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# First-principles calculation of the ultrafast spin manipulation of two-center metallic clusters with a CO molecule attached to one center as an infrared marker

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We present a fully *ab initio* ultrafast spin manipulation calculation in two-magnetic-center clusters with CO attached to one of the magnetic centers. CO serves as an experimental marker for certain magnetic states between which spin flip and transfer can be achieved. The predicted spin-state-dependent CO vibrational frequencies indicate that spin manipulation can be readily monitored through the infrared spectrum. The feasibility is demonstrated by two charged clusters $[CoMg_2Ni\text{-}CO]^+$ and $[NiCo\text{-}CO]^+$. Spin transfer between magnetic centers is achieved with a fidelity of 99.8%.

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The applications of magnetic storage and magnetic logical devices have been attracting more and more attention due to the fact that the present magnetic storage media and the corresponding read-write speed are reaching their physical limits. Exploiting the spin degree of freedom for computational device applications is appealing because of the potential for increasing their information density and speed. Using ultrafast optical pulses to manipulate the spin state of matter is a topic that has become one of the most intriguing issues of magnetism.[1,2] Ever since the light-induced demagnetization of ferromagnets was discovered,[3,4] several light-driven scenarios and mechanisms have been proposed,[5,6] and it has already been demonstrated that subpicosecond magnetic switching can be achieved by exploiting the ultrafast electron-photon interaction.[7,8] Furthermore, it has experimentally been assessed that the electronic excitations can nonthermally control spin dynamics[9] and magnetic phases[10,11] in magnetic materials. Laser manipulation is well understood in atomic and molecular systems, which stimulates the demand for an implementation of these mechanisms in device applications.

Small magnetic clusters are good candidates for these devices since they form narrow band systems and provide great potential for coherent spin manipulation.[12,13] Multicenter magnetic clusters have turned out to be good prototypes to realize all basic logic operations.[14] Previous investigations have shown that the spin dynamics induced by a nonadiabatic $\Lambda$ process is faster than the spin dynamics in ordinary semiconductors.[15,16] The idea is that to generate a fast transition between two almost degenerate states split by the Zeeman effect (the two feet of $\Lambda$) with different spins we need a laser excitation to a highly excited state (the tip of $\Lambda$), which is a spin-mixed state due to spin-orbit coupling (SOC), and a de-excitation to the state of opposite spin.[17–20] However, spin transfer from one atom to another is hard to achieve, especially for clusters with direct connections between the magnetic centers, which can be easily manufactured in experiments. In order to implement multifunctional logic computation and ultrafast information storage, magnetic transfer will play a decisive role. Ideally the spin transfer and flip must be realizable in the same cluster, a fact which calls for a development of systems with more magnetic centers where coherent dynamics can take place.

In this Rapid Communication, we demonstrate using first-principles calculations that local spin flip and spin transfer can be best achieved in magnetic clusters with two neighboring magnetic atoms. By choosing triplet rather than doublet systems we move away from a one-carrier-for-all picture, thus separating spin and charge dynamics. Although it is possible to theoretically predict the spin state of matter, it is still one of the significant problems that experiment will encounter. Besides the well-known Stern-Gerlach experiment, to the best of our knowledge, spin can only be detected in a spatially resolved way by magnetic scanning tunneling microscopy on surfaces.[21,22] However, alternative solutions to render these "hidden" properties "visible" are possible. Considering electron-phonon coupling,[20] it is our first attempt to map spin dynamics to vibrational modes as an alternative to nonlinear optics.[23] If a marker such as CO is attached to a magnetic cluster, the electronic structure of the original cluster will remain almost unchanged, and the marker will lower the symmetry of the cluster. If certain magnetic states of the cluster in the gas phase correspond to specific CO vibrational frequencies, experiment can reveal the spin state indirectly from the infrared (IR) spectrum of CO, a known skilled and reliable technique. Similar markers can be designed for electrolyte (liquid phase) environments.

In this Rapid Communication two magnetic clusters ($[CoMg_2Ni]^+$ and $[NiCo]^+$) with CO attached to one of the magnetic atoms (Ni or Co) and the mapping of their magnetic states to the IR spectrum of CO are studied. 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 $\mathbf{B}_{\text{stat}}$,

$$\hat{H} = \sum_{i=1}^{N_{\text{el}}} \frac{Z_a^{\text{eff}}}{2c^2 R_i^3} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} + \sum_{i=1}^{N_{\text{el}}} \mu_L \hat{\mathbf{L}} \cdot \mathbf{B}_{\text{stat}} + \sum_{i=1}^{N_{\text{el}}} \mu_S \hat{\mathbf{S}} \cdot \mathbf{B}_{\text{stat}} + \sum_{i=1} \sum_{\mathbf{q}} \lambda_a^{\mathbf{q}} \langle \mathbf{q} \rangle, \quad (1)$$

where for the SOC the effective nuclear charges ($Z_a^{\text{eff}}$) is used. $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are the orbital and spin momentum operators, respectively, $\mu_L$ and $\mu_S$ are their respective gyromagnetic ratios, $c$ is the speed of light, $\mathbf{q}$ is the normal mode coordi-

 

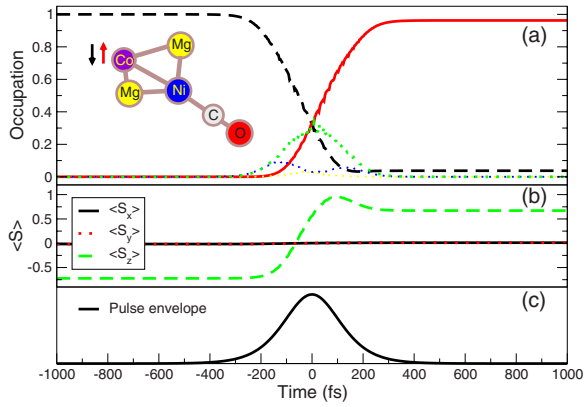


FIG. 1. (Color online) Local magnetic switch at the Co end of the cluster $[CoMg_2Ni\text{-}CO]^+$ (with SOC). (a) The occupations of the initial (dashed), target (solid), and intermediate (dotted) states vs time. Inset: sketch of the optimized cluster. (b) Time-resolved expectation values of the spin components. (c) The laser pulse envelope that induces the switching.

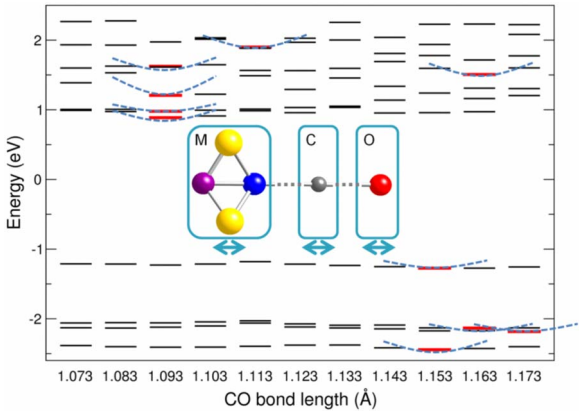


FIG. 2. (Color online) Calculated low-lying magnetic (triplet) states with respect to different CO bond lengths. The thick solid levels indicate the minimum energy of a state with respect to the CO bond lengths (the dashed curves near these levels show the minimum trends). The inset shows the separation of the cluster into three blocks for the frequency calculations.

nate, and $\lambda_a^{\mathbf{q}}$ is the electron-vibron coupling. To simulate the light-matter interaction, in the second step, a suitably tailored laser field is turned on by adding a time-dependent laser pulse Hamiltonian to the above system.[19,20] Here we do not distinguish between different nonlinear optical effects but present a unified picture of electron and spin dynamics in our calculations.

We independently optimize the geometry of the clusters for certain spin states and subsequently calculate the CO stretch frequency. The predicted frequency shifts provide a possible approach to monitor the magnetic state of matter in experiment. Our quantum chemical calculations show that the low-energy electronic states of these clusters exhibit a very high spin localization either at the Co or the Ni site. Spin flip on the same magnetic center and transfer from one magnetic center to another are achieved on structurally optimized clusters. In order to accurately describe the complex electronic structure of strongly correlated materials, such as the Ni-Co clusters studied in the present work, a fully *ab initio* quantum chemistry method is adopted, which also allows us to calculate not only the energy levels but the wave functions as well. All the first-principles calculations start with GAUSSIAN.[24] On top, our own codes are implemented for the computation of relativistic effects and time-propagation information during the flip and transfer processes.[17–20]

A sketch of the optimized $[CoMg_2Ni\text{-}CO]^+$ cluster is shown in the inset of Fig. 1(a): two magnetic atoms (Ni and Co) and two nonmagnetic atoms (Mg) constitute the metallic part; CO is attached to the Ni atom. We add one unit charge to the whole structure since we focus on the magnetic ground state (triplet). Our calculations also show that the energetically low-lying states of the optimized cluster are triplets. Another important advantage of the charged cluster is that it can be easily produced and manipulated through mass selection in the gas phase. Thus the scenario clearly lies within experimental reach.

The geometry optimizations are carried out as follows: (i) the metallic part (without CO) is fully optimized within the restricted Hartree-Fock (RHF) approximation, and the normal modes and frequencies are calculated to confirm the minimum-energy geometry. (ii) The relaxation procedure is repeated with CO attached to the previously obtained structure (RHF). (iii) Further optimizations of the whole cluster, especially the local geometry of CO, are performed with the symmetry-adapted cluster configuration interaction (SAC-CI) methods.[25]

After the structural relaxation, the metallic part of the cluster consists of two adjacent triangles with a dihedral angle of about 170°. The magnetic centers occupy the antidiametric edges of this quasirhomb and together with the Ni-Co bond form an almost straight line, as shown in the inset of Fig. 1(a). The ten lowest triplet states for various CO bond lengths, calculated with the SAC-CI method, are shown in Fig. 2, where the dependence is evident: the energetic minima of the spin states not only lie at different C-O distances but their corresponding parabolas have also different curvatures, leading to different frequencies. This offers a unique opportunity to separate them through the IR spectrum of the respective systems. The IR shifts are typically on the order of 20–100 $cm^{-1}$. The energy difference between initial and final states is on the order of 20 K; thus, they can be selectively populated without substantial unwanted relaxations.

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 are selected as initial and final states for the flip scenario. A genetic algorithm is used for the optimization of the laser pulse.[19,26,27] Note that we do not concentrate only on several specific states but include all the magnetic states obtained from our high level (SAC-CI) calculations. This is also one of the reasons why we develop the genetic algorithm program to perform global search in order to find the suitable intermediate states. 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

TABLE I. Calculated CO frequencies for the clusters $[CoMg_2Ni\text{-}CO]^+$ and $[NiCo\text{-}CO]^+$ 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 for each of the two clusters.

| Cluster | State | Bond length (Å) | Frequency ($cm^{-1}$) |
|---|---|---|---|
| | 1 | 1.1561 | 2080 |
| $[CoMg_2Ni\text{-}CO]^+$ | 3 | 1.1550 | 2100 |
| | 5 | 1.1467 | 2264 |
| | 1 | 1.1518 | 2252 |
| $[NiCo\text{-}CO]^+$ | 3 | 1.1509 | 2257 |
| | 5 | 1.1514 | 2208 |

local spin flip on the Co end. The external magnetic field is almost perpendicular to the Ni-Co axis with a strength of $|B|=10^{-5}$ a.u. in order to lift the degeneracy of the triplet. A population transfer of 96.3% is achieved during the process. The properties of the linearly polarized laser pulse are $\theta=30.4°$, $\gamma=267.0°$, and $\phi=127.6°$ ($\theta$ and $\gamma$ denote the angles of incidence in spherical coordinates and $\phi$ denotes the angle between the polarization of the light and the optical plane) with the FWHM=260.8 fs of the pulse (FWHM is the full width at half maximum of the laser pulse).[28] Figure 1(b) clearly demonstrates nearly perfect spin switching within 500 fs.

To determine the CO frequencies for different spin states of $[CoMg_2Ni\text{-}CO]^+$ we divide the whole structure into three blocks: metallic part (M), carbon atom (C), and oxygen atom (O) (see inset of Fig. 2). This is necessary since the structure contains 6 atoms and has 12 normal modes apart from the rotational and translational degrees of freedom, an intractable problem at the SAC-CI level. Additionally a Hartree-Fock (HF) calculation of the normal modes shows that the CO frequency lies far away from the internal metallic-part modes, so they can be decoupled. To obtain the CO frequencies, we use the force matrix formalism along the CO bond direction. The forces are computed from the derivatives of the energies with respect to the displacements: the three blocks are moved by $5\times10^{-3}$ Å from their equilibrium positions along the CO bond direction, and the energies are calculated at the SAC-CI level. Thus a force constant matrix is set up, the eigenvalues of which give the frequencies. The three predicted CO frequencies at the corresponding optimized CO distances (Table I) exhibit clear dependence on the magnetic states.

We have demonstrated magnetic flip on the cluster $[CoMg_2Ni\text{-}CO]^+$, a necessity in order to design a nanoscale logic unit. The next step is to transfer the spin from one magnetic center to the other, which is very important in multifunctional magnetic logic devices. It is especially desirable to achieve spin switch and transfer on one unit. However we could not achieve spin transfer on this cluster. Both processes are now implemented on the bimetallic cluster $[NiCo\text{-}CO]^+$. The same method used for the cluster $[CoMg_2Ni\text{-}CO]^+$ is utilized to optimize the geometry and shows that CO prefers to bind to the Co site. The optimized

TABLE II. Energies and total spin and orbital angular momentum of some states of the $[NiCo\text{-}CO]^+$ cluster—SOC included. States marked bold are included in the spin transfer from Ni to Co.

| State | Energy (eV) | $\langle \mathbf{S}_{tot} \rangle$ | $\langle \mathbf{L}_{tot} \rangle$ | Spin localization |
|---|---|---|---|---|
| **80** | **4.2617** | **0.466** | **0.396** | – |
| ⋮ | ⋮ | ⋮ | ⋮ | ⋮ |
| 17 | 0.9954 | 0.823 | 0.789 | Co |
| **16** | **0.9941** | **0.823** | **0.789** | Co |
| 15 | 0.8236 | 0.829 | 0.006 | Ni |
| **14** | **0.8225** | **0.828** | **0.005** | Ni |

$[NiCo\text{-}CO]^+$ cluster is almost linear with the two bond angles of 172° for Ni-Co-C and 178° for Co-C-O. Further optimizations of the CO distance are also performed using the SAC-CI method for the ground state and two excited states, respectively. The frequency calculations show that the CO frequency shifts between certain electronic states are distinguishable and can be recognized by IR experiments (Table I).

Table II shows some low-lying triplet states and magnetic moments of the states of the cluster $[NiCo\text{-}CO]^+$, where the SOC and the effect of an external magnetic field are included. Strictly speaking, when including SOC, triplet and singlet are not good characterizations; however, for the low-lying states the expectation value of $\langle S^2 \rangle$ is close to 0 or 2. Although the spin localization is not as pronounced as in the previous case, both spin flip and transfer can be achieved. Since the spin-flip scenario is similar to the $[CoMg_2Ni\text{-}CO]^+$ case, here we show the spin transfer from one magnetic center to the other. States $|14\rangle$ and $|16\rangle$ exhibit spin localization at the Ni and Co atom, respectively, and serve as initial and final states for the transfer scenario. A perfect $\Lambda$ process starts ideally from a state energetically close to the ground state in order to be easier processed in experiment. Although

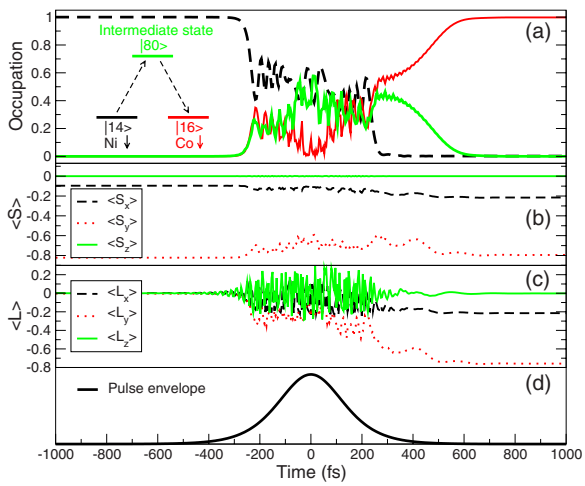


FIG. 3. (Color online) (a) Spin transfer from Ni to Co for $[NiCo\text{-}CO]^+$. The inset shows a sketch of the transfer scenario. (b) and (c) The time-resolved expectation values of the spin and orbital angular momentum components, respectively. (d) The laser pulse envelope for the transfer.

the selected two states are not so close to the ground state, their spin localization and energy difference are suitable for a $\Lambda$ process (Table II). As a prototype, the present model is sufficient to demonstrate the feasibility of our key idea. The laser pulse is optimized with the same genetic algorithm as above.[19] The population transfer between the initial state $|14\rangle$ and the final state $|16\rangle$ via only one intermediate state $|80\rangle$ is shown in Fig. 3(a). For this transfer, the external magnetic field is chosen to be almost perpendicular to the axis of the approximately linear structure with a strength of $|B|=10^{-5}$ a.u. to lift the degeneracy of the triplet. For this scenario a population transfer of 99.8% is achieved. The properties of the laser pulse are $\theta=65.3°$, $\gamma=261.7°$, $\phi=253.0°$, and FWHM=300.0 fs. The process is completed in the subpicosecond regime.

In conclusion, through first-principles calculations, laser-induced ultrafast magnetic manipulation is implemented in optimized two-magnetic-center clusters with CO attached to one of the magnetic centers. Time-resolved propagation of the spin density shows that the spin at the Co site of the cluster $[CoMg_2Ni\text{-}CO]^+$ can be flipped with linearly polarized light. In particular, a $[NiCo\text{-}CO]^+$ cluster is best suited for spin flip at Co and transfer from Ni to Co in a subpicosecond regime with linearly polarized light and external magnetic field.[29] Both spin flip and transfer are theoretically demonstrated on the same cluster. Furthermore, the predicted CO frequencies for certain magnetic states indicate that spin manipulation processes can clearly be monitored with IR experiments. The present theoretical prediction bears a close relationship to experiment and could serve as a reference for future investigations and applications of nanomagnetic-logic devices.

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[1] J. Berezovsky *et al.*, Science **320**, 349 (2008).
[2] A. M. Kalashnikova, A. V. Kimel, R. V. Pisarev, V. N. Gridnev, A. Kirilyuk, T. Rasing, Phys. Rev. Lett. **99**, 167205 (2007).
[3] E. Beaurepaire, J.-C. Merle, A. Daunois, and J.-Y. Bigot, Phys. Rev. Lett. **76**, 4250 (1996).
[4] J. Hohlfeld, E. Matthias, R. Knorren, and K. H. Bennemann, Phys. Rev. Lett. **78**, 4861 (1997).
[5] B. Koopmans, J. J. M. Ruigrok, F. Dalla Longa, and W. J. M. de Jonge, Phys. Rev. Lett. **95**, 267207 (2005).
[6] J. Chovan, E. G. Kavousanaki, and I. E. Perakis, Phys. Rev. Lett. **96**, 057402 (2006).
[7] G. P. Zhang and W. Hübner, Phys. Rev. Lett. **85**, 3025 (2000).
[8] R. Gómez-Abal, O. Ney, K. Satitkovitchai, and W. Hübner, Phys. Rev. Lett. **92**, 227402 (2004).
[9] A. V. Kimel *et al.*, Nature (London) **435**, 655 (2005).
[10] T. Lottermoser *et al.*, Nature (London) **430**, 541 (2004).
[11] M. I. Kurkin, N. B. Bakulina, and R. V. Pisarev, Phys. Rev. B **78**, 134430 (2008).
[12] V. V. Dobrovitski, M. I. Katsnelson, and B. N. Harmon, Phys. Rev. Lett. **84**, 3458 (2000).
[13] M. N. Leuenberger and D. Loss, Nature (London) **410**, 789 (2001).
[14] W. Hübner, S. P. Kersten, and G. Lefkidis, Phys. Rev. B **79**, 184431 (2009).
[15] R. Gómez-Abal and W. Hübner, Phys. Rev. B **65**, 195114 (2002).
[16] R. Gómez-Abal and W. Hübner, J. Phys.: Condens. Matter **15**, S709 (2003).
[17] G. Lefkidis and W. Hübner, Phys. Rev. B **74**, 155106 (2006).
[18] G. Lefkidis and W. Hübner, Phys. Rev. B **76**, 014418 (2007).
[19] T. Hartenstein, C. Li, G. Lefkidis, and W. Hübner, J. Phys. D **41**, 164006 (2008).
[20] G. Lefkidis and W. Hübner, J. Magn. Magn. Mater. **321**, 979 (2009).
[21] U. Kaiser, A. Schwarz, and R. Wiesendanger, Nature (London) **446**, 522 (2007).
[22] U. Schlickum, W. Wulfhekel, and J. Kirschner, Appl. Phys. Lett. **83**, 2016 (2003).
[23] G. Lefkidis and W. Hübner, Phys. Rev. Lett. **95**, 077401 (2005).
[24] M. J. Frisch *et al.*, in *GAUSSIAN 03, Revision B.03* (Gaussian Inc., Wallingford, CT, 2004).
[25] H. Nakatsuji *et al.*, http://www.sbchem.kyoto-u.ac.jp/nakatsuji-lab/sacci.html.
[26] R. S. Judson and H. Rabitz, Phys. Rev. Lett. **68**, 1500 (1992).
[27] B. Amstrup *et al.*, J. Phys. Chem. **99**, 5206 (1995).
[28] To achieve the $\Lambda$ process, linearly rather than circularly polarized light must be used, but a tilted magnetic field may always allow for it (see the details in Ref. 18).
[29] T. Hartenstein, *et al.*, J. Appl. Phys. **105**, 07D305 (2009).