored in real time. *A priori*, one would expect to see
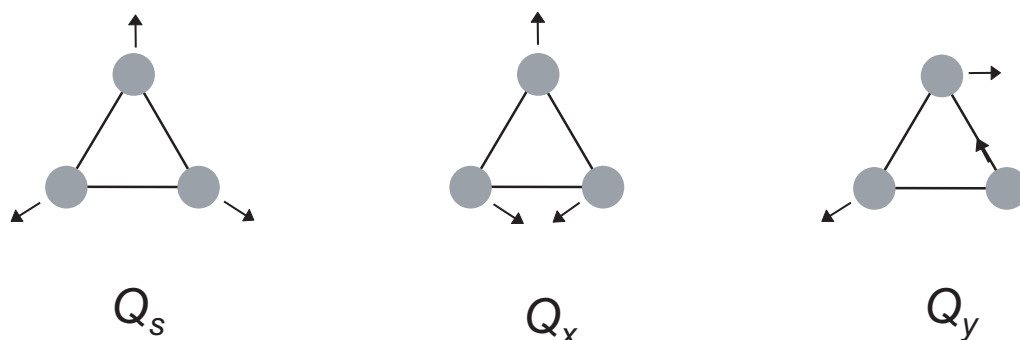
Figure 3.4: The normal vibrational modes of a triatomic molecule, where Q_s represents the symmetric stretching mode, Q_x the bending mode and Q_y the antisymmetric stretching mode. The black arrows indicate the motion of the atoms which are depicted as grey spheres.

vibrational features in the transient signal of the neutral triatomic molecule but, as seen from Fig. 3.2, no oscillations can be identified in the NeNePo spectrum. This is due to the fast intramolecular vibrational energy redistribution (IVR) process, which sets in after the collision of the two terminal atoms of the clusters and is practically completed after a few picoseconds.[77]

In contrast to this, the NeNePo spectra reveal a pronounced oscillatory behavior in the case of Ag_4 clusters, where the anionic, neutral and cationic tetramers have a rhombic structure with slightly different bond lengths and angles. These oscillations were assigned to the antisymmetric stretching mode of the silver tetramer. It is important to note that in the case of the silver tetramer, the oscillation of the wave packet can be observed over more than 20 ps in comparison with the silver trimer, where the IVR process is finished on a time scale of 2 ps.[74,75]

In conclusion, the NeNePo method is a general technique for the investigation of the nuclear dynamics of a molecular system on the neutral ground state potential energy surface. In the last years, a systematic investigation of the fs-dynamics of small noble metal clusters could be carried out by employing this spectroscopic method. Specifically, the significant influence of size and chemical composition on the dynamic behavior of silver, gold and mixed silver-gold clusters was characterized.[75,79] The results of the NeNePo measurements on gold clusters will be presented in detail in chapter 6.