Two-Photon Excitation of Low-Lying Electronic Quadrupole States in Atomic Clusters

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A simple scheme of population and detection of low-lying electronic quadrupole modes in free small deformed metal clusters is proposed. The scheme is analyzed in terms of the TDLDA (time-dependent local density approximation) calculations. As test case, the deformed cluster Na\textsubscript{12} is considered. Long-living quadrupole oscillations are generated via resonant two-photon (two-dipole) excitation and then detected through the appearance of satellites in the photoelectron spectra generated by a probe pulse. Femtosecond pump and probe pulses with intensities \(I = 2 \cdot 10^{12} - 2 \cdot 10^{13}\) W/cm\(^2\) and pulse duration \(T = 200 - 500\) fs are found to be optimal. The modes of interest are dominated by a single electron-hole pair and so their energies, being combined with the photoelectron data for hole states, allow to gather new information about mean-field spectra of valence electrons in the HOMO-LUMO region. Besides, the scheme allows to estimate the lifetime of electron-hole pairs and hence the relaxation time of electronic energy into ionic heat.

In recent years, the analysis of cluster structure and dynamics has made remarkable progress in going beyond mere optical absorption spectroscopy. More and more observables are now being accessed with methods which had been applied successfully in atomic and molecular physics, as e.g. measuring angular distributions, photoelectron spectra (PES), or pump and probe scenarios, for an overview see \footnote{1}. For example, PES have attracted much interest, see e.g. \footnote{2}, \footnote{3}, \footnote{4}, \footnote{5}. They allow to determine the energies \(\epsilon_{h}\) of the occupied (hole) electron levels in the mean field of the cluster. Altogether, cluster studies are shifting from the investigation of global properties (like, e.g. the dipole plasmon) to exploring more detailed features, as e.g. the single-electron states in the cluster mean field. These novel observables are important not only for clusters but for any nano-system since they deepen the understanding and promote the development of experimental techniques.

In spite of impressive achievements, atomic clusters bear still a variety of unexplored features. For example, clusters have a rich excitation spectrum of higher multipoles \(\lambda > 1\), beyond the well studied dipole modes. As is discussed below, low-lying non-collective excitations of this family give access to the single-electron spectra and allow to estimate some principle time scales relevant for clusters and other nano-systems. However, the standard one-photon absorption experiments are blind to non-dipole states. Other means of analysis as, e.g., inelastic electron scattering did not yet come very far due to the small energies involved. It is the aim of present contribution to discuss a possible pathway to the particular kind of non-dipole spectra, quadrupole (\(\lambda = 2\)) non-collective modes. The novel pump/probe technique with using laser two-photon process will be proposed for population and detection of these modes.

It is a challenging task as such to get access to quadrupole modes. Moreover, the low-lying quadrupoles carry useful information about the unoccupied electron states near the Fermi surface. The modes are predominantly of electron-hole (\(eh\)) type \footnote{6}, whose spectra are the mere energy differences \(\epsilon_{eh} = \epsilon_{e} - \epsilon_{h}\). Knowing the hole state \(\epsilon_{h}\) from other sources, allows then to conclude on the involved particle energies \(\epsilon_{e}\). A further interesting observable is the lifetime \(\tau_{eh}\) of an \(eh\) pair since it provides the time scale of the transfer of electronic energy into internal energy (mainly ionic motion and to some extend higher correlated electron states). The value \(\tau_{eh}\) is important for many processes, e.g., for defining different regimes of multi-photon ionization (MPI) in atomic clusters \footnote{7}. Being determined by electron-ion correlations, \(\tau_{eh}\) should be much longer than the lifetime of the dipole plasmon. However, very little is known experimentally. As is shown below, the scheme we propose is also appropriate for measurement of the lifetime \(\tau_{eh}\).

Low-lying (infrared=IR) electronic quadrupole states in free small deformed clusters seem to be most appropriate for our aims \footnote{8}. Beams of size selected small clusters are readily available. In free small clusters, the IR electronic spectra are dilute, which simplifies their experimental discrimination. Thus we concentrate here on these species. Deformed clusters are needed, because most of the IR quadrupole states arise due to the cluster deformation and are absent in spherical clusters (see the upper plot in Fig. \footnote{9}). This then provides a further indicator of the cluster shape. And, as outlined above, low-lying quadrupole states in small deformed clusters give access to \(eh\) energies since they can be, to a good approximation, considered as pure \(eh\) states \footnote{10}.

Quadrupole states cannot be populated in mere photoabsorption where dipole modes dominate. One has to use
two-photon (two-dipole) processes. An option is one of the different versions of the stimulated Raman process (e.g., off-resonant Raman or stimulated Raman adiabatic passage [STIRAP]) which steps up via an intermediate dipole state. These methods use three laser pulses: pump, Stokes and probe. They may be applicable to atomic clusters when choosing appropriate laser parameters.

In the present paper, we will consider an alternative, probably simpler, scheme using direct two-photon excitation in resonance with the final quadrupole state (see Fig.1b)). To detect the successful population of the quadrupole states, the cluster is irradiated by a probe pulse (with appropriate delay) leading to MPI. The corresponding PES are recorded. The quadrupole oscillation couples with the single-electron PES structures and thus manifests itself via satellites in the PES. In this scheme we need only two lasers, pump and probe. As is shown below, intense fs lasers are most appropriate.

As a test case for our computational simulation, we consider Na$^{+}_{11}$ in jellium approximation. This cluster is strongly prolate and displays well separated low-lying quadrupole states. The calculations are performed within the time-dependent local density approximation (TDLDA) with the exchange-correlation functional. The ions are treated in the soft jellium approximation. This approximation, although a bit daring to small metal clusters, is well suited for the exploration of the two-photon method in Na$^{+}_{11}$ which is axially symmetric in jellium. Besides, this allows to perform the calculations on an axial grid in coordinate space. Absorbing boundary conditions are employed for the description of photoionization. The excitation spectra in the linear response regime are computed using TDLDA by standard techniques of spectral analysis. The laser induced dynamics is simulated by adding to the TDLDA the laser pulses (propagating in $z$-direction) as classical external dipole fields of the form $W(t) = E_0 z \sin^2(t/T) \cos(\omega t)$ where $E_0$ is the field strength, $\omega$ the frequency, and $T$ the pulse duration.

Fig. 1 demonstrates the spectra of Na$^{+}_{11}$. Panel a) shows the single-electron states. The ground state is deformed. Comparison with the spherical spectrum shows that the axial deformation splits the single-electron spectra and hence the energies of $eh$ pairs. Following the scheme, only three low-lying quadrupole $eh$ excitations, $\{[220],[200]\}_{20}$, $\{[220],[211]\}_{21}$, and $\{[220],[202]\}_{22}$, exist in Na$^{+}_{11}$ and the last two of them are fully driven by the cluster deformation. The associated excitation energies are small because they are mainly determined by the deformation splitting. Panel b) shows the relevant part of the excitation spectrum in terms of the dipole ($\lambda \mu = 10$) and quadrupole ($\lambda \mu = 20$) strengths. The modes with $\mu > 0$ (and thus the excitations $\lambda \mu = 21$ and 22) are not presented here. To illustrate our method it is quite enough to consider only one low-energy quadrupole mode, namely that of $\lambda \mu = 20$. This mode is seen as a peak at the energy $\epsilon_{20} = 0.8$ eV.

Figure 1 shows that the only inhabitants of the IR region below 1.3 eV are three low-energy quadrupole excitations indicated by arrows in the panel a). Both dipole and quadrupole plasmons lie well above. The lowest dipole $eh$ excitation also resides above, at 1.4 eV. So, the IR part of the spectrum we are interested in is indeed very dilute. This favors the experimental discrimination of the quadrupole levels. Moreover, the well separated levels are not subject to collective mixing and thus preserve their $eh$ nature.

The lifetime of the low-lying quadrupole states probably does not exceed several ps. The exciting laser pulses should be shorter, say hundreds fs. They have to be intense enough to excite the quadrupole mode in the two-photon process and to yield a measurable PES. On the other hand, the pulses should not be too intense in order to keep the resolution in the PES. As is shown below, the optimal intensity is $I = 2 \cdot 10^{10} - 2 \cdot 10^{11}$ W/cm$^2$. The simplest case of one-photon (n=1) ionization cannot be applied here, since the low-order ionization would demand lasers operating in the ultraviolet (UV). But UV
LASERS WITH SUFFICIENT INTENSITIES ARE AVAILABLE ONLY IN THE ns REGIME WHICH IS USELESS FOR OUR PURPOSES. SO, WE ARE ENFORCED TO DEAL WITH fs LASERS AND MULTI-PHOTON IONIZATION (MPI). TO MINIMIZE THE MPI ORDER N, IT IS DESIRABLE TO WORK AT THE MINIMAL WAVELENGTH AVAILABLE FROM fs LASER SYSTEMS. IN THE PRESENT STUDY, WE USE THE LASER RADIATION AT $\hbar\omega_{\text{probe}} = 3.2$ eV, WHICH CORRESPONDS TO THE SECOND HARMONIC FREQUENCY OF A TITANIUM SAPPHIRE LASER. THE MPI ORDER IS THEN $n = 2$. THE TUNABLE IR PUMP PULSE MAY BE PROVIDED BY fs OPTICAL-PARAMETRIC GENERATORS.

FIG. 2: Resonant and off-resonant excitations in Na$_{11}^-$. The left panels exhibit quadrupole and dipole strengths as function of the excitation energy. The right panels depict the electronic quadrupole and dipole moments (in atomic units) as a function of time. The pump (first) and probe (second) pulses are clearly seen. The calculations are performed for laser intensities $I_{\text{pump}} = I_{\text{probe}} = 10^{11}$ W/cm$^2$ and pulse durations $T_{\text{pump}} = T_{\text{probe}} = 300$ fs.

Lasers with sufficient intensities are available only in the ns regime which is useless for our purposes. So, we are enforced to deal with fs lasers and multi-photon ionization (MPI). To minimize the MPI order $n$, it is desirable to work at the minimal wavelength available from fs laser systems. In the present study, we use the laser radiation at $\hbar\omega_{\text{probe}} = 3.2$ eV, which corresponds to the second harmonic frequency of a titanium sapphire laser. The MPI order is then $n = 2$. The tunable IR pump pulse may be provided by fs optical-parametric generators.

Fig. 2 exhibits the first step of our scheme, the population of the $\lambda\mu = 20$ quadrupole state. The right panels show time evolution of the dipole and quadrupole oscillations caused by the pump pulse. The resonant ($2\hbar\omega_{\text{pump}} = 2 \cdot 0.40$ eV = $\epsilon_{20} = 0.80$ eV) and off-resonant ($2\hbar\omega_{\text{pump}} = 2 \cdot 0.34$ eV $\neq \epsilon_{20} = 0.80$ eV) cases are considered. It is obvious that only the resonant case develops self-sustaining quadrupole oscillation. Since electron-ion relaxation is not taken into account here, this oscillation persists for several ps and further. But the dipole oscillates only during the pump pulse at $t = 0 - 300$ fs. In the off-resonant case, both quadrupole and dipole modes respond only during the pump pulse. The left panels exhibit the corresponding dipole and quadrupole strengths. Note that in the resonant case (left upper panel), the quadrupole mode of interest at $0.80$ eV dominates all other modes. This resonant suppression of competitors is crucial for producing the clean satellites in PES later on. The quadrupole mode as excited by the resonant two-photon excitation continues to oscillate for a while. The population of this mode can thus be checked by a sufficiently delayed probe pulse. This pulse is shown at $t = 600 - 900$ fs. The pulse delay $600$ fs (equal to the double pulse duration) suffices to all other (virtual) modes to relax to zero, except of the long-living mode of interest.

The probe pulse leads to strong photoionization and the resulting PES provides information about the cluster state before ionization. The upper panel of Fig. 3 shows the PES for the off-resonant case, which is typical for the cluster ground state $^{13}$Na. The structures corresponding to single-electron hole states $1d$, $1p$ and $1s$ are well visible. The lower panel shows the PES for the resonant case. One recognizes additional satellites in the spectra which are shifted just by the quadrupole energy $\pm 0.8$ eV with respect to the leading peaks, as indicated by the arrows. They emerge from the coupling of the quadrupole mode with the single-electron states. Only the strongest $1d$ and $1p$ PES structures have significant satellites. The most remarkable satellite is at $\epsilon_{1s\text{kin}} \approx 1$ eV. The interpretation of the quadrupole energy in terms of $e\hbar$ differences $\epsilon_{eh} = \epsilon - \epsilon_h$ is to be taken with a bit of care. The state can involve a small coupling to collective quadrupole strength. Detailed analysis shows that the $\lambda\mu = 20$ mode in Fig. 2 contains a small collective blue-shift of $< 0.1$ eV as compared with the energy of the pure $\{220\}, [200]_{20}$ configuration. However, this shift is within the accuracy of the typical PES measurements.

The proposed scheme allows to obtain not only the frequency of the quadrupole mode but also its lifetime. To that end, one should simply increase, step by step, the delay between the pump and probe pulses. The relaxation of quadrupole oscillation will finally lead to an extinction of the satellites from which one can read off the lifetime. This feature cannot be tested in our present model where $eh$ states have infinite lifetime.

In Fig. 4 the sensitivity of the process to the pulse intensity is tested. The PES structures and their satellites are strong and can be well discriminated for intensities $I = 2 \cdot 10^{10} - 2 \cdot 10^{11}$ W/cm$^2$. Smaller intensities result in

FIG. 3: The photoelectron yield in Na$_{11}^+$ at time $t=1200$ fs for the off-resonant and resonant cases. Parameters of the calculations are the same as in Fig. 2.
FIG. 4: The resonant photoelectron yield in Na\(^+\) calculations with the fixed intensity to considerable broadening the PES (see also [13]). The too weak photoelectron yield while higher intensities lead the same as in Figs. 2 and 3.

The low-energy spectra are sensitive to thermal fluctuations of the cluster configuration. Our survey deals with a fixed ground state configuration. Thus it is advisable to work at low temperatures (less 100 K) to avoid broadening of the signal and other artifacts. Our calculations show that the photoelectron yield from the satellites should be \(n_e \sim 10^{-5}\) electrons per cluster and laser pulse. Then, assuming typical parameters of available cluster beams [14] and lasers with kHz repetition, one finds that \(n_e\) still should be measurable even under additional damping effects (electron-ion correlations, possible probe-induced multi-plasmon excitations [15], random orientation of clusters in the beam).

In conclusion, we propose a simple scheme for the population and detection of non-collective (electron-hole) infrared quadrupole states in small deformed atomic clusters. It relies on a pump-and-probe technique where the pump pulse excites the quadrupole mode via a two-photon process and the probe pulse explores the resulting quadrupole oscillations through satellites in the photoelectron spectra. Already the measurement of low-lying quadrupole states in itself is an achievement as such. Moreover, it can deliver information about the single-electron spectrum directly above the Fermi energy and about the relaxation time for the electron-hole pairs. The proposed scheme is quite general and can be applied to any clusters provided their electronic infrared spectrum is sufficiently dilute.

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