Electronic Supplementary Information for:

Photon-Driven Charge Transfer and Photocatalysis of p-Aminothiophenol in Metal Nanogaps: A DFT Study of SERS

De-Yin Wu,*[a] Liu-Bin Zhao[a], Xiu-Min Liu[a], Rong Huang[a], Yi-Fan Huang[a], Bin Ren[a], and Zhong-Qun Tian[a]

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X
First published on the web Xth XXXXXXXXX 200X
DOI: 10.1039/b000000x

Computational Details

DFT calculations were carried out with the hybrid exchange-correlation functionals, such as B3LYP [1, 2] for PATP-metal cluster complexes. The generalized gradient approximation (GGA) for exchange-correlation functionals PW91PW91[3] was used for DMAB. The main reason is due to that the N=N bond in DMAB is very sensitive to theoretical functionals, significantly influencing peak frequencies and relative Raman intensities in simulated Raman spectra of DMAB.[4] The basis sets for C, N, S and H atoms of PATP and DMAB were 6-311+G(d, p), which included a polarization function to all four kinds of atoms and a diffuse function to the C, N and S atoms.[5, 6] For Ag and Au atoms, the valence electrons and the inner shells were described by the basis set of LANL2DZ, and the corresponding relativistic effective core potentials, respectively.[7, 8] Full geometry optimizations and analytic frequency analysis were carried out by using Gaussian 03 package.[9]

All the fundamental vibrational bands were assigned on the basis of the scaled quantum mechanics force field (SQMF) procedure [10]. We chose the scaling factors of 0.935 for N-H and C-H bonds as well as 0.963 for the other internal coordinators to the force constant matrix calculated at the B3LYP/6-311+G** level. For DMAB the vibrational frequencies calculated at the PW91PW91 level have not been scaled here due to a good agreement with the observed frequencies. Absolute Raman intensities were calculated on top of the differential Raman scattering cross section (DRSC) from the Raman scattering factors (RSF) under the double-harmonic approximation, as published in our previous works.[11] In order to make direct comparison with the SERS experiments, the simulated Raman spectra were presented in terms of the Lorentzian expansion of the DRSC magnitudes. The frequency-dependent RSF magnitudes were calculated by using the coupled perturbation Hartree-Fock (CPHF) methods.[12]

References:

1. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
2. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
3. J. P. Perdew, K. Burke and Y. Wang, *Phys. Rev. B*, 1996, **54**, 16533.
4. D. Y. Wu, X. M. Liu, Y. F. Huang, B. Ren, X. Xu and Z. Q. Tian, *J. Phys. Chem. C*, 2009, **113**, 18212-18222.
5. A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639.
6. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 650.
7. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.
8. P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
9. M. J. Frisch, G. W. Trucks, H. B. Schiegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, T. Vreven, Jr., K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. J. Salvador, J. Dannenberg, V. G.

Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Rahgavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, B. A. G., S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, Editon edn., 2003.

10. P. M. Kozlowski, T. S. Rush, A. A. Jarzecki, M. Z. Zgierski, B. Chase, C. Piffat, B. H. Ye, X. Y. Li, P. Pulay and T. G. Spiro, *J. Phys. Chem. A*, 1999, **103**, 1357-1366.
11. D. Y. Wu, X. M. Liu, S. Duan, X. Xu, B. Ren, S. H. Lin and Z. Q. Tian, *J. Phys. Chem. C*, 2008, **112**, 4195-4204.
12. P. Pulay, *J. Chem. Phys.*, 1983, **78**, 5043.