Exploration of electronic quadrupole states in atomic clusters by two-photon processes

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Abstract
We analyse particular two-photon processes as possible means to explore electronic quadrupole states in free small deformed atomic clusters. The analysis is done in the time-dependent local density approximation (TDLDA). It is shown that direct two-photon population (DTP) and off-resonant stimulated Raman (ORSR) scattering can be effectively used for excitation of the quadrupole states in high-frequency (quadrupole plasmon) and low-frequency (infrared) regions, respectively. In ORSR, isolated dipole particle–hole states as well as the tail of the dipole plasmon can serve as an intermediate state. A simultaneous study of low- and high-frequency quadrupoles, combining DTP and ORSR, is most effective. Femtosecond pulses with intensities $I = 2 \times 10^{10}$ to $2 \times 10^{11}$ W cm$^{-2}$ and pulse durations $T = 200–500$ fs are found to be optimal. Since the low-lying quadrupole states are dominated by one single electron–hole pair, their energies, being combined with the photoelectron data for hole states, allow us to get the electron spectrum above the Fermi level and thus greatly extend our knowledge on the single-particle spectra of clusters. Besides, the developed schemes allow us to estimate the lifetime of the quadrupole states.

1. Introduction
In recent years, the achievements in laser technologies have led to a remarkable progress in the analysis of electronic degrees of freedom in atomic clusters, for an extensive review
see [1]. For example, photoelectron spectra (PES) can now be measured with high accuracy and for a broad variety of clusters [2–8]. However, a wealth of electronic modes still remains unexplored. In clusters with the diameter far below the laser wavelength (i.e. in clusters with the number of atoms \( N < 10^6–10^8 \)), the laser light couples only to dipole (\( \lambda = 1 \)) states. Hence we gain the well-known dipole plasmon. At the same time, it is still very hard to access the electronic modes with higher multipolarity \( \lambda > 1 \). Multi-photon processes can generally give a way to these modes [9]. For example, two photons couple to quadrupole (\( \lambda = 2 \)) modes [9, 10]. Just this case, investigation of quadrupole modes of valence electrons in two-photon processes, will be scrutinized in the present paper. In a previous publication [11], we have studied the scenario of two-photon processes where both photons originate from the same laser pulse and so have the same frequency. In this paper, we will analyse an alternative two-photon technique employing two different laser frequencies. It will be shown that the combined implementation of both techniques is most optimal for the exploration of electronic quadrupole states.

A particularly interesting aspect emerges for low-frequency (infrared) quadrupole modes in small deformed clusters. It was found that these modes are dominated by a single electron–hole (1eh) pair [10, 11] and their spectra are close to the pure 1eh energy differences \( \epsilon_{1eh} = \epsilon_e - \epsilon_h \). As a result, measuring the energy \( \epsilon_{1eh} \) in a two-photon process and the energy of the hole (occupied) state \( \epsilon_h \) by PES [2–4], we gain information on the particle energy \( \epsilon_e \). This allows us to determine the full single-particle spectrum of valence electrons near the HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) gap. Being sensitive to diverse features of a cluster (equilibrium shape, ionic structure, . . . ), the electronic spectra can in turn serve for investigations of these features. Besides, they constitute a critical test of any theoretical description.

It is worth noting that, unlike the dipole states with their high frequencies and strong collective mixing, the quadrupole states of interest mainly originate from deformation splitting [10, 11]. Their energy scale is thus quite small and they usually lie in the infrared region \(<1 \) eV. In small clusters the spectrum of these states is very dilute. This prevents collective mixing of the states, favours their 1eh nature, and simplifies the experimental discrimination. Different kinds of small deformed clusters (free, supported, embedded) can be explored for the infrared quadrupole modes. In this paper, we will consider the simplest case of free clusters.

Two-photon processes allow us to excite not only the low-frequency quadrupole modes, but also high-frequency quadrupole states in the regime of the quadrupole plasmon. In fact, these plasmon states carry a large quadrupole strength and thus rather easily respond to two-photon probes. The two sorts of quadrupole modes can be characterized in terms of transitions between major quantum shells of the cluster mean field [10]. The low-frequency quadrupole modes correspond to 1eh excitations within the valence quantum shell \( N (\Delta N = 0 \text{ modes}) \). The high-frequency states in the quadrupole plasmon range correspond to excitations over two major shells (\( \Delta N = 2 \) modes). There are still no experimental data about either kind of modes. But their investigation could deliver valuable spectroscopic information.

As mentioned above, the excitation of quadrupole states needs at least a two-photon process. A variety of such processes is known in atomic and molecular spectroscopy [12–15]. However, to our knowledge, none has been applied so far in experimental investigations of atomic clusters. Some of these processes, namely direct two-photon population (DTP) [11], off-resonant stimulated Raman scattering (ORSR) [13], and stimulated Raman adiabatic passage (STIRAP) [14, 15], seem to be quite promising [16] and are thus worth closer inspection. As is shown below, some particular cluster properties, e.g. high probability of undesirable plasmon population, complicates implementation of two-photon schemes. Hence
Figure 1. Schemes of two-photon processes: direct two-photon (DTP) in a two-level system and off-resonant stimulated Raman (ORSR) in a three-level $\Lambda$-system. The initial $|0\rangle$, intermediate $|1\rangle$ and target $|2\rangle$ states have the orbital moments $\lambda = 0$, 1 and 2, respectively. In ORSR the pump dipole pulse couples the ground and intermediate states while the Stokes dipole pulse provides the coupling of the intermediate and target states. $\Delta$ is the detuning from the intermediate dipole state $|1\rangle$. The purpose of both DTP and ORSR is the population of the target quadrupole state $|2\rangle$.

we need a detailed analysis on the basis of realistic calculations. As a first step in this direction, the pump–probe DTP method was recently investigated [11]. In this method the electronic infrared quadrupole state is generated via the direct resonant two-photon (two-dipole) excitation by the pump laser; see the DTP scheme at the left part of figure 1. The population of the quadrupole state is detected through the appearance of satellites in the photoelectron spectra produced by a probe pulse (not shown in figure 1). Femtosecond pump and probe pulses with intensities $I = 2 \times 10^{10}$ to $2 \times 10^{11}$ W cm$^{-2}$ and pulse duration $T = 200–500$ fs were found to be optimal. The systematic TDLDA calculations have shown that the method is very robust and delivers not only the 1eh spectrum but also the lifetime of the 1eh pairs.

In the present paper, we aim to inspect an alternative two-photon method, off-resonant stimulated Raman scattering (ORSR). In this method, the target quadrupole state is populated by two different dipole transitions via an intermediate dipole state. Hence we deal with the so-called $\Lambda$-system; see right part of figure 1. The pump pulse provides the coupling of the initial (ground) state $|0\rangle$ to the intermediate state $|1\rangle$. The Stokes pulse couples $|1\rangle$ with the quadrupole target state $|2\rangle$, altogether stimulating the transition to the target state. The pulses have to maintain the two-photon resonance condition $\omega_p - \omega_s = \omega_2$, i.e. the difference of the pump and Stokes frequencies must coincide with the frequency of the target quadrupole state. Isolated dipole states of 1eh nature as well as the dipole plasmon can serve as the intermediate state $|1\rangle$. However, one should avoid a real population of the intermediate state to prevent undesirable leaking into competing channels. This is especially important for the dipole plasmon which decays via a fast Landau damping associated with a short lifetime ($\sim 10–20$ fs) [1]. To avoid the actual population of $|1\rangle$, we will use an appreciable detuning $\Delta$ from the energy of this state, hence the reference to an off-resonant process. A considerable detuning is the crucial point in our scheme. Detection of the population of the target quadrupole states (both at low- and high-frequency) in ORSR can be done by a probe pulse in the same way as in DTP [11]. As compared with DTP, the ORSR scheme is more involved since it requires not two but three different pulses (pump, Stokes and probe). At the same time, ORSR allows us to explore the low-lying quadrupole states using lasers in the region of visible light and hence is an interesting alternative to DTP. Besides, ORSR is widely used in atomic and molecular physics. It is certainly worth assaying this method for atomic clusters as well.

In the present study, we will apply ORSR to low-frequency quadrupole states. However, as is shown below, it is hard to explore these states without touching the high-frequency quadrupoles which very easily respond to any two-photon probes. Both kinds of quadrupole
states should thus be involved into a realistic exploration scheme. The high-frequency quadrupoles can hardly be studied within ORSR in \( \Lambda \)-configuration because in this case we would need the intermediate dipole state lying above the quadrupole plasmon\(^5\). It is hence better to explore these quadrupoles by DTP. As a result, we naturally come to a combined analysis implementing ORSR for the low-frequency quadrupoles and DTP for their high-frequency counterparts. The aim of the present paper is to develop optimal schemes for the combined DTP–ORSR method.

The paper is outlined as follows. In section 2 the calculation scheme is sketched. In section 3 the ORSR excitation of the low-frequency quadrupole is discussed for two cases of the intermediate state: an isolated dipole state and tail of the dipole plasmon. Stability of the process to variation of the main parameters is scrutinized. The DTP population of the quadrupole plasmon states is outlined and the general scheme for the combined DTP–ORSR experiment is developed. Conclusions are drawn in section 4.

2. Calculation scheme and test case

The theoretical and numerical framework of our study are explained in detail elsewhere \([1, 17]\). So we summarize here only the key points. The calculations are performed within the time-dependent local density approximation (TDLDA) using the exchange-correlation functional of \([18]\) and an averaged self-interaction correction \([19]\). As a first step, the static single-electron wavefunctions \(\bar{\phi}_i(\vec{r})\) are calculated from the stationary Kohn–Sham equations. Then time evolution of the single-electron wavefunctions \(\phi_i(\vec{r}, t)\) is computed starting from the initial condition \(\phi_i(\vec{r}, t = 0) = \bar{\phi}_i(\vec{r})\). The ionic background is treated in the soft jellium approximation \([1]\). This approximation, although a bit daring, is capable of reproducing the basic trends of shapes and subsequent plasmon spectra of Na clusters \([20–22]\). In the present paper, we consider axially deformed clusters and therefore Na\(^{11}\) as a particularly suitable test case. The axial symmetry and jellium approximation together greatly reduce the computational effort and thus allow huge scans in the multi-parameter space of multi-photon processes even in deformed clusters. Absorbing boundary conditions are employed for the description of photoionization. The numerical handling is performed by standard methods (gradient iterations for the ground state, time splitting for time propagation). The excitation spectra in the linear response regime are computed in TDLDA by standard techniques of spectral analysis \([17, 23]\). The laser-induced dynamics is simulated by adding to the TDLDA the laser pulses as classical external dipole fields of the form \(W(t) = E_0 z \sin^2(\pi t / T) \cos(\omega t)\) with the field strength \(E_0 \propto \sqrt{\text{square root of the intensity}}\) lasting for one half-cycle of the profile function \(\sin^2(\pi t / T)\). The field is applied in the \(z\)-direction (the symmetry axis of the system); \(\omega\) is the frequency and \(T\) is the pulse duration. Small deformed sodium clusters are optimal for a first exploratory analysis. We consider here the test case Na\(^{11}\). Parameters of the quadrupole and hexadecapole deformations in this cluster are \(\beta_2 = 0.32\) and \(\beta_4 = 0.24\) (see definitions of the parameters in \([24]\]). So, it is strongly prolate which provides a comfortably strong collective splitting of the plasmon resonance and of the single-electron spectrum. Its infrared spectrum below 1 eV is very dilute and displays only three well separated electronic levels, namely the quadrupole modes of multipolarity \(\lambda\mu = 20, 21\) and 22 (see table 1). Following our estimations \([10]\), these modes almost correspond to pure 1eh states as indicated in table 1. The collective shifts of these states through the Coulomb residual interaction are modest, e.g. \(\sim 0.05\) eV for \(\lambda\mu = 20\), which corroborates their 1eh structure. This feature

\(^5\) In principle, the quadrupole plasmon can be also explored by ORSR in the ladder configuration when the successive levels lie higher than the predecessors. However, as is shown in section 3.4 this option is not optimal.
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Figure 2. Dipole ($\lambda\mu = 10$) and quadrupole ($\lambda\mu = 20$) strength distributions in Na$^{+}_{11}$. The large peaks above 2 eV represent the states of the dipole and quadrupole plasmons. The sets of horizontal arrows depict two-photon (two-dipole) processes: DTP (pump + pump) and ORSR (pump + Stokes). The latter runs via the isolated dipole state at 1.35 eV and the tail of the dipole plasmon. The low- and high-frequency quadrupole states of interest are seen as peaks at 0.8 and 2.6 eV.

Table 1. The spectrum of the quadrupole states below 1 eV in Na$^{+}_{11}$, approximated by the energies of the dominant 1eh pairs. The structure of 1eh pairs is done in terms of the Nilsson–Clemenger quantum numbers $[N\pi, \Lambda_l]$. See text for more details.

| $\lambda\mu$ | $\hbar\omega$ [eV] | $[N\pi, \Lambda_l]$ | $[N\pi, \Lambda_h]$ |
|--------------|-------------------|-------------------|-------------------|
| 21           | 0.41              | [211]             | [220]             |
| 22           | 0.60              | [202]             | [220]             |
| 20           | 0.75              | [200]             | [220]             |

is a direct consequence of the dilute spectrum, because large energy intervals between the levels prevent their collective mixture. In Na$^{+}_{11}$ dipole states start above 1 eV and so are well separated from the low-frequency quadrupole modes. Such a spectral separation is a general feature of small deformed clusters. As was mentioned above and as can be seen from table 1, the low-frequency quadrupole modes are represented by the 1eh transitions inside the valence shell ($\Delta N = 0$). Moreover, most of these modes arise due to the deformation splitting of the levels and so their energy scale is small. Instead, the dipole modes are generated by $\Delta N = 1$ electron–hole transitions between the neighbour quantum shells and thus acquire much higher energies. The effective energy separation of the quadrupole and dipole modes favours discrimination of the low-frequency quadrupole spectrum. In what follows, we will concentrate on the states with $\lambda\mu = 20$. This suffices for our exploration. Besides, the limitation to $\lambda\mu = 20$ allows us to maintain the axial symmetry which, in turn, reduces computational expense. Figure 2 shows the relevant part of the excitation spectrum in terms of the dipole ($\lambda\mu = 10$) and quadrupole ($\lambda\mu = 20$) photo-absorption strengths. The low- and high-frequency quadrupole modes of interest are seen at the energies $\epsilon_{20} = 0.8$ and 2.6 eV. The horizontal arrows depict the DTP and ORSR processes considered below. Two ORSR versions are discussed. In the first case, the process runs via the isolated dipole state at 1.35 eV. In the second case, it proceeds via the intermediate region between the isolated dipole state at 1.9 eV and the dipole plasmon. In both cases, there is an appreciable detuning from the dipole states such that one deals only with remote tails of the states.
3. Results and discussion

3.1. ORSR for low-frequency isolated quadrupole

Figure 3 shows the ORSR via the isolated dipole state at 1.35 eV with a detuning of $\Delta \sim 0.08$ eV. The right panels show time evolution of the dipole and quadrupole moments. It is seen that the ORSR mechanism leads to enduring quadrupole oscillation. Since electron–ion and electron–electron relaxations are not taken into account here, these oscillations persist for several ps and further. The dipole oscillations, on the other hand, exist only during the pulses at $t = 0–300$ fs. The left panels display the corresponding dipole and quadrupole strengths in the frequency domain, obtained as the Fourier transforms of the oscillating moments. The quadrupole mode of interest at 0.81 eV dominates all other quadrupole excitations, even the quadrupole plasmon. So, just this mode is presented in the enduring oscillation seen in the right-top panel. The dipole strength is negligible (compare different scales of the top and bottom panels) and so should not noticeably compete with the quadrupole mode of interest. As was shown in [11], a significant decoupling of competing modes is crucial for detection of the target quadrupole state.

Figure 4 shows results for the ORSR via the region between two close dipole structures. The pump laser frequency 2.05 eV is placed between the isolated 1eh peak at 1.9 eV and the tail of the dipole plasmon lying at 2.3 eV, thus representing a considerable detuning from both dipole structures. As these structures are much stronger than the intermediate dipole in the previous case, it becomes possible to get double the quadrupole signal even at the lower laser intensity ($I_s = 1.5 I_p = 1.44 \times 10^{10}$ W cm$^{-2}$ against $I_s = 1.5 I_p = 2.2 \times 10^{10}$ W cm$^{-2}$ in figure 3). Like in the previous case, we have no appreciable competitors though now the pump
frequency is rather close to the dipole plasmon. Altogether, figures 3 and 4 justify that one can get robust ORSR signals in clusters via both isolated dipole states and tail of the dipole plasmon.

One may observe in the right-top panel of figure 4 that the quadrupole oscillation leads to some shift of the average quadrupole moment. Indeed, the oscillation starts at the moment $26.6 a_0^2$ but then proceeds around a bit lower average value $\sim 26.4 a_0^2$. Our analysis shows that this effect is caused by a non-isotropic emission of electrons from the cluster. Indeed, the axial cluster Na$_{11}^+$ has a shape of the prolate ellipsoid. The quadrupole oscillation of multipolarity $\lambda \mu = 20$ drives electrons along the symmetry axis of the cluster and thus favours emission of electrons from the poles of the cluster ellipsoid. This makes the shape of the electron subsystem more spherical and therefore effectively decreases the quadrupole moment. The stronger the oscillation, the larger the moment shift. Hence the effect is most apparent in figure 4 which exhibits the strongest quadrupole mode. However, even in this case the moment shift is quite modest (2%) and thus should not noticeably influence the accuracy of measurements of the energy of the quadrupole mode in ORSR experiments.

3.2. Coherence and population for the target state

Figures 3 and 4 were obtained with simultaneously active pump and Stokes pulses, i.e. with the relative time shift $T_{\text{shift}} = 0$. The dependence of the quadrupole peak height on the time shift is shown in figure 5. It is seen that the maximal quadrupole strength is achieved at coincident pump and Stokes pulses. A similar picture emerges for stimulated Raman scattering, when plotting the population of the state instead of its strength [12–14]. However, such a correlation between the strength and population arises only at low population and does not imply equality of these two characteristics. This point deserves closer inspection.
Let us confine the formal considerations to the active subspace. At any time \( t \), the many-body wavefunction of the three-level \( \Lambda \) system can be represented as a superposition

\[ \psi(t) = c_0(t)|0\rangle + c_1(t)|1\rangle + c_2(t)|2\rangle \]

(1)

where \( c_0(t), c_1(t) \) and \( c_2(t) \) are time-dependent amplitudes of the initial, intermediate and final bare states, respectively. The population of the target quadrupole state then reads \( |c_2(t)|^2 \). But the strength of the quadrupole transition (considered in figures 3–5) is \( \sim |c_0(t) * c_2(t)|^2 |E_2| \langle 0 | \) and so corresponds not to the population but to the coherence \( c_0(t) * c_2(t) \) of the initial and target states. The population and coherence have different behaviours. They both grow at the onset of the population of the level \( |2\rangle \) but then the coherence reaches a maximum at \( c_0^2(t) = c_2^2(t) = 0 \). When further increasing \( |c_2(t)|^2 \) from 0.5 to 1.

The calculation of the population \( |c_2(t)|^2 \) in TDLDA is somewhat involved. So, in the present study, we will only consider a simple estimate. We know that the dominant component of the low-frequency quadrupole state is the 1eh configuration [200]e[220]h (see table 1). To populate this configuration, the electron from the occupied state [220] should be transferred to the unoccupied state [200]. This should manifest itself in the time-dependent single-particle wavefunction \( \phi_{[220]}(\vec{r}, t) \). Namely, it has to coincide with the initial state \( \phi_{[200]}(\vec{r}) \) at \( t = 0 \) and then acquire large contribution of \( \phi_{[200]}(\vec{r}) \) in the course of time. Hence the population \( P_{2\text{eh}}^\text{eh}(t) \) of the [200]e[220]h quadrupole component can be estimated as the squared overlap

\[ P_{2\text{eh}}^\text{eh}(t) = \left| \int d\vec{r} \phi_{[220]}(\vec{r}, t) \phi_{[200]}(\vec{r}) \right|^2. \]

(2)

This estimate yields for \( t > 600 \) fs (i.e. for the time when, following figures 3 and 4, only the low-lying quadrupole mode survives) quite small population 0.01–0.03. Instead, the overlap with the initial static state

\[ P_{2\text{eh}}^\text{en}(t) = \left| \int d\vec{r} \phi_{[220]}(\vec{r}, t) \phi_{[220]}(\vec{r}) \right|^2 \]

(3)

turns out to contribute the complementing 99–97%. Similar relations were obtained for the direct two-photon (DTP) excitation of the quadrupole, described in [11]. During the time

\[ \text{Figure 5. The quadrupole strength as a function of the pulse shift for ORSR via the isolated dipole state and the dipole plasmon.} \]
evolution, the single-electron wavefunctions thus mainly keep their initial structure and only a small fraction (a few per cent) of the intended 1eh quadrupole configuration \([200]e[220]h\) is really populated. This is mainly the consequence of using the large detuning. One might be tempted to decreasing the detuning or, alternatively, enhance the population by increasing the laser intensity. But then we would run into the non-linear regime of TDLDA where the cross-coupling between numerous states of the system takes place and hence the three-level picture most probably fails. This trouble reflects the more complex dynamics of metal clusters as compared to simple molecules. In any case, even a population of a few per cent has to be sufficient to detect the quadrupole state in experiments. The TDLDA calculations for the DTP in \(\text{Na}^+\) showed measurable signatures of the low-lying quadrupole state in PES \([11]\). A similar situation is expected for the ORSR.

3.3. ORSR stability

It is still necessary to check the stability of the ORSR scheme to variations of the process parameters. Our tests are illustrated in figure 6. It shows ORSR via the isolated dipole. The process via the tail of the dipole plasmon (not shown here) produces the same features.

The panels (a) of figure 6 show the quadrupole and dipole strengths at larger pulse intensities. The intensities are increased by a factor 3.4 as compared to figure 3. This allows us to get a two times stronger quadrupole mode at 0.81 eV. However, we are punished by stronger dipole excitations and a coupling to the quadrupole mode at 2.8 eV (as a part of the quadrupole plasmon), which can complicate discrimination of the target state in PES. So, though the ORSR works even at high intensities, the lower intensities are better suited for the experimental analysis. On the other hand, it is not worth going below the optimal intensities of figure 3 since this would lead to an unnecessary weakening of the quadrupole strength.

Figure 6. The strengths calculated as in figure 3 but (a) for larger intensities \(I_t = 1.5 I_p = 7.44 \times 10^{10} \text{ W cm}^{-2}\); (b) with small deviation 0.03 eV from the two-photon resonance; (c) without detuning from the intermediate dipole state. See text for more details.
The panels (b) in figure 6 show that small deviations from the two-photon resonance condition $\omega_p - \omega_s = \omega_2$ lead to weakening of the target mode. Nevertheless, because of the finite width of the mode, the signal does not vanish too rapidly. In fact the width of the mode determines the maximal deviation for $\omega_s$ while looking for the mode in the experiment.

Finally, the panels (c) of the figure demonstrate what happens without detuning from the intermediate dipole state. In this case, the dipole strength of the intermediate state is considerably increased while the population of the target quadrupole state shrinks. Besides that, a large fraction of competing high-frequency quadrupoles appear. So, considerable detuning is crucial for the success of the ORSR scheme.

3.4. DTP exploration of quadrupole plasmon

The top panel of figure 6(c) deserves a deeper analysis because it demonstrates an important feature of ORSR and similar two-photon processes in metal clusters. Indeed, if two photons from the pump and/or Stokes pulses happen to come into resonance with one of the peaks of the quadrupole plasmon, then this peak is strongly excited. Such a case is observed in the top panel of figure 6(c). Comparison of this plot with figure 2 shows that $2\hbar\omega_p = 2.7\ eV$ and $2\hbar\omega_p + 2\hbar\omega_s = 3.7\ eV$: this approximately covers two of the plasmon states and thus results in two prominent spikes at these energies. Obviously, such undesirable excitation of the quadrupole plasmon can spoil the discrimination of low-frequency quadrupole modes in PES. At the same time, this provides new possibilities for simultaneous investigation of low- and high-frequency quadrupoles.

The example above indicates that implementation of two lasers with different frequencies complicates the analysis of the quadrupole plasmon because we may have more than one resonance at once. This would hinder the detection procedure. For the same reason is not optimal to use ORSR in the ladder configuration for investigation of high-frequency states. It is much better to apply the DTP method proposed in [11], where the quadrupole state of interest is populated by absorption of two photons from one laser, as shown in figures 1 and 2. An example of such a DTP process is presented in figure 7 where the resonant absorption of two photons from the pump laser results in a strong excitation of the quadrupole plasmon state at 2.6 eV. Unlike the top panel of figure 6(c), only one frequency is involved and thus only one resonant peak excited. A properly tuned DTP with scanning frequency allows us to investigate the quadrupole plasmon state by state.

3.5. Proposed experiment

The discussion above shows that the most optimal way is a simultaneous investigation of the low- and high-frequency quadrupole states by a combination of ORSR and DTP methods, respectively. For this aim we need three synchronized lasers: tunable infrared pump and Stokes lasers and an ultraviolet probe laser.

The detection scheme can be the same as that proposed in [11]. Namely, the cluster is irradiated by a probe pulse (with an appropriate delay) leading to a direct emission of an electron out of the excited quadrupole state. The coupling of the quadrupole oscillation to the single-electron PES structures will create satellites in the PES. Thus, by recording the PES and measuring the relative frequencies of the satellites, one may determine the frequency of the quadrupole state.

The experiment should follow three steps.

(1) As a first step, we should find the optimal parameters (intensity, duration, . . . ) for the probe pulse responsible for the photoionization of the cluster and detection process. For
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Figure 7. Direct two-photon excitation of the quadrupole plasmon state at 2.6 eV in Na$_{11}$. The cluster is irradiated by the pump laser only, with characteristics $\hbar\omega_p = 1.31$ eV, $I_p = 2.2 \times 10^{10}$ W cm$^{-2}$ and $T_s = 300$ fs.

In this aim we should scan the pulse parameters so as to get the strongest and, at the same time, distinct single-particle PES from the ground state. Our predictions [11] for the optimal pulse intensities and durations ($I = 2 \times 10^{10}$ to $2 \times 10^{11}$ W cm$^{-2}$ and $T = 200$–500 fs) can be used here as a first guess. These predictions are relevant for all three pulses (pump, Stokes and probe) which may have similar characteristics, apart from the photon frequency.

In principle, photoionization can be also provided by a coherent synchrotron source with high-frequency photons. Then the two-photon ionization proposed in [11] can be replaced by a more effective one-photon ionization. In this case, the characteristics of the pump and Stokes pulses can be taken again from [11], while the parameters of the probe irradiation needs independent adjusting.

(2) Now we can proceed with the next step: to explore the high-frequency states of the quadrupole plasmon. We use here only the pump and probe lasers. The pump frequency is scanned until its double value comes into resonance with the states of the quadrupole plasmon. The probe pulse should have sufficient delay with respect to the pump pulse so as to be safely decoupled from it and to measure self-sustaining oscillations only. Since the quadrupole plasmon has high energy, one-photon ionization by a probe laser in the visible range suffices for our aims. The maximum satellite signal provides the quadrupole energy in two ways, first as the double pump frequency and second (as a countercheck) from the offset of the satellites. Thus one can explore, state by state, all the quadrupole plasmon$^6$.

(3) In a final step, one can refine the measurement of the low-frequency quadrupole state. First, one should choose the optimal intermediate dipole frequency by combining a suitable

$^6$ The pump frequency can accidentally coincide with one of the isolated dipole states below the dipole plasmon and thus result in additional PES satellites. However, these satellites can easily be recognized through a slight shift of the probe frequency; see [26] for more details.
detuning above or below the dipole state with the feature that the double-pump frequency lies between the peaks of the quadrupole plasmon and thus avoids their resonance excitation. In such a way we will hopefully minimize the influence of the quadrupole plasmon. Then one should scan the Stokes laser until the two-photon resonance $\omega_p - \omega_s = \omega_2$ with a low-frequency quadrupole is achieved.

The proposed scheme allows us to obtain not only the frequencies of the quadrupole states but also their 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.

It should be noted that the low-energy spectra are sensitive to some damping effects (variations in deformation, temperature smoothing, electron–ion correlations, probe-induced multi-plasmon excitations [26], random orientation of clusters in the beam, etc) which are not taken into account in the present calculations. We have deliberately left the full-scale analysis of these involved and delicate effects to further studies since, by our opinion, one should first solve some principle problems and develop reasonable schemes of future experiments. Now we content ourselves with comments and simple estimations of the damping effects. First, it is advisable to run the proposed experiments at low temperatures (less 100 K) so as to avoid broadening of the signal due to variations of the cluster configurations and other artifacts. Further, 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 and lasers with kHz repetition, one finds that $n_e$ still should be measurable even under the damping effects. Further, the experimental data [2, 3] show that PES obtained in clusters like Na$_{11}$ at temperature $\sim$100 K are distinct enough in spite of all the smoothing effects. Following these arguments, our schemes seem to be relevant despite omission of the detailed treatment of the damping factors.

4. Conclusions

In this paper, we have proposed a combined exploration of electronic quadrupole low-frequency (infrared region) and high-frequency (region of the quadrupole plasmon) states in free metal clusters by means of two-photon processes: direct two-photon (DTP) excitation and off-resonant stimulated Raman (ORSR) scattering. DTP uses one pump laser and retrieves two photons from it while ORSR employs pump and Stokes pulses with different frequencies. The final proof of the successful excitation of a quadrupole mode is achieved by a probe pulse with a subsequent measurement of the photo-electron spectra (PES). The present analysis is based on realistic simulations within the time-dependent local density approximation. Most attention is paid to ORSR which, to our knowledge, still has never been considered for atomic clusters.

The calculations show that the high-frequency quadrupole states in the regime of the quadrupole plasmon are preferably explored by DTP. The more flexible ORSR is a powerful tool to investigate the isolated low-frequency (infrared) quadrupoles. ORSR allows us to use various intermediate dipole states, from the isolated infrared dipoles to the dipole plasmon. In all cases, an appreciable detuning from true dipole states is crucial to avoid unwanted cross talk. A proper combination of both methods (DTP, ORSR) should allow us to explore both spectra and lifetimes of the quadrupole states. We have worked out optimal parameters of DTP and ORSR schemes and checked the sensitivity of the schemes to parameter variations. The proposed two-photon schemes are quite general and, in principle, can be used for a variety of clusters including supported and embedded ones.
The low- and high-frequency quadrupole states can deliver important information on electron–hole excitations inside the valence shell ($\Delta N = 0$) and through two shells ($\Delta N = 2$). By combining the two-photon and photoelectron data, one can get the single-electron energies above the Fermi level and thus greatly enlarge our knowledge on the mean field spectra of valence electrons. These spectra give access to other cluster features (mean field, deformation) and provide a critical test for the theory of cluster structure.

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