Optical and magnetic excitations of metal-encapsulating Si cages: A systematic study by time-dependent density functional theory

Micael J. T. Oliveira,1,2 Paulo V. C. Medeiros,3 José R. F. Sousa,1 Fernando Nogueira,1,2 and Gueorgui K. Gueorguiev3

1 Center for Computational Physics, University of Coimbra, Rua Larga, 3004-516 Coimbra, Portugal
2 European Theoretical Spectroscopy Facility (ETSF)
3 Department of Physics, Chemistry and Biology (IFM), Linköping University, 58183 Linköping, Sweden

Systematic study of the optical and magnetic excitations of twelve MSi12 and four MSi10 transition metal encapsulating Si cages has been carried out by employing real time time-dependent density functional theory. Criteria for the choice of transition metals (M) are clusters stability, synthesizability, and diversity. It was found that both the optical absorption and the spin-susceptibility spectra are mainly determined by, in decreasing order of importance: 1) the cage shape, 2) the group in the Periodic Table M belongs to, and 3) the period of M in the Periodic Table. Cages with similar structures and metal species that are close to each other in the Periodic Table possess spectra sharing many similarities, e. g., the optical absorption spectra of the MSi12 (M = V, Nb, Ta, Cr, Mo, and W), which are highly symmetric and belong to groups 4 and 5 of the Periodic Table, all share a very distinctive peak at around 4 eV. In all cases, although some of the observed transitions are located at the Si skeleton of the cages, the transition metal specie is always significant for the optical absorption and the spin-susceptibility spectra. Our results provide finger-print data for identification of gas-phase MSi12 and MSi10 by optical absorption spectroscopy.

I. INTRODUCTION

After mixed silicon-transition metal clusters (MSiₙ) were obtained and studied by Becq et al. in the late eighties, the first theoretical calculations indicated the stability of species containing one transition metal atom such as ZrSi₂₀, MSi₁₅ (M = Cr, Mo, W) and MSi₁₆ (M = Ti, Hf, Zr). In 2001, a major breakthrough in the field of silicon-transition metal clusters was achieved by Hiura et al. They successfully synthesized MSi₁₃⁺ species by employing gas phase reactions of single transition metal atoms with silane (SiH₄). Abundance of clusters with 12 silicon atoms (MSi₁₂) for the cases of M = Ta, W, Re, and Ir was measured by mass-spectrometry. Initial computer simulations conducted by the same research team suggested for MSi₁₂ the shape of a regular hexagonal prism. Subsequent theoretical studies by others confirmed similar cage-like geometries for neutral species such as CrSi₁₂ as well as for CuSi₁₂, MoSi₁₂, and WSi₁₂.

In a series of two works, in an attempt to systematize the behavior of a wide variety of neutral MSiₙ clusters, we studied these species by means of first-principles calculations within the framework of density functional theory (DFT). A total of 336 different MSiₙ clusters, for 24 transition elements grouped into the following subgroups: M = [Cr, Mo, W], [Mn, Tc, Re], [Fe, Ru, Os], [Co, Rh, Ir], [Ti, Zr, Hf], [V, Nb, Ta], [Ni, Pd, Pt], and [Cu, Ag, Au], were addressed. The geometries of most MSi₁₂ and of some MSi₁₀ are not only symmetric, but - apart from minor distortions - independent on the transition metal involved. Importantly, the electronic properties of structurally nearly equivalent clusters depend sensitively on M, thus providing diversity of building blocks for synthesizing cluster-assembled materials and for designing nano-devices. In order to investigate cluster-assembled materials, i.e., solids in which the MSi₁₂ clusters play the role of building blocks, we also conducted Langevin molecular dynamics simulations to investigate the possibility of forming NbSi₁₂ and WSi₁₂ solid phases. In an important contribution to this emerging field, Uchida et al. synthesized hydrogenated TaSi₁₀₁₃ clusters, successfully deposited them onto a Si(111)-(7 x 7) surface and by taking scanning tunneling microscope (STM) observations demonstrated that these units do not decompose after their deposition on the Si surface. The preserved integrity of such cage-like molecules deposited on a surface gives credibility to this first attempt for MSi₁₂ manipulation and assembly into thin films and low-dimensional structures. More recently, we have also predicted nano-wires with metallic properties assembled from MSi₁₂ species and found most stable those containing light transition metal atoms such as Ni, Co, Ti, and V. The feasibility of MSi₁₂-based nanowires has been successfully explored also by others for M = Ni, Fe, and even in the case of M = Be. Cluster-assembled materials are expected to exhibit distinct properties from the pure substances, compounds, and alloys of the chemical elements they contain. In addition, silicon is the chemical element most worked out in current microelectronics. Logically, the endohedral silicon-metal clusters and the corresponding cluster-assembled materials based on them are expected to exhibit distinct electronic but also optical properties from those of existing Si-based materials. Therefore, the MSiₙ-based materials are seen as prospective compounds for achieving integrated nano-opto-electro-mechanical devices.

While structural and ground-state properties of MSiₙ clusters and corresponding extended phases have already attracted significant research effort the excited state properties of MSiₙ units, let alone those of possible ex-
tended phases made upon them, are just starting to be investigated. A very appropriate tool for approaching the excited state properties of this type of clusters is the time-dependent density functional theory (TDDFT)\cite{22,23}. Indeed, TDDFT has previously been used to study the optical properties of a wide variety of clusters, including clusters containing transition-metal species and hydrogenated silicon clusters\cite{26,27}. Nevertheless, the only previous TDDFT studies of MSi\textsubscript{n} clusters is the recent work of He et al.\cite{28} in which the second-order hyperpolarizabilities and the optical absorption spectra in the UV-Visible region of \((\text{Sc} - \text{Zn})\text{Si}_{12}\) were addressed using TDDFT at the B3LYP and B3PW91 levels of theory.

In the present work, by applying real-time TDDFT methodology, we report systematic results on the optical absorption spectra and dynamical spin susceptibility of a range of stable MSi\textsubscript{12} (M = Ti, V, Cr, Ni, Zr, Nb, Mo, Pd, Hf, Ta, W, Pt), and MSi\textsubscript{10} (M = Ni, Cu, Ag, Au) species. The choice of the MSi\textsubscript{n} explored is motivated by their structural stability (at DFT level), synthesizability, and our determination to study a wide diversity of metals (M).

**II. METHODOLOGY AND COMPUTATIONAL DETAILS**

A great deal of information can be obtained about the electronic structure of a given system by studying how it interacts with an electromagnetic field. The mathematical objects that describe how the electrons redistribute in a finite system after being perturbed by an external electromagnetic field are called susceptibilities. A susceptibility thus relates some observable of the system to the electromagnetic field are called susceptibilities. For example, the optical absorption spectra and dynamical spin susceptibility of the system was applied, and we kept track of the dipole moment of the system as a function of time:

\[
p(t) = \int \text{d}r \ r \ n(r, t),
\]

where \(n(r, t)\) is the time-dependent electronic density. The components of the polarization tensor are then simply obtained from the induced dipole \(\delta p(\omega)\):

\[
a_{ij}^{[nn]}(\omega) = \frac{\delta p_{ij}(\omega)}{E_j},
\]

where all the quantities were now moved to the more convenient frequency domain, and the superscript \([nm]\) indicates that we are looking at the density variation after a density perturbation.

Computing now the spin-susceptibility spectra, the applied perturbation was made to be spin-dependent in the following way:

\[
\delta \sigma(r, t) = -E_j x_j \delta(t)\sigma_z,
\]

where \(\sigma_z\) is the usual Pauli matrix, and we kept track of the spin-dipole moment:

\[
s(t) = \int \text{d}r \ r \ m(r, t),
\]

where \(m(r, t)\) is the time-dependent electronic density. In this case, the dynamical spin susceptibility tensor is obtained from the induced spin-dipole \(\delta s(\omega)\):

\[
a_{ij}^{[mm]}(\omega) = \frac{\delta s_{ij}(\omega)}{E_j},
\]

where the superscript \([mm]\) indicates that we are looking at the magnetization density variation after a perturbation of the magnetization density. The dynamical spin susceptibility calculated by following this scheme is just the spin contribution to the magnetizability of the system\cite{39} which, in turn, contains information about the spin-dependent electronic excitations of the system\cite{39,40,41,42,43}.

Before performing the TDDFT calculations, the geometries of the MSi\textsubscript{n} clusters (in their ground state) were
optimized at the DFT level of theory by employing a plane-wave basis set for the expansion of the Kohn-Sham orbitals. The calculations were performed by using the VASP code\textsuperscript{35} Projector Augmented-Wave (PAW) potential\textsuperscript{36} were employed and the Generalized Gradient Approximation (GGA) was adopted. The exchange-correlation functional chosen is the PBE (Perdew, Burke and Ernzerhof)\textsuperscript{37} A cut-off of 300 eV was used for the kinetic energies of the plane waves included in the basis set, and a Gaussian smearing scheme was employed to set the partial occupancies of electronic states, with a width of 0.05 eV. The level of theory employed in the present work has been demonstrated to be successful for addressing the structural and electronic properties of a wide range of nano-structured systems\textsuperscript{38,39}

The geometries of the MSi\textsubscript{n} cages were fully relaxed until the absolute value of the largest projection component of the Hellmann-Feynman forces acting on the atoms became smaller than 1x10\textsuperscript{-2} eV/Å. The convergence of the self-consistent electronic cycles was considered to have been achieved when both the Kohn-Sham eigenvalues and the total energies calculated in two consecutive iterations differed by less than 10\textsuperscript{-5} eV.

In the case of the TDDFT calculations, the core electrons were treated using norm-conserving pseudopotentials of the Troullier-Martins type\textsuperscript{40} For some of the species (Ti, V, Cr, Nb, and Mo), the generation of accurate pseudopotentials required the inclusion of semi-core states in the valence space. For these cases, the corresponding extension of the Troullier-Martins scheme\textsuperscript{40} as implemented in the Atomic Pseudopotentials Engine (APE) code\textsuperscript{41} was used. In octopus, all the relevant functions are discretized in a real-space regular rectangular grid, and we chose the simulation box to be composed of spheres around each atom. Therefore, there are essentially two parameters that control the convergence of the spectra: the grid spacing and the radius of the spheres. We found that a radius of 4.5 Å and spacings of 0.10 Å (M = Ti, V, Cr, Ni, Cu), 0.13 Å (M = Zr, Nb, Mo), and 0.14 Å (M = Pd, Ag, Hf, Ta, W, Pt, Au) were required in order to achieve a convergence of better than 0.1 eV in the spectra. Since some of the cage geometries exhibit several spatial symmetries, it was possible to considerably reduce the total number of calculations needed to obtain the full polarizability tensor\textsuperscript{35} As for the choice of the exchange and correlation functional, it has already been shown that only small differences are found in the excited state properties obtained within the Local Density Approximation (LDA) and the GGA for this kind of systems\textsuperscript{42} Therefore, all TDDFT calculations were performed using the LDA for the exchange and correlation potential\textsuperscript{42} Nevertheless, for some selected clusters we also performed the same calculations using the PBE functional, but found only very minor differences in the spectra, as expected.

A hydrogenated empty cage Si\textsubscript{n}H\textsubscript{n} can be derived from each of the geometrically optimized MSi\textsubscript{n} clusters (n = 12, 10). These hydrogenated empty cages Si\textsubscript{n}H\textsubscript{n} were obtained by removal of the centrally located transition metal atom, followed by passivation with H atoms of the dangling bonds of the remaining pure silicon cage. The positions of the H atoms were then relaxed by employing the described above method and convergence criteria. The positions of the silicon atoms were kept fixed, thus preserving the skeleton of the corresponding optimized MSi\textsubscript{n} cages.

III. RESULTS AND DISCUSSION

The detailed study of the structural properties of these clusters has already been done elsewhere\textsuperscript{43} As such, here we will only briefly present our results for the ground-state geometries of the cages insofar as these can influence the optical properties. Indeed, the presence of the metal atom contributes to the optical properties of the cluster in a direct way, through its own electronic structure and its bonds with the silicon atoms, but also in an indirect way, as it will also influence the geometry of the cluster. Concerning this later contribution, the overall shape of the cluster and its symmetries are usually more important for its optical properties than the actual values of the bond-lengths. In particular, the spectral structure of more symmetrical clusters tends to be simpler than the spectral structure of clusters with less symmetries, as the number of available electronic transitions will be reduced by the degeneracies introduced by the symmetries. On the other hand, changes in bond-lengths
that keep the overall shape typically only introduce small shifts of the peaks of the observed spectra, and change their relative intensities.

Therefore, in order to make the relationship between the metal species and the computed excited-state properties more obvious, the obtained geometries for the selected MSi_{12} clusters were divided into three classes. The first class corresponds to geometries with perfect $D_{6h}$ symmetry and includes the clusters with $M = V, Cr, Nb, Mo, Pd, Ta, W$, and Pt. The second class of geometries includes the clusters with $M = Ti, Zr, and Hf$, while the third class includes the cluster with $M = Ni$. Both the second and third classes correspond to two different distortions of the perfect $D_{6h}$ symmetry. In the case of the selected MSi_{10} clusters, there is only one class of geometries, which corresponds to a small distortion of the perfect endohedral bicapped tetragonal antiprism ($D_{h}$).

Representative equilibrium geometries for the three differences classes of MSi_{12} clusters as well as for the single class of MSi_{10} clusters are shown in Fig. 1.

### A. MSi_{12} clusters

In Fig. 2, we present the calculated optical absorption and spin-susceptibility spectra of the MSi_{12} clusters studied in this work. In these plots, the spectra are arranged with respect to each other in a similar way as the corresponding metal species are arranged in the Periodic Table. As for the color of the curves, it is used to differentiate the shapes of the cages.

As seen from upper panel of Fig. 2, the optical absorption spectra of cages with perfect $D_{6h}$ symmetry (light gray curves) share significant similarities. Looking in more detail at those spectra, we see that the ones corresponding to cages whose metal species belong to groups 4 and 5 of the Periodic Table (VSi_{12}, NbSi_{12}, TaSi_{12}, CrSi_{12}, MoSi_{12}, and WSi_{12}) all share a very distinctive peak at around 4 eV. A similar peak seems to be present in the absorption spectra of the group 10 cages (PdSi_{12} and PtSi_{12}), albeit shifted towards lower energy at around 3.5 eV and, in the case of the PtSi_{12}, split in two peaks close in energy. These differences can be explained by the fact that the metal species belonging to groups 4 and 5 (V, Nb, Ta, Cr, Mo, and W) are close to each other in the Periodic Table, while the metal species belonging to group 10 (Pd and Pt) are further away. A smaller peak in the visible region, at around 3 eV, also seems to be shared by all the spectra of these MSi_{12} clusters. Other peaks are common to several of these spectra, but not to all. We note that such similar features are usually shared by cages for which the metal species are close to each other in the Periodic Table. For example, the VSi_{12} and CrSi_{12} absorption spectra are very similar. The same applies to the NbSi_{12} and TaSi_{12} cages. At this point, it is worth to consider how the optical absorption spectra change along a given group of the Periodic Table, as elements from the same group have similar electronic configurations. Concerning the elements from group 4 (VSi_{12}, NbSi_{12}, and TaSi_{12}), we see that, with the exception of the peak at around 4 eV, all the other peaks are slightly shifted towards higher energies when increasing the atomic number. There is also a peak that appears at around 3.6 eV in the optical absorption spectra of NbSi_{12} which increases in intensity when moving to TaSi_{12}. As for the elements from group 5 (CrSi_{12}, MoSi_{12}, and WSi_{12}), the most noticeable changes in their spectra are found in two peaks at around 3.5 eV and 4.5 eV that shift towards higher energies. In the former case, the peak relative intensity also seems to increase when going from CrSi_{12} to WSi_{12}. Finally, concerning the elements from group 10 (PdSi_{12} and PtSi_{12}), besides the aforementioned peaks at around 3.0 and 3.5 eV, we also note the existence of similar peaks at around 1 and 4 eV, although slightly shifted towards lower energies in the case of PtSi_{12}.

The same kind of analysis can also be provided for the spin-susceptibility spectra shown in the lower panel of Fig. 2, although in this case the similarities are clearly more pronounced among spectra of cages for which the metal species belong to the same group. Concerning this point, we note that the total magnetic moments of the cages with perfect $D_{6h}$ symmetry are the same for metal elements that belong to the same group, but different for cages for which the metal elements belong to different groups (1 $\mu_b$, 0 $\mu_b$, and 2 $\mu_b$ for groups 4, 5, and 10 of the Periodic Table, respectively). Looking in more detail at the spin-susceptibility spectra of the group 4 cages (VSi_{12}, NbSi_{12}, and TaSi_{12}), we observe that the structure of the NbSi_{12} and TaSi_{12} spectra are almost identical, while some differences are found for the VSi_{12} spectra outside the 2-3 eV range. These differences include the lowest energy peak, which is shifted almost 1 eV towards higher energy in the case of the VSi_{12} spectra, and the relative intensities of the peaks found in the 3-3.5 eV range. Nevertheless, there are three peaks between 2 and 3 eV that feature in the spectra of all these cages. We also note that the relative intensity of the peak at around 2.2 eV increases with the increasing of the atomic number of the metal species. As for the group 5 cages (CrSi_{12}, MoSi_{12}, and WSi_{12}), three peaks are also found between 2 and 3 eV in all cases, but there is no clear trend regarding their relative intensities. Finally, in the case of the group 10 cages (PdSi_{12} and PtSi_{12}), three peaks are again found between 2 and 3 eV for all cases with no clear trend regarding their relative intensities. Furthermore, two peaks with similar intensities are found between 0.8 and 1.2 eV, although slightly shifted towards lower energies in the case of PtSi_{12}.

Concerning the more distorted MSi_{12} clusters belonging to the second and third classes of geometries shown in Fig. 1, we note that both their optical absorption and spin-susceptibility spectra are clearly distinct from the ones of the clusters with perfect $D_{6h}$ symmetry. In particular, the spectra of these cages have a more complex structure, as expected. Furthermore, we note that the
FIG. 2: (color online) Optical absorption spectra (top panel) and spin-susceptibility spectra (lower panel) of selected MSi$_{12}$ clusters. The color of each curve indicates the type of geometry of the corresponding cage: The light gray corresponds to the perfect hexagonal prism with $D_{6h}$ symmetry, while the blue and dark green correspond to the two distortions of the $D_{6h}$ symmetry (see Fig. 1 for the equilibrium geometries of each of these classes of MSi$_{12}$ clusters).

change of the metal species within the group 3 of the Periodic Table (TiSi$_{12}$, ZrSi$_{12}$, and HfSi$_{12}$), which correspond to the clusters belonging to our second class of geometries, does change both the optical absorption and spin-susceptibility spectra in a noticeable way. It is possible that the same peaks appear in the spectra of these three clusters, but the complexity of the spectra does not allow us to ascertain it.

From the discussion above, it is clear that the cage geometry is important in determining the excited-state properties of these clusters. Since the spectra of cages with the same geometry share significant spectral features, it is quite likely that some of the calculated excitations only involve states localized at the cage itself, i.e., at the silicon atoms. In order to verify this hypothesis, we calculated the optical absorption spectra of the corresponding “empty” hydrogenated cages, using the geometries obtained as explained in Sec. II. This also allows for a better understanding of the direct contribution of the metal atom to the excited-state properties of the clusters.

In Fig. 3, a comparison between the optical absorption spectra of the MSi$_{12}$ clusters and their corresponding hydrogenated “empty” cages is provided. Looking first at the spectra of the cages with perfect $D_{6h}$ symmetry, we note the presence of a distinct peak located between 4.0 and 4.3 eV in all the Si$_{12}$H$_{12}$ spectra. These are quite close to the similar peak found at around 4.0 eV in the case of the corresponding MSi$_{12}$ clusters, with the notable exception of PdSi$_{12}$ and PtSi$_{12}$, where the peak is found at around 3.5 eV. Nevertheless, it is well noticeable
that in the case of the group 4 and group 5 cages (VSi$_{12}$, NbSi$_{12}$, TaSi$_{12}$, CrSi$_{12}$, MoSi$_{12}$, and WSi$_{12}$), the position of this peak changes a lot more in the case of the corresponding Si$_{12}$H$_{12}$ clusters than in the case of the MSi$_{12}$ clusters. The fact that the peak position changes in the case of the Si$_{12}$H$_{12}$ clusters is to be expected, as the distance between the Si atoms increases with increasing atomic number of the metal species of the corresponding MSi$_{12}$ cluster. This raises the question of why a similar thing does not happen in the case of the corresponding MSi$_{12}$ clusters. A possible explanation would be that the presence of the metal atom counteracts the change in the spectra induced by the stretching of the Si bonds. A peak at 3.5 eV is also shared by all the Si$_{12}$H$_{12}$ cages, although in the case of the Nb and Ta ones, its relative intensity is quite small. We find a peak with similar relative intensity in the spectra of VSi$_{12}$ and CrSi$_{12}$. A similar peak also appears in the spectra of MoSi$_{12}$ and WSi$_{12}$, but at higher energies and with higher relative intensities. From the results presented in Fig. 3, we conclude that some of the observed transitions are, indeed, located at the silicon atoms, but that the presence of the metal atom cannot be neglected. Once again, the complexity of the spectra of the remaining two classes of equilibrium geometries (TiSi$_{12}$, ZrSi$_{12}$, HfSi$_{12}$, and NiSi$_{12}$) complicates their analysis, making it difficult to assign specific peaks to the cage itself.

B. MSi$_{10}$ clusters

In Fig. 3 the calculated optical absorption and spin-susceptibility spectra of the MSi$_{10}$ clusters are shown. Like for the MSi$_{12}$ species, the spectra are arranged with respect to each other in a similar way as the corresponding metal species are arranged in the Periodic Table.

From Fig. 4 several clear trends can be identified in the optical absorption spectra of the group 11 cages (CuSi$_{10}$, AgSi$_{10}$, and AuSi$_{10}$). When going from CuSi$_{10}$ to AuSi$_{10}$, i.e., when going to heavier metal species, we observe that the peak found between 1.5 and 2.0 eV is shifted towards higher energies, the peak around 2.6 eV remains practically unchanged, and the peak found between 3.0 and 3.5 eV is shifted towards lower energies and its relative intensity increases. For the spectral features above 3.5 eV the situation is not so clear. Despite this, we note that the overall shapes of the CuSi$_{10}$ and AgSi$_{10}$ spectra are quite similar, which is not the case when comparing these spectra to the one of AuSi$_{10}$. Similarly, in the case for the spin-susceptibility spectra, we observe that the peak found between 1.5 and 2.0 eV is shifted towards higher energies when going to heavier metal species. As for the two peaks found between 2.0 and 2.5 eV in the spin-susceptibility spectra, we observe that the peak at higher energy is shifted towards lower energies when going to heavier metal species, eventually leading to the merging of these two peaks in the AuSi$_{10}$ spectra. A similar situation is also observed for the two peaks found between 2.5 and 3.0 eV. Finally, the peak found around 3.6 eV remains practically unchanged when going from CuSi$_{10}$ to AgSi$_{10}$, while a splitting of the same peak seem to occur when going from AgSi$_{10}$ to AuSi$_{10}$. Comparing the NiSi$_{10}$ spectra with the ones of the group 11 cages, we find many similarities. For the optical absorption spectra, we find peaks at around 2.6, 3.7, 4.0, and 4.3 with similar relative intensities for all the four clusters NiSi$_{10}$, CuSi$_{10}$, AgSi$_{10}$, and AuSi$_{10}$. As for the spin-susceptibility spectra, we find peaks close to 1.7, 2.3, 2.8,
and 3.5 eV with similar relative intensities in all cases. These similarities can be explained by the similar geometry of these cages.

As in the case of the MSi\textsubscript{12} clusters, we also calculated the optical absorption spectra of the corresponding “empty” hydrogenated cages for the MSi\textsubscript{10} clusters. The results can be seen in Fig. 5. The spectra of the Si\textsubscript{10}H\textsubscript{10} clusters are more complex than those of MSi\textsubscript{10}, but it is still possible to identify peaks shared with the spectra of the MSi\textsubscript{10} clusters. We observe such peaks at around 1.7, 2.5 eV, and 3.1 eV, although their relative intensities are not quite the same. We also point out that the spectra of the Si\textsubscript{10}H\textsubscript{10} cages corresponding to group 11 metal species (CuSi\textsubscript{10}, AgSi\textsubscript{10}, and AuSi\textsubscript{10}) are almost identical, while some differences are found with respect to the spectra corresponding to the NiSi\textsubscript{10} cluster. This confirms our previous conclusion drawn with respect to the MSi\textsubscript{12} clusters that some of the observed transitions are, indeed, located at the silicon atoms, but that the presence of the metal atom cannot be neglected.

FIG. 4: (color online) Optical absorption spectra (top panel) and spin-susceptibility spectra (lower panel) of selected MSi\textsubscript{10} clusters.

FIG. 5: (color online) Optical absorption spectra of selected MSi\textsubscript{10} clusters (light gray curves) and their corresponding “empty” Si\textsubscript{10}H\textsubscript{10} clusters (blue curves). The scales of the Si\textsubscript{10}H\textsubscript{10} curves were adjusted to make the intensities of their highest peak coincide with the highest peak of the corresponding MSi\textsubscript{10} curves.

IV. CONCLUSIONS

In this work, we have studied optical and magnetic excitations of selected endohedral MSi\textsubscript{12} and MSi\textsubscript{10} clusters. The geometries of the clusters were determined using density functional theory, while a real-time formulation of time-dependent density functional theory was used to calculate their optical absorption and spin-susceptibility spectra. The obtained results were then analyzed by taking into account the position of the metal species in the Periodic Table. From the calculated spectra, we found that these are mainly determined by, in decreasing order of importance: 1) the cage shape, 2) the group in the Periodic Table the metal specie belongs to, and 3) the period of the metal species in the Periodic Table. This means that cages with similar structures and metal species that are close to each other in the Periodic Table will have spectra that share many similarities. This implies that the fine tuning of the excited-state properties for such cages might be better achieved by replacing the metal atom by one belonging to the same group or, to a lesser extent, to the same period, provided that this substitution does not alter the shape of the cage. In this respect, the MSi\textsubscript{10} clusters (M = Ni, Cu, Ag, Au) and the MSi\textsubscript{12} clusters with perfect D\textsubscript{6h} symmetry (M = V, Cr, Zr, Nb, Mo, Pd, Ta, W, Pt) studied in this work seem to be particularly suited as tunable building blocks for self-assembled nano-opto-electro-mechanical devices. Finally, we point out that our results indicate that optical absorption spectroscopy could be a useful tool for the structural identification of MSi\textsubscript{10} and MSi\textsubscript{12} clusters produced in experiments.
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