UV RAMAN SPECTROSCOPY OF BA AND PHBA IN AQUEOUS SOLUTION AND SILVER COLLOID

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Abstract: This report provides the UV Raman spectra of BA and PHBA in aqueous solution and silver colloid. We find that there’s not any enhancement of above-mentioned samples in silver colloid with UV excitation. And possible reasons are discussed.

Employing photons as probes, Raman spectroscopy is potentially an ideal technique for studying chemical structures and physical interface phenomena [1]. The recent development of ultraviolet (UV) laser sources has made possible experiments in UV Raman spectroscopy. The first major advantage of UV Raman over visible Raman spectroscopy is that fluorescence would not interfere and all samples could be measured with UV excitation. The UV Raman technique also benefits by the increased Raman efficiency due to the $\sim \cdot^4$ dependence of the Raman scattering efficiency. Furthermore, with resonance excitation, the Raman cross sections could be exceptionally large [2]. And it’s possible to observe the Raman bands of typical sample at low concentrations.

Most likely, Surface-enhanced Raman scattering (SERS) is combined force of the chemical effect and the electromagnetic effect that gives rise to the total enhancement of $\sim 10^6$ [3]. But in the ultraviolet region, the Raman spectra are focused up on rather than the enhancement effects. However, the researches on the enhancement mechanism in UV region could help to understand the puzzling properties associated with SERS.

There are some differences in the $1600 \cdot 1700$ cm$^{-1}$ region and one-to-one correspondence below $1600$ cm$^{-1}$ between curve $a$ and $b$ in Fig.1 and 2 apart from a general small increase in linewidth with respect to the solution. In comparison with the UV Raman spectrum of corresponding solid powder, an additional band appears at about $1687$ cm$^{-1}$ in Fig.1b and 2b which are due to C=O stretching mode. In crystals, pairs of molecules are linked through hydrogen bonds between carboxyl groups to form dimers [4]. So the band at about $1687$ cm$^{-1}$ attributed to C=O stretching is absent in Fig.1a and 2a. And in the aqueous solution, hydrogen bond established between carboxylic groups is destroyed and the dimer turns into molecule or ion, and the band located at $1687$ cm$^{-1}$ appears due to decomposition of dimer.

It’s worthwhile to note there’s not any enhancement after silver colloid is added into aqueous BA or PHBA solution. When an aliquot silver colloid is added into aqueous BA or PHBA solution, the interaction between them takes place immediately. We not only observe the color change of mixture, but also obtain the visible SERS, which could elucidate the interaction between the molecules and the silver particles. But we could observe any enhancement with the UV excitation. We call it Surface-Unenhanced Raman Scattering (SUERS).

The poor performance of enhancement in UV region can be explained by the absence of both surface-plasmon resonance and charge transfer excitation. The surface-plasmon resonance condition
is that the real part of dielectric constant must be negative and the imaginary part should approach to zero as much as possible. Silver works best because its dielectric constant is almost real and negative in the visible region [5]. There’s no surface-plasmon resonance because the real part of dielectric constant for Ag is positive while the imaginary part increases rapidly for transition between energy bands.

The charge transfer excitation occurs from the highest occupied state of the metal to the electron affinity level of the molecule. The energy required for this CT excitation is found to become resonance with the laser frequencies used in SERS experiments. The photon energy of ultraviolet used in experiments is about 3.8 ev so the CT excitation condition can’t be satisfied in this region.

References: