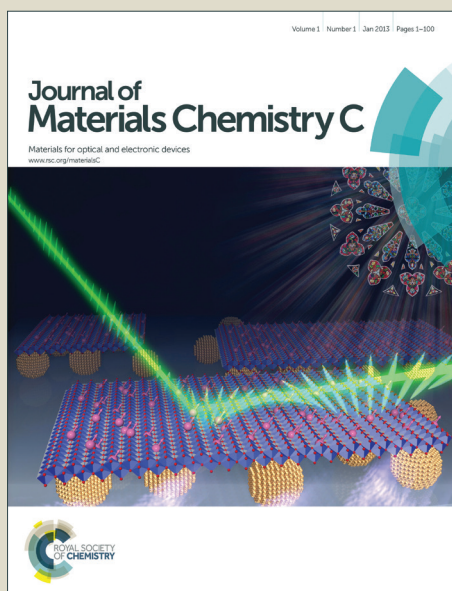


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Photo-Switching of Magnetization in Iron Nanoparticles

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Abstract

We report the theoretical study of light induced switching of magnetization in core-shell nanoparticles. The core of the nanoparticle is made of iron (Fe) coated with the shell of azobenzene compound. Azobenzene is a photochromic material with the reversible *trans-cis* photoisomerization upon irradiation by UV and visible light. The magnetization of nanoparticles can be reversibly switched by using specific wavelengths of light. Using an *ab initio* parameterization of magnetic interactions we have performed Monte Carlo simulations of magnetization of the core-shell nanoparticle as a function of temperature. The results show that Fe nanoparticles magnetization can be switched by at least 50% due to photoisomerization of azobenzene at room temperature. *Ab initio* calculations show that the exchange interaction in Fe dimer is ferromagnetic (FM) and shows a strong modification of exchange interaction parameters by 40% due to *trans-cis* photoisomerization of azobenzene. An infinite planar Fe monolayer mimicking the surface of nanoparticle shows a strong modification of exchange interaction parameters (up to 50%) in the monolayer due to *trans-cis* photoisomerization. The local magnetic moments of Fe sheet increase by only 0.5% due to photoisomerization.

Keywords: core-shell Fe nanoparticles, magnetization switching, *trans-cis* photoisomerization, exchange interactions

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1. Introduction

In recent years, interest in the nanoparticle magnetism has led to many advances in magnetic memory, biomedicine, and spintronics among other fields.^{1,2} The size and temperature dependence of magnetization as well as magnetization reversal were studied both experimentally and theoretically in a variety of systems.³⁻⁹ The obtained results are system dependent suggesting strong effects of the surface morphology on magnetic properties of nanoparticles which may differ drastically from the properties of bulk materials. Because of their extreme size, nanoparticles are sensitive to the properties of their surfaces, i.e. surface termination, roughness, and symmetry. Furthermore, the termination at the surface reduces the number of neighbors surface (coordination) atoms interact with. Because of this, the atomic local magnetic moments, and more importantly, the magnetic exchange interactions of the surface atoms can be strongly modified. Such sensitivity of the nanoparticle properties to the surface modification can be used to tune its magnetic properties by external stimuli like an electric field^{10,11} or a pulse of light granting.¹² Particularly, core-shell nanoparticles where shell is sensitive to the external stimuli can serve this purpose.¹³

It has been recently observed that the magnetic properties of core-shell nanoparticles can be modified by using specific wavelengths of light.¹³ The shell of these particles can be manufactured out of photo-sensitive molecules, such as azobenzene or other photochromic materials.¹⁴ Molecules like azobenzene display photoisomerization, or structural change in response to irradiation. This process is reversed by using light of a different wavelength. Azobenzene chromophores can be switched between two geometric (*trans* and *cis*) isomers using ultraviolet and visible light pulses.¹⁵ This photoisomerization is rapid, reversible, and high quantum yield. The wavelengths effecting the transformation can be tuned synthetically with

substituent groups to the chromophores. Upon isomerization, there can be significant changes to the optical, geometric, mechanical, and chemical properties of azobenzene molecules, and these photoswitchable properties can often be transferred to large host systems into which azobenzene is incorporated.¹⁵ In the *cis* or excited state, azobenzene exhibits an overall dipole moment of 3.0D whereas in the *trans* or ‘ground’ state the molecule has zero dipole moment.^{16,17}

Reversible photoswitchable nanoparticles were achieved experimentally.¹⁸⁻²¹ Suda et al. designed reversible photoswitchable ferromagnetic (FM) FePt nanoparticles coated with azobenzene-derivatized ligands.²² They controlled the magnetic properties of the FM composite nanoparticles by alternating the photoillumination at room temperature. Also a reversible photoswitching of magnetization of iron oxide nanoparticles was achieved at room temperature by Mikami et al.²³ However, the possible mechanisms for the controlling of the magnetization in the nanoparticle systems are yet to be clarified. The photoisomerization of azobenzene and other molecules with similar properties may provide a mechanism of varying the exchange interactions on the surfaces of the nanoparticles, and the exchange interactions affect the magnetization.

In this study we performed Monte Carlo simulations of magnetization of the core-shell nanoparticle as a function of temperature to show that the magnetization of Fe nanoparticles can change due to photoisomerization of azobenzene compound in the selected range of temperature. We examine from first principles methods the effects of *trans-cis* photoisomerization of azobenzene on changing the surface local magnetic moments and the surface exchange interactions of the Fe dimer and the planar iron surface modeled by monolayer.

2. Model and Computational Methods

The interatomic exchange interactions parameters of Heisenberg model are calculated from the energy difference of the FM and anti-ferromagnetic (AFM) configurations. This

approach to the finite temperature magnetic properties of base- (*bcc*) and face- (*fcc*) centered cubic structures of Fe have shown that the Heisenberg model based on electronic structure calculations predicts Curie temperature in a good agreement with experimental results.²⁴ We employ the Monte Carlo (MC) method with the Heisenberg Hamiltonian

$$H = - \sum J_{ij} \vec{S}_i \cdot \vec{S}_j$$

where J_{ij} is the pair exchange parameter and summation is performed over nearest neighbors. J_{ij} is derived from *ab initio* electronic structure calculations. If $J_{ij} > 0$ the exchange interaction is FM, and $J_{ij} < 0$ results in AFM interaction. We use Statistical MC method and Metropolis algorithm^{25,26} to simulate the magnetization as a function of temperature in nanoparticle. Effective exchange parameter, $J_0 = -\sum J_{0j}$ determines the corresponding to Curie temperature in bulk systems.²⁴ Here, we consider a core-shell nanoparticle in the shape of truncated octahedron terminated by (1 1 1) and (0 0 1) facets, mimicking experimentally synthesized nanoparticles.^{27,28} The nanoparticle consists of 1297 atoms in face centered cubic *fcc* structure.

The self-consistent spin-polarized density functional theory (DFT) calculations are performed using SIESTA package,²⁹ which use numerical atomic orbitals as basis sets and Troullier-Martin type³⁰ norm-conserving pseudopotentials. The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) form³¹ is used for the exchange-correlation functional. The self-consistent calculations are performed with a 400 Ry mesh cutoff. A linear combination of numerical atomic orbitals with double- ξ polarizations (DZP) basis set is used. The conjugate gradient method is used to relax all the atoms until the maximum absolute force was less than 0.01 eV/Å. We have performed spin polarized calculations of Fe sheet for two configurations: (1) the FM states (all spin up), and (2) the AFM alignment of one atomic

spin (down) keeping the rest of the lattice in the initial state to determine the effective exchange interaction for the Fe systems in all cases.

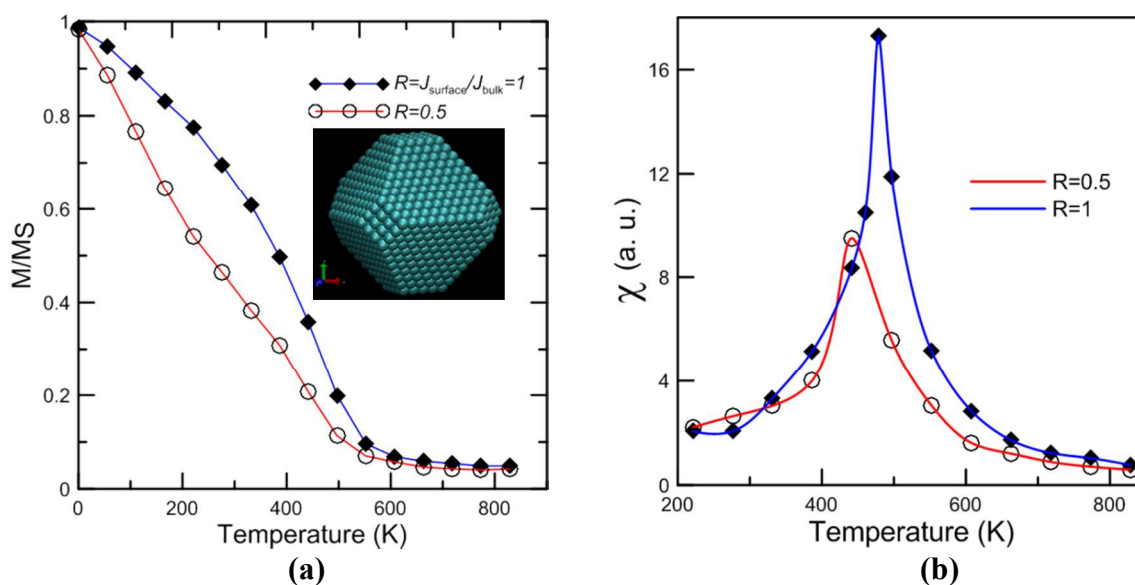
The core of the nanoparticle is made of Fe coated with the shell of azobenzene compound. The azobenzene molecule has to be modified to attach to the surface. We consider here a molecule $N(CH_3)_2C_6H_4-N-N-C_6H_4O-(CH_2)_7-COOH$. It has been shown that this termination allows the molecule to attach to Fe sites on the surface.²² This molecule can form a self-assembled monolayer on the surfaces of metals and metal oxide.

3. Results and Discussion

To elucidate the effect of surface exchange coupling on magnetization of nanoparticle we performed MC simulations of magnetization of the model nanoparticle as a function of temperature. The effect of the *trans-cis* transition upon UV/visible light irradiation is modeled by altering the surface exchange parameters as derived from *ab-initio* calculations. We considered nearest exchange interactions between sites in the bulk (J_{0B}), between surface sites (J_{0S}), and between surface and bulk sites (J_{0SB}) in the 1297 atom particle of *fcc* structure truncated in the shape of cube-octahedron. Exchange interactions in the nanoparticle were altered from $R=J_{0B}/J_{0SB}=1^{32}$ to 0.5 accounting for 50% drop in the surface exchange coupling upon photo-isomerization derived from *ab-initio* calculations. Using parameterization of the exchange interactions on the surface of Fe nanoparticle, we obtained the magnetization as a function of temperature for Fe nanoparticle which is shown in Figure 1(a). The red curve (with circle points) shows the resulting magnetization with respect to temperature, $M(T)$, in case of smaller surface exchange parameter and the blue curve (with square points) shows the $M(T)$ in case of larger surface exchange, corresponding to *cis* and *trans* azobenzene isomers, respectively. Figure 1(a) shows that Fe nanoparticles magnetization at selected temperatures ($T\sim 300K$ for our exchange

parameters) can be switched by at least $R = 2 \cdot \frac{M^{trans} - M^{cis}}{(M^{trans} + M^{cis})} = 50\%$ due to *trans-cis*

photoisomerization of azobenzene. These results clearly show that magnetization switching is possible by modification of surface exchange coupling alone. This effect can also be clearly seen in enhancement in magnetic susceptibility³³ near this range of temperatures as shown in Figure 1(b). Figure 1(c) illustrates schematically photo-induced changes in the core-shell nanoparticles due to photoisomerization and potential change in Fe core magnetization. The *trans-cis* photoisomerization of azobenzene attached to the surface of magnetic nanoparticle may prove to be a way of optical stimulation of magnetization switching. This mechanism should not be confused with the all optical magnetization reversal by circularly polarized light proposed for magnetic structures¹² or similar approaches.



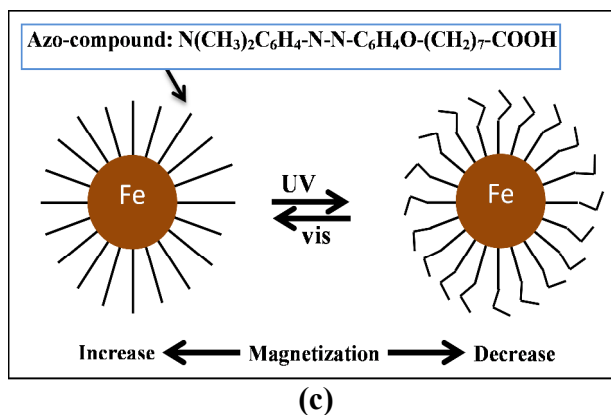


Figure 1. (a) Simulated magnetization as function of temperature for *trans* ($R=1$) and *cis* ($R=0.5$) photoisomerization of a 1297 atom nanoparticle. M/M_s is the magnetization scaled to magnetic saturation (M_s) of the nanoparticle; (b) magnetic susceptibility as function of temperature for the nanoparticle shown in (a); (c) Schematic illustration of photoswitching of the magnetization of iron core due to photoisomerization of the azobenzene shell in core-shell nanoparticle.

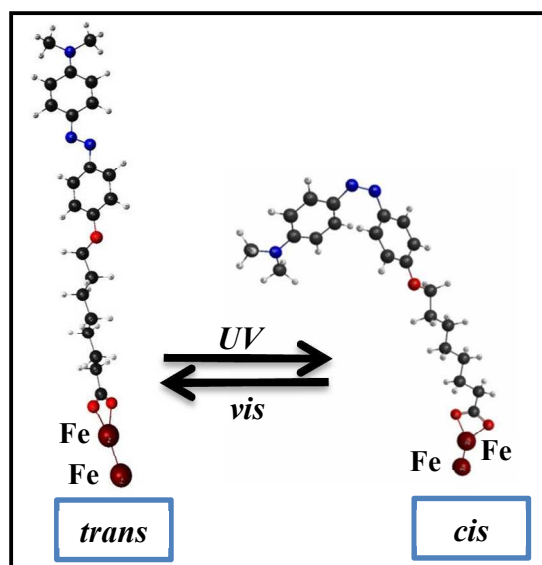


Figure 2. Fe-Fe dimer attached to azobenzene compound ($Fe_2-N(CH_3)_2C_6H_4-N-N-C_6H_4O-(CH_2)_7-COOH$) in *trans* and *cis* isomers. The small red balls and the blue balls represent O and N atoms, respectively.

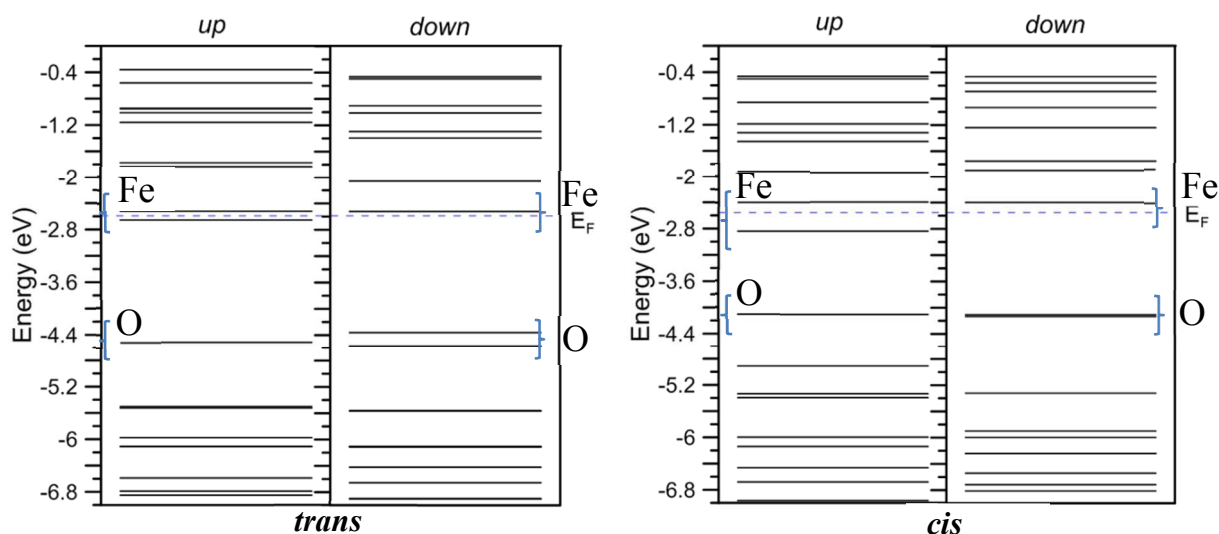


Figure 3. Energy levels diagram of Fe₂-azobenzene compound (Fe₂- N(CH₃)₂C₆H₄-N-N-C₆H₄O-(CH₂)₇-COOH) for *trans* and *cis* isomers in antiferromagnetic (AP) configuration.

In order to quantify the effect of photoisomerization of azobenzene on exchange interactions in nanoparticles we have performed first-principle calculations of magnetic properties of Fe systems modified by absorbed azobenzene. We started from the simplest system which the exchange interactions can be derived, i.e. Fe dimer attached to an azobenzene molecule through the COOH termination. The molecule forms coordination bonds with the dimer. The relaxed structures of Fe-Fe pair that attached to azobenzene in case of *trans* and *cis* isomers, as shown in Figure 2, indicate bonds formation between one of Fe atoms and two oxygen atoms of azobenzene with bond length of 2.1 Å, in good agreement with the experimental value of the Fe-O bond length of 2.03 Å in FeO molecule.³⁴

Pair exchange parameter (J_0) calculated as difference in energy of a dimer with co-aligned, $E(P)$, and oppositely aligned, $E(AP)$, local magnetic moments on Fe sites: $J_0 = E(AP) - E(P)$. The calculations show that the exchange interaction is FM and the exchange parameter (J_0) in Fe dimer increase from 0.15 to 0.24 eV due to *trans-cis* photoisomerization of azobenzene. The photoisomerization changes the energy states of azobenzene, also noticeably shifts energy states of Fe-dimer that are hybridized with states of azobenzene molecule. Figure 3 shows the

energy levels diagram of molecular orbitals in Fe₂-azobenzene compound (Fe₂-N(CH₃)₂C₆H₄-N-N-C₆H₄O-(CH₂)₇-COOH) in AFM alignment of Fe local moments. It is interesting that there are small changes in Fe states near Fermi energy upon trans-cis transformation in co-aligned spin case. However, in anti-aligned spin configuration there is noticeable difference between *trans* and *cis* isomers cases, as can be seen in Figure 3. There is minor variation in energy of minority (down) orbitals of Fe₂ states. However, there is noticeable shift in the energy of Fe₂ states of majority (up) states near Fermi level. Besides energies of Fe state, *cis-trans* isomerization induces a shift and splitting of the O state about 1.8eV below HOMO as shown in Figure 3. This is an indication of change in interactions between oxygen electrons with ones of Fe, as well as Fe-Fe hybridization. As a result, the exchange coupling between Fe sites changes. One electron energy $E = \sum_{i=1..N} \varepsilon_i \cdot n_i$ in scope of force theorem approach is related to the exchange coupling parameter of Heisenberg model.³⁵ With “one-electron” eigenvalues, ε_i , shifting by 0.1-0.2eV *trans-cis* isomerization is clearly affecting the energies on the scale of the exchange interactions magnitudes.

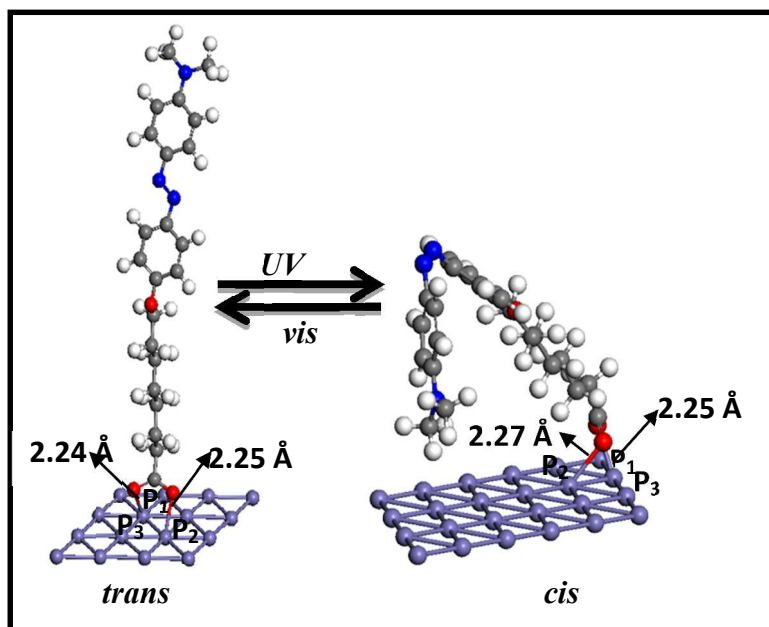


Figure 4. Fe sheets attached to azobenzene compound $[N(CH_3)_2C_6H_4-N-N-C_6H_4O-(CH_2)_7-COOH]$ in case of *trans* and *cis* isomers.

To study the effects of *trans-cis* photoisomerization of the azobenzene on the exchange interactions at the surface of Fe nanoparticle, we attached *trans* azobenzene isomer to a planar Fe sheets containing 16 Fe atoms, and *cis* azobenzene isomer to a planar Fe sheets containing 24 Fe atoms, as shown in Figure 4. Although, the planar sheet of Fe may have exchange interactions that are somewhat different from the surface of Fe nanoparticle, the effect of the photoisomerization on the exchange coupling in a planar sheet can be estimated quantitatively using DFT calculations. The percentile of the change in exchange interaction in the planar sheet, mimicking the surface layer of nanoparticle, upon isomerization can be calculated. The lattice constant of the consider Fe planar sheet was taken as 3.593 Å corresponding to calculated bulk *fcc* Fe. Calculations show the formation of Fe-O bonds at the interface of the molecule and Fe sheet. We find that after ionic relaxation the Fe-O bonds are formed having bond lengths around 2.25Å, as shown in Figure 4. These bond lengths are longer by 0.15 Å than that in Fe dimer with azobenzene. This is probably due to the additional bonding within the infinite Fe sheet (compared to Fe dimer) which reduces the number of electrons participating in Fe-O bonding. The change in the atom positions at the contact points and formation of chemical bonds may play role in changing the local magnetic moments and induce magnetization on the surface of the nanoparticle. This correlates well with substantial atomic displacements in the interfacial TiO₂ and PbO planes, in ferroelectric/piezomagnetic hetrostructures that also exhibit switchable magnetic state in the interfaces.³⁶

Table 1. Calculated J (eV) exchange coupling constant for Fe monolayer.

Fe position (P _x)	<i>pure-Fe sheet</i>	<i>Trans</i>	<i>Cis</i>
P1	-0.1915745	-0.0824860	-0.0628000
P2	-0.1915985	-0.0718345	-0.0426015
P3	-0.1915600	-0.0711970	-0.0518270

Table 2. Electric Dipole moments (Debye) of studied systems.

	Trans	Cis
AZO: N(CH ₃) ₂ C ₆ H ₄ -N-N-C ₆ H ₄ O-(CH ₂) ₇ -COOH	5.5	-4.5
AZO with Fe-monolayer	4.2	-4.8

Our calculations show that the Fe sheet displays only a small change of the local magnetic moments due to *trans-cis* photoisomerization of azobenzene. The local magnetic moments of Fe sheet increase by only 0.5% (from 3.580 μ_B with *trans* to 3.595 μ_B with *cis* isomer attached) due to photoisomerization. Upon reversal of local magnetic moment of Fe in positions nearest to the adsorption sites, P_x, shown in Figure 4, the local magnetic moment on the reversed site is about 4.2 μ_B . There is small change in magnitude of local magnetic moment of reversed Fe by less than 2% upon *trans-cis* isomerization. Thus, we expect only a marginal effect on the magnetization due to the changes induced in local magnetic moments.

The pristine (without azobenzene) planar Fe sheet exhibits AFM effective exchange interactions, i.e. negative J₀. Fe sheet with azobenzene attached still exhibit AFM coupling, but the exchange interaction parameter decreases in both *trans* and *cis* isomers of azobenzene as show in Table 1. Note, that the calculated exchange interaction parameter has small variation in

the values at three different Fe sites P_x , (P_1 , P_2 , P_3) sites as shown in Figure 4, due to the difference in Fe-O distances for these sites. Thus this variation on the exchange interaction parameters indicates that the response of Fe surface atoms to the photoisomerization depends on the local surface atomic environment. Furthermore, the exchange interaction in Fe sheet is more AFM in case of *trans* isomer than that in *cis* azobenzene isomer case. If we introduce a photo-switching coefficient as difference of exchange interaction parameter over its average value in two isomer configurations $R_{exch} = 2 \cdot \frac{J^{trans} - J^{cis}}{(J^{trans} + J^{cis})}$, we find that R_{exch} is about 25 ~50%. Because

the effective exchange parameter is linearly proportional to the Curie temperature in bulk ferromagnet $\left(T_C = \frac{2J_0}{3k_B}\right)$ or Neel temperature of antiferromagnet, the change in the exchange parameter will affect magnetization variation as function of the temperature in nanostructures.

The calculated switching in exchange parameters comes from changes in electron density distribution at the interface between molecule and Fe sheet when *trans-cis* transformation occurs. This redistribution comes both from the formation of the dipole moment in the molecule and also the change in the Fe-O bond strength at the interface. We should point out that both azobenzene and COOH groups have large dipole moments which are altered by the *trans-cis* transformation. Table 2 summarizes the values of the electric dipole moments for *trans* and *cis* azobenzene isomers with terminating molecules before and after attached to the Fe sheet. The electric dipole moments of *trans* and *cis* azobenzene isomers were changed due to the interaction with Fe sheet. This change may be possible case of switching magnetization on the surface of Fe nanoparticle due to *trans-cis* photoisomerization of azobenzene. The electric Dipole moment of Fe-monolayer-azobenzene system is changed from 4.2 to -4.8D due to *trans-cis* photoisomerization. This suggests that photo-induced changes in the electronic polarization of the electrons of the

surface Fe atoms affect the magnetic properties of the Fe nanoparticle. Recently it was found that changing the direction of electric polarization in the ferroelectric phase controlled the induced magnetization in the systems. This agrees also with *ab initio* calculations show that reversal of the polarization results in change of the net magnetization in the ferroelectric/piezomagnetic heterostructures system by more than 50%.³⁶

The switching in the magnetization is induced due to the modification of the exchange interactions on the surfaces of the Fe nanoparticle coupled to the switching in dipole moments of attached functionalized azobenzene molecule. Note, that the interaction of Fe with O across the interface between molecule and nanoparticle is critical for large observed switching. The unattached azobenzene molecules would change its dipole and switch the electric field near the surface of the nanoparticle. However, this field would only marginally affect the exchange parameters between Fe spins and does not result in noticeable magnetization switching.

4. Conclusions

we investigate the mechanism of magnetization switching in core-shell nanoparticles (Fe-core) due to photoisomerization of the shell (azobenzene). The results of Monte Carlo simulations show that Fe nanoparticle magnetization at select temperature range can be switched reversibly by at least 50% due to photoisomerization of azobenzene caused by a light pulse. *Ab initio* calculations show that the exchange interaction in Fe dimer is FM and shows a strong modification of exchange interaction parameters by 40% due to *trans-cis* photoisomerization of azobenzene. Moreover, the calculations show that an infinite planar Fe monolayer displays a small change on the surface local magnetic moments and a strong change on the exchange interactions of the surface atoms as result of *trans-cis* azobenzene photoisomerization. The exchange interaction in Fe sheet is more AFM in case of *trans* isomer than that in *cis* azobenzene

isomer case. Our calculations show up to 50% change in the exchange interaction parameters between *trans* and *cis* azobenzene isomers.

We believe that the magnetic photoswitching mechanism in nanoparticles due to photoisomerization that described in this work should be helpful in practical research of the nanomaterials with enhanced photomagnetic switching ratio. Therefore we hope that our results will stimulate experimental work on reversible photoswitching of the magnetization of nanoparticles and nanostructures.

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