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Photoabsorption in sodium clusters on the basis of time-dependent density-functional theory

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Photoabsorption in sodium clusters on the basis of time-dependent density-functional theory

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The photoabsorption spectra of a continuous series of Na_n clusters ($n \leqslant 14$, $n=20$, $n=40$) have been calculated using a time-dependent density-functional scheme. Accordingly, we present these spectra and show that they are in very good agreement with other theoretically and experimentally obtained photoabsorption spectra. Furthermore, we discuss the influence of the cluster structure on the photoabsorption spectrum for some selected clusters and present for several cluster sizes photoabsorption spectra of different geometrical isomers. The spectra of clusters with five or more atoms are dominated by a few large peaks which can be interpreted as collective plasmon excitations. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2814161]

I. INTRODUCTION

Clusters and nanoparticles are widely investigated since they have become important in science and technology. They feature several extraordinary properties that differ from those that we know from macroscopic materials science. The most remarkable changes in properties of nanosized objects are certainly those arising from quantum-confinement or quantum-size effects.[1–5] Since the electronic wave functions are confined to the size of the particle, a discretization of the energy eigenvalues is the consequence and, thus, electronic and optical properties depend critically on the particle size. An example is the optical absorption which can be approximated by the gap between the highest occupied states and the lowest unoccupied states. Decreasing the particle size increases this gap. Consequently, optical properties are tunable by varying the particle size.

One way of dealing with optical properties is, in fact, to measure the energy dependence of the absorption of a substance. This is done, e.g., in photoabsorption spectroscopy. However, it is crucial to be able to select the clusters by size before the measurement is performed, since only then we can assign a spectrum to a particular stoichiometry or cluster size. Although size-selective chemical production of clusters in solution has been improved significantly, it is still impossible to assure that a solution contains particles of a single composition. The spectroscopical way of investigating optical properties of clusters is, thus, still limited to the gas phase. Here, mass-selection processes can be quite easily performed by means of spectrometry, e.g., in a time-of-flight mass spectrometer.

Because photoabsorption spectra give insight into the electronic nature of the investigated systems, they have also been approached by theoreticians already at an early stage. Both Hartree-Fock and density-functional theory (DFT) based methods have been employed in this task. Although the quantum-chemical calculations, such as configuration interaction (CI) and calculations beyond, are particularly demanding with respect to computer time, there have been numerous calculations on small systems. Also density-functional theory gives access to photoabsorption processes, especially in the time-dependent DFT (TDDFT) formulated in 1980s.

In this study we focus on small sodium clusters. They have been very popular since the discovery of the magic numbers by Knight and co-workers[6–8] in early 1980s. Since then, these systems have been studied extensively, both experimentally and theoretically. Besides other properties, the photoabsorption spectra of sodium clusters have also been the target of experimental investigations. Since they have to be recorded in the gas phase and, moreover, since a proper size selection of the clusters is crucial, experimental studies are rare. Early studies, therefore, fixed the wavelength of the exciting light beam. These studies resulted in size-dependent absorption cross sections at fixed absorption energies.[9–11] Wang and co-workers[12,13] obtained the absorption spectra by photodepletion spectroscopy. These spectra have been recorded for small size-selected neutral Na clusters with less than ten atoms and cover the energy range of approximately 1.5–3.0 eV.

Photoabsorption spectra of Na clusters have also been calculated with different methods. Many different cluster sizes have been investigated. The photoabsorption cross sections of different Na_n jellium clusters ($n=1-10,20,21$) have been calculated by Koskinen *et al.*[14] applying the analog of the nuclear shell model. Several large investigations of single clusters—neutral and positively or negatively charged—and their absorption spectra have been performed by Bonačić-Koutecký and co-workers,[15–18] whereas Vasiliev *et al.*[19] investigated different approximations within TDDFT for a set of three small Na clusters. Single clusters have been investigated by Onida *et al.*[20] (Na_4 using the *GW* approximation), Marques and co-workers[21,22] (Na_2 and Na_4 employing

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TDDFT), and Gatti *et al.*[23] (Na_8 using the random-phase approximation). Solov'yov *et al.*[24] performed a large study of structural and electronic properties of neutral and positively charged sodium clusters and also investigated photoabsorption spectra of a selection of these clusters,[25] whereas Moseler *et al.*[26] focused on the photoabsorption spectra of some small charged Na_n^+ clusters only. Finally, Na clusters have also been studied on surfaces, e.g., by Rytkönen *et al.*[27]

In the present study we have focused on the photoabsorption spectra of small Na_n clusters ($n \leqslant 14$). Selectively, we have also chosen two larger magic clusters (Na_{20} and Na_{40}) to cover a larger size range. For several cluster sizes, we have calculated the absorption spectra for different structural isomers.

This article is organized as follows. In Sec. II we will shortly review how the photoabsorption spectrum is calculated within TDDFT and how the comparison to the experiment is made. In Sec. III we will give some information about the computational details, in Sec. IV we present our results and their analysis and, finally, we conclude in Sec. V.

II. PHOTOABSORPTION SPECTRA FROM TIME-DEPENDENT DENSITY-FUNCTIONAL THEORY

Photoabsorption is a time-dependent process and, thus, TDDFT (Refs. 28 and 29) can be employed to calculate the photoabsorption spectrum of the system of interest. To perform these calculations, we have to employ the time-dependent one-particle Schrödinger equation,

$$i\hbar \frac{\partial}{\partial t}\psi_i(\mathbf{r},t) = \hat{H}\psi_i(\mathbf{r},t), \tag{1}$$

where $\psi_i(\mathbf{r},t)$ are the one-electron wave functions of the noninteracting time-dependent Kohn-Sham system, and the Hamiltonian $\hat{H}$ reads

$$\hat{H} = -\frac{\hbar^2\nabla^2}{2m_e} + v_{\mathrm{ext}}(\mathbf{r},t) + v_{\mathrm{H}}(\mathbf{r},t) + v_{\mathrm{xc}}(\mathbf{r},t), \tag{2}$$

and, thus, consists of the kinetic energy of the electrons, a time-dependent external potential $v_{\mathrm{ext}}(\mathbf{r},t)$, the Hartree potential $v_{\mathrm{H}}(\mathbf{r},t)$, and the exchange-correlation potential $v_{\mathrm{xc}}(\mathbf{r},t)$. The nuclei are treated classically through the Born-Oppenheimer approximation and the Coulomb interactions and are included in $v_{\mathrm{ext}}(\mathbf{r},t)$.

In principle, there are two ways of calculating the photoabsorption spectrum within TDDFT, either by propagating the time-dependent Kohn-Sham equations in real time[30–32] or by calculating the linear response of the electrons to the external potential in the frequency domain.[33,34] In this paper, we will use the first approach. The initial state at time $t=0$ is perturbed with a time-dependent potential,

$$v(\mathbf{r},t) = -\hbar k_0 x_\nu \delta(t), \tag{3}$$

so that $v_{\mathrm{ext}}(\mathbf{r},t) = v_{\mathrm{static}}(\mathbf{r}) + v(\mathbf{r},t)$.[30–32] In Eq. (3), $x_\nu = x,y,z$ and k_0 is a momentum transferred to the system, which has to be small in order to assure that the response of the system is linear and that only dipole transitions are excited. By this means, all frequencies of the system are excited with equal weight.

If we define $\varphi_i(\mathbf{r})$ to be the ground-state Kohn-Sham wave functions of our system, the initial state for the time evolution at $t=0^+$ is

$$\psi_i(\mathbf{r},0^+) = \exp(ik_0 x_\nu)\varphi_i(\mathbf{r}). \tag{4}$$

After this initial step, the Kohn-Sham wave functions are propagated during a finite, but very long, time.

The information of the excitations is deduced from the dipole-strength function $S(\omega)$. It measures how strongly a given frequency ω excites the system and it can be written as[30–32]

$$S(\omega) = \frac{2m_e\omega}{\pi\hbar e^2}\Im\sum_\nu \alpha_{\nu\nu}(\omega), \tag{5}$$

where the dynamical polarizability $\alpha_{\mu\nu}$ is

$$\alpha_{\mu\nu}(\omega) = \frac{e^2}{\hbar k_0}\int \mathrm{d}\mathbf{r}\, x_\nu \delta n(\mathbf{r},\omega). \tag{6}$$

III. COMPUTATIONAL DETAILS

The cluster structures used for the calculations have been obtained by first performing genetic-algorithm calculations[35,36] using an empirical pair potential.[37] The resulting structures have been reoptimized with an electronic-structure method [SIESTA (Ref. 38)] as described below. Especially for large structures, e.g., Na_{40}, this approach was necessary because the number of local-minimum structures increases very fast with the cluster size. Second, we have used those structures which are reported in the literature, as cited in the discussion. These have also been optimized with SIESTA. In this way we ended up with several structures for each cluster size and chose those, which were lowest in energy, to perform the calculations of the photoabsorption spectra. In some cases, which are explicitly mentioned, we have used more than one structure for a specific cluster size.

The geometry optimizations of the cluster structures have been performed using the SIESTA code[38] which employs density-functional theory.[39,40] The local-density approximation (LDA) has been used as an approximation to the exchange-correlation functional and, moreover, the frozen-core approximation together with norm-conserving pseudopotentials[41,42] have been used to describe the ionic environment of the electronic system. Furthermore, double-zeta pseudoatomic orbitals for the $3s$ shell together with single-zeta polarization orbital for the $3p$ shell are employed as the basis set.

The photoabsorption spectra have been calculated using the octopus code.[22] Herein, the electronic wave functions are evolved in real space and real time.[30–32] The dipole-strength function, which is directly proportional to the photoabsorption cross section, is then obtained by a Fourier transform of the time-dependent dipole moment. The exchange-correlation potential has been approximated through the adiabatic LDA, in which the exchange-correlation potential at time t is taken to be the LDA of that ground state giving the time-dependent density $n(\mathbf{r},t)$. This will be referred to as

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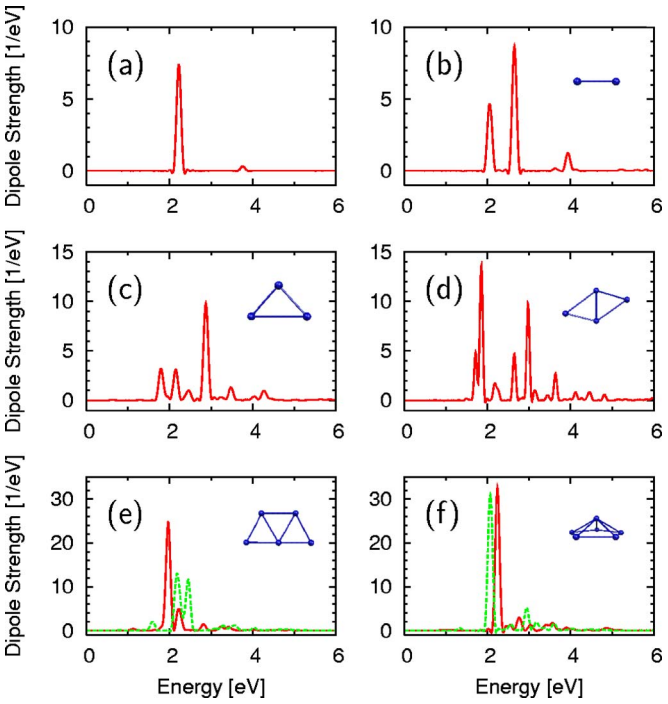

FIG. 1. (Color online) TDLDA spectra of (a) the sodium atom and [(b)–(f)] the clusters Na_2–Na_6. Note the different scalings of the axes of ordinates. For Na_5 (e), spectra of a planar (red/solid) and a pyramidal isomer (green/dashed) are shown, and for Na_6, spectra of a pentagonal pyramidal (red/solid) and a planar isomer (green/dashed) are shown. The displayed structures are lowest in total energy. The corresponding spectra are shown in red (solid).

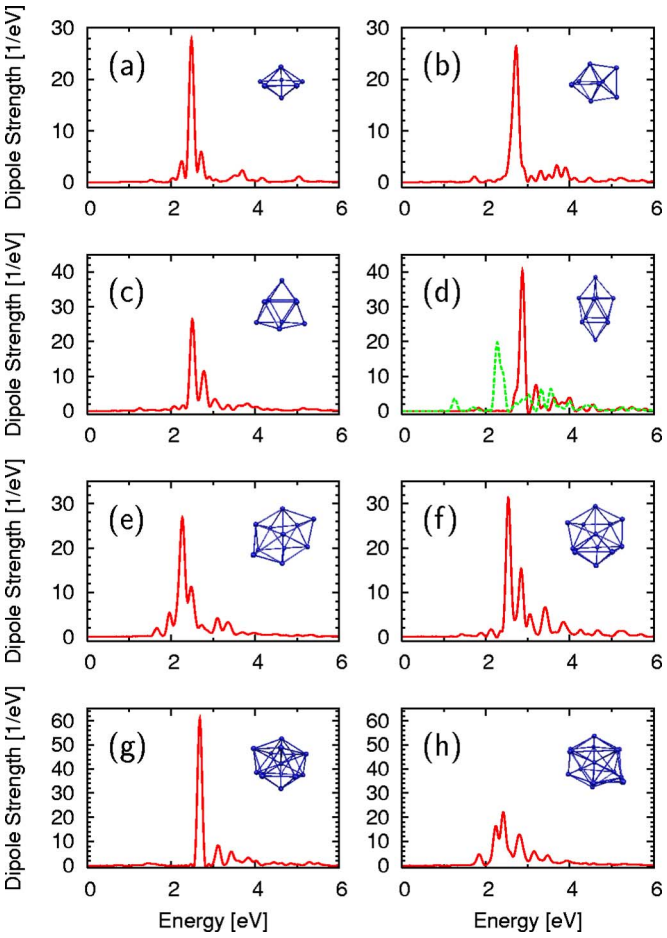

FIG. 2. (Color online) TDLDA spectra of the clusters Na_7–Na_{14}. Note the different scalings of the axes of ordinates. For Na_{10} (d), spectra of a D_{4d} (red/solid) and a trigonal pyramidal (tetrahedral) isomer (green/dashed) are shown.

TDLDA in the following. The same norm-conserving pseudopotentials[41,42] as for the static calculations mentioned above have been utilized.

Octopus uses a uniform grid in real space, which is located inside the sum of n spheres, one around each atom of the n-atomic cluster. The radius of each sphere is 10.0 Å and the grid spacing is 0.25 Å throughout all calculations. The propagation in real time has been performed with 20 000 time steps of each 1.65 as which is a total simulation time of around 33 fs. This gives a good resolution of the spectra. The Fourier transform has been performed using a polynomial damping, i.e., the dipole moment has been multiplied with the third-order polynomial,

$$1 - 3\left(\frac{t}{T}\right)^2 + 2\left(\frac{t}{T}\right)^3, \tag{7}$$

before performing the transform. Finally, we note that spin polarization has been taken into account, if the number of electrons is odd.

IV. RESULTS

The calculated photoabsorption spectra for clusters with up to 14 atoms are presented in Figs. 1 and 2. The corresponding cluster structures that have been found to be lowest in energy are depicted as insets. In some cases the spectra of other structural isomers are shown additionally.

The whole series of absorption spectra shows some general trends that will be summarized in the following: (1) The intensity in terms of the dipole-strength function increases with increasing cluster size. (2) The number of absorption peaks in the spectra increases in systems with one to four atoms [Figs. 1(a)–1(d)], but stays more or less constant (one or two major peaks) for larger clusters. (3) There are no significant changes in the fine structure of the spectra of clusters with more than five atoms. (4) Several spectra show similarly shaped absorption peaks, e.g., those of Na_9 and Na_{12} and those of Na_7, Na_8, and Na_{13}. (5) The first major excitation peaks occur in an energy range between 2 and 3 eV for nearly all displayed spectra. (6) The spectrum of Na_{13} shows an exceptional intensity of a single absorption peak at 2.6 eV, which is double as high as any peak in the other displayed spectra.

The spectrum of the single sodium atom [Fig. 1(a)] consists of a large peak at 2.23 eV and a minor peak at 3.76 eV. The corresponding spectroscopic data[43] are 2.10 and 3.19 eV for the energy differences between the $3s$ level and the $3p$ and $4s$ levels, respectively. Thus, the dipole-allowed $3s \rightarrow 3p$ transition is reproduced with reasonable accuracy, whereas the forbidden transition is shifted towards higher energies.

The sodium dimer has been investigated experimentally already in 1920s by Fredrickson and Watson.[44] They studied the first two major peaks which they have located at 1.86 and 2.52 eV showing a 1:2 ratio with respect to the intensities.

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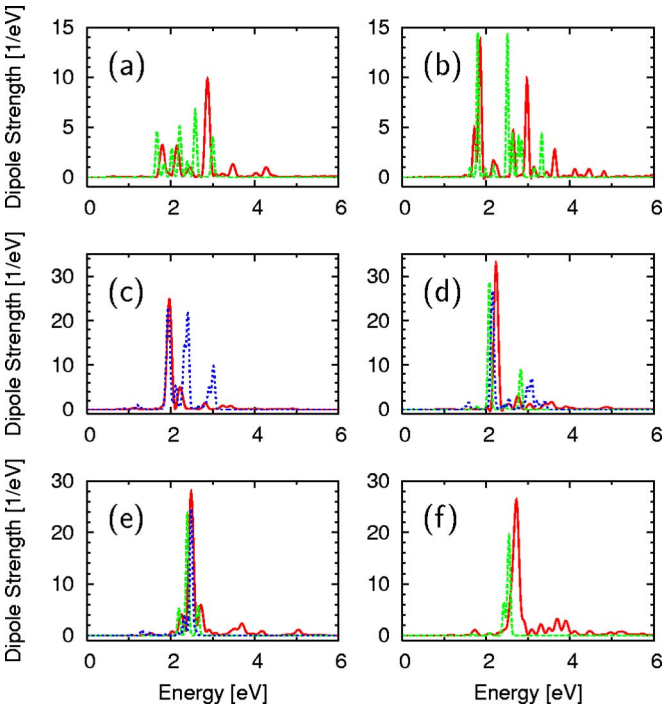

FIG. 3. (Color online) TDLDA spectra (red/solid) of the clusters Na_3–Na_8 which are lowest in total energy. Note the different scalings of the axes of ordinates. Experimental spectra (green/dashed) are adapted from Refs. 12 and 13. These have been measured in the energy range of 1.48–3.35 eV only. Theoretical CI spectra (Ref. 17) are also displayed (blue/dotted).

The TDLDA spectrum of the dimer [Fig. 1(b)] presents these two peaks at 2.06 and 2.65 eV. Thus, they are again shifted towards higher energies by 0.1–0.2 eV. In contrast to the study by Fredrickson and Watson, Sinha[45,46] concentrated on the energy range from 3.41 to 4.96 eV and found three absorption peaks at 3.67, 3.96, and 4.12 eV. The first two of these peaks are correctly reproduced in the TDLDA spectrum at 3.63 and 3.94 eV, whereas the latter is located at 5.02 eV with almost zero intensity. The Na_2 spectra of Marques *et al.*[21] and Vasiliev *et al.*[19] are very similar to the TDLDA spectrum in Fig. 1(b), especially with respect to the shift of the first two dominant peaks compared to the experimental spectra.

In Fig. 3 we compare several TDLDA spectra to available theoretical and experimental data. For the clusters with three to eight atoms the experimental spectra have been measured by Wang and co-workers.[12,13] In case of the Na_3 cluster [Fig. 3(a)] we found absorption peaks in the energy range that has been scanned in the experiment (1.48–3.35 eV). The agreement is not obvious, but the five peaks between 1.5 and 3.5 eV in the TDLDA spectrum can be found in the experimental spectrum as well, although their heights match only partly. This is also observed by Vasiliev and co-workers[47–50] who suggest that the "floppy" structure, due to the absence of a pronounced minimum in the potential energy surface of the sodium trimer, may be responsible.

The agreement with the experiment is much better for Na_4 [Fig. 3(b)] and the larger clusters. The TDLDA spectrum of Na_4 shows two major peaks at 1.86 and 2.98 eV and two smaller peaks at 1.72 and 2.65 eV. In the experimental spectrum, the first two peaks can be found together at 1.80 eV. The peaks above 2 eV are shifted towards higher energies in the calculation. In total, the agreement of the onset peak is very good and better resolved in the calculation than in the experiment.

Using the *GW* approximation, Onida *et al.*[20] have calculated the excitation spectrum of the Na_4 cluster in the D_{2h} symmetry. Compared to the experiment,[12] their resulting spectrum is shifted to higher energies by approximately 0.2 eV. In contrast, the Na_4 spectrum presented in this work matches the experimental one much better, since the position of the first strong excitation is exactly at the experimentally measured energy and only the peaks above 2.5 eV are slightly shifted with respect to the experiment. However, since the Na_4 structure in Ref. 20 is a regular planar rhombus, it differs from ours which is a slightly distorted, nonplanar rhombus (torsion angle: 8.1°). We found the occupied and unoccupied orbitals to be of the same shape and symmetry, despite a slight asymmetry due to the distorted geometry.

For Na_5, the experimental data[13] are not as clear as for the other clusters. The main absorption band is centered around 605 nm (2.05 eV). This corresponds well to the absorption peak in the displayed TDLDA spectrum which is at 1.97 eV. For all spectra displayed in Fig. 3 we find good agreement between the calculated TDLDA spectra and the experimentally obtained photoabsorption spectra, especially with respect to the relative heights of the peaks, the positions of the onset peaks, and the overall shape of the spectra. The excitation energies of the most significant peaks are summarized in Table I.

Figures 3(c)–3(e) show also a comparison with spectra obtained by CI calculations. These have been adapted from the data given in the work of Bonačić-Koutecký *et al.*[17] The agreement is very good, especially regarding the positions of the onset peaks. However, in the Na_5 spectrum two larger

TABLE I. Excitation energies of the most significant peaks in the calculated absorption spectra. Abbreviations are used for planar (pl), pyramidal (py), and double-icosahedral (d-ico) isomers.

Cluster	E (eV)
Na_1	2.23
Na_2	2.06, 2.65, 3.94
Na_3	1.80, 2.15, 2.88
Na_4	1.72, 1.86, 2.65, 2.98
Na_5 (pl)	1.97, 2.22
Na_5 (py)	2.18, 2.45
Na_6 (pl)	2.07, 2.56
Na_6 (py)	2.24, 3.05
Na_7	2.26, 2.49, 2.72
Na_8	2.73
Na_9	2.51, 2.79
Na_{10} (D_{4d})	2.88, 3.20
Na_{10} (py)	1.26, 2.28
Na_{11}	1.97, 2.27, 2.48
Na_{12}	2.54, 2.85, 3.42
Na_{13}	2.69, 3.12
Na_{14}	1.84, 2.24, 2.43, 2.81
Na_{20} (d-ico)	2.60, 2.89
Na_{20} (py)	2.24, 2.37
Na_{40}	2.56, 2.86, 3.10, 3.60

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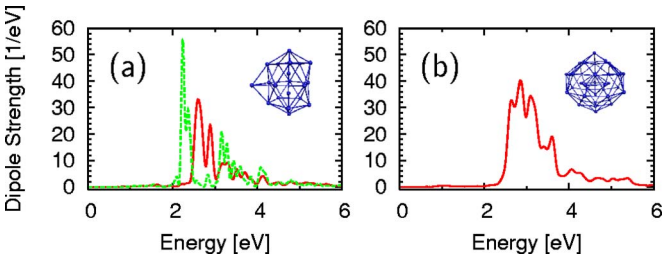

FIG. 4. (Color online) TDLDA spectra of (a) Na_{20} and (b) Na_{40}. For Na_{20} (a), the spectra of two isomers are shown: a capped double-icosahedron (red/solid) and a trigonal pyramid (green/dashed).

peaks are present which have not been computed by TDLDA. Since CI calculations are computationally very demanding, the good agreement underlines the advantages of the method and code used within this study.

Two larger cluster sizes have been considered as well [Na_{20} and Na_{40} (cf. Fig. 4)], which are considered as magic clusters due to an electronic shell closing within the jellium model. For Na_{20}, the two peaks in the experimental spectrum measured by Pollack *et al.*[51] are at 2.42 and 2.78 eV, which corresponds well to 2.60 and 2.89 eV. However, whereas Pollack *et al.* find a ratio of 1:3, the TDLDA spectrum (red/solid curve) shows a 3:2 ratio. The excitations in the spectrum of the second Na_{20} isomer, a pyramid, are located at 2.24 and 2.37 eV.

For Na_{40}, it is very difficult to find the most stable structure. Moreover, in an experiment where several thousand ions per second are counted and their spectra taken, the geometries of large clusters might not be distinct at all and the spectrum will be a mixture from the excitations of all present geometrical isomers. If the number of local minima on the potential energy surface is very large (as it is for Na_{40}), more than just one isomer will be present in the beam. Therefore, we have chosen to take just one isomer, in order to show its spectrum.

Moreover, such a large alkali cluster may be seen as small metal sphere, in which the electronic excitation have a collective (plasmonic) character. These collective features result in single outstanding excitation peaks. The Na_{40} spectrum shows four dominant peaks (at 2.56, 2.86, 3.10, and 3.60 eV), which are not totally resolved. Especially the peaks at around 2.6 and 2.8 eV in the Na_{20} and Na_{40} correspond well to similar excitation energies in the smaller clusters, e.g., Na_{12}.

For some selected cluster sizes we have calculated the spectra of different structural isomers. The TDLDA spectra of Na_5 (planar and bipyramidal), Na_6 (pyramidal and planar), Na_{10} (D_{4d} and pyramidal), and Na_{20} (capped double-icosahedral and pyramidal isomers) are depicted in Figs. 1(e), 1(f), 2(d), and 4(a), respectively. For three cluster sizes ($n=5,10,20$) the spectra of the isomers look rather different. An experimental determination of the cluster structure by means of measuring the photoabsorption spectra could be possible. However, for Na_6 the spectra of the two isomers (planar and pyramidal) are very similar. The two isomers are energetically very close ($\Delta E=0.02$ eV) and structurally very related, so that an experimental distinction is impossible. These few examples show that the underlying geometry of a cluster has an important influence on the shape of the absorption spectrum.

In Fig. 2 we have already displayed the spectra of two isomers of Na_{10}. The most stable D_{4d} structure (red/solid) shows two main peaks at 2.88 and 3.20 eV, whereas the pyramidal isomer (green/dashed) absorbs at 2.28 eV and, additionally, has peaks at 1.26, 3.03, 3.33, and 3.55 eV. Peak positions and intensities of these two isomers are very different.

As we have mentioned in the beginning, the spectra of clusters with more than five atoms (cf. Figs. 1 and 2) do not show an increasing number of peaks, but consist mainly of one or two peaks at around 2.50 and 2.80 eV. Comparing their oscillator strengths to those in the spectra of the clusters with less than five atoms shows also that these peaks are much more intense. Both facts point towards the appearance of collective plasmon excitations in these clusters. Moreover, the fine structure in the spectra of the smallest clusters is much more distinctive than in the spectra of larger clusters, where collective plasmon excitations dominate the spectra. This is in good agreement with other theoretical and experimental studies.[9–11,25,52]

V. CONCLUSIONS

The photoabsorption spectra for a continuous series of small sodium clusters with up to 14 atoms have been calculated using TDDFT. Additionally, the spectra for Na_{20} and Na_{40} have been obtained as well. For some clusters, the spectra of geometrical isomers have been calculated.

The spectra show increasing intensities with increasing cluster size, but the number of peaks does not increase. Exceptions are the spectra of the very smallest clusters. Moreover, several spectra show similar absorption bands. These observations strongly point to occurring collective plasmon excitations, which have also been observed experimentally.[9–11,25,52]

In total, we have found an excellent agreement with the experimental obtained absorption spectra of Wang and co-workers.[12,13] The spectra also match well with those of Bonačić-Koutecký and co-workers[16–18] and others.

The influence of the geometry with respect to position and intensity of the absorption peaks is of crucial importance. We have presented photoabsorption spectra of different isomers of Na_5, Na_6, Na_{10}, and Na_{20}. In case of the two nearly planar and energetically almost degenerate Na_6 structures, a determination of the cluster structure via the experimental photoabsorption spectrum would be difficult, if not impossible.

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