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SURFACE SELECTION RULES OF SURFACE ENHANCED RAMAN SCATTERING

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ABSTRACT

Surface Enhanced Raman Scattering (SERS) is an important spectroscopic tool for studying molecules adsorbed on noble metal surfaces. The surface selection rules for SERS are discussed.

Key words : Surface enhanced Raman scattering (SERS), Surface selection rules.

INTRODUCTION

SERS refers to the observation that for certain molecules adsorbed on specially prepared metal surfaces a Raman spectrum is observed, whose intensity exceeds by a factor of $10^5 - 10^6$, what one expects on the basis of simple calculations. The first such observation was made by Fleischmann et al[1] on the molecule of pyridine adsorbed from aqueous solution onto a silver electrode roughened by means of successive oxidation–reduction cycles. An understanding of the surface selection rule is an important part of SERS theory, since it determines the activity or silence of normal modes, and whether or not the intensity of the normal mode is enhanced in the Raman scattering process. Two theoretical models have been developed to explain the SERS effect : the classical electromagnetic enhancement (EM) model[2] and the charge (CT) model[3] .The electromagnetic surface selection rules in the EM model and the distance dependence of the Raman scatterer from the surface[4–6] are essential for the interpretation of the SERS spectra. In addition, the metal–electron–mediated resonance Raman effect (CT model)[3] with the CT surface selection rules plays an important role. The ability to couple the dipole moment fluctuation accompanying the molecular vibrations with the electric field at the metal surface is decisive for the observed SERS intensity. The EM related surface selection rules suggest that vibrational modes possessing polarizability tensors along the surface normal will experience the greatest intensity enhancement. Consequently, the result of these rules is that vibration motion perpendicular to the surface will couple more effectively with the enhanced surface

electromagnetic fields than vibrational motions parallel to the surface. There are two popular ways of stating the surface selection rules for SERS, the Image Field Model[7–8] and Electromagnetic field model [2,9–11].

The Image Field Model

In this model, the modes belonging to irreducible representations spanning the X^2, Y^2, Z^2, XY and YX components of the derived polarizability will be active while those transforming as XZ and YZ will be extinguished on the surface. [Here Z axis of the Cartesian coordinates is taken to be normal to the surface]. The major advantage of the model is that it uses a simple image charge model to simulate the surface effect on the adsorbed molecule.

The Electromagnetic Field Model

For flat surface the local electromagnetic field consists of the electric field vector of the sum of the incident and reflected light. Hence, the tangential component is generally diminished while the normal component is augmented. Due to this, the scattering intensities of the vibrational modes normal to the surface are reinforced. For small metal spherical surfaces, two cases must be considered. One is that at visible optical frequencies the electromagnetic field component parallel to the surface of the metals is non zero; another is that the molecular polarizability is a tensor rather than a vector.

CONCLUSION

In SERS, a strong band feature is often observed in the 1300 – 1600 cm^{-1} region, which is usually ascribed to graphite formed by photodecomposition of organic materials near the surface[12–14]. When a molecule is adsorbed onto a metal surface, some of its vibrational frequencies are modified, because of the interaction between the molecule and the metal[15,16]. In particular, the vibrational modes involving the atom(s) bound directly to the surface are more affected than others. In the case of monosubstituted benzenes, the ring–breathing modes are known to undergo a red–shift of more than 10 cm^{-1} with substantial band broadening, when adsorbed flat on the surface via surface–ring π orbital interactions[17–19]. Surface Raman electromagnetic enhancement is estimated to be proportional to the fourth power of the field enhancement, and the normal (z) component is greater than the tangential field component[20,21]. Therefore, zz (follow by xz and yz) components of the polarizability derivative tensor would be preferentially enhanced to the red of the plasmon frequency. According to electromagnetic theory of SERS, using a small sphere model, a greater mean intensity of radiation at the surface polarized radially than that polarized tangentially. Consequently, when the molecule lies nearly flat on the silver surface, the enhancement factor of the in–plane modes would be lower than that of the out–of plane modes[22]. The general trend that a molecule lying on the surface of low coverage may stand up as the surface become fully covered, but when more than one layer of adsorbate is present, the average percentage of molecules interacting with the metal surface is

less, and other types of interactions can be observed[23]. For a more complete understanding of the surface selection rules for SERS, one has to consider the surface complex and surface local electromagnetic field.

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