Optical response of small magnesium clusters

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We predict the strong enhancement in the photoabsorption of small Mg clusters in the region of 4-5 eV due to the resonant excitation of the plasmon oscillations of cluster electrons. The photoabsorption spectra for neutral Mg clusters consisting of up to \( N = 11 \) atoms have been calculated using \textit{ab initio} framework based on the time dependent density functional theory (TDDFT). The nature of predicted resonances has been elucidated by comparison of the results of the \textit{ab initio} calculations with the results of the classical Mie theory. The splitting of the plasmon resonances caused by the cluster deformation is analysed. The reliability of the used calculation scheme has been proved by performing the test calculation for a number of sodium clusters and the comparison of the results obtained with the results of other methods and experiment.

I. INTRODUCTION

Optical spectroscopy is a powerful instrument for investigation of the electronic and ionic structure of clusters as well as their thermal and dynamical properties. During the last decades these issues have been intensively investigated both experimentally by means of photodepletion and photodetachment spectroscopy and theoretically by employing the time-dependent density functional theory (TDDFT), configuration interaction (CI) and random-phase approximation (RPA) (for review see \cite{1,2} and references therein). These methods have been used in conjunction with either jellium model \cite{2} defined by a Hamiltonian, which

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treats the electrons in a cluster in the usual quantum mechanical way, but approximates
the field of the ionic core treating it as a uniform positively charged background, or with \textit{ab initio} calculations of the electronic and ionic cluster structure, where all or at least valence
electrons in the system are treated accurately.

During the last years, numerous theoretical and experimental investigations have been
devoted to the study of optical response properties of alkali metal clusters. The plasmon
resonances formation in Na, K and Li clusters has been studied both theoretically and
experimentally (see \cite{1, 2, 3, 4, 5} and references therein). Some attention was also devoted to
the splitting and broadening of the plasmon resonances (see citations above). The mentioned
metal elements belong to the first group of the periodic table, i.e. possess one \textit{s}-valence
electron.

The situation differs for clusters of the alkali-earth metals of the second group of the
periodic table, such as Be, Mg, Ca. Study of these clusters is of particular interest, because
they exhibit a transition from the weak van der Waals bonding being the characteristic
of the diatomic molecule to the metallic bonding present in the bulk. Thus, significant
attention was paid to the magnesium clusters. Various properties of Mg clusters, such
as their structure, the binding energy, ionization potentials, HOMO-LUMO gap, average
distances, and their evolution with the cluster size have been investigated theoretically (see
\cite{6, 7, 8} and references therein). Recently, the mass spectrum of Mg clusters was recorded
\cite{9} and the sequence of magic numbers was determined. The investigation of optical response
of small Mg clusters has not been performed so far in spite of the fact that it should carry
a lot of useful information about the dynamic properties of magnesium clusters.

In this paper we predict the strong enhancement in the photoabsorption of small \textit{Mg}
clusters in the region of 4-5 eV due to the resonant excitation of the plasmon oscillations of
the cluster electrons. Using all electron \textit{ab initio} TDDFT we calculate the spectra for cluster
structures with up to 11 atoms possessing the lowest energy. The geometries of these clusters
were calculated using all electron DFT methods and described in our recent work \cite{6}. In
this work we focus on the formation of the plasmon resonances in magnesium clusters. We
elucidate their nature by comparing our results with the results of the classical Mie theory
and analyse the splitting of the plasmon resonances caused by the cluster deformation.
II. THEORETICAL METHOD

Theoretical methods used in our calculations are based on the density functional theory and many-body-perturbation theory. In the present work we use the gradient-corrected Becke-type three-parameter exchange functional \cite{10} paired with the gradient-corrected Lee, Yang and Parr correlation functional (B3LYP) \cite{11}, as well as with the gradient-corrected Perdew-Wang 91 correlation functional (B3PW91) \cite{12}. We do not present the explicit forms of these functionals, because they are somewhat lengthy, and refer to the original papers \cite{10, 11, 12, 13, 14}. Our calculations have been performed with the use of the Gaussian 98 software package \cite{15}. We have utilized the 6-311+G(d) basis set of primitive Gaussian functions to expand the cluster orbitals \cite{13, 15}.

The absorption of light by small metal spheres has been investigated theoretically by Mie long ago (see e.g. \cite{16}). For particles with the diameter being considerably smaller than the wavelength, the absorption cross section based on the Drude dielectric function reads as:

$$\sigma(\omega) = \frac{4\pi N_e e^2}{m_e c} \frac{\omega^2 \Gamma}{(\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2}$$

where $\omega_0$ is the surface-plasma frequency of a sphere with $N_e$ free electrons, $\omega$ is the photon frequency, $\Gamma$ represents the width of the resonance, $m_e$ is the electron mass, $e$ is its charge and $c$ is the light velocity. Equation (1) assumes that the dipole oscillator strengths are exhausted by the surface plasma resonance at $\omega_0$. In metal clusters this resonance corresponds to the collective oscillation of the spherical valence-electron cloud against the positive background.

Using the sum rule one can easily show (see e.g. \cite{16}) that $\omega_0 = \sqrt{N_e e^2 / m_e \alpha}$, where $\alpha$ is the static polarizability of the cluster. For a classical metal sphere, $\alpha = N_e r_s^3$, where $r_s$ is the Wigner-Seitz radius. With $r_s = 4.0$ a.u. for Na and $r_s = 2.66$ for Mg \cite{17}, one derives the classical surface-plasma-resonance energies $\omega_0^{Na} = 3.40$ eV and $\omega_0^{Mg} = 6.27$ eV for Na and Mg respectively.

For small metal clusters the photoabsorption pattern differs significantly from the Mie prediction. In these systems the plasmon resonance energy is smaller as compared to the metal sphere case. The lowering of the plasmon energies in small metal clusters occurs because of the spill out effect according to which the electron density is spilled out of the cluster, increasing its volume and polarizability. For example, for spherical Na$_8$ and Na$_{20}$ clusters the average static polarizability is 796.840 (a.u) and 1964.484 (a.u.) respectively.
Thus, the plasmon resonance energies, $\omega_0$, read as 2.73 and 2.75 (eV) for Na$_8$ and Na$_{20}$ respectively. Beside the lowering of the plasmon resonance energy in small metal clusters the photoabsorption pattern is splitted. This fragmentation arises mainly due to the cluster deformation. With the use of the sum rule, equation (11) can be generalized and written in the following form (see e.g. [16]):

$$
\sigma(\omega) = \frac{4\pi e^2}{m_e c} \sum_{i=1}^{n} \frac{f_i \omega^2 \Gamma_i}{(\omega_i^2 - \omega^2)^2 + \omega^2 \Gamma_i^2}
$$

where $\omega_i$ are the transition energies, $f_i$ and $\Gamma_i$ are the corresponding oscillator strengths and widths, $n$ is the total number of the resonant transitions.

In the case of the triaxial cluster deformation the photoabsorption cross section possesses the three peak structure. The splitting of the plasmon resonance into three peaks can easily be understood assuming the ellipsoidal form of the cluster surface. Within the framework of the deformed jeilium model the ionic density is considered to be uniform within the volume confined by the ellipsoid surface defined by $\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1$. If one assumes that the electron density fills in entirely in the interior of the ionic ellipsoid, one finds the following dipole plasmon energies corresponding to the electron density oscillations in three directions $x$, $y$, $z$, (for more details see [18]):

$$
\omega_x = \omega_0 \left[ 1 + \frac{\delta \cos \gamma}{5} (1 - \sqrt{3} \tan \gamma) \right]
$$

$$
\omega_y = \omega_0 \left[ 1 + \frac{\delta \cos \gamma}{5} (1 + \sqrt{3} \tan \gamma) \right]
$$

$$
\omega_z = \omega_0 \left[ 1 - \frac{2 \delta \cos \gamma}{5} \right]
$$

Where $\omega_0$ is the classical Mie frequency being the average of $\omega_x$, $\omega_y$ and $\omega_z$, $\delta$ and $\gamma$ are the deformation parameters defined by equations: $\delta \cos \gamma = \frac{3}{4} \frac{2c^2 - a^2 - b^2}{a^2 + b^2 + c^2}$, $\tan \gamma = \sqrt{3} \frac{a^2 - b^2}{2c^2 - a^2 - b^2}$.

Note that in the axially symmetric case one derives $\gamma = 0$ and $\omega_z = \omega_y$.

III. RESULTS AND DISCUSSION

In figure we present the oscillator strengths for the dipole transitions calculated for the most stable cluster isomers of Mg$_2$-Mg$_{11}$. Cluster geometries are shown in the insets to the
FIG. 1: Photoabsorption cross section calculated for Mg clusters with $N \leq 11$ using the $B3PW91/6 - 311 + G(d)$ method. Vertical solid lines show the oscillator strengths for the optically allowed transitions. Their values are shown in the left hand side of the plots. The right hand side of each plot shows the scale for the corresponding photoabsorption cross section. Cluster geometries calculated in [6] are shown in the insets. The label near each cluster image shows the sum of the oscillator strengths and the excitation energy range considered. By solid and dotted arrows we show the adiabatic and vertical ionization potentials respectively, calculated in [6].
figure. They were calculated and discussed in [6].

For sodium [2], the plasmon resonance arises for the clusters with less than 10 atoms. Thus, it is natural to expect that for the magnesium clusters with \( N \leq 10 \) the formation of the plasmon resonance should be clearly seen.

Calculating the oscillator strengths \( f_i \) and substituting the found values in equation [2] we obtain the photoabsorption cross sections for magnesium clusters plotted in figure [1]. In this calculation we have used the width \( \Gamma_0 = 0.4 \) eV, which is the average width for Na clusters at room temperature [2]. In this paper we do not calculate the excitation line widths for Mg clusters and do not investigate the line widths temperature dependence. These interesting problems are beyond the scope of the present paper and deserve a separate careful consideration.

In the photoabsorption spectra for \( Mg_2 \) and \( Mg_3 \) one can identify the strong resonances in the vicinity of 4 eV, which can be interpreted as the plasmon resonances splitted due to the cluster deformation. Below, we discuss this splitting in more detail. For larger clusters, the plasmon resonance energy increases slowly and evolves towards the bulk value, 6.26 eV, see dots in figure [2]. The lowering of the plasmon resonance energy in small Mg clusters as compared to its bulk value occurs because of the spill out effect.

There are two main factors, which determine the resonance pattern of the photoabsorption spectra for magnesium clusters: collective plasmon excitations of the delocalized electrons and the resonant transitions of the electrons bound in a single magnesium atom. In the excitation energy range considered, the photoabsorption spectrum of a single Mg atom exhibits the two strong resonant excitations: \( 3s(^1S_0) \rightarrow 3p(^1P_0) \) and \( 3s(^1S_0) \rightarrow 4p(^1P_0) \) with the energies (oscillation strengths) 4.346 (1.8) and 6.118 (0.2) eV respectively [19]. The TD/B3PW91/6-311+G(d) method gives the following energies and the oscillator strengths for these lines: 4.225 (1.63) and 5.765 (0.29) eV, which are in the reasonable agreement with the data given in [19]. The \( 3p(^1P_0) \) line can be easily identified in the photoabsorption spectrum for \( Mg_2 \). In terms of the plasmon resonance excitations, this line corresponds to the oscillations of the electronic density perpendicular to the cluster axis, while the strong line in the vicinity of 3 eV corresponds to the collective electron oscillations along the cluster axis. For larger clusters, the \( 3p(^1P_0) \) line is strongly coupled with the plasmon resonance excitation occurring at the close energy. The situation is different for the \( 4p(^1P_0) \) line. Due to its higher energy, this excitation line does not couple that strongly with the plasmon
FIG. 2: Size dependence of the plasmon resonance energies $\omega_x$, $\omega_y$, $\omega_z$: $x$ (upper triangles), $y$ (lower triangles) and $z$ (left triangle). Circles are the Mie-frequencies $\omega_0$ being the average of $\omega_x$, $\omega_y$ and $\omega_z$.

resonance and can be identified in the photoabsorption spectra for the $Mg_2$, $Mg_3$, $Mg_6$ and $Mg_7$ clusters in addition to the plasmon resonances. For larger clusters (e.g. $Mg_8$, $Mg_9$, $Mg_{10}$), due to the growth of their plasmon resonance energies, the $4p(1P_0^1)$ line becomes more and more of the plasmon resonance type.

For many clusters the plasmon resonance is splitted. This splitting arises mainly due to the cluster deformation. In order to illustrate this effect we plot in figure 2 the energies $\omega_x$, $\omega_y$, $\omega_z$ of the strongest resonances versus the cluster size. Using equation (3), we determine the deformation parameters $\delta$ and $\gamma$ and present them in figure 3. One can distinguish four different cases: i) $\delta = \gamma = 0$ the cluster is spherical (see $N = 4$); ii) $\delta < 0$, $\gamma = 0$ the cluster is oblate (see $N = 3, 7, 9$); iii) $\delta > 0$, $\gamma = 0$ the cluster is prolate (see $N = 2, 5, 10, 11$); iv) $\delta \neq 0$, $\gamma \neq 0$ the cluster is triaxially deformed (see $N = 6, 8$). This analysis shows that most of the clusters considered are close to the axially symmetric form, although some clusters ($Mg_6$ and $Mg_8$) are triaxially deformed. Note that many additional satellite resonances
FIG. 3: Cluster deformation parameters versus the cluster size. The labels indicate the cluster deformation type.

appear in the photoabsorption spectra. The additional satellite lines are often the result of higher order cluster deformations. Thus, they are beyond the ellipsoidal model.

To show the connection between the plasmon resonance splitting and the cluster deformation we have determined the plasmon resonance energies for $Mg_2$ and $Mg_3$ from the Mie theory via the static dipole polarizabilities of the clusters and compared them with the TDDFT result. The principle values of cluster polarizability tensor $\alpha_{xx}$, $\alpha_{yy}, \alpha_{zz}$ are 130.386, 130.386, 246.769 (a.u) for $Mg_2$ and 282.412, 282.412, 159.757 (a.u.) for $Mg_3$ respectively. Thus, the plasmon resonance energies $\omega_x$, $\omega_y$ and $\omega_z$ read as 4.82, 4.82, 3.39 (eV) for $Mg_2$ and 3.8, 3.8, 5.46 (eV) for $Mg_3$ respectively. These values are very close to those obtained directly from the photoabsorption spectra analysis and presented in figure 2. This fact independently proves that the plasmon resonance is already formed in such small systems.

In insets to figure we present the sum of the oscillator strengths and the excitation energy range considered for each cluster. The sum of the oscillator strengths characterises the valence electrons delocalization rate. Note, that for many clusters it is close to the
total number of valence electrons in the system. For some clusters the total sum of the oscillator strengths is significantly smaller than the number of the valence electrons (see, for example, $Mg_{10}$, $Mg_{11}$). To increase the sum of the oscillator strengths one has to calculate the photoabsorption spectra up to the higher excitation energies. The calculation of cluster excited states becomes an increasingly difficult problem with the growth of the cluster size, because of the rapid growth of the number of possible excited states in the system. In this paper we focus on the investigation of the plasmon resonances in small $Mg$ clusters, manifesting themselves in the energy range about 4-5 eV as it is clear from our discussion. Therefore, for clusters with $N > 8$, we have calculated the photoabsorption spectra only up to the excitation energies of about 6 eV, which is significant for the elucidation of the plasmon resonance structure and at the same time it does not acquire substantial computer power.

Photoabsorption spectra for sodium clusters have been earlier investigated in a large number of papers. There were performed experimental measurements, as well as theoretical calculations involving $ab$ $initio$ and model approaches. In order to check the level of accuracy of our calculation method, in figure 4 we compare the photoabsorption spectra for a few selected neutral and singly charged sodium clusters, calculated with the use of the methods described above, with the results of experimental measurements and other calculations. In figure 4 the experimentally measured photoabsorption spectra for $Na_{3-5}^+$, $Na_{4-8}$ are plotted by dots. The results of our TDDFT calculation performed with the use of the B3LYP functional are shown by solid lines. The CI results of Bonačić-Koutecký et al are shown by dashed lines.

In [14] we demonstrated that the B3LYP functional is well applicable for the description of sodium clusters. Thus, we used it for the photoabsorption spectra computations. The comparison shown in figure 4 demonstrates that our calculation method is a good alternative to the CI method, and our results are in a good agreement with the experimental data.

The photoabsorption spectrum of $Na_5$ has a prominent peak at the energy about 2.3 eV, which can be identified as a Mie plasmon resonance. This peak is also seen in the photoabsorption spectra of $Na_6$, $Na_7$ and $Na_8$. The plasmon resonance energy for these clusters is smaller than the bulk value, 3.4 eV, because of the spill out effect. As it is seen from figure 4 the resonance energy evolves slowly towards the bulk limit with increasing cluster size. For the $Na_3^+$, $Na_4^+$ and $Na_5^+$, the plasmon peak is hardly to identify in the
FIG. 4: Photoabsorption cross section calculated for $Na_{3-5}^+$, $Na_{4-8}$ using the B3LYP functional (solid lines). Vertical lines show the oscillator strengths for the optically allowed transitions. Cluster geometries calculated in [14] are shown in the insets. The label near each cluster image shows the sum of the oscillator strengths, the excitation energy range considered and the line width. We compare our results with experimentally measured photoabsorption spectra [1, 2] (dots) and with the results of previous $ab\ initio$ CI calculation [1, 2] (dashed lines).
distribution of oscillator strengths, which means that the number of delocalized electrons in these clusters turns out to be insufficient for the formation of the plasmon resonance in this system, see figure 4.

Note, that often the plasmon peaks for sodium clusters are splitted due to the cluster axial quadrupole deformation. Using equations (5), we have calculated the deformation parameters for axially symmetric $Na_6$ and $Na_7$. The result reads as $\delta = -0.55$ and $-0.34$ respectively. The deformation parameter $\gamma$ vanishes for both clusters. The axially symmetric jelium model leads to the following values of $\delta$: $\delta_{JM} = -0.48$ and $-0.24$ for $Na_6$ and $Na_7$ respectively. Comparison shows that the splitting of the plasmon resonances can be explained by cluster deformation.

IV. CONCLUSION

In this paper we predict the enhancement of the photoabsorption spectra for small Mg clusters in the vicinity of plasmon resonance. The photoabsorption spectra for neutral $Mg$ clusters consisting of up to $N = 11$ atoms have been calculated using ab initio framework based on the time dependent density functional theory. The nature of predicted resonances have been elucidated by comparison of the results of the ab initio calculations with the results of the classical Mie theory. The splitting of the plasmon resonances caused by the cluster deformation is analysed. The reliability of the used calculation scheme has been proved by performing the test calculation for a number of sodium clusters and the comparison of the results obtained with the results of other methods and experiment. The calculation of the photoabsorption spectra for larger clusters requires much more computer power and is left open for further investigations.

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