



CHEMICAL EDUCATION

SURFACE ENHANCED RAMAN SCATTERING

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ABSTRACT

Surface Enhanced Raman Scattering is an important spectroscopic tool for studying molecules adsorbed on noble metal surfaces. The electromagnetic enhancement mechanism and charge transfer mechanism theories are discussed.

Key words : Surface Enhanced Raman Scattering (SERS)

INTRODUCTION

Surface Enhanced Raman Scattering (SERS) was first demonstrated by Fleischmann et al.¹ in 1974¹. In a study of the adsorption of pyridine at a silver electrode, they noted that the Raman scattering was considerably stronger when the surface of the electrode was roughened. In the works of Albrecht and Creighton² and Jeanmaire and Van Duyne³, it was independently proposed that the increase of the scattering intensity could not be a consequence of the increase of the number of scatterers present in the surface, but it occurred due to the adsorption of the molecules on the metal surface. Jeanmaire and Van Duyne³ proposed an electric field enhancement mechanism whereas according to Albrecht and Creighton², the origin of the enhancement might be the Resonance Raman Scattering from molecular electronic states broadened by the interaction of the molecules with the surface. There exist many papers and reviews describing the experimental results using SERS and its developments^{4–13}. It was shown^{14,15} that there are two major types of mechanisms of the SERS effects – (i) the electromagnetic effect and (ii) the charge transfer mechanism (or the chemical effect).

Electromagnetic (EM) enhancement mechanism

In the EM model, the properties of the surface itself undoubtedly play very important roles in SERS. The creation of the surface plasmons – the collective excitations of the surface conduction electrons in metal by the incident photon provide the main contribution to the electromagnetic enhancement. The metal becomes highly polarizable resulting in the large field

– induced polarizations and therefore, large local fields on the surface at the plasmon frequency. The Raman emission intensity, which is proportional to the square of the applied electric field at the molecules is increased by these local fields. The excitation of the surface plasmon by the Raman emitted photon also creates the additional enhancement. There exist many types of electromagnetic enhancement mechanisms which occur either in the presence or in the absence of radiation field beside of the surface plasmons. In general due to the electromagnetic effect the Raman cross-section for a molecule on a surface may be enhanced¹⁶ by factors up to 10^6 . When the SERS effect is combined with an optical resonance in the molecule, even larger factors were observed⁸.

A molecule adsorbed on a single metal particle embedded in a homogeneous medium is the simple model of the EM effect^{17–20}. In this model the enhancement results from two main mechanisms : (i) due to the addition of a field caused by the polarization of the metal particle, the incident electromagnetic field acting on the molecule is increased and (ii) the molecule polarizes the metal particle acting as an antenna and amplifying the Raman scattered radiation. In the case of the first mechanism, the electric field E_{in} inside the spherical particle is related to

the applied electric field E_0 by $E_{in} = \frac{\epsilon(\omega) - \epsilon_0}{\epsilon(\omega) + 2\epsilon_0} E_0$

where $\epsilon(\omega)$ and ϵ_0 are dielectric constants of the bulk metal and the surrounding medium, respectively, but $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$. When there is resonance with the plasmon frequency $\epsilon_1(\omega) + 2\epsilon_0 = 0$, the value of E_{in} is maximum. In addition, if $\epsilon_2(\omega)$ is very small, then the enhancement occurs. The surface plasmons in the metal particle enhance incident electromagnetic field and the scattered Raman radiation. There exist other types of electromagnetic enhancement mechanisms, beside the enhancement due to the surface plasmons : the “lighting rod” effect^{21,22}, the image effect^{23,24} and the Fresnel reflection effect. A review of the mechanisms of the electromagnetic effect was given by Moscovits²⁵.

Charge transfer mechanisms (Chemical effect)

The chemical enhancement due to the charge transfer mechanism operates independently of the electromagnetic mechanism²⁶. The charge transfer mechanisms are associated with the overlap of the wave functions of the electron in the metal and the electron in the adsorbate molecule resulting in the tunneling of electrons between the metal and the molecule. As a result, a negative ion (electron–molecule complex) is produced. This electron transfer is called chemical effect and if the energy of the negative ion is in resonance with the incident photon then the enhancement occurs. Different charge transfer mechanisms have been proposed. The mechanism proposed by Chang²⁷ involves the following steps:

1. An incident photon creates an electron–hole pair in the metal.

2. The electron of this pair transfers to the excited state electronic level of the adsorbate via tunneling for physisorbed adsorbates or via hybridization for chemisorbed adsorbates.
3. The electron from the excited level comes back to the metal into a state with lower energy in comparison with the electron simultaneously created together with the holes, leaving the adsorbate in the higher vibrational level.
4. The recombination of the electron from this lower state with the hole resulting in the emission of a photon with lower energy.

There exist also other chemical effect mechanisms with the transfer of an electron between the adsorbed molecule and the metal.

- (a) The incident photon excites an electron from the molecular ground state upward shifted and broadened due to the chemisorption to an unoccupied metal state above the Fermi level by the intermediate of some excited molecular state²⁸.
- (b) The incident photon excites an electron in a partially filled molecular state in the vicinity of the Fermi level to a vacant metal state through the intermediate of the states in the occupied part of initial partially filled molecular state²⁹.
- (c) The incident photon excites an electron from the metal with the energy near the Fermi level to an excited state of the negative electron-molecule complex³⁰.

REFERENCES

1. M. Fleischmann, P. Hendra and A.J. McQuillan, Chem. Phys. Lett., **26**, 163 (1974).
2. M. G. Albrecht and J. A. Creighton, J. Am. Chem. Soc., **99**, 5215 (1977).
3. D. L. Jeanmaire and R. P. Van Duyne, J. Electroanal. Chem. **84**, 1 (1977).
4. R. L. Birke and T. Lu, J. Chem. Phys., **84**, 4174 (1986).
5. R. J. H. Clark and R. E. Herster (Eds), Spectroscopy of Surfaces, John Wiley and Sons, New York (1988).
6. A. Otto, J. Raman Spectrosc., **22**, 743 (1991).
7. W. Kiefer, Special Techniques and Applications in Infrared and Raman Spectroscopy, VCH, Weinheim (1995).
8. S. Nie and S. R. Emory, Science, **275**, 1102 (1997).
9. K. Kneipp, H. Kneipp, G. Deinum, I. Itzkan, R. R. Dasari and M. S. Feld, Appl. Spectrosc., **52**, 175 (1998).
10. N. Felidj, J. Aubard and G. Le'vi, J. Raman Spectrosc., **29**, 651 (1998).
11. A. Bruckbauer and A. Otto, J. Raman Spectrosc., **29**, 665 (1998).
12. W. B. Lacy, L. G. Olson and J. M. Harris, Anal. Chem., **71**, 2564 (1999).

13. W. Demtroeder, Laserspektroskopie, Springer Verlag, Berlin (2000).
14. T. Vo-Dinh, Surface-Enhanced Raman Spectroscopy, in Chemical Analysis of Polycyclic Aromatic Compounds, T. Vo-Dinh (Ed.), John Wiley and Sons, New York (1989).
15. R. K. Chang and T. E. Furtak (Eds.), Surface-Enhanced Raman Scattering, Plenum, New York (1982).
16. K. Kneipp, H. Kneipp, R. Manoharan, E. B. Hanlon, I. Itzkan, R. R. Dasari and M. S. Feld, Appl. Spectrosc., **52**, 1493 (1998).
17. F. J. Adrian, Chem. Phys. Lett., **78**, 45 (1981).
18. D. S. Wang and M. Kerker, Phys. Rev. B, **B24**, 1777 (1981).
19. R. Aroca and F. Martin, J. Raman Spectrosc., **16**, 156 (1985).
20. P. W. Barber, R. K. Chang and H. Massoudi, Phys. Rev. Lett., **50**, 997 (1983).
21. J. Gersten and A. Nitzan, J. Chem. Phys., **73**, 3023 (1980).
22. J. I. Gersten, J. Chem. Phys., **72** (1980).
23. G. C. Schatz and R. P. Van Duyne, Surf. Sci., **101**, 425 (1980).
24. A. Otto, Surf. Sci., **75**, 1392 (1978).
25. M. Moskovits, Rev. Mod. Phys., **57**, 783 (1985).
26. A. Ruperez and J. J. Laserna, Surface-Enhanced Raman Scattering in "Modern Techniques in Raman Spectroscopy", J. J. Laserna (Ed.), John Wiley and Sons, New York (1996).
27. R. K. Chang, Ber. Bunsenges, Phys. Chem., **91**, 296 (1987).
28. K. Arya and R. Zeyher, Phys. Rev., **B24**, 1852 (1982).
29. B. N. J. Persson, Chem. Phys. Lett., **82**, 561 (1981).
30. A. Otto, J. Timper, J. Billmann and I. Pokrand, Phys. Rev. Lett., **45**, 46 (1980).
31. H. Ueba, Surf. Sci. **131**, 347 (1983).
32. K. Kneipp, H. Kneipp, I. Itzan, R. R. Dasari and M. S. Feld, Chem. Rev., **99**, 2957 (1999).

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