Observation of Biradical Spin Coupling through Hydrogen Bonds

He, Yang; Li, Na; Castelli, Ivano E.; Li, Ruoning; Zhang, Yajie; Zhang, Xue; Li, Chao; Wang, Bingwu; Gao, Song; Peng, Lianmao; Hou, Shimin; Shen, Ziyong; Lu, Jing-Tao; Wu, Kai; Hedegard, Per; Wang, Yongfeng

Published in:
Physical Review Letters

DOI:
10.1103/PhysRevLett.128.236401

Publication date:
2022

Document version
Publisher’s PDF, also known as Version of record

Citation for published version (APA):
Observation of Biradical Spin Coupling through Hydrogen Bonds

Yang He,1 Na Li,1 Ivan E. Castelli,2 Ruoning Li,1 Yajie Zhang,1 Xue Zhang,1 Chao Li,1 Bingwu Wang,3 Song Gao,3 Lianmao Peng,1 Shimin Hou,1 Ziyong Shen,1 Jing-Tao Liu,5,* Kai Wu,3,†
Per Hedegård,5‡ and Yongfeng Wang1,6,‡

1Center for Carbon-Based Electronics and Key Laboratory for the Physics and Chemistry of Nanodevices, Department of Electronics, Peking University, Beijing 100871, China
2Department of Energy Conversion and Storage, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark
3Beijing National Laboratory for Molecular Science, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China
4School of Physics, Institute for Quantum Science and Engineering, and Wuhan National High Magnetic Field Center, Huazhong University of Science and Technology, 430074 Wuhan, China
5Niels Bohr Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark
6Beijing Academy of Quantum Information Sciences, Beijing 100193, China

(Received 16 September 2019; revised 9 February 2022; accepted 3 May 2022; published 6 June 2022)

Investigation of intermolecular electron spin interaction is of fundamental importance in both science and technology. Here, radical pairs of all-trans retinoic acid molecules on Au(111) are created using an ultralow temperature scanning tunneling microscope. Antiferromagnetic coupling between two radicals is identified by magnetic-field-dependent spectroscopy. The measured exchange energies are from 0.1 to 1.0 meV. The biradical spin coupling is mediated through O─H···O hydrogen bonds, as elucidated from analysis combining density functional theory calculation and a modern version of valence bond theory.

DOI: 10.1103/PhysRevLett.128.236401

Electron spin interactions play pivotal roles in both fundamental science and applied technology. Spin-related quantum effects have been intensively investigated in solid materials. Electron spins can couple via exchange, double exchange, superexchange, and conduction-electron-mediated Ruderman-Kittel-Kasuya-Yosida interactions. Scanning tunneling microscope (STM) is a powerful tool to investigate spin properties for its capability of high-resolution spectroscopy at the single-atom level [1,2]. Spin interactions between magnetic metal atoms were intensively investigated by STM [3–7]. Data storage and logic operation have been realized based on the manipulation of spin states of nanometals [8,9].

By probing Kondo resonance and spin excitation, magnetic properties of organic molecules were characterized using STM [10–16]. Intermolecular spin interactions were rarely investigated even though they are of fundamental importance [17]. The hydrogen bond is an unique attractive interaction in molecular crystals and biological structures. Spin couplings through hydrogen bonds have been studied by electron spin resonance and magnetic neutron diffraction [18]. These methods average out spectroscopic signals from a large number of molecules, including their mutual interactions. The experimental investigation at the single-molecule level has not been reported.

All-trans retinoic acid [ReA, Fig. 1(a)] can be transited into a radical via biphotonic processes [19]. Here, we use a low-temperature STM to construct radical pairs of ReA molecules on Au(111). The spin generation, spin distribution, and exchange interaction of radical pairs are studied by a combination of STM and density functional theory (DFT) calculations [20–23]. The singlet ground state of the hydrogen-bonded radical pair is determined and the exchange energy ranges from 0.1 to 1.0 meV. Analysis based on a modern version of valence bond theory (VBT) reveals that the biradical superexchange antiferromagnetic (AFM) coupling is mediated by hydrogen bonds.

The experiments are performed using an ultrahigh vacuum scanning tunneling microscope (UNISOKU USM-1300-He) with magnetic field up to 11 T. Single crystalline Au(111) (MaTecK GmbH) surfaces are cleaned by cycles of Argon ion sputtering and annealing. ReA molecules (Sigma Aldrich) are evaporated from a homemade tantalum boat onto Au(111) kept at room temperature. The measurements are conducted at 0.5 to 0.6 K with an etched tungsten tip. Differential conductance (dI/dV) spectra are collected by a lock-in amplifier with the modulation voltage of 0.06 mV. All STM images are slightly processed using the software of WSxM [24].

ReA molecules interact with each other mainly through O─H···O hydrogen bonds, as shown by the optimized model of a ReA dimer [Fig. 1(a)]. At high coverage, ReA molecules arrange themselves in parallel dimers [Fig. 1(b)] [25]. The molecular bulky 1,3,3-trimethylcyclohexene group appears as the highest protrusion, denoted as head
yields the Zeeman splitting as a function of magnetic field. A linear fit between singlet and triplet states in magnetic fields. (h) Extracted vertically shifted for clarity. (g) Illustration of spin transitions solid color curves represent fits of the spectra. All plots are state A field-dependent −

ReA radical pair. (a) Chemical structure of a ReA dimer. (b) FIG. 1. Formation and characterization of a hydrogen-bonded ReA radical pair. (a) Chemical structure of a ReA dimer. (b)–(d) STM images showing the formation process of a ReA radical pair. The molecular nonmagnetic, spin-carrying, and spin-coupled states are denoted by U, A, and A′, respectively. Imaging parameters: (b) V = −4 mV, I = 16 pA; (c) V = −10 mV, I = 16 pA; (d) V = −10 mV, I = 16 pA. The sizes of all three STM images are 4.5 × 4.5 nm². (e) dI/dV spectra measured over the centers of molecular bulky heads of different states (U, A, A′, A″). The STM is operated at V = 11 mV and I = 0.5 nA before opening the current feedback loop when taking constant-height spectroscopic measurements. (f) Magnetic-field-dependent dI/dV spectra recorded on the head group of state A′ with the set point of −5.7 mV and 1.2 nA. In both (e) and (f), all black dotted curves were experimentally obtained and solid color curves represent fits of the spectra. All plots are vertically shifted for clarity. (g) Illustration of spin transitions between singlet and triplet states in magnetic fields. (h) Extracted Zeeman splitting as a function of magnetic field. A linear fit yields the g = 1.7.

group. The rest of the molecule, 3,7-dimethylnona-2,4,6,8-tetraanoic acid, appears lower and is denoted as polyene. ReA molecules could be switched to spin-carrying states by positioning the tip over the molecular bulky heads and shifting the sample voltage from −2.0 to −2.8 V with current feedback disabled [26]. After switching the ReA molecule (marked by U) to a spin-carrying state (marked by A), the head group appears as an elliptical protrusion and is around 50 pm higher than others [Fig. 1(c)]. As in the previous Letter [26], the molecule can be further switched to two other magnetic states, which are presented in Fig. S1 in the Supplemental Material (SM) [27]. The dI/dV spectra measured over centers of the molecular bulky heads of U and A states are presented in Fig. 1(e). The spectrum of U state is featureless. Meanwhile, the spectrum of the switched A state shows a zero bias resonance. We attribute the resonance to Kondo effect resulting from screening of the molecular spin by the conducting electrons of Au(111) [28]. The spectrum is fitted by Frota function and the fitted Kondo temperature is 4.7 K [29,30], which gives a better fitting than the perturbation approach (Fig. S2 in the SM) [31–33]. Interestingly, a molecule in state A further changes to state A′ when its partner molecule in a dimer is switched to the A″ state by the same procedure [Fig. 1(d)]. Correspondingly, a small voltage gap is observed in the dI/dV spectrum [Fig. 1(e)]. A similar spectrum is obtained on the paired A″-state molecule [Fig. 1(e)].

The gapped spectra originate from the singlet-triplet spin transition, which can be well interpreted by the two-impurity Anderson model. There are two electron spins in one ReA radical pair. A competition arises between screening of molecular spin by conducting electrons and intermolecular spin coupling. The former process favors the formation of a Kondo state, while the latter prefers to form a singlet or triplet state via AFM or ferromagnetic coupling. The evolution of dI/dV spectra in magnetic fields confirms that two electron spins form a local singlet in the radical pair. Figure 1(f) shows a series of spectra recorded on the head group of ReA in state A″ with the field strength up to 11 T. When increasing the strength of magnetic field, the zero-bias gap gradually splits and a clear threefold splitting is observed when the field reaches 11 T. The energy gaps in the spectra correspond to spin transitions from the ground singlet state (S = 0; m = 0) to triplet excited states (S = 1; m = 1, 0, −1), as schematically shown in Fig. 1(g). All spectra of spin transitions are fitted using the scattering theory proposed by Appelbaum et al., revised and implemented by Ternes [33]. Since there is still a strong spin-flip Kondo scattering at the spin excitation step at the low experimental temperature, we have replaced the logarithmic function by the Frota function in the fitting, which provides a better fitting of the spectra at the two steps [34]. The Hamiltonian is

\[ H = \sum_{i=A',A''} g \mu_B \mathbf{B} \cdot \mathbf{S}_i + J \mathbf{S}_i \cdot \mathbf{S}_i', \]

Here, the index i represents molecules in the dimer, J is the Heisenberg exchange coupling, g is the Landé g factor, and \( \mu_B \) is the Bohr magneton. For B = 0, we get J = 1 meV from the fitting. An average effective g factor, g = 1.7, is extracted by fitting the magnetic-field-dependent spectra [Fig. 1(b)]. All other fitting parameters are listed in Fig. S3 in the SM.

When two ReA radicals are not connected through hydrogen bonds, only the Kondo resonance of single ReA radical is observed. One example is shown in Fig. 2(a), where two ReA molecules packed side by side are manipulated to magnetic A states. The measured spectra

236401-2
at different positions have not shown any feature of spin coupling [Fig. 2(b)]. The fitted Kondo temperatures of the spectra are presented in Fig. S4 in the SM. The \( \frac{dI}{dV} \) measurements at 11 white-dotted positions marked in Fig. 2(c) indicate that the electron spin is delocalized on the ReA radical [Fig. 2(d)]. The spin delocalization has been reported for other organic molecules [35–38]. The fitted asymmetric factors and Kondo temperatures are listed in Fig. S5 in the SM. The spin delocalization is found for all ReA radicals and the related measurements for two other single ReA radicals and one radical dimer are presented in Figs. S6 and S7 in the SM. The spin delocalization allows spin coupling through hydrogen bonds. In the following, we perform DFT calculations [27] and VBT analysis to elucidate the mechanism of spin delocalization, position-dependent Kondo spectra of sing ReA radical and spin coupling of a ReA radical pair through hydrogen bonds.

The dehydrogenation process has been used to generate spin on the graphene nanostructure [39]. In a previous report, a magnetic ReA molecule was considered as a radical that was generated by H-atom transfer and sigmatropic reaction [40]. However, the mechanism leads to a localized spin. Here, we propose another possible activation mechanism that involves only the transfer of H atom from ReA to Au(111) [Fig. 3(a)]. A neutral radical is formed after losing the hydrogen atom at the radical carbon position, as shown in Fig. 3(b). The calculated activation barrier is roughly 3 eV (Fig. S8 in the SM). A delocalized spin distribution is found on the ReA radical (Fig. S9 in the SM). The calculated spin density at each atom of a ReA radical on Au(111) is represented with red arrows of different length in Fig. 3(c). The values are listed in Table 1 in the SM. From molecular head to the carboxyl group, the spin densities of six carbon atoms marked by red spin-up arrows [Fig. 3(c)] are 0.19, 0.24, 0.21, 0.18, 0.17, and 0.13, which show a clear decay. After removing the H atom, the reactive C atom interacts more strongly with the substrates than other atoms. For these two reasons, the amplitude of Kondo resonance decays from molecular head to the carboxyl group. The oscillatory behavior of the Kondo peak originates from the stronger amplitude of spectra at methyl group compared with other positions, which might be due to structure dependent molecule-substrate coupling. The asymmetric factor \( \phi \) is determined by the ratio between the electron tunneling into the Kondo resonance and substrate. So, position-dependent spin density and coupling between ReA and Au(111) are tentatively suggested to interpret why the fitted asymmetry factor and Kondo temperature (Fig. S3 in the SM) are not constant. Two ReA radicals form a singlet ground state via AFM interaction [Fig. 3(d)]. The calculated exchange energy of
the optimized dimer is 0.50 meV, which nicely matches the experimental result ranging from 0.1 to 1.0 meV (Fig. S11 in the SM).

Furthermore, the analysis based on a modern version of VBT [41–44] reveals the physical nature of biradical spin coupling. A brief introduction about the theory is shown in the section of valence bond theory in the SM (Figs. S12 to S15). The ReA radical is conjugated and one of its resonant formulas is shown in Fig. 4(a). Only the marked part of the ReA radical is used in the VBT model [Fig. 4(b)], which simplifies the theoretical analysis. A total of nine valence bond states are displayed in Fig. 4(c). A red line represents a singlet electron pair residing on the atoms at the ends of the line. The electron spin can move to two oxygen atoms in the $\text{COOH}$ group and their spin polarities are the same as that of the ReA radical.

The order of exchange energy can be estimated from the VBT. The biradical spin coupling acts as a perturbation to the uncoupled molecules. The theory includes hopping terms between $p_z$ orbitals and Coulomb interaction between charged atoms. The effective Hamiltonian coupling the $\pi$ system in the O–H$\cdots$O hydrogen bond [Fig. 4(d)] is

$$H_{\text{exch}} = -J_H \left( \frac{1}{4} - \vec{S}_1 \cdot \vec{S}_2 \right).$$  \hspace{1cm} (2)

Here, the exchange coupling parameter $J_H$ is given by

$$J_H = \frac{12t_1^2 t_2^2}{(E_1 - E)(E_2 - E)(E_3 - E)},$$  \hspace{1cm} (3)

where $E_i$ ($i = 1, 2, 3$) is the energy of the intermediate state and $E$ is the energy of the unperturbed ground state. The constant is positive, resulting again in an AFM exchange coupling across the hydrogen bond. It is exponential in the distance between atoms, which is the reason why an exponentially decaying exchange coupling is found in the DFT result (Fig. S10 in the SM). We use $\vec{S}_1$ ($\vec{S}_2$) and $\vec{S}_a$ ($\vec{S}_b$) to represent the spin operators of the oxygen atom and whole ReA radical, respectively. The Wigner-Eckard theorem ensures that these two operators are proportional. The proportionality constant can be determined by evaluating their expectation value in the ground state of the molecules. We get $\vec{S}_1 = M_1 \vec{S}_a$, with $M_1 = 2\langle \vec{S}_1 \rangle$. The coupling between two ReA radicals through hydrogen bonds thus becomes

$$H_{\text{exch}} = -J_H M_1 M_2 \left( \frac{1}{4} - \vec{S}_a \cdot \vec{S}_b \right).$$  \hspace{1cm} (4)
In vacuum, the spin densities of two oxygen atoms are 0.056 and 0.013 (Table 1 in the SM), respectively. An extra factor 2 is introduced because there are two hydrogen bonds in a dimer. Therefore, the singlet-triplet splitting energy is around $2J_H \times 2 \times 0.056 \times 2 \times 0.013 = 0.0058J_H$. When comparing to DFT calculated exchange energy of 0.5 meV, we estimate the value of $J_H$ is roughly 0.1 eV. When considering the molecule-surface interaction, the spin densities of carbonyl and hydroxy oxygen atoms reduce to 0.035 and 0.008, which leads to an exchange energy reduction from 0.5 meV in vacuum to 0.22 meV on Au(111).

In summary, biradical spin coupling through hydrogen bonds has been studied by a combination of LT STM, DFT calculations, and VBT analysis. The AFM interaction between two ReA radicals is identified by magnetic-field-dependent spectroscopy. The measured exchange energies range from 0.1 to 1.0 meV, which are in agreement with the DFT calculated results. The VBT analysis reveals that spin coupling in ReA radical pairs is through $\text{O} \cdots \text{O}$ hydrogen bonds via superexchange processes. This work provides a way to study spin properties of single radial pairs.

This work was supported by the Ministry of Science and Technology (Grants No. 2017YFA0050003, 2017YFA0050004, 2017YFA0050005, and 2017YFA0050006) and National Natural Science Foundation of China (Grants No. 21433011, 91527303, 21522301, 21523033, and 2162501). This work provides a way to study spin properties of single radial pairs.

Y. H., N. L., I. E. C., and R. N. L. contributed equally to this work.

*Corresponding author. jilha@hust.edu.cn
†Corresponding author. kaiwu@pku.edu.cn
‡Corresponding author. hedegard@nbi.ku.dk
§Corresponding author. yongfengwang@pku.edu.cn


[27] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.128.236401 for three manipulated magnetic states of ReA molecules; Method of fitting Kondo spectra; Position-dependent dI/dV spectra of magnetic ReA radicals; Details of DFT calculation and VAT analysis; Exchange energies of different ReA-radical pairs.


