

Charge-Transfer and SERS Coupling on TiO₂

Syed K. Islam, Antonio Ponte

Department of Physical Sciences, Eastern Connecticut State University, Willimantic, CT, USA

Email: islams@easternct.edu

How to cite this paper: Islam, S.K. and Ponte, A. (2023) Charge-Transfer and SERS Coupling on TiO₂. *American Journal of Analytical Chemistry*, 14, 519-530.

<https://doi.org/10.4236/ajac.2023.1411030>

Received: October 8, 2023

Accepted: November 27, 2023

Published: November 30, 2023

Copyright © 2023 by author(s) and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

We report the SERS enhancements of Raman forbidden surface modes of TiO₂ in different sized TiO₂ crystals. This current study utilizes the relationship between the vibronic coupling and the degree of charge-transfer to explain the differences of Surface Enhanced Raman Scattering (SERS) enhancements. Our study shows a direct correlation between the degree of charge-transfer and vibronic coupling. This relationship suggests that charge-transfer between the N-719 dye and TiO₂ due to vibronic coupling plays a fundamental role in SERS enhancements. Furthermore, this study shows a strong dependence of the enhancements of the N-719 dye molecular modes to that of the surface modes. This indicates that the mechanism that governs the enhancements of the surface modes in TiO₂ crystals most likely also dictates the enhancements of the N-719 dyes.

Keywords

Charge-Transfer, Vibronic Coupling, Fano Profile, TiO₂, Surface Modes

1. Introduction

The explanation for the observation of Raman forbidden characters in SERS spectra of semiconductors was initially proposed by Lombardi and Birke [1]. In their study, the authors attributed the SERS enhancements to the presence of charge-transfer (CT) which may borrow intensity through vibronic (Herzberg-Teller) coupling between excitonic and molecular transitions in molecule-semiconductor systems. Charge-transfer (CT) transitions, allowing intensity borrowing through vibronic coupling, is indicated to be the primary mechanism through which Raman forbidden modes of molecules as well as the SERS substrates (phonon modes) are enhanced in SERS spectra. In a recent study, we reported the first observation of SERS enhancements of Raman forbidden surface phonon modes of A_{2u} symmetry in TiO₂ nanoparticles modified with N-719 dyes [2]. Vi-

bronic coupling between the discrete levels of N-719 dyes and TiO₂ nanoparticles allowing intensity borrowing due to the presence of charge-transfer (CT) was concluded to be responsible for the enhancements of these Raman forbidden characters.

As an extension to our previous study, this current study shows the SERS enhancements of the same Raman forbidden surface phonon modes in different size TiO₂ crystals upon the adsorption of N-719 dyes. The sizes of the TiO₂ crystals used in this study varied from 7 nm to 100 nm which are considerably larger than the exciton Bohr radius of TiO₂ (about 2.4 nm) [3]. Based on the observed enhancements, an excitation profile of the surface modes as a function of particle size is constructed. The profile shows the strongest enhancements originating from 30 nm size TiO₂ crystals.

A similar study to investigate size dependent resonant effects on SERS enhancements was previously reported using larger size TiO₂ crystals (larger than the exciton Bohr radius) [4]. In this study, different size TiO₂ crystals ranging from 6.8 nm to 14.2 nm were modified with 4-MBA molecules and the size at which the largest enhancement was observed was 10.9 nm. This maximum enhancement was attributed to strong vibronic coupling between the discrete states of 4-MBA molecules and different size TiO₂ crystals. Additional studies of SERS enhancements as a function of particle size were previously demonstrated in PbS and CdSe quantum dots [5] [6]. Note, the sizes of these quantum dots were smaller than the size of the exciton radius of these two semiconductors. These studies show strong enhancements based on size dependent charge-transfer transitions in a molecule-semiconductor complex as a result of quantum confinement.

Vibronic coupling in a molecule-solid substrate complex was originally explored in detail by Fano [7]. In this study, he proposed a solution to the interaction of the discrete states between a molecule and a solid substrate to measure the extent that these two systems are coupled. His exploration of the interaction between a discrete state and a continuum result in an asymmetric line shape (Fano profile) with a net reduction of intensity in some regions and a net enhancement of intensity in others. Application of the Fano solution to vibronic coupling contributing to SERS enhancements of several different molecules has been previously reported [8] [9]. In these studies, the authors attributed the observed differences of enhancements to the extent that a molecule and a SERS substrate are coupled. Their study further obtained a fit between the SERS excitation profile and the Fano Profile indicating that the differences of coupling between a molecule and SERS substrate contributes to the differences of SERS enhancements. In this study, we utilize the close match between the SERS excitation profile and the Fano profile to explain the observed variations of SERS enhancements of the surface modes in TiO₂ due to the adsorption of N-719 dyes. This study shows that the coupling between the N-719 dye and the TiO₂ varies for different size TiO₂ crystals based on the fit between the SERS profile of N-719 dyes and the Fano pro-

file. This study further suggests that the difference of coupling contributes to the degree of charge-transfer (CT) between the N-719 dye and the TiO₂ crystals affecting the SERS enhancements. Furthermore, this study shows that the excitation profile of N-719 dyes follows a similar trend to that of the surface modes. This observed phenomenon indicates that mechanism that governs the enhancements of the surface modes in TiO₂ crystals, most likely also dictates the enhancements of the N-719 dyes as well.

2. Experimental Methods

2.1. Chemical Reagents

N-719 dye (99.0%) samples were purchased commercially from Fisher Scientific and used without further purification. TiO₂ nanocrystals (99.5%, anatase) were purchased commercially from Sigma Aldrich. Triple distilled water was used for sample preparation.

2.2. Raman Spectroscopy

Solutions of N-719 dye were prepared by dissolving the dye powder in distilled water at 10⁻⁵ M concentration. Adsorption of N-719 dye molecules on TiO₂ nanoparticles was obtained by dispersing 5 mg of TiO₂ nanoparticles in 10 ml of N-719 dye solutions. This procedure was followed for each of the different size TiO₂ nanoparticles to prepare the mixture. The mixtures were stirred overnight, and the precipitate was then centrifuged and rinsed three times with deionized water. Finally, a small amount of TiO₂ nanoparticles modified with the selected adsorbate was dropped onto a glass slide and allowed to spread into a circle of about 2 cm in diameter. After solvent evaporation, Raman measurements of these samples were investigated using Spectra Pro 2750 (0.75 m Triple Grating Monochromator 1200 gratings/Spectrograph) at the excitation wavelength of 488 nm obtained from an Ar⁺ laser (Spectra Physics). The laser was focused on the sample by using a 10× objective lens attached to a confocal microscope and the power of the laser on stage was 1.50 mW. The laser spot size was 2 μm and the slit width was 20 μm. The Raman measurement of the sample was taken with 5 accumulations over 10 s acquisition. The silicon line at 520 nm was used to calibrate the observed wavenumbers.

3. Results/Discussion

3.1. SERS Profile of the Surface Modes

Figure 1 displays Raman intensity of two peaks—a narrow peak at 690 cm⁻¹ and a relatively broad peak at 790 cm⁻¹ for six different size TiO₂ crystals. Enhancements of these two peaks are observed in the SERS spectra upon the adsorption of N-719 dyes on TiO₂ crystals.

In a recent study, we showed the appearance of these same two peaks after the modification of the TiO₂ particles with N-719 dyes [2]. We showed that these two peaks belong to surface optical (SO) phonon modes of TiO₂ and only appear

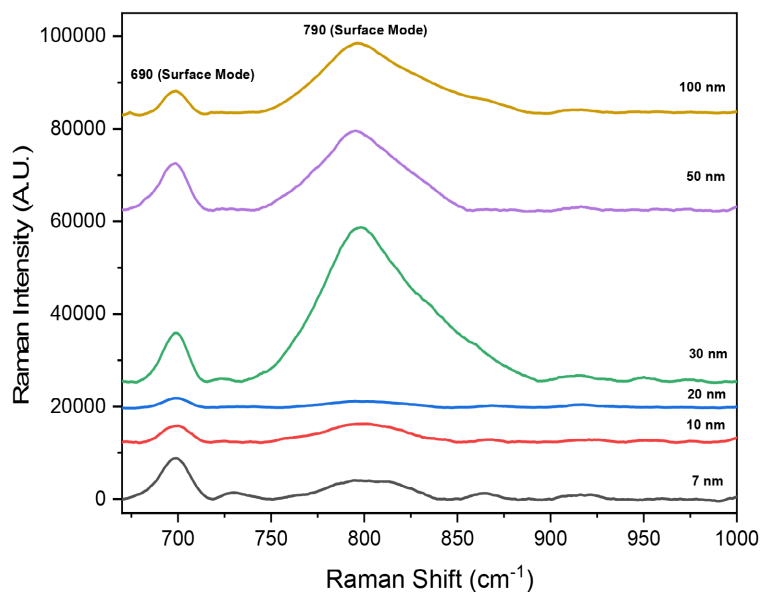


Figure 1. SERS spectra of the Raman forbidden surface modes at 690 cm^{-1} and at 790 cm^{-1} for different size TiO_2 crystals after the adsorption of N-719 dyes. Excitation is at 488 nm .

upon the adsorption of N-719 dyes on TiO_2 crystals. We further identified the symmetry of these surface modes to be of Raman forbidden a_{2u} symmetry originating from the (100) face of TiO_2 crystals. A figure displaying the SERS enhancements of the surface modes upon the modification with N-719 dyes compared to the bare TiO_2 particles from our previous study is included in the supplemental information.

In our previous analysis of the enhancement of the Raman forbidden surface modes using 10.9 nm size TiO_2 crystals, we demonstrated the presence of charge-transfer (CT) transitions between the TiO_2 crystals, and the N-719 dyes adsorbed on the surface of the TiO_2 crystals. An energy level diagram of TiO_2 and N-719 dyes is presented in **Figure 2** to illustrate the possible charge-transfer transitions between the TiO_2 crystals and the adsorbed dye. Note, this figure is reproduced from our previous study.

The diagram shows that the energy gap between the HOMO of N-719 dyes and the conduction band (CB) of TiO_2 is 1.48 eV which is within the range of the excitation laser 488 nm (2.56 eV) to excite a charge-transfer transition (μ_{CT}) from the (HOMO) of N-719 dyes to the (CB) of TiO_2 . In addition, a molecular transition (μ_{mol}) can also be obtained between the (HOMO) and the unfilled (π^*) molecular orbital at -2.84 eV of N-719 dyes. In this study we concluded that the presence of the charge-transfer transitions (μ_{CT}) between the dye and the TiO_2 crystals indicates the energy states of these two systems must be coupled. This coupling between the dye and the TiO_2 crystals is the primary mechanism through which intensity is borrowed from the nearby excitonic (μ_{exct}) or molecular transition (μ_{mol}) for the enhancement of the surface modes in TiO_2 . Enhancements of these Raman forbidden surface modes are akin to the observations of forbidden

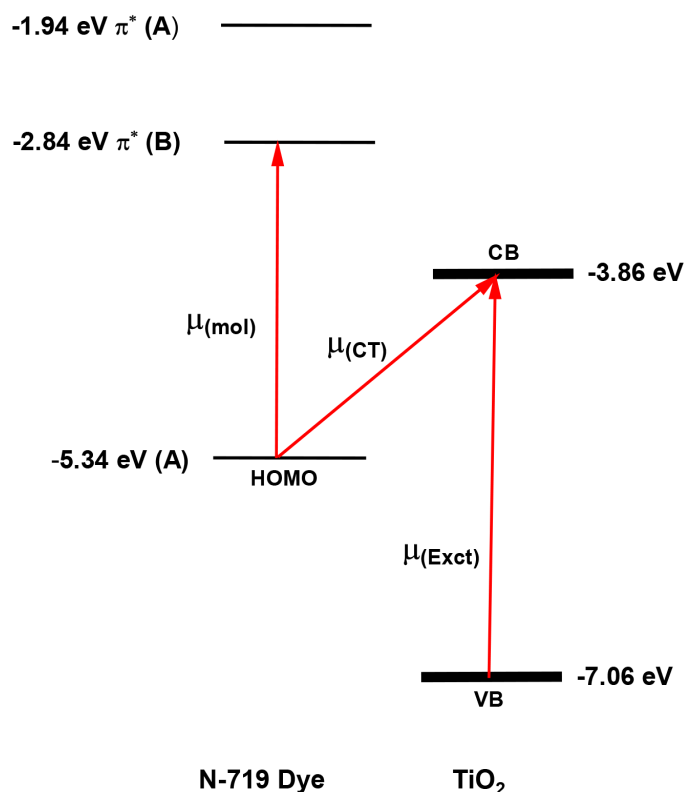


Figure 2. Energy level diagram of bulk TiO₂ and N-719 dye molecules. All levels are measured from the vacuum. Arrows indicate possible charge transfer transitions. (Reproduced from *Chem. Phys. Lett.* Vol 806, 2022, 140040)

character in both optical and Raman spectra by Albrecht contributing to the chemical enhancement in SERS [10].

In the current study, appearance of the same Raman forbidden surface modes at 690 cm⁻¹ and at 790 cm⁻¹ in different size TiO₂ crystals suggests the presence of the same mechanism governing the SERS enhancements. While **Figure 1** shows the enhancement of the same two surface modes in all different sized TiO₂ crystals, the figure also exhibits differences of SERS intensity of these two surface modes in different sized TiO₂ crystals. Among the six different sized TiO₂ crystals, the maximum enhancements for both surface modes appear in 30 nm sized TiO₂ crystals whereas the 20 nm TiO₂ crystals show the least enhancements. In **Figure 3**, a comparison of the SERS excitation profile for these two surface modes for all six different sized TiO₂ crystals is displayed.

Figure 3 exhibits a similar trend of the excitation profile for both surface modes. Raman intensity for both of these two surface modes initially drops from 7 nm to 20 nm size TiO₂ crystals before reaching its maximum for 30 nm size TiO₂ crystals. The intensity then gradually decreases as the size for TiO₂ crystals increases to 100 nm. Results in this figure clearly show differences in SERS enhancements of the two surface modes for different sized TiO₂ crystals. Unlike PbS and CdSe quantum dots where differences in charge-transfers transitions due to quantum confinement played a major role in generating the resonance

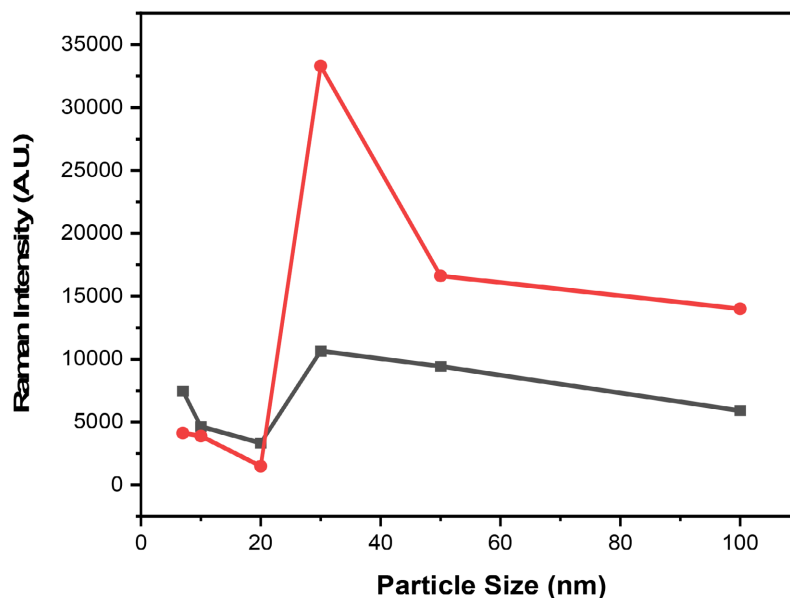


Figure 3. Comparison of the excitation profiles of TiO₂ surface modes at 690 cm⁻¹ (black) and at 790 cm⁻¹ (red) for different size TiO₂ crystals.

condition, the same phenomenon cannot be attributed to differences of SERS enhancements in this study. The size of the TiO₂ crystals used in this study are well above the exciton Bohr radius thus the differences in charge-transfer transitions owing to quantum confinement does not apply here.

3.2. Vibronic Coupling and Fano Profile

The differences of SERS enhancements of several different probing molecules adsorbed on larger sized crystals (larger than Bohr radius) was previously reported [8] [9]. In this study, the authors utilized the Fano solutions to vibronic coupling following the equation below to analyze the variation of the observed SERS enhancements.

$$\text{SERS Intensity} \propto \frac{(q + \epsilon)^2}{1 + \epsilon^2}$$

Note, q is regarded as an asymmetry parameter which varies from 0 to larger values and measures the degree of coupling of the discrete states between the molecule and the SERS substrate. ϵ is a dimensionless parameter. The Fano line shape (Fano profile) results from this equation shows a drop in intensity at sufficiently negative values of ϵ before reaching the maximum intensity. The curve then decreases asymmetrically at higher positive values of ϵ . The maximum resonance in this Fano profile reported to indicate a strong vibronic coupling between the discrete states of an adsorbent (molecule) and a SERS substrate. On the contrary, the minimum resonance in the profile suggested to indicate a weak vibronic coupling between the two systems. To examine the correlation between the vibronic coupling and charge-transfer (CT) transitions, the authors in the previous study constructed SERS excitation profiles of different molecules based

on the differences of charge-transfer (CT). Their study showed a fit between the SERS excitation profile and the Fano profile suggesting that the degree of charge-transfer (CT) transition is strongly dependent on the degree of coupling between a molecule and a SERS substrate.

In our current study, we constructed a Fano profile based on the Fano equation as previously reported to compare with the excitation profile of the two surface modes with that of the Fano profile in **Figure 4(a)** and **Figure 4(b)**. The Fano line shape in this figure shows a characteristic drop in intensity (minimum resonance) at sufficiently negative values of ϵ before reaching its maximum

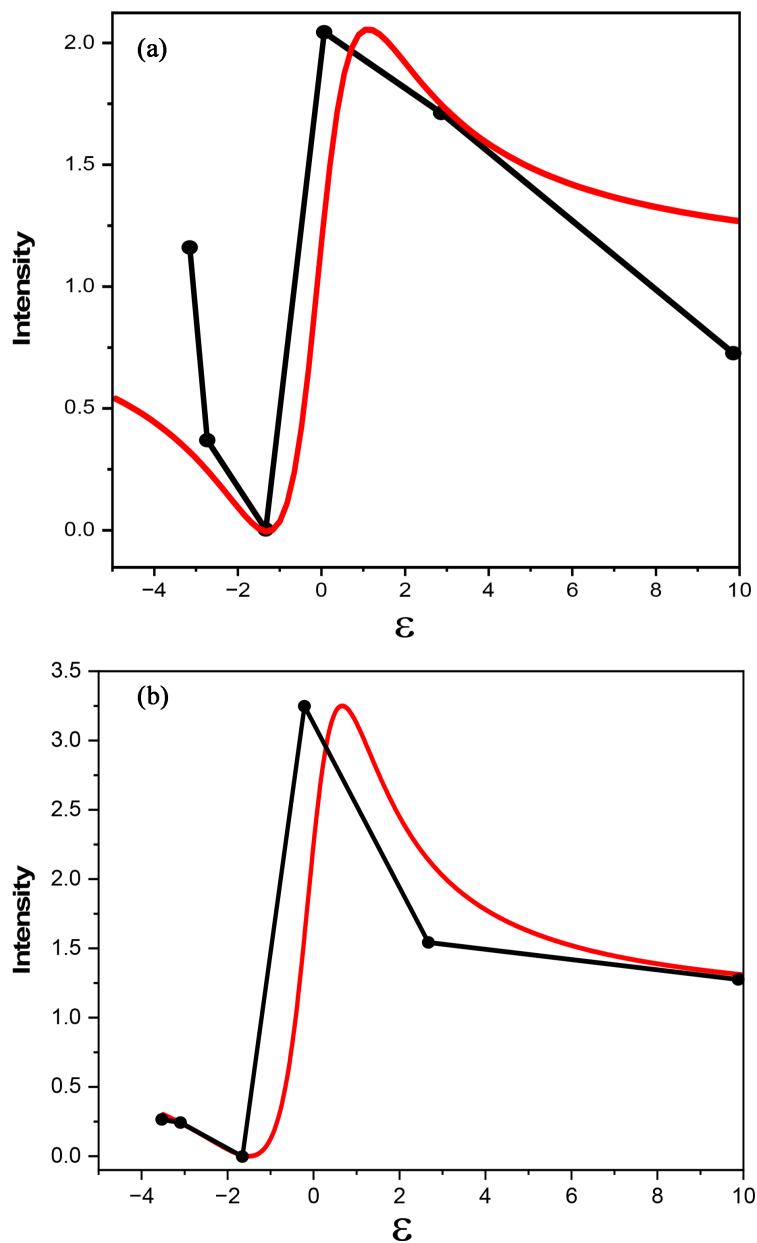


Figure 4. (a) Excitation profiles of TiO₂ surface mode at 690 cm⁻¹ (black) and the Fano profile (red); (b) Excitation profiles of TiO₂ surface mode at 790 cm⁻¹ (black) and the Fano profile (red).

intensity (maximum resonance). The line then decreases asymmetrically at higher positive values of ϵ . This Fano profile is similar to those previously reported [7] [8] [9]. The figure also shows excitation profiles of the surface modes at 690 cm^{-1} (**Figure 4(a)**) and at 790 cm^{-1} (**Figure 4(b)**). It can be seen that the excitation profiles of the two surface modes closely fit to that of the Fano profile. We obtained the optimum fit of the SERS profile to that of the Fano profile with a value of $q = 1.0$ for the surface mode at 690 cm^{-1} in **Figure 4(a)** and with a value of $q = 1.5$ for the surface mode at 790 cm^{-1} in **Figure 4(b)**. The excitation profiles of the two surface modes show the presence of resonances similar to those in the Fano profile.

The figures show the highest enhancements (maximum resonance) of the surface modes at 30 nm and the lowest enhancements (minimum resonance) of the surface modes at 20 nm .

The close fit between the excitation profile and the Fano profile indicates a strong coupling between the N-719 dye and TiO_2 in 30 nm sized crystals compared to that of the 20 nm sized TiO_2 . Furthermore, the strong coupling suggests a higher degree of charge-transfer between the N-719 dyes and the 30 nm size TiO_2 crystals compared to that of the 20 nm size crystals.

3.3. Degree of Charge-Transfer $\rho_{\text{CT}}(k)$

To quantify the degree of charge-transfer $\rho_{\text{CT}}(k)$ for the enhancements of the two surface modes in different size TiO_2 crystals, we employ the following equation as previously reported to measure the degree of charge-transfer in a N-719 dye- TiO_2 complex [11] [12]:

$$\rho_{\text{CT}}(k) = \frac{\frac{I^k(\text{CT})}{I^0(\text{CT})}}{1 + \frac{I^k(\text{CT})}{I^0(\text{CT})}} \quad (1)$$

Herein, k is an index used to identify individual vibrational mode in the Raman spectrum. $I^k(\text{CT})$ is the Raman intensity of the vibrational mode which is strongly enhanced by charge-transfer and $I^0(\text{CT})$ is the Raman intensity of the vibrational mode whose enhancement is considered free from charge-transfer. Since the enhancements of the two surface modes are strongly affected by the charge-transfer (CT) process, we need to examine the vibrational mode which is free from the effect of charge-transfer (CT).

In **Figure 5**, we display the comparison of the Raman spectra of N-719 dyes with that of N-719 dyes adsorbed on different size TiO_2 crystals. The figure shows enhancements of the molecular peaks of N-719 dyes at 1030 cm^{-1} , 1268 cm^{-1} , 1472 cm^{-1} , 1542 cm^{-1} and 1610 cm^{-1} .

The molecular line at 1030 cm^{-1} corresponds to ring breathing (bpy) mode, the line at 1268 cm^{-1} corresponds to inter-ring (bpy) mode, and the three lines at 1472 cm^{-1} , 1542 cm^{-1} and 1610 cm^{-1} correspond to ring stretching mode (bpy) [13] [14]. Among these molecular lines, the ring breathing mode at 1030 cm^{-1} is

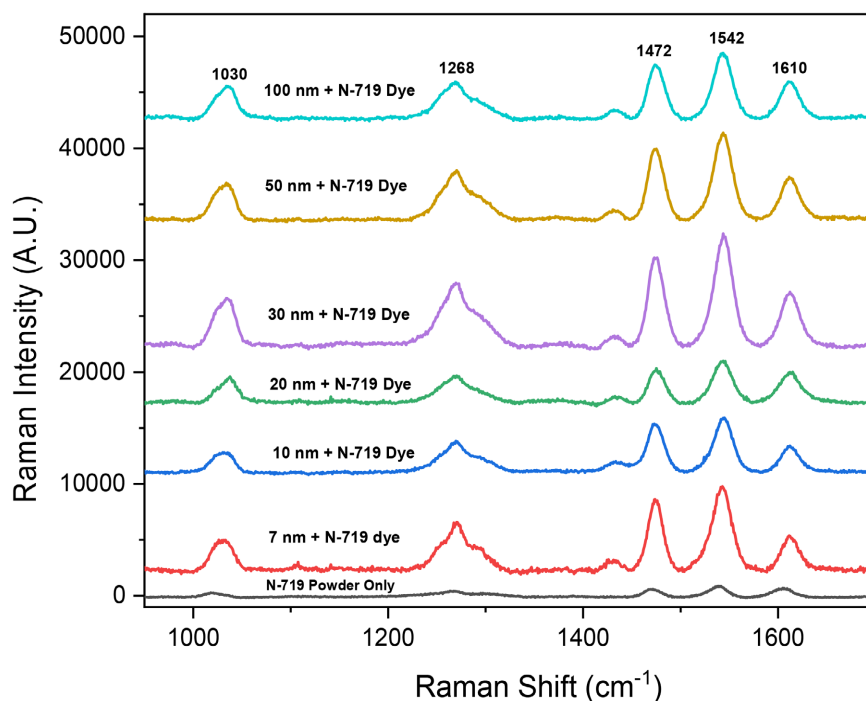


Figure 5. Enhancements of the N-719 dyes adsorbed different size TiO₂ crystals. Excitation wavelength 488 nm.

considered to be least affected by the charge-transfer (CT) effect [11] [12]. Therefore, to quantify the degree of charge-transfer, we select the surface mode at 690 cm⁻¹ and at 790 cm⁻¹ which are strongly affected by CT process as $\tilde{\nu}^*$ (CT) and the N-719 dye line as $\tilde{\nu}$ (CT). Thus, to measure the degree of charge-transfer for the enhancement of the surface mode at 690 cm⁻¹ Equation (1) can be expressed as follows:

$$\rho_{CT}(k) = \frac{\frac{I_{690}}{I_{1030}}}{1 + \frac{I_{690}}{I_{1030}}} \quad (2)$$

Note, to measure the degree of charge-transfer for the enhancement of the surface mode at 790 cm⁻¹, we simply replace I_{690} with I_{790} in Equation (2).

In **Figure 6**, we plot the degree of charge-transfer of the two surface modes based on different particle sizes. The figure shows the 30 nm sized TiO₂ crystals have the highest degree of charge-transfer whereas the 20 nm sized crystals have the lowest degree of charge-transfer.

In addition, for 690 cm⁻¹ peak, the degree of charge-transfer gradually decreases between 7 nm to 10 nm and between 50 nm to 100 nm. For 790 cm⁻¹ peak, the degree of charge-transfer level off between 7 nm to 10 nm and between 50 nm to 100 nm. The degree of charge-transfer in **Figure 6** is similar to the excitation profiles of the two surface modes in **Figure 3**. Results in **Figure 6** suggest that higher degree of charge-transfer in 30 nm sized TiO₂ is due to strong coupling between the TiO₂ and N-719 dye contributing to maximum SERS

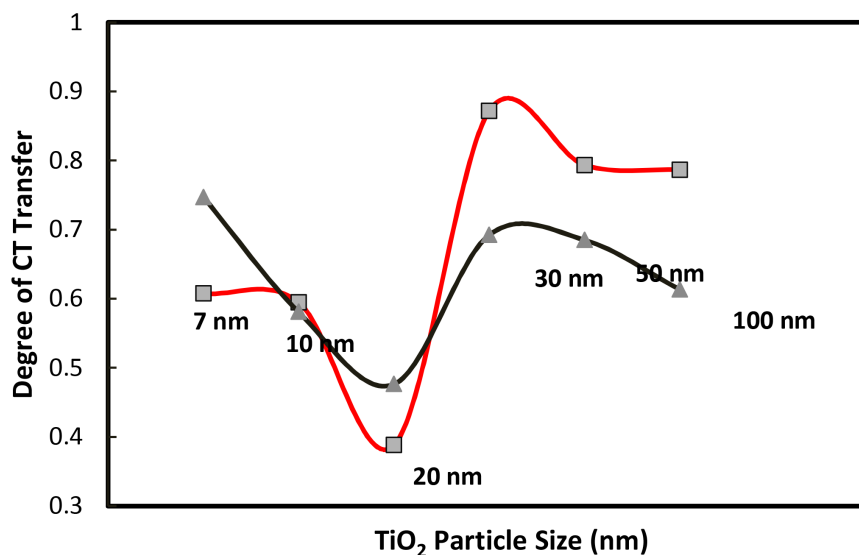


Figure 6. Comparison of the degree of charge-transfer (CT) of the surface modes at 690 cm^{-1} (black) and at 790 cm^{-1} (red) for different size TiO_2 crystals.

enhancements. This coupling is the weakest in 20 nm sized TiO_2 crystals resulting in a smaller degree of charge-transfer generating the weakest enhancements. The figure also shows the relative degree of charge-transfer resulting in the enhancement of the 790 cm^{-1} in each of the TiO_2 crystals is higher than that of the 690 cm^{-1} . In addition, in **Figure 4**, the best fit between the excitation profile of 790 cm^{-1} and the Fano profile was achieved for the value of $q = 1.5$ whereas for 690 cm^{-1} , the value of $q = 1.0$ shows the optimum fit. The higher value of q for 790 cm^{-1} indicates that the coupling between the N-719 dye and the TiO_2 crystals generating is stronger for 790 cm^{-1} line compared to the 690 cm^{-1} line. We do not know why the coupling and the degree of charge-transfer is different for the two surface modes in each of the different size crystals.

Looking back at **Figure 5**, we can see that the molecular enhancements of N-719 dyes are similar to the enhancements of the surface modes. It can be seen in the figure that the 30 nm size TiO_2 crystals produce the strongest enhancements of N-719 dyes while the 20 nm size TiO_2 crystals show the least. To compare the relative enhancements of the molecular modes to those of the surface modes, the SERS excitation profiles of the 1542 cm^{-1} line of N-719 dyes and the two surface modes at 690 cm^{-1} and at 790 cm^{-1} are presented in **Figure 7**.

Note, the molecular line at 1542 cm^{-1} is selected as it is the most enhanced molecular peak in all six different size TiO_2 crystals. The figure shows the excitation profile of N-719 dyes follows the same trend as the excitation profile of the two surface modes. Similar to the excitation profile of the surface modes, Raman intensity of the N-719 dye at 1542 cm^{-1} initially drops for 7 nm to 20 nm size TiO_2 crystals before reaching its maximum for 30 nm size TiO_2 crystals. The intensity then gradually decreases as the size for TiO_2 crystals increases to 100 nm. Similarity of this enhancement pattern between the surface modes and the molecular mode suggests that the degree of charge-transfer between N-719 dye and

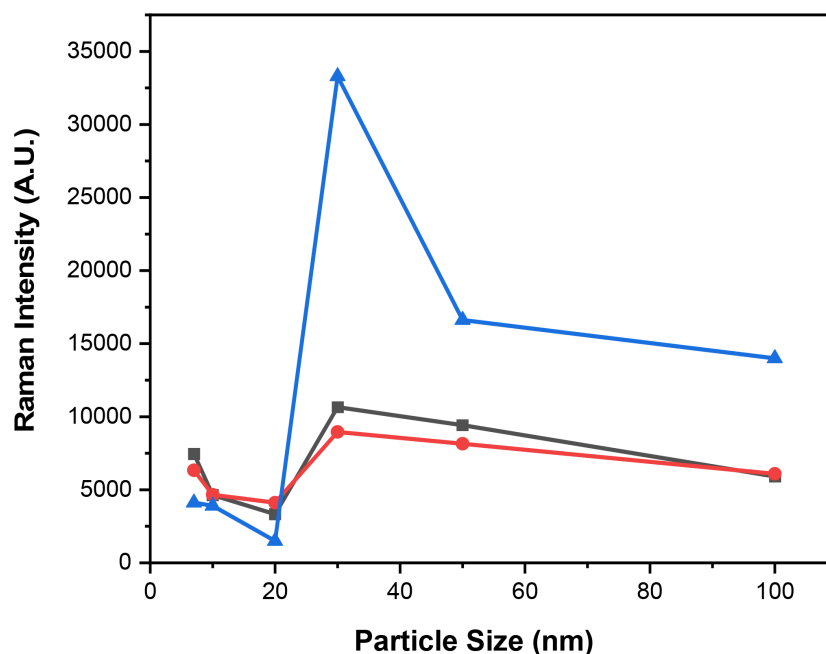


Figure 7. Comparison of the excitation profiles of the N-719 dye mode at 1542 cm^{-1} (red), TiO_2 surface modes at 690 cm^{-1} (black) and at 790 cm^{-1} (blue) for different size TiO_2 crystals.

the TiO_2 crystals is governed by the strength of vibronic coupling which plays an important role in SERS enhancements of the surface modes and of N-719 dyes.

4. Conclusion

Following previous studies, we relied on the Fano profile resulting from the Fano solutions to vibronic coupling to examine SERS profile of the N-719 dyes in different sized TiO_2 crystals. The SERS profile generated for N-719 dyes closely fits that of the Fano profile. This close fit of the two profiles indicates that the degree of charge-transfer is dependent on the vibronic coupling between N-179 dye and TiO_2 contributing to the SERS enhancements of the surface modes in TiO_2 crystals. Furthermore, this study shows a strong dependence of the enhancements of the N-719 dye molecular modes to that of the surface modes. This suggests that enhancement of the surface modes of TiO_2 and the molecular modes of N-719 dyes are most likely linked by the same mechanism.

Acknowledgements

We are indebted to the National Science Foundation (CHE-1402750) for partial funding of this project. This work was also partially supported by NSF grant number HRD-1547830 (IDEALS CREST).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Lombardi, J.R. and Birke, R.L.J. (2014) The Theory of Surface Enhanced Raman Scattering in Semiconductors. *The Journal of Physical Chemistry C*, **118**, 11120-11130. <https://doi.org/10.1021/jp5020675>
- [2] Islam, S. and Lombardi, J.R. (2022) Raman Enhancements (SERS) of the Surface Phonon Modes of TiO₂. *The Journal of Physical Chemistry Letters*, **806**, Article Number 140040. <https://doi.org/10.1016/j.cplett.2022.140040>
- [3] Hormann, U., Kaiser, U., Albrecht M., Geserick, J. and Husing, N. (2010) Structure and Luminescence of Sol-Gel Synthesized Anatase Nanoparticles. *Journal of Physics: Conference Series*, **209**, Article Number 012039. <https://doi.org/10.1088/1742-6596/209/1/012039>
- [4] Xue, X., Ji, W., Mao, Z., Mao, H., Wang, Y., Wang, X., Ruan, W., Zhao, B. and Lombardi, J.R. (2012) Raman Investigation of Nanosized TiO₂: Effect of Crystallite Size and Quantum Confinement. *The Journal of Physical Chemistry C*, **116**, 8792-8797. <https://doi.org/10.1021/jp2122196>
- [5] Fu, X., Pan, Y., Wang, X. and Lombardi, J.R. (2011) Quantum Confinement Effects on Charge-Transfer between PbS Quantum Dots and 4-Mercaptopyridine. *The Journal of Chemical Physics*, **134**, Article Number 024707. <https://doi.org/10.1063/1.3523646>
- [6] Islam, S.K., Sohel, M.A. and Lombardi, J.R. (2014) Coupled Exciton and Charge-Transfer Resonances in the Raman Enhancement of Phonon Modes of CdSe Quantum Dots (QDs). *The Journal of Physical Chemistry C*, **118**, 19415-19421. <https://doi.org/10.1021/jp5051035>
- [7] Fano, U. (1961) Effects of Configuration Interaction on Intensities and Phase Shift. *Physical Review*, **124**, 1866. <https://doi.org/10.1103/PhysRev.124.1866>
- [8] Lombardi, J.R. and Birke, L.R. (2010) Excitation Profile and the Continuum in SERS: Identification of Fano Line Shapes. *The Journal of Physical Chemistry C*, **114**, 7812-7815. <https://doi.org/10.1021/jp100568b>
- [9] Lombardi, J.R. and Birke, L.R. (2012) The Theory of Surface-Enhanced Raman Scattering. *The Journal of Chemical Physics*, **136**, Article Number 144704. <https://doi.org/10.1063/1.3698292>
- [10] Albrecht, A.C. (1960) "Forbidden" Character in Allowed Electronic Transitions. *The Journal of Chemical Physics*, **33**, 156-169. <https://doi.org/10.1063/1.1731071>
- [11] Wang, X., Zhao, B., Li, P., Han, X. and Ozaki, Y. (2017) Charge Transfer at the TiO₂/N₃/Ag Interface Monitored by Surface Enhanced Raman Spectroscopy. *The Journal of Physical Chemistry C*, **121**, 5145-5153. <https://doi.org/10.1021/acs.jpcc.7b00153>
- [12] Wang, X., Wang, Y., Sui, H., Zhang, H., Su, H., Cheng, W., Han, X. and Zhao, B.J. (2016) Investigation of Charge Transfer in Ag/N719/TiO₂ Interface by Surface-Enhanced Raman Spectroscopy. *The Journal of Physical Chemistry C*, **120**, 13078-13086. <https://doi.org/10.1021/acs.jpcc.6b03228>
- [13] León, C., Kador, L., Peng, B. and Thelakkat, M. (2005) Influence of the Solvent on the Surface-Enhanced Raman Spectra of Ruthenium(II) Bipyridyl Complexes. *The Journal of Physical Chemistry B*, **109**, 5783-5789. <https://doi.org/10.1021/jp044946x>
- [14] Birke, R. and Lombardi, J. (2021) DFT and TD-DFT Investigation of a Charge Transfer Surface Resonance Raman Model of N₃ Dye Bound to a Small TiO₂ Nanoparticle. *Nanomaterials*, **11**, 1491. <https://doi.org/10.3390/nano11061491>