HYPER-RAYLEIGH SCATTERING AND SURFACE-ENHANCED RAMAN SCATTERING STUDIES OF PLATINUM NANOPARTICLE SUSPENSIONS

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ABSTRACT
Platinum nanoparticles (ptNPs) in the water are synthesized by nanosecond pulsed laser ablation of a pure platinum plate in the distilled water. Using hyper-Rayleigh scattering (HRS) spectroscopy is observed considerable HRS responses. Pt nanoparticles do not have visible-region plasmon absorption, do not represent clear HRS signals, whereas surprisingly, they exhibit strong surface-enhanced Raman scattering.

1. INTRODUCTION
Colloidal nanoparticles of metals represent useful optical properties. Their linear optical response is dominated by the surface plasmon resonance related to the collective oscillation of the conduction band electrons. These nanoparticles can be used for second-order nonlinear optical application. Second-order nonlinear optical behavior commonly is measured by first hyperpolarizability tensor $\beta$. Hyper-Rayleigh scattering (HRS) over the past decade has known as a useful technique to measure the $\beta$ of species in solution [1]. HRS works, despite the orientational randomization, because signals scale as the variance of the orientation of the species in solution with respect to the incident radiation field [2]. Metallic nanoparticles also exhibit an interesting phenomenon known as surface-enhanced Raman scattering (SERS). In this effect, the scattering cross section is considerably increased for absorbed molecules on the nanoparticles [3]. It has been recently reported that single molecule spectroscopy also is possible by SERS [4-6]. But unfortunately, SERS is not developed as a powerful surface technique. In order for SERS to happen, the Raman excitation wavelength may have to be close to that surface plasmon oscillation. Creighton and Eadon [7] calculated optical absorption of platinum nanoparticles based on the Mie theory and determined that the plasmon peak occurs at 215 nm. Henglein et al. [8] showed experimentally that there is a peak at 215 nm for nanoparticles prepared by the radiolytic reduction of $\text{PtCl}_2^{2-}$. However, it has been found that the UV/Vis absorption spectrum of Pt nanoparticles is almost independent of the particle size and thus the plasmon oscillation must contribute very little to the total absorption. Hence, compared with the Au nanoparticles, the size and the size distribution of the Pt nanoparticles cannot be estimated from their UV/Vis absorption spectrum.

According to the above description, SERS spectra can not be obtained for pt nanoparticles under visible light wavelengths. But surprisingly, we observed that the SERS spectra can be recorded even under visible light wavelengths for pt nanoparticles. In this work, we also report that pt nanoparticles suspended in water do not show considerable HRS under two-photon plasmon resonance conditions. The key reason is absence of the visible-region plasmon band, necessary for resonance enhancement.

2. EXPERIMENTAL DETAILS
Platinum nanoparticles were prepared by nanosecond pulsed laser ablation of pure platinum target in the water. The laser ablation of platinum was carried out using a Q-switched Nd:YAG laser operating at fundamental wavelength. The laser generated 18 ns pulses at 1064 nm with a repetition rate of 1 Hz. The laser beam was focused by a 20 cm focal length lens on the surface of a platinum plate placed inside a 10 mm cell. The spatial profile of the laser pulse was Gaussian with 136μm (FWHM) beam waist at the target. The volume fraction of the platinum nanoparticles was 2.9x10^{-4}. The prepared samples were studied using transmission electron microscopy (TEM), and a UV-Vis optical absorption spectrophotometer.

HRS responses were measured by using a described setup [10]. The output from a mode-locked Ti:sapphire laser (82 MHz, 1.0 W average power at 820 nm) was focused into a solution of nanoparticles. The scattered light was focused onto a photomultiplier tube for detection. Optical filters were used to ensure detection of only the frequency-doubled light. A small section of incident beam was directed through a doubling crystal and onto a fast photodiode; this signal was collected with the scattering to account for fluctuations in laser power during the experiments. HRS experiments were done using Nd:YAG laser operating at 10 Hz pulses and at 1064 nm. Raman spectra were obtained using a Renishaw Raman system Model 2000 spectrometer equipped with an integral microscope. The 514.5 nm line from a 20 mW Ar + laser was used as the excitation source, and Raman scattering was detected with 180° geometry with a Peltier cooled charged-coupled device (CCD) camera.
3. RESULTS and DISCUSSION

Figure 1 shows the absorption spectra of Pt nanoparticles suspended in the water. One can see that the solution possess a strong absorption band corresponding to the surface plasmon of the platinum nanoparticles at about 267 nm.

![Absorption spectra of Pt solution.](image1.png)

The size distribution of the platinum nanoparticles is studied by TEM. Figure 2 presents the TEM image and size distribution of the platinum nanoparticles in the water. Average platinum nanoparticles radius is found to be about 9 nm with a standard deviation of 3 nm.

![TEM images and size distribution of the platinum nanoparticles in the water.](image2.png)

As is shown in Figure 1, platinum nanoparticles have a featureless spectrum that is consistent with the Mie theory. The extinction cross section of these small particles, $C$, is roughly proportional to $Im\left[\left(\frac{\varepsilon_m}{\varepsilon_s}\right) - 1\right]/\left[\left(\frac{\varepsilon_m}{\varepsilon_s}\right) + 2\right]$, where $\varepsilon_s$ and $\varepsilon_m$ are the dielectric constant of the surrounding medium and the frequency-dependent dielectric
constant of the metal nanoparticle respectively [9]. The plasmon resonance in the linear spectrum occurs at wavelengths for which $Re(\varepsilon_m) \approx -2\varepsilon_s$. The width of the resonance is determined by $Im\left(\frac{2m}{\varepsilon_s}\right)$. Above description shows that the resonance condition for Pt is satisfied at wavelengths shorter than 267 nm, and since $Im(\varepsilon_m)$ is especially large for Pt, the resonance is extremely broad and hardly distinguishable.

HRS experiments on solution of Pt nanoparticles, do not show a substantial HRS signals at extinction wavelength 820 nm while for the Au nanoparticles, have been recorded HRS signal at 820 nm [10]. Vance et al. [10] have calculated $\beta' = \frac{\beta_{\text{particle}}}{\varepsilon_{\text{atom}}}$ for Au nanoparticles \( \sim 2800 \times 10^{-30} \) esu for incident light at 820 nm. The reason of this important difference between Pt and Au is lack visible-region plasmon band. Since Ag as well as Au has visible-region plasmon band, $\lambda = 410$ nm, available theories such as theory by Agarwal and Jha [11] suggest that 2-photon plasmon-resonance enhancement effects should exist. In the Agarwal-Jha theory, the power radiated at $2\omega$ and integrated over all solid angles is found to be

$$S = 192\pi^2c|E(\omega)|^4 \left(\frac{2\omega R}{c}\right)^6 \times \left\{ \frac{|e^2(2\omega - 1)|/\beta n_\omega^2}{|e(2\omega)|^2 + 2e^2(2\omega) + 2}\right\} \right\} \left(\frac{2\omega R}{c}\right)^6$$

where $c$ and $m$ are the electron charge and effective mass, $E(\omega)$ is the field at the fundamental frequency, $R$ is the sphere radius, $c$ is the velocity of light, $\varepsilon(\omega)$ is the relative dielectric constant (defined as $\varepsilon_m/\varepsilon_s$) at incident radiation frequency ($\omega$), and $e(2\omega)$ is the corresponding quantity at $2\omega$. Notice that the first term in the large brackets has the characteristic dipole plasmon resonance denominator $|e(\omega) + 2|^{-1}$. Strong enhancement of the HRS signal is expected, therefore, at incident wavelengths coincident with the dipole plasmon absorption maximum. Additionally, the term containing the factor $|e(2\omega) + 2|^{-2}$ indicates strong HRS enhancement at an incident wavelength that is double the dipole plasmon absorption wavelength. We have used the Agarwal-Jha theory to calculate HRS intensity (per atom) at 820 nm. The dielectric constant for Pt was taken from Palik [12]. We obtain the intensity per atom of 0.1 for Pt. Ag indicates a much larger HRS signal at 820 nm than the other metals, about 80. Because the dipole plasmon resonance peak occurs at this wavelength.

For obtaining the Raman spectra, Benzenethiol (BT) was chosen as a model adsorbate in this work since BT was known not only to be a strong Raman scatterer but also to adsorb strongly on Pt. A noticeable change takes place upon the addition of BT to the Pt solution as can be seen in Fig. 3. A very broad but distinct band is developed around 500 nm, probably due to the aggregation of Pt nanoparticles caused by adsorption of BT onto the Pt surfaces [7, 8].

![Absorption spectra of Pt solution after adding BT](Fig3).
Figures 4 (a), 4 (b) show the Raman spectra of BT in the neat liquid state and in the adsorbed state on Pt, respectively. The peaks at 3060, 1584 and 1000 cm\(^{-1}\) in Fig. 4 (a) are due to the CH stretching, the CC stretching \((\nu_{CH})\), and the ring CCC in plane bending \((\nu_{12})\) modes of BT, respectively, while the peaks at 2567 and 917 cm\(^{-1}\) are due to the SH stretching and CSH bending vibration, respectively [13]. The counterparts of the latter two vibrational bands are found in Fig. 4 (b), however. Nevertheless, all the peaks in Fig. 4 (a) can be correlated with those in Fig. 4 (a).

![Raman spectra of BT](image)

**Fig 4. Raman spectra of BT (A-a) in liquid state and (A-b) in adsorbed state on Pt nanoparticles.**

We have calculated the surface enhancement factor (EF) by using the following relationship [14]:

\[
EF = \frac{I_S}{I_O} \left( \frac{N_O}{N_S} \right)
\]  

(2)

in which \(I_S\) and \(I_O\) are the SERS intensity of BT on Pt nanoparticles and the ordinary Raman (OR) intensity of BT in bulk, respectively, and \(N_S\) and \(N_O\) are the number of BT molecules illuminated by the laser light to obtain the corresponding SERS and OR spectra, respectively. \(I_S\) and \(I_O\) were measured, and \(N_S\) and \(N_O\) were estimated on the basis of the density of bulk BT, and the concentration of surface BT species. We have accounted \(N_S = 7.4 \times 10^{-17} \text{ mol}\) and \(N_O = 1.1 \times 10^{-14} \text{ mol}\). Since the intensity ratio, \(I_S/I_O\), is \(\sim 1\), EF can be as large as \(1.5 \times 10^2\). This clearly shows that the SERS can be induced even on Pt substrate by visible laser irradiation. The origin of SERS at Pt nanoparticles is unknown yet, but considering the fact that EF is dependent on the particle size strongly, chemical effects may be important in the present system.

4. **CONCLUSIONS**

The nonlinear optical responses of platinum nanoparticles were examined by Hyper-Rayleigh scattering and surface-enhanced Raman scattering. Pt nanoparticles, which lack surface plasmon absorption in the visible, and for which the plasmon is strongly damped, yield no detectable HRS at 820 nm, but after adding BT to the Pt solution the SERS can be induced even on Pt substrate by visible laser irradiation.
REFERENCES


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