

# Experimental and theoretical evidence for the chemical mechanism in SERRS of rhodamine 6G adsorbed on colloidal silver excited at 1064 nm

Bin Dong,<sup>a,b</sup> Liwei Liu,<sup>c</sup> Hongxing Xu<sup>a,d</sup> and Mengtao Sun<sup>a\*</sup>



The evidence for the existence of a chemical mechanism in surface-enhanced resonance Raman scattering (SERRS) of rhodamine 6G (R6G) adsorbed on colloidal silver excited at 1064 nm is reported on the basis of experimental and theoretical analyses. A weak absorption peak at around 1060 nm for R6G-functionalized silver nanoparticles was observed, which is not present in the individual spectra of R6G or silver nanoparticles. Theoretically, the charge difference density reveals that this weak absorption is a metal-to-molecule charge transfer excited state. Copyright © 2010 John Wiley & Sons, Ltd.

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**Keywords:** SERS; chemical mechanism; 1064 nm; charge transfer excited state

## Introduction

Since the discoveries of surface-enhanced Raman scattering (SERS) and surface-enhanced resonance Raman scattering (SERRS), the mechanisms of electromagnetic (EM) and chemical enhancement via charge transfer (CT) have been widely accepted.<sup>[1,2]</sup> The coupling of metals at suitable distances produces EM enhancements which give rise to SERS signal enhancements reaching values as high as  $10^{11}$ .<sup>[3]</sup> Because of the interaction between molecules and metals, the intensity of the signal can be enhanced by a factor of up to  $10^4$ – $10^6$ , when the wavelength of the radiation is close to an electronic excitation of the molecule–metal system, which is referred to as SERRS via CT between the molecule and metal.<sup>[4,5]</sup> In fact, it is not easy to experimentally distinguish the CT mechanism from the EM mechanism in SERS or SERRS. In this article, we report experimental and theoretical evidence for the existence of chemical mechanism in SERRS of rhodamine 6G adsorbed on colloidal silver excited at 1064 nm.

## Experimental

The SERS-active silver colloid was prepared according to the process specified in Ref. [6]. The Ag particle concentration was estimated to be  $\sim 35$  pM with an average diameter of around 100 nm.<sup>[7]</sup> R6G ( $5 \times 10^{-6}$  M) was dissolved in the water and silver sol solution, respectively, and the absorption spectra were measured using a UV–VIS spectrometer (Cary 5000). A 50- $\mu$ l volume of R6G ( $5 \times 10^{-4}$  M) was added to a 5-ml silver sol solution (R6G in silver sol is  $5 \times 10^{-6}$  M) which was dropped and allowed to dry on a glass slide. The Raman spectra were obtained with an RFS 100/s Bruker NIR-FT spectrophotometer using an operating wavelength of 1064 nm. The maximum resolution of this instrument was  $3 \text{ cm}^{-1}$ , and a  $180^\circ$  geometry was employed.

All quantum chemical calculations were performed using Gaussian 03 suite.<sup>[8]</sup> The detailed calculations and methods are described in the supporting information. The orientation of CT was visualized with charge difference density.<sup>[9]</sup>

## Results and Discussion

Figure 1(a) and (b) shows the experimental normal Raman spectrum of R6G powder and the SERS spectrum of R6G adsorbed on the silver nanoparticles using an excitation wavelength of 1064 nm. It is found that these two profiles are similar. Experimentally, we measured the absorption spectra of R6G, silver colloid, and R6G with silver colloids, respectively, in the 250–1300 nm wavelength range (Fig. 2(a)). One can see that at around 1060 nm, there is a weak absorption peak for R6G-functionalized silver nanoparticles, which is not present in the individual spectra of R6G or silver nanoparticles. Thus we conclude that the weak absorption peak at around 1060 nm for R6G-functionalized silver nanoparticles arises from the interaction between silver and the N atoms of R6G, which is a new CT electronic excitation state. The Raman spectrum obtained from R6G adsorbed on silver nanoparticles using an incident light of 1064 nm should be SERRS enhanced by chemical mechanism via CT.

To confirm the experimental result shown above, the absorption spectrum of the R6G–Ag<sub>2</sub> complex was calculated using time-dependent density functional theory.<sup>[10]</sup> Depending on the nature of the interaction between R6G and silver, new CT excited states can occur. The calculated optical absorption spectrum of R6G–Ag<sub>2</sub>

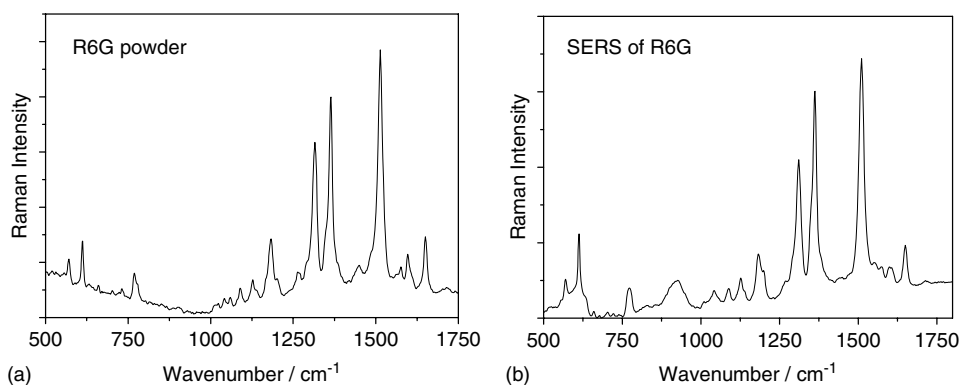
\* Correspondence to: Mengtao Sun, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, P. O. Box 603-146, Beijing 100190, P. R. China. E-mail: mtsun@aphy.iphy.ac.cn

a Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, P. R. China

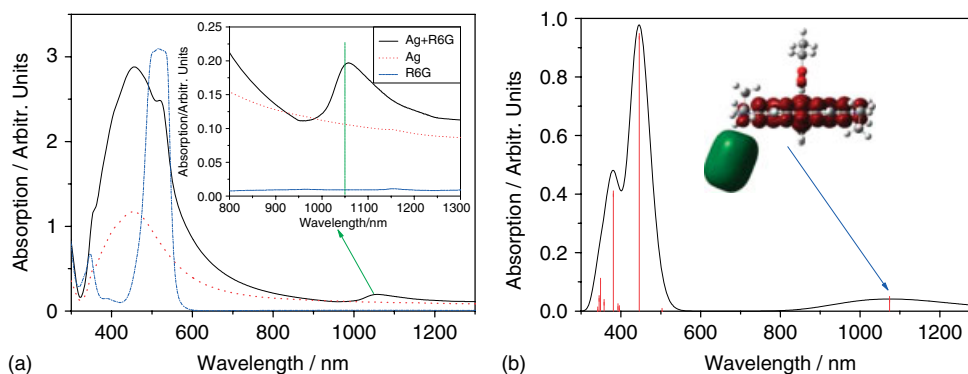
b School of Science, Dalian Nationalities University, Dalian 116600, P. R. China

c Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215125, P. R. China

d Division of Solid State Physics, Lund University, Lund 22100, Sweden



**Figure 1.** (a) Raman spectrum of R6G powder and (b) SERS of R6G using an incident light of 1064 nm.



**Figure 2.** (a) The absorption spectra of R6G, silver colloid and R6G with silver colloids from 300 to 1300 nm, where the inset shows the absorption spectra of those from 800 to 1300 nm; and (b) the calculated optical absorption of R6G–Ag<sub>2</sub> cluster, where the green and red colours indicate hole and electron, respectively, in the inset.

reveals the weak absorption peak at around 1064 nm (Fig. 2(b)). The charge difference density in the inset of Fig. 2(b) reveals that this excited state is a pure metal-to-molecular CT-excited state (electrons transfer from Ag<sub>2</sub> to R6G; see Fig. 2(b)), since all the holes and electrons are localized on the Ag<sub>2</sub> cluster and the R6G molecule, respectively. Because the electrons on the Ag<sub>2</sub> cluster are equally transferred to the xanthene group of R6G without any orientation using the incident light of 1064 nm, the profiles of the Raman spectra in Fig. 1(a) and (b) are almost the same.

## Conclusion

We have provided experimental and theoretical evidence for the existence of chemical mechanism in SERRS of R6G adsorbed on colloidal silver excited at 1064 nm. The weak absorption at around 1064 nm was observed experimentally, and the charge difference density reveals that it is a pure metal-to-molecular CT excited state.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No: 10874234, 20703064, 90923003 and 1080401) and the National Basic Research Program of China (Grant No: 2009 CB930701).

## Supporting information

Supporting information may be found in the online version of this article.

## References

- [1] M. Moskovits, *Rev. Mod. Phys.* **1985**, *57*, 783.
- [2] A. Otto, I. Mrozek, H. Grabhorn, W. Akemann, *J. Phys. Condens. Matter* **1992**, *4*, 1143.
- [3] H. X. Xu, E. J. Bjerneld, M. Kall, L. Borjesson, *Phys. Rev. Lett.* **1999**, *83*, 4357.
- [4] L. L. Zhao, L. Jensen, G. C. Schatz, *Nano Lett.* **2006**, *6*, 1229.
- [5] L. L. Zhao, L. Jensen, G. C. Schatz, *J. Am. Chem. Soc.* **2006**, *128*, 2911.
- [6] P. C. Lee, D. Meisel, *J. Phys. Chem.* **1982**, *86*, 3391.
- [7] H. X. Xu, M. Käll, *ChemPhysChem* **2005**, *4*, 1001.
- [8] 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, 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, D. J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, **2009**.
- [9] M. T. Sun, S. Liu, M. Chen, H. X. Xu, *J. Raman Spectrosc.* **2009**, *40*, 137.
- [10] E. K. U. Gross, W. Kohn, *Phys. Rev. Lett.* **1985**, *55*, 2850.