Electronic Supplementary Information for : Experimental and Theoretical Investigations on the Negative Influence of an Applied Magnetic Field on SERS of Ag nanoparticles

Experimental Section

All reagents were of analytical grade and were used as received without further purification. 0.5 g of polyvinylpyrrolidone (PVP, K-30) and 0.1 g of AgNO₃ were dissolved in 20 ml distilled water in dark. Subsequently, 30 ml ethylene glycol was added dropwise into the solution under stirring. Then the mixture was transferred into a Teflon-lined autoclave with a capacity of 50 ml and heated to and maintained at 170 °C. After 10 h, the autoclave was cooled naturally to room temperature. The products were collected and rinsed with distilled water and ethanol several times, and then dried in a vacuum oven at 60 °C for 6 h. A Rhodamine 6G aqueous solution at a concentration of 10^{-8} mol/L of was prepared. 0.03 g of the product was loaded on a clean glass slide, making a SERS substrate. Then the SERS signals were detected by adding 50 μ L of R6G solution on the substrate.

Computational Details

All the quantum chemical calculations were performed using Gaussian 09 suite software.[1] It was hard to introduce MF in Gaussian 09. Here we devised a new method to settle this problem. As known to all, the magnetism of transition atom originated in its unpaired d electrons. So it was available to adjust Ni atom's multiplicity (M) to control the number of its unpaired electrons, and then to bring MF. We selected Ag-Ni to construct a two atoms cluster. The M of Ni was changed from 2 to 4 to alter its magnetism and the mulliken atomic spin densities were shown in Table S1. The ground state geometries of pyridine-Ag-Ni (both M=2 and M=4) were optimized by density functional theory (DFT) with the B3LYP functional and there were no imaginary frequencies ensuring our structures were stable. The 6-311+G** basis set which supplemented the polarization functions to C, N and H and the diffuse function to C and N atoms was used for C, N, H atoms and LanL2DZ was selected for Ag, Ni atoms. The Raman scattering factors and orbital electron energy were calculated by pre-resonance and Natural Bond Orbital (NBO), respectively. In this work, we did not use any scale factors in calculation of Raman spectra for only their relative value were meaningful.

Reference:

[1] Gaussian 09, Revision B.01,M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.



Figure S1 XRD pattern of this sample



Figure S2 SEM of this sample



Figure S3 Raman spectra of the sample using R6G as probe molecules. Spectrum measured before a magnetic field applied (A), with a 0.15 T magnetic field applied (B) and then removing the magnetic field (C). Inset: the magnification spectra between 1300 and 1700 cm⁻¹.



Figure SS3 Subtracting Raman spectra of FigureS3. Red line stands for spectrum B - spectrum A. Black line stands for spectrum B – spectrum C. The peaks are all adown, which means that the peaks of spectrum B (with applied magnetic field) are weaker than those of spectrum A (before applying magnetic field) or spectrum C (after removing magnetic field)



Figure S4 The optimized structure of pyridine-Ag-Ni. Inset table is the Ag-N bond distance of doublet and quartet.



Figure S5 Mulliken charge distribution at ground state for pyridine-Ag-Ni of doublet and quartet.



Figure S6 Calculated NRS spectroscopy of (a) isolated pyridine, (b) pyridine-Ag-Ni of doublet, (c) pyridine-Ag-Ni of quartet.



Figure S7 Calculated pre-resonance Raman spectrum of (a) pyridine-Ag-Ni of doublet, (b) pyridine-Ag-Ni of quartet. The wavelength of incident light is 540nm.

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Figure S8 Natural bond orbital calculation result of the α spin orbitals.

	Doublet	Quartet
1 Ni	1.068201	2.444732
2 Ag	-0.066269	0.510449
3 N	-0.008148	-0.007650
4 C	-0.000750	0.002378
5 C	0.002642	0.027724
6 C	0.002776	-0.018871
7 C	0.002644	0.027797
8 C	-0.000744	0.002182
9 H	0.000003	0.000279
10 H	-0.000130	0.004333
11 H	-0.000047	0.001158
12 H	-0.000047	0.001157
13 H	-0.000130	0.004333

Table S1 Calculated Mulliken atomic spin densities of doublet and quartet in units of au.

Modes	Doublet	Quartet
v6a	12053.9 (635.3)	4826.5 (628.7)
v1	81325.3 (1024.6)	5154.6 (1019.2)
v12	6628.0 (1050.4)	3933.4 (1047.2)
v9a	168924.1 (1240.1)	16630.4 (1237.7)
v8a	414283.1 (1635.9)	7993.9 (1631.7)

Table S2 Calculated pre-resonance Raman scattering activities in Units of $Å^4$ /amu and according frequencies (in Parentheses) in Units of cm⁻¹.