First-principles calculation of monitoring spin states of small magnetic nanostructures with IR spectrum of CO

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Abstract. A fully \textit{ab initio} controlled ultrafast magnetooptical switching mechanism in small magnetic clusters is achieved through exploiting spin-orbit-coupling enabled Λ processes. The idea is that in the magnetic molecules a fast transition between two almost degenerate states with different spins can be triggered by a laser pulse, which leads to an electron excitation from one of the degenerate states to a highly spin-mixed state and a deexcitation to the state of opposite spin. In this paper a CO molecule is attached to one magnetic center of the clusters, which serves as an experimental marker to map the laser-induced spin manipulation to the IR spectrum of CO. The predicted spin-state-dependent CO frequencies can facilitate experimental monitoring of the processes. We show that spin flip in magnetic atoms can be achieved in structurally optimized magnetic clusters in a subpicosecond regime with linearly polarized light.

1. Introduction
In recent years there has been a continuous strain to increase the storage capacity as well as to minimize as much as possible the time needed to record data on magnetic materials. However, the tremendous increase in the storage density and read-write speed in magnetic storage media is reaching its physical limits. Manipulation of the spin degree of freedom is attracting more and more attention due to its potential to increase the information density and speed in computational device applications. Many light-driven scenarios and mechanisms of demagnetization have already been proposed [1, 2, 3], and it has been demonstrated that subpicosecond magnetic switching can be achieved by exploiting the ultrafast electron-photon interaction [4, 5]. Laser manipulation has been well understood in atomic and molecular systems, which stimulates the implementation of these mechanisms in practical device applications.

At the same time, monitoring spin manipulation is another important and necessary aspect in device realization. Although it is possible to theoretically predict the spin state of matter, it is still one of the significant problems that experiment will encounter. Here a possible solution to this problem is proposed. We use a CO molecule as an experimental marker attached to the investigated magnetic clusters. The CO marker changes the electronic structure of the magnetic cluster only minimally, however it lowers its symmetry. If certain magnetic states of the cluster correspond to specific CO vibrational frequencies, experiment can reveal the spin state indirectly from the infrared (IR) spectrum of CO, which is a common and reliable technique in experiment.
In this paper, we demonstrate using first-principles quantum chemistry calculations that laser-induced spin switching can be achieved in small magnetic clusters through a nonadiabatic Λ process, which can be substantially faster than the dynamics in conventional semiconductors [6, 7]. In the present calculations, two different clusters Co-Co and [Co-Ni]+ are studied. Both clusters are realistic systems that can be synthesized in experiment. Especially, a CO molecule is attached as an experimental marker to one magnetic center of each cluster. The predicted CO vibrational frequencies for certain states show that it is possible to monitor the spin dynamics by mapping spin states to the IR spectrum of CO.

2. Methods and technical details

In order to properly describe the laser-matter interaction, as demonstrated in previous works [8, 9], the Hamiltonian of the interacting system is solved in two steps. The first step is to solve the time-independent Hamiltonian in a static magnetic field $B_{\text{stat}}$:

$$
\hat{H} = \sum_{i=1}^{N_{el}} \frac{Z_{eff}^i}{2c^2R_i^2} \hat{L} \cdot \hat{S} + \sum_{i=1}^{N_{el}} \mu_L \hat{L} \cdot B_{\text{stat}} + \sum_{i=1}^{N_{el}} \mu_S \hat{S} \cdot B_{\text{stat}} + \sum_{i=1}^{N_{el}} \sum_{q} \lambda^q_{\alpha}(q)
$$

where effective nuclear charges ($Z_{eff}^i$) are used for the SOC. $\hat{L}$ and $\hat{S}$ are the orbital and spin momentum operators, respectively, $\mu_L$ and $\mu_S$ their respective gyromagnetic ratios, $c$ is the speed of light. It should be noted that the last item on the right hand side provides a new contribution from the electron-phonon interaction, the validity of which has been proven in a recent work of a magnetic switching scenario in NiO [9]. Here $q$ represents the quantized normal mode coordinate, and $\lambda^q_{\alpha}$ the electron-vibron coupling. $\langle q \rangle$ denotes integration over the phononic wavefunction. In order to accurately describe the complex electronic structure of strongly correlated materials, such as the magnetic clusters studied in the present work, a fully ab initio quantum chemistry method is adopted in this step, which allows us to calculate not only the energy levels but the wavefunctions as well. All the first-principles calculations start with Gaussian03 [10]. In the second step, a suitably tailored laser pulse, which accounts for the electron-laser interaction, is turned on by adding a time-dependent term to the above system. In this step, our own codes are implemented for the computation of time-propagation information during the switching processes and the optimization of laser pulse as well [11, 12, 13, 14].

All the clusters studied here have been optimized with the following steps: Firstly, the metallic part without CO is fully optimized within the Hartree-Fock (HF) approximation, and the normal modes and frequencies are calculated as well in order to confirm the stable geometry. Then the relaxation procedure is repeated with CO attached to the previously obtained structure. In the third step, further optimizations of the whole cluster, especially the local geometry of CO, are performed with the symmetry-adapted cluster configuration interaction (SAC-CI) methods [15], which is a high level post-HF method and also used in our accurate electronic structure calculations. The sketches of the optimized clusters are shown in the insets of Figures 1 and 2.

3. Spin flip at Co site of the cluster Co-Co-CO

After geometry optimization, Co-Co-C forms a bond angle of about 136°, and the bonds Co-C and C-O are almost in the same line with the bond angle Co-C-O of 173°, as shown in the inset of Figure 1. The spin localization is determined from the spin population analysis of the states (not shown here). The two lower states exhibiting spin localization with opposite direction at the Co atom near the CO molecule are selected as initial and final states for the flip scenario. Figure 1(a) shows the population transfer between the initial state (dashed) and the final state (solid) via several intermediate states, which amounts to a local spin flip on the Co cite. The external magnetic field is in the same plane of the cluster with a angle of 31° between the Co-Co
Table 1. Calculated CO frequencies for the cluster [Co-Ni-CO]$^+$ with respect to certain spin states as well as the optimized CO bond lengths. The results of the first, third, and fifth low-lying triplet states are shown.

| Cluster | Triplet state | Bond length (Å) | Frequency (cm$^{-1}$) |
|---------|---------------|-----------------|-----------------------|
| [Co-Ni-CO]$^+$ | 1 | 1.1532 | 2149 |
|          | 3 | 1.1545 | 2363 |
|          | 5 | 1.1518 | 2160 |

axis and a strength of $|B| = 10^{-5}$ a.u. in order to lift the degeneracy of the triplet. A population transfer of 98.1% is achieved during the process. The properties of the linearly polarized laser pulse are $\theta = 10.0^\circ$, $\gamma = 307.9^\circ$, $\phi = 286.8^\circ$ ($\theta$ and $\gamma$ denote the angles of incidence in spherical coordinates and $\phi$ is the angle between the polarization of the light and the optical plane) with the FWHM = 300.0 fs of the pulse (FWHM is the full width at half maximum of the laser pulse). Figure 1(b) clearly demonstrates nearly perfect spin switching within 500 fs. The time-resolved expectation values of the orbital angular momentum components are also shown in Figure 1(c), showing that the switching of the orbital angular momentum is also achieved at the same time.

Figure 1. Local magnetic switch at a Co site of the cluster Co-Co-CO. (a) The occupations of the initial (dashed), target (solid), and intermediate (dotted) states vs. time. Inset: sketch of the optimized cluster. (b) and (c): Time-resolved expectation values of the spin and orbital angular momentum components, respectively. (d) The laser pulse envelope for the switching.

4. Mapping spin states of cluster [Co-Ni-CO]$^+$ to IR spectrum of CO

The same computational methods for the structure optimization and electronic structure calculations have been adopted for the cluster [Co-Ni-CO]$^+$, which is an almost linear structure after optimization (inset of Figure 2(a)). Here one unit charge is added to the whole structure since we focus on a magnetic triplet ground state. One advantage of the CO marker is that it is commonly used in experiment and will not affect the electronic structure of the original cluster significantly. Magnetic switching on the Co site is also achieved with an appropriate external magnetic field and laser pulse in the cluster [Co-Ni-CO]$^+$ via our $\Lambda$ process, as shown in Figure 2. A population transfer of 99.8% is achieved during the switching process. The properties of the linearly polarized laser pulse are $\theta = 94.4^\circ$, $\gamma = 8.81^\circ$, $\phi = 9.97^\circ$ and FWHM = 305.6 fs. As shown in Figure 2(b), although the spin localization is not as pronounced as in the case of Co-Co-CO, the $z$-component of the total magnetic moment $<J_z>$ exhibits a clear switching within 500 fs.
Figure 2. Local magnetic switch at a Co end of the cluster [Co-Ni-CO]+. (a) The occupations of the initial (dashed), target (solid), and intermediate (dotted) states vs. time. Inset: sketch of the optimized cluster. (b) Time-resolved expectation values of the total magnetic moments components. The dash-dotted line shows the $z$-component of the expectation value of the spin. (c) The laser pulse envelope that induces the switching.

The CO frequency is indirectly calculated in order to combine accuracy with computational efficiency. The steps taken are similar to the ones for our previously investigated structures [14]. Firstly, the fully optimized cluster is divided into three blocks: metallic part, carbon atom, and oxygen atom. Next, the forces are computed using the SAC-CI method when the three blocks are slightly displaced by 0.005 Å along the CO bond direction from their equilibrium positions. Finally, using the force matrix formalism, the frequencies are obtained by evaluating the eigenvalues of the force constant matrix. The three predicted CO frequencies at the corresponding optimized CO bond lengths are shown in Table 1, and exhibit a clear dependence on the magnetic states.

5. Conclusions
In conclusion, using first-principles calculations, we present laser-induced local magnetic switching at the Co site in the two-magnetic-center clusters Co-Co-CO and [Co-Ni-CO]+, respectively. In particular, the CO molecule attached to one magnetic center of each cluster can serve as an experimental marker of the spin state before and after the switching has occurred. The predicted magnetic-state-dependent CO frequencies provide a way of monitoring magnetic switching through the IR spectrum of the respective systems.

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