

# Surface-Enhanced Raman Scattering and Surface-Enhanced Resonance Raman Scattering Excitation Profiles of Ag-2,2'-Bipyridine Surface Complexes and of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> on Ag Colloidal Surfaces: Manifestations of the Charge-Transfer Resonance Contributions to the Overall Surface Enhancement of Raman Scattering<sup>#</sup>

Ivana Srnová-Šloufová and Blanka Vlčková\*

Department of Physical and Macromolecular Chemistry, Charles University, Hlavova 2030, 128 40 Prague 2, Czech Republic

Theo L. Snoeck and Derk J. Stufkens

Institute of Molecular Chemistry, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Pavel Matějka

Department of Analytical Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

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Excitation profiles of SERS (surface-enhanced Raman scattering) and/or SERRS (surface-enhanced resonance Raman scattering) spectral bands of two forms of a Ag–bpy (bpy = 2,2'-bipyridine) surface complex and of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> on Ag nanoparticle (hydrosol) surfaces were determined from the spectra excited in the 458–600 nm region and are reported together with the FT-SERS spectra of the Ag–bpy surface complex and FT Raman spectra of [Ru(bpy)<sub>3</sub>] Cl<sub>2</sub>. Seven of the observed 11 fundamentals as well as their first overtones and combination bands are selectively enhanced in SERS of the Ag–bpy surface complex formed in the Ag colloid/HCl/bpy system. The profiles of these bands show a common maximum at ~540 nm. The selectively enhanced bands of the Ag–bpy surface complex have nearly the same wavenumbers as those enhanced in the SERRS and resonance Raman spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> upon excitation close to the 453 nm maximum of its MLCT absorption band. Moreover, the intensity patterns of the bpy vibrations of the two species match both in resonance (541 nm excitation for Ag–bpy, 458 nm for [Ru(bpy)<sub>3</sub>]<sup>2+</sup>) and in off-resonance (458 and 1064 nm for Ag–bpy, 1064 nm for [Ru(bpy)<sub>3</sub>]<sup>2+</sup>). The distinct band shapes of the excitation profiles of the selectively enhanced vibrational modes of the Ag–bpy surface complex, as well as the observation of overtones and combination bands in the SERS spectra upon excitation into this “band”, are interpreted in terms of a charge-transfer resonance contribution to the overall SERS enhancement. In view of the near-coincidence of the vibrational modes coupled to the resonant electronic transition of Ag–bpy with those coupled to the MLCT transition of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, the resonant electronic transition is tentatively assigned to a Ag metal to bpy ( $\pi^*$ ) CT transition.

## Introduction

During more than 20 years of thorough investigation of the phenomenon of SERS (surface-enhanced Raman scattering), the electromagnetic (EM) mechanism was proved to be the major mechanism responsible for the enhancement of Raman scattering of species (molecules, ions, radicals) located at or in proximity to nanostructures, nanoparticles, and/or nanoparticle assemblies of free-electron-like metals such as Ag, Au, and Cu.<sup>1</sup> This mechanism operates provided that the frequency of the incident radiation is close to the excitation frequencies of surface plasmons localized on the nanostructures<sup>2</sup> and gives rise to enhancement factors up to 10<sup>4</sup>–10<sup>5</sup>.<sup>1</sup> Recently, Campion and co-

workers<sup>3</sup> showed that a resonance enhancement by a factor of ~100 is achieved when the exciting radiation coincides with a charge transfer (CT) electronic transition within a metal–molecule surface complex formed upon chemisorption of pyromellitic dianhydride on atomically smooth Cu (111) and Cu (100) single-crystal faces. The existence of such an electronic transition has been proved by EEL (electron energy loss) and RR (resonance Raman) spectra. The authors proposed that the observed resonance Raman scattering via the CT intermediate state is the chemical mechanism of SERS. In these experiments,<sup>3</sup> the chemical (i.e., CT) mechanism of SERS was well separated

<sup>#</sup> Dedicated to the memory of Professor A. A. Vlček.

\* To whom correspondence should be addressed.

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from the EM mechanism, which enabled an unambiguous proof of its existence. Low-energy CT bands were also observed in the EEL spectra of adsorbed pyridine (py) and pyrazine (pz),<sup>4</sup> and the SERS spectra of py adsorbed on Ag island films were interpreted in terms of the chemical mechanism of SERS, operating simultaneously with the EM mechanism.<sup>5</sup>

Recently, we have accumulated experimental results indicating a CT mechanism contribution to the overall SERS enhancement of one specific form of 2,2'-bipyridine (bpy) adsorbed on the surface of Ag colloidal particles in an aqueous medium. Two spectrally different forms of adsorbed bpy denoted as form I (observed at neutral pH) and form III (observed at low pH adjusted by HCl, HBr, HI but not by H<sub>2</sub>SO<sub>4</sub>) were described by Kim and Itoh.<sup>6</sup> The notation of forms I and III (adopted also in this paper) was based on their earlier study of SERS of bpy adsorbed on the surface of a roughened Ag electrode as a function of the applied potential in which four spectrally different species were identified.<sup>7</sup> By contrast, only one form of adsorbed bpy, in particular form III in Kim and Itoh's notation, was observed in SERS of bpy adsorbed on a roughened Ag electrode in nonaqueous media throughout the -0.8 to 1.8 V potential range, although some potential-dependent frequency shifts of SERS spectral bands were observed.<sup>8</sup>

In previous experiments with bpy and [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as testing adsorbates for Ag colloids, we noticed already a striking similarity between the SERS spectra of form III of adsorbed bpy upon 514.5 nm excitation and both the SERRS (surface-enhanced resonance Raman scattering) and RR spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> excited with 457.9 nm.<sup>9</sup> Similarities and differences between the SERS spectra of form III of bpy and [Ru(bpy)<sub>3</sub>]<sup>2+</sup> adsorbed on a Ag electrode in dimethylformamide as a function of the applied potential were also noted in connection with an investigation of the various reduction steps of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>.<sup>8</sup> Furthermore, the SERRS spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> adsorbed on Ag colloid and excited by the 488 nm laser line revealed the occurrence of overtone and combination bands.<sup>10</sup> In our preliminary experiments, these overtones and combination bands appeared in the SERRS spectra upon 457.9 nm excitation but not upon 514.5 nm excitation.<sup>9</sup> Importantly, the SERRS spectrum of form III in the Ag colloid/bpy/HCl system (obtained with 514.5 nm excitation) showed overtone and combination bands at nearly the same frequencies as in the above-mentioned SERRS of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> excited with 457.9 nm.<sup>11</sup> These and other observations suggested that the 514.5 nm excitation line falls within the contour of a CT band specific for form III of the Ag-bpy surface complex.<sup>11</sup> Such a CT transition can be either molecule to metal or metal to molecule. The latter type of CT has been assumed to occur in surface complexes of N-containing heterocycles. In particular, a metal to molecule character of the CT was assumed in calculations of the changes in molecular geometry of pyrazine (pz) upon excitation of the CT, which in turn were found to be compatible with the relative band intensities in the SERS spectrum of the Ag-pz complex

formed on the Ag electrode and excited with 514.5 nm excitation.<sup>12</sup> The structure of the photoproduct resulting from surface photochemistry of phthalazine (pht) was interpreted in terms of excitation of a metal to molecule CT by 514.5 and 457.9 nm laser lines in the course of a SERS experiment.<sup>13</sup>

In this paper, we first focus on verification of our hypothesis about a CT contribution to SERS of form III of the Ag-bpy surface complex upon 514.5 nm excitation. We present SERS spectra of both form I and form III of bpy adsorbed on aggregated Ag colloidal nanoparticles measured in the 300–3200 cm<sup>-1</sup> region as a function of excitation wavelengths ranging from 457.9 to 600 nm and excitation profiles of all SERS spectral bands of each of the forms calculated from them. Furthermore, we explore in detail the origin of the analogy between the SERS spectral pattern of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> excited with the 457.9 nm excitation and SERS of form III of the Ag-bpy complex excited with 514.5 nm wavelength. We report SERRS spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> acquired with the same excitation wavelengths as SERS of bpy. SERRS spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> probe the long wavelength part of the 453 nm MLCT<sup>14,15</sup> band of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>. It is now well established that relative band intensities in the resonance Raman (RR) spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> are governed by the molecular geometry changes accompanying the transfer of charge from Ru(II) to one bpy ligand and formation of bpy<sup>-</sup>.<sup>16–18</sup> By contrast, the off-resonance relative band intensities in the Raman spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> are not known. We thus acquired FT Raman spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> as well as the FT-Raman SERS spectra of form III of bpy, which provided us with the off-resonance (with respect to CT resonance contribution) spectral patterns of the species. Comparison of both the resonance (457.9 nm excitation) and off-resonance (1064 nm) relative band intensities in the spectra of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> to the excitation-wavelength-dependent relative band intensities in the SERS spectra of form III of adsorbed bpy, as well as the SERS excitation profiles themselves, provides us with conclusive evidence of the existence of a Ag metal to bpy CT transition in form III of the Ag-bpy surface complex.

## Experimental Section

**Materials.** Redistilled, deionized water, and p.a. grade chemicals were used for all sample preparations.

**Preparation Procedures.** The Ag colloid was prepared by reduction of AgNO<sub>3</sub> by NaBH<sub>4</sub> (Merck) using procedure I described in ref 19. The Ag colloid/bpy (form I) system was prepared by adding 20 μL of a 10<sup>-2</sup> M aqueous solution of bpy and 10 μL of 10<sup>-2</sup> M aqueous HCl to 2 mL of Ag colloid. Ethanol (240 μL) was introduced into the system as an internal intensity standard for the SERS spectral measurements. SERS spectra of form I of adsorbed bpy were reproducibly obtained from the system. The Ag colloid/bpy (form III) system was prepared from the Ag colloid/bpy (form I) system (containing ethanol as the standard) by adding 10 μL of 1 M HCl. The efficiency and reproducibility of the procedure were confirmed by the reproducibility of the SERS spectra of form III obtained from the system upon 514.5 nm

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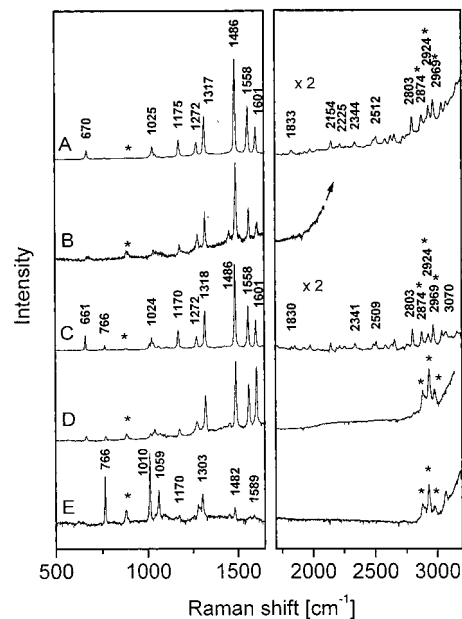
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excitation. The same system was used for the FT-SERS spectral measurement. The Ag colloid/ $[\text{Ru}(\text{bpy})_3]^{2+}$  system employed for the SERRS spectral measurements was obtained by introducing 20  $\mu\text{L}$  of a  $10^{-3}$  M aqueous solution of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  and 10  $\mu\text{L}$  of  $10^{-2}$  M HCl into 2 mL of Ag colloid and by a subsequent addition of 240  $\mu\text{L}$  of ethanol. The reproducibility of the surface plasmon absorption (SPA) of the systems described above was followed by UV/vis absorption spectroscopy. A  $10^{-4}$  M aqueous solution of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  was employed for the RR spectral measurements of  $[\text{Ru}(\text{bpy})_3]^{2+}$ , and a  $10^{-2}$  M aqueous solution of bpy was used to obtain the normal Raman (NR) spectrum of bpy. Both samples contained ethanol as the internal intensity standard. A solid sample of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  was employed for the FT Raman measurement.

**Instrumentation.** All types of Raman spectra (SERS, SERRS, RR, and NR) excited with laser lines in the visible spectral region were measured with a multichannel Raman spectrometer Dilor XY. A Spectra Physics 2016 argon ion laser was used as the source of exciting radiation, both directly (457.9, 476.5, 488.0, 496.5, 514.5 nm) and indirectly in combination with either a CR model 590 dye laser filled with coumarine 450 (541 and 552 nm exciting lines) or a CR model 490 dye laser filled with rhodamine 6G (584, 600, and 607 nm exciting lines). The laser power at the sample varied from 50 to 100 mW. The SERS spectra are the result of five spectral accumulations with a 7 s accumulation time. The accumulation time was reduced to 1 s for the SERRS of  $[\text{Ru}(\text{bpy})_3]^{2+}$ . UV/vis absorption spectra of the SERS samples were obtained with a Perkin-Elmer Lambda 5 spectrometer. For both types of measurements, samples were placed in a quartz cell (10 mm optical path). FT-Raman spectra were acquired with a Fourier transform near-infrared (FT-NIR) spectrometer Equinox 55/S (Bruker) equipped with a FT-Raman module FRA 106/S (Bruker) and a liquid  $\text{N}_2$  cooled Ge detector. The samples placed on a motorized XYZ sample stage were irradiated by the 1064 nm line of a Nd:YAG laser (Coherent Radiation). The scattered light was collected in the backscattering geometry.

**Acquisition of SERS Spectra as a Function of Excitation Wavelength.** Two strategies were adopted for the acquisition of SERS spectra of form III of adsorbed bpy at different excitation wavelengths. (i) At each of the excitation wavelengths employed, a SERS spectrum of a freshly prepared sample of the Ag colloid/bpy (form I) system was measured, yielding a SERS spectrum of form I of adsorbed bpy. Subsequently, 10  $\mu\text{L}$  of 1 M HCl was added and a SERS spectrum of form III was acquired (set M1). (ii) SERS spectra of the same sample of Ag colloid/bpy (form III) were measured for excitations ranging from 457.9 to 514.5 nm (set M2). SERS excitation profiles were constructed from both sets of measurements and mutually compared in order to eliminate any artifacts in the SERS excitation profiles that might possibly have arisen in set M1 from a random error in the sample preparation and in set M2 from the limited stability of the SERS active system that may cause sedimentation of aggregates accompanied by a decrease of SERS signal. A significant error or irreproducibility in the sample preparation in set M1 was also eliminated by measuring and mutually comparing the SPA spectra of the systems both prior to and after the SERS spectral measurements. Furthermore, to enable a precise normalization of the SERS spectra obtained from all the SERS-active systems studied, ethanol was employed not only as an internal intensity standard but also as an external intensity standard.

**Normalization of the SERS Spectra and Calculation of the SERS Excitation Profiles.** The intensities of the spectral bands of the samples expressed in terms of peak areas were first normalized with respect to that of the most intense and well-separated  $881\text{ cm}^{-1}$  band of ethanol (internal intensity standard). The concentration of ethanol was chosen in such a way that the  $881\text{ cm}^{-1}$  band, which did not interfere with any spectral band of the samples, was the only band of ethanol that could clearly be distinguished in the spectra. Since the response of the detector was strongly dependent on the wavelength (particularly in the red spectral region), the following refinement of the normalization procedure was applied to the spectral bands of the samples positioned above  $1100\text{ cm}^{-1}$  (i.e., for those far removed from the  $881\text{ cm}^{-1}$  ethanol band). The ratios of peak areas of the spectral bands of pure ethanol (external intensity standard), that is,  $1281\text{ cm}^{-1}/881\text{ cm}^{-1}$  ( $F_1$ ),  $1457\text{ cm}^{-1}/881\text{ cm}^{-1}$  ( $F_2$ ), and triplet  $2874, 2924, 2969\text{ cm}^{-1}/881\text{ cm}^{-1}$  ( $F_3$ ), were determined from the measurements at each excitation wavelength



**Figure 1.** (A) SERRS spectrum of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (457.9 nm excitation). (B) RR spectrum of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (457.9 nm excitation). (C) SERS spectrum of form III Ag–bpy surface complex (514.5 nm excitation). (D) SERS spectrum of form III Ag–bpy surface complex (457.9 nm excitation). (E) SERS spectrum of form I Ag–bpy surface complex (514.5 nm excitation). Raman bands of ethanol are marked by asterisks.

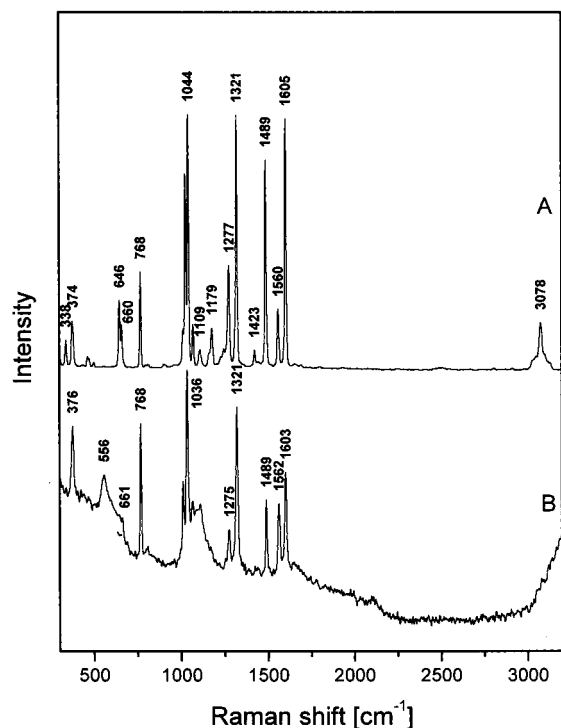
and employed as a correction factor ( $F_i$ ) by which the intensities of the SERS spectral bands obtained by normalization to the intensity of the  $881\text{ cm}^{-1}$  band of the ethanol internal standard were multiplied. Factor  $F_1$  was used for the sample spectral bands in the  $1000\text{--}1350\text{ cm}^{-1}$  region,  $F_2$  for the  $1350\text{--}1650\text{ cm}^{-1}$  region, and  $F_3$  for the  $2800\text{--}3100\text{ cm}^{-1}$  region. This procedure was actually used as a substitute for the normalization to the 1281, 1457, and triplet  $2874, 2924, 2969\text{ cm}^{-1}$  bands, respectively, of the ethanol internal standard. This overall normalization procedure thus ensured a proper correction for changes of the laser beam power at each wavelength, the  $\nu^4$  dependence of Raman intensities, and the wavelength dependence of the detector response. The validity of this normalization procedure was verified by measuring the wavelength dependence of the NR spectrum of bpy, which yielded a straight line for all normalized bands of bpy. To facilitate the mutual comparison of the excitation profiles, the profile of each band is presented as the wavelength dependence of the relative enhancement of this band, obtained for each wavelength as the ratio of the band intensity at that particular wavelength to the minimum value of the band intensity in the overall profile.

## Results and Discussion

**SERS Spectra of the Ag–bpy Surface Complexes in Comparison to the SERRS Resonance and Off-Resonance Raman Spectra of  $[\text{Ru}(\text{bpy})_3]^{2+}$ .** RR and SERRS spectra of  $[\text{Ru}(\text{bpy})_3]^{2+}$  excited at 457.9 nm, SERS spectra of form III of the Ag–bpy surface complex excited at 514.5 and 457.9 nm, and the SERS spectrum of form I of the Ag–bpy surface complex excited at 514.5 nm are presented in Figure 1. The RR spectrum (Figure 1B) and SERRS spectrum (Figure 1A) of  $[\text{Ru}(\text{bpy})_3]^{2+}$  excited at 457.9 nm correspond closely, both in frequencies and relative band intensities, with the RR spectrum that was employed for the NCA calculation of the Ru(II)–bpy system in refs 20 and 21. Figure 1 also demonstrates a striking similarity between the SERRS spectrum of  $[\text{Ru}(\text{bpy})_3]^{2+}$  excited at 457.9 nm (spectrum A) and the SERS spectrum of form III

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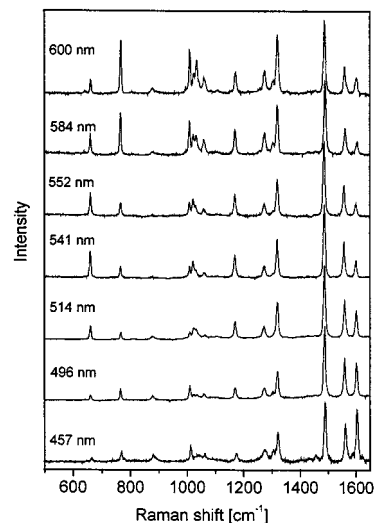


**Figure 2.** (A) FT Raman spectrum of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (1064 nm excitation). (B) FT-SERS spectrum of form III Ag-bpy surface complex (1064 nm excitation).

of the Ag-bpy surface complex excited at 514.5 nm (spectrum C). This similarity encompasses both the frequencies (note that the wavenumbers of the 766, 1010, 1272, 1486, 1558, and 1601 cm<sup>-1</sup> bands are identical in both spectra) and the relative band intensities and comprises both the fundamentals (bands in the 300 to ca. 1650 cm<sup>-1</sup> region and the 3070 cm<sup>-1</sup> band) and the overtones and combination bands (in the ca. 1650–3200 cm<sup>-1</sup> spectral region).

On the other hand, a comparison of the SERS spectra of form III (Figure 1C) and form I (Figure 1E) of the Ag-bpy surface complex (both at 514.5 nm excitation) clearly demonstrates the spectral differences of the two forms of bpy adsorbed on Ag colloidal nanoparticles. Whereas the differences in the frequencies of fundamentals of these two forms were pointed out and discussed earlier,<sup>6,7</sup> the presence of overtones and combination bands in the SERS of form III and their absence in the SERS of form I (upon 514.5 nm excitation) are reported here for the first time. The analogy between the SERS spectrum of form I and the normal Raman spectrum of [Ag(bpy)<sub>2</sub>]NO<sub>3</sub> was pointed out in refs 6 and 7. The synthetically prepared complex was later characterized by X-ray structure determination.<sup>22</sup>

The SERS spectrum of form III of the Ag-bpy surface complex excited at 457.9 nm (Figure 1D) shows significant differences from that excited at 514.5 nm (Figure 1C), namely, the absence of overtones and combination bands as well as the changes of the relative band intensities of fundamentals (note, for example, the increase of the relative intensity of the 766 cm<sup>-1</sup> band with respect to the 661 cm<sup>-1</sup> band and the changes of the relative intensities of the 1486, 1558, and 1601 cm<sup>-1</sup> bands). Interestingly, the SERS spectrum of form III of the Ag-bpy surface complex excited at 1064 nm and acquired by the FT Raman technique (Figure 2B) shows a relative band intensity pattern that is analogous to that obtained upon 457.9 nm



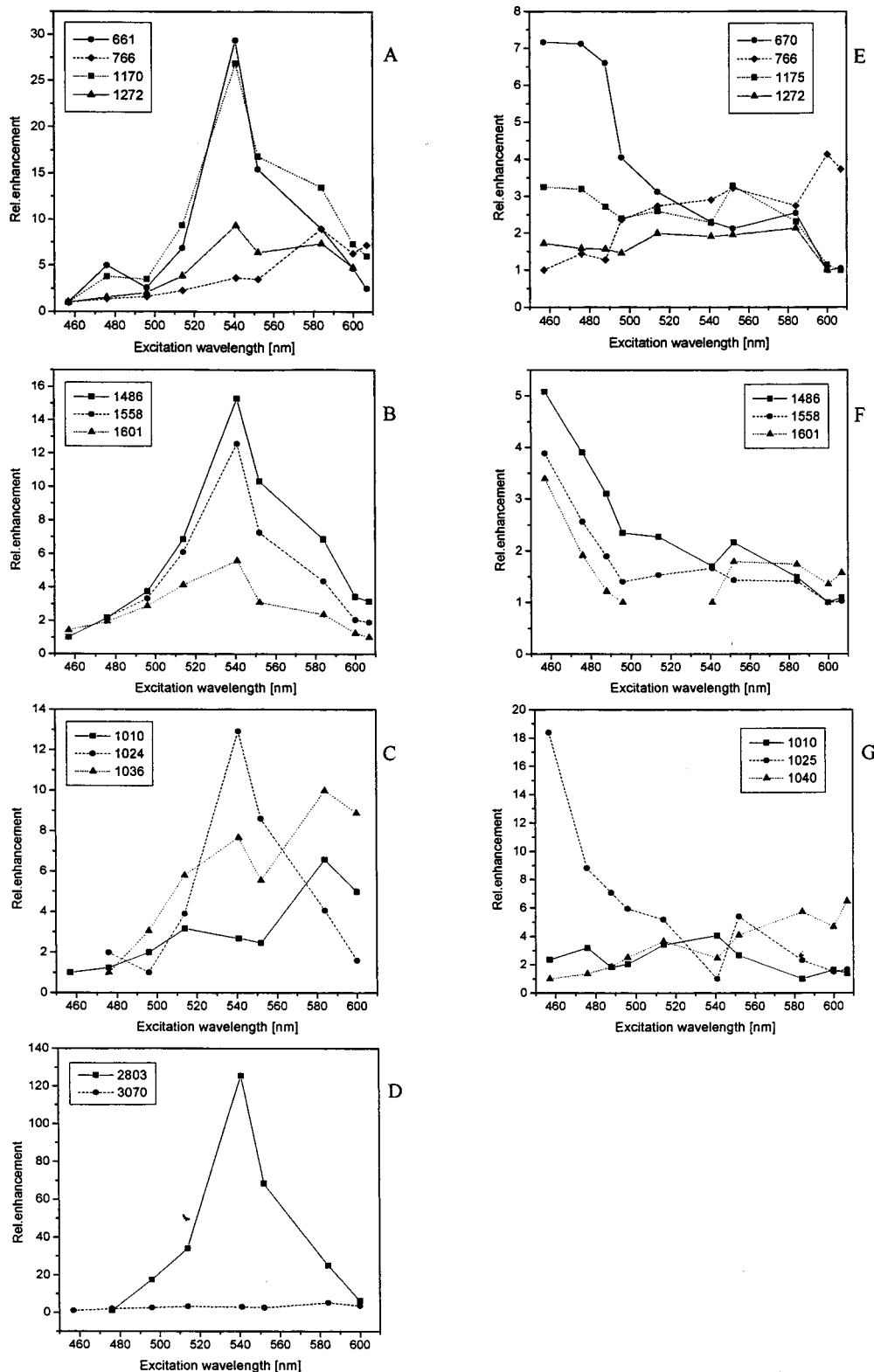
**Figure 3.** SERS spectra of form III Ag-bpy surface complex as a function of excitation wavelength: 457.9, 496.5, 514.5, 541, 552, 584, and 600 nm.

excitation owing to the absence of overtones and combination bands and to the relative intensities of the 661 and 768 (766) cm<sup>-1</sup> and of the 1489 (1486), 1562 (1558), and 1603 (1601) cm<sup>-1</sup> bands. This pattern, in turn, corresponds closely with that observed in the normal Raman spectrum of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> obtained by FT Raman spectroscopy at 1064 nm (Figure 2A). Since there is no electronic transition within the [Ru(bpy)<sub>3</sub>]<sup>2+</sup> cation that could be in resonance with the 1064 nm excitation, the spectral pattern of spectrum A in Figure 2 is an off-resonance pattern, i.e., normal Raman spectral pattern of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>. By contrast, the RR and SERRS spectral patterns of spectra B and A, respectively, in Figure 1 result from a close match between the 457.9 nm excitation and the 453 nm maximum of the MLCT band of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>.<sup>14–18,20,21</sup>

**Excitation Profiles of the SERS Spectral Bands of the Ag-bpy Surface Complexes and the SERRS Bands of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>.** An explanation of the above-mentioned analogies and differences in spectral patterns emerges from a detailed analysis of the SERS excitation profiles of form III and form I of the Ag-bpy surface complex and of the SERRS excitation profile of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (Figures 4–6). The profiles were calculated from the corresponding SERS and/or SERRS spectra measured at 10 different excitation wavelengths in the 457.9–601 nm region (Figure 3). Excitation profiles of 11 fundamentals and of a combination band at 2803 cm<sup>-1</sup> (originating probably from 1318 + 1486 cm<sup>-1</sup>) of form III of the Ag-bpy surface complex are shown in parts A–D of Figure 4. Distinct maxima are observed in the excitation profiles of the combination band (Figure 4D) and the fundamental bands at 661, 1024, 1170, 1486, and 1558 cm<sup>-1</sup>; less pronounced maxima are present in the profiles of the 1272 and 1601 cm<sup>-1</sup> bands. The positions of these maxima cannot be determined exactly, since the profiles consist of distinct points between which lines are drawn only as a guideline. However, we can conclude that the profiles have a common maximum that lies between 514.5 and 540 nm and is located close to 540 nm. On the other hand, no such a maximum is observed in the excitation profiles of the 766, 1010, 1036, and 3070 cm<sup>-1</sup> bands. The former three bands show a varying degree of a monotonic intensity increase toward the red spectral region.

To verify the results obtained, we compare, in Figure 5, the parts of the excitation profiles of form III of Ag-bpy, which were obtained by two independent sets of measurements denoted

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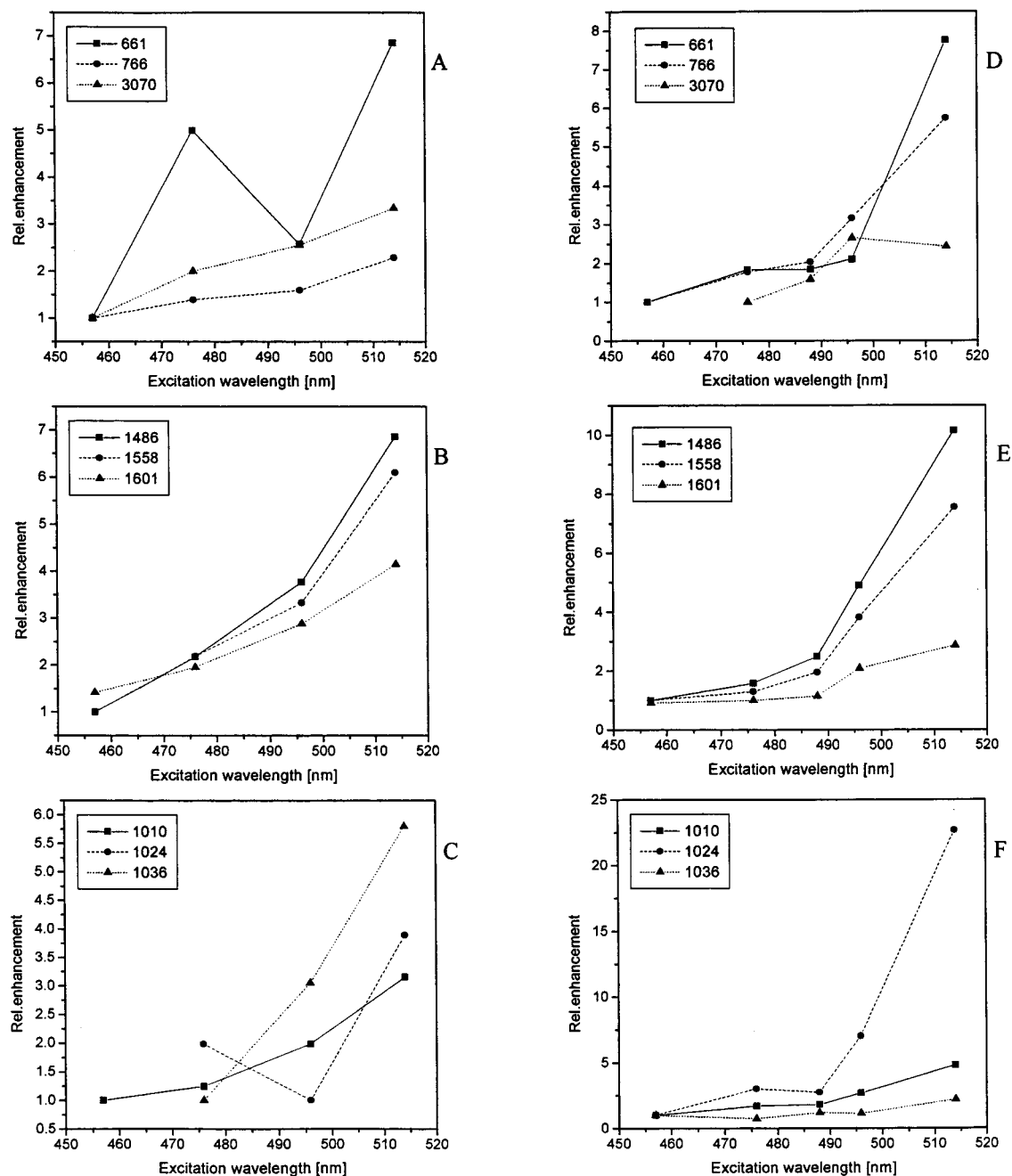
**Figure 4.** Excitation profiles of the SERS spectral bands of form III Ag-bpy surface complex (A-D) and of the SERRS spectral bands of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> (E-G).

as M1 and M2 in the Experimental Section. Both sets of profiles match reasonably well for all bands except for the 1036 cm<sup>-1</sup> band, which shows enhancement in set M1 but not in set M2. However, the complete profile obtained from the M1 data (Figure 4C) does not actually maximize at 540 nm but increases further to the red spectral region, and thus, the 1036 cm<sup>-1</sup> band is not among the resonance-enhanced bands in sets M1 and M2. One should also take into account that the set of close-lying

bands in the 1010–1040 cm<sup>-1</sup> region had to be subjected to a computer separation that might also have induced some differences between the two sets.<sup>23</sup>

In contrast to the excitation profiles of form III of the Ag-bpy surface complex, no excitation profile of any spectral band

(23) Separation of the SERS and SERRS spectral bands of Ag-bpy surface complexes and of [Ru(bpy)<sub>3</sub>]<sup>2+</sup> in the 1000–1100 cm<sup>-1</sup> region was carried out by the Origin computer program.



**Figure 5.** Excitation profiles of the SERS spectral bands of form III Ag–bpy surface complex obtained by the M1 (A–C) and M2 (D–F) sets of measurements.

of form I shows a distinct maximum. This is demonstrated in Figure 6, which shows for comparison the excitation profiles of selected bands of form III and form I. Most illustrative is the comparison between the profiles of the 1486  $\text{cm}^{-1}$  band of form III and the 1482  $\text{cm}^{-1}$  band of form I in Figure 6A; whereas the profile of the 1486  $\text{cm}^{-1}$  band shows a distinct maximum (the relative enhancement at 540 nm being  $\sim 15$ ), the profile of the 1482  $\text{cm}^{-1}$  band is essentially flat with the relative enhancement factor at 540 nm being close to 1. The existence of a maximum close to 540 nm in the SERS excitation profiles of several (7 of the total amount of 11) observed fundamentals is thus a specific feature of form III of the Ag–bpy surface complex. Furthermore, the observation that (i) the  $\sim 540$  nm maximum occurs only in the excitation profiles of some of the  $A_1$  modes of adsorbed bpy (compare, for example, profiles of the 661 and 766  $\text{cm}^{-1}$  in Figure 4A) and that (ii) this selectivity is not systematically related to the mode

frequency indicates that the enhancement is due to a resonance mechanism analogous to RR, i.e., due to the chemical mechanism of SERS.<sup>3</sup>

**Manifestation of the Chemical (CT) and EM Mechanism of SERS in the Shapes of the Excitation Profiles of Form III Ag–bpy Surface Complex Modes.** In the system with Ag colloidal aggregates, a chemical mechanism operates in addition to the electromagnetic (EM) mechanism of SERS. We thus inspected the morphology and optical responses of Ag colloidal aggregates in the Ag colloid/bpy (form III) system. TEM micrographs (not presented here) show the presence of large aggregates. UV/vis spectra of the Ag colloid/bpy (form III) system (Figure 7) are in good agreement with the calculated SPA spectra of fractal colloidal aggregates.<sup>24</sup> In accord with

(24) Markel, V. N.; Shalaev, V. M.; Stechel, E. B.; Kim, W.; Armstrong, R. *Phys. Rev. B* **1996**, *53*, 2425.

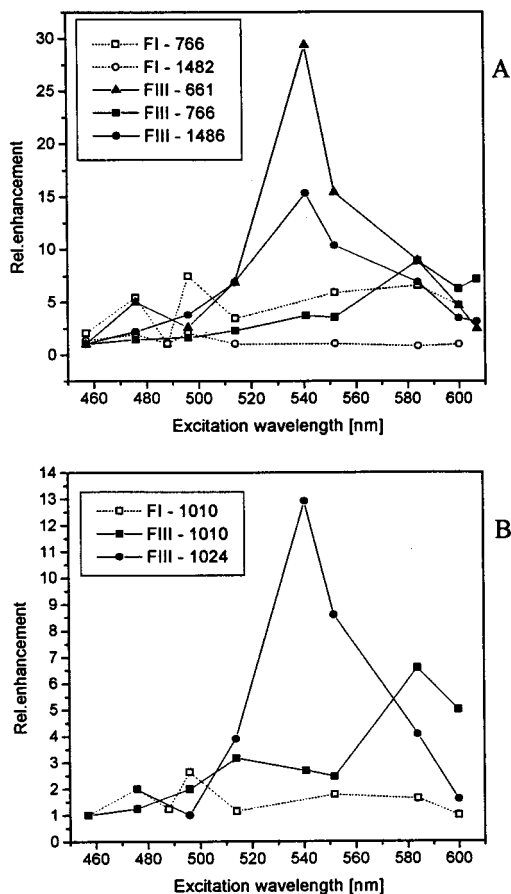


Figure 6. Comparison of the excitation profiles of the SERS spectral bands of form I (FI) and form III (FIII) of the Ag-bpy surface complex.

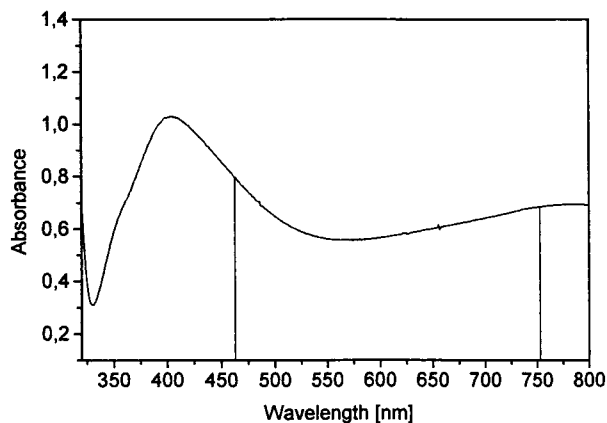


Figure 7. UV/vis absorption spectrum of Ag colloid/HCl/bpy system from which SERS spectra of form III of Ag-bpy surface complex were obtained.

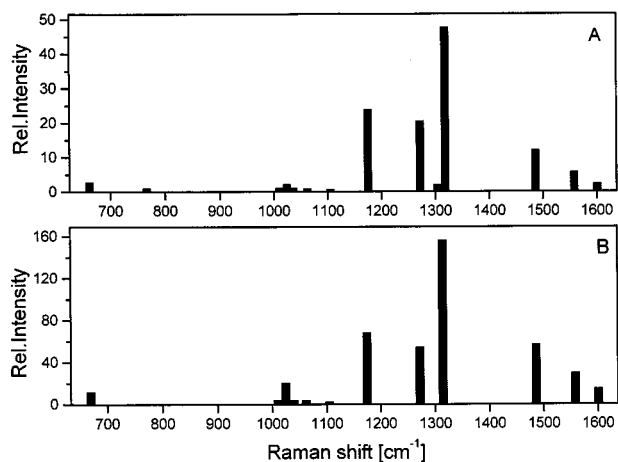
these calculated SPA spectra, no distinct maximum appears on the SPA spectrum of the Ag colloid/bpy (form III) in the particular region spanned by our SERS spectral measurements (marked in Figure 7). We can thus exclude the possibility that the maximum in the excitation profiles of certain bands of Ag-bpy form III originates from the EM mechanism of SERS. On the other hand, the increase of the SERS spectral intensity toward the red spectral region clearly observed in those excitation profiles that do not show a maximum at 540 nm (such as those of the 766, 1010, and 1036  $\text{cm}^{-1}$  modes) is in good agreement with the predicted and experimentally observed wavelength dependence of SERS spectra of adsorbates on fractal Ag colloidal aggregates in the absence of a chemical mechanism

enhancement (such as those of phthalazine at excitation wavelengths longer than 514.5 nm in ref 25). While the presence of the  $\sim 540$  nm maximum in the excitation profiles of certain bands (parts A–D of Figure 4) is attributed to the chemical mechanism of SERS, the asymmetric shape of the profiles, namely, the slow decrease of the SERS spectral intensity at wavelengths longer than the 540 nm maximum, can be explained as a contribution of the wavelength dependence of the SERS enhancement by the EM mechanism.

The already-mentioned similarities and differences between the intensity patterns of the spectra in Figures 1 and 2 can now be explained. The matching spectral patterns in spectra A–C of Figure 1 are the resonance intensity patterns of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and of form III Ag-bpy surface complex. By contrast, the matching spectral patterns of spectrum A in Figure 2, spectrum B in Figure 2, and spectrum D in Figure 1 are the off-resonance intensity patterns of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and of form III Ag-bpy surface complex. It should be noted that for the form III Ag-bpy surface complex, the off-resonance pattern is obtained both at shorter (457.9 nm) and longer (1064 nm) excitation wavelengths relative to the resonance excitation (541 nm). This is indeed expected in the case of a molecular resonance (chemical mechanism) contribution to the overall SERS enhancement, in contrast to the case of the enhancement entirely by the surface plasmon resonance (EM mechanism). We thus postulate the existence of a resonance CT electronic transition (with an absorption band maximum close to 540 nm) responsible for the chemical mechanism contribution to the SERS of the form III Ag-bpy surface complex.

**Character of the CT Transition of the Form III Ag-bpy Surface Complex.** A comparison between the excitation profiles of the matching SERS spectral bands of form III Ag-bpy surface complex (parts A–D of Figure 4) and the SERS SERS spectral bands of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (parts E–G of Figure 4) enables us to elucidate the nature of the above-mentioned CT electronic transition on the basis of the following arguments. The SERS SERS spectral bands of  $[\text{Ru}(\text{bpy})_3]^{2+}$  at 661, 1024, 1170, 1486, 1558, and 1601  $\text{cm}^{-1}$ , which show a distinct intensity increase when the excitation wavelength approaches the 453 nm maximum of the MLCT band, are the matching counterparts of those bands of form III of the Ag-bpy surface complex, which show a distinct maximum at 540 nm on their excitation profiles. Analogously, the resonance nonenhanced bands of  $[\text{Ru}(\text{bpy})_3]^{2+}$  at 766, 1010, and 1040  $\text{cm}^{-1}$  are also not enhanced for form III of Ag-bpy upon 541 nm excitation. The only exception is the 1272  $\text{cm}^{-1}$  band, which is not enhanced for  $[\text{Ru}(\text{bpy})_3]^{2+}$  but weakly enhanced for form III Ag-bpy upon 541 nm excitation. Profiles of the 3072  $\text{cm}^{-1}$  fundamental and the 2802  $\text{cm}^{-1}$  combination bands of  $[\text{Ru}(\text{bpy})_3]^{2+}$  could not be obtained because of an increase of the spectral background in the high-wavenumber region. Summarizing the results, we conclude that of the 10 matching fundamentals inspected, 9 show analogous trends in intensities (i) for  $[\text{Ru}(\text{bpy})_3]^{2+}$  at excitations approaching the maximum of the MLCT electronic transition at 453 nm and (ii) for form III Ag-bpy at excitations approaching 540 nm at which the maximum appears in the excitation profiles of the resonance-enhanced modes.

In addition, we evaluated quantitatively the relative band intensity patterns in both the SERRS spectrum of  $[\text{Ru}(\text{bpy})_3]^{2+}$  excited at 457.9 nm (Figure 8A) and the SERS spectrum of the form III Ag-bpy surface complex excited at 541 nm (Figure 8B), i.e., in the spectra obtained, for each species, by excitation



**Figure 8.** Relative band intensity patterns in (A) SERRS spectrum of  $[\text{Ru}(\text{bpy})_3]^{2+}$  excited at 457.9 nm. (B) SERS spectrum of form III Ag–bpy surface complex excited at 541 nm.

close to the resonant electronic transition. The relative band intensity patterns (Figure 8) relate, in each of the normalized spectra, the intensities of the individual bands to that of the  $766\text{ cm}^{-1}$  band. This band was selected as a common standard because it experiences no resonance enhancement, as apparent from the shape of its profile for both species (parts A and E of Figure 4). There is, indeed, a striking agreement between these intensity patterns (apart from the different intensity scale originating from different overall enhancement factors and the difference in the relative band intensities of the  $\sim 1170\text{ cm}^{-1}$  bands). Applying the well-known empirical rule of Tsuboi<sup>26</sup> justified by several theoretical treatments of the RR effect,<sup>27,28</sup> we conclude that coordinated bpy undergoes analogous geometry changes in the form III Ag–bpy surface complex upon the electronic transition at 540 nm as in  $[\text{Ru}(\text{bpy})_3]^{2+}$  upon MLCT excitation (at 453 nm). The geometry changes of  $[\text{Ru}(\text{bpy})_3]^{2+}$  that accompany this MLCT transition originate from the transfer of charge from Ru(II) to the lowest  $\pi^*$  orbital of one of the three bpy ligands. Accordingly, the normal modes that are most enhanced in the RR and/or SERRS spectra excited by a wavelength matching this transition are associated with population of this  $\pi^*$  orbital of bpy and formation of  $\text{bpy}^-$ . Since the same modes are selectively enhanced in the SERS spectra of the form III Ag–bpy surface complex excited close to the 540 nm maximum (Figures 3 and 8), we conclude that their enhancement is associated with the same change of the bpy ligand geometry as upon MLCT transition in  $[\text{Ru}(\text{bpy})_3]^{2+}$ , i.e., by a transfer of charge to the lowest  $\pi^*$  orbital of bpy. We thus attribute the observation of the maxima in the excitation profiles of the form III Ag–bpy surface complex to resonance with a Ag metal to bpy molecule (adsorbate) charge-transfer transition.

**Differences between the Form I and Form III Ag–bpy Surface Complexes.** The results described in this paper allow us to discuss the differences between form I and form III of the Ag–bpy surface complex. Form I is a vibrational spectral analogue of  $[\text{Ag}(\text{bpy})_2]^+$  in which the bpy ligand is bidentately coordinated to a single  $\text{Ag}^+$  cation.<sup>22</sup> None of these species shows a CT transition in the visible region, as witnessed by the

electronic absorption spectrum of  $[\text{Ag}(\text{bpy})_2]^+$ <sup>11</sup> and by the SERS excitation profile of form I of Ag–bpy. In light of the results obtained, we assume that form I is actually a  $[\text{Ag}(\text{bpy})_2]^+$  species attached to the Ag colloidal surface via interaction with adsorbed chlorides.

On the other hand, there is the above-mentioned striking match between the frequencies of the SERS bands of form III of Ag–bpy and the SERRS/RRS bands of  $[\text{Ru}(\text{bpy})_3]^{2+}$ . On the basis of the NCA calculation of the Ru(II)–bpy fragment,<sup>20,21,29</sup> all SERRS bands of  $[\text{Ru}(\text{bpy})_3]^{2+}$ , the profiles of which are presented in parts E–G of Figure 4, are assigned to vibrational modes of a bpy ligand in the cis conformation bidentately chelated to Ru(II). We thus assume that in the form III Ag–bpy surface complex, bpy is also coordinated as a chelate. Nevertheless, the wavenumber of the bpy breathing mode, which shifts from  $991\text{ cm}^{-1}$  in free bpy (trans form) to  $1001\text{ cm}^{-1}$  in  $\text{bpy}\cdot\text{H}_2\text{O}$  (cis form)<sup>30,31</sup> to  $1010\text{ cm}^{-1}$  in form I and to  $1024\text{ cm}^{-1}$  in form III, and the wavenumbers of the other bpy bands indicate a stronger bonding interaction in form III compared to form I. Furthermore, it should be noted that the frequencies of the resonance-enhanced bands of coordinated bpy in the spectra of other transition metal complexes, namely,  $[\text{Os}(\text{bpy})_3]^{2+}$  and  $[\text{Fe}(\text{bpy})_3]^{2+}$ ,<sup>10,17,32</sup> are very close to those of  $[\text{Ru}(\text{bpy})_3]^{2+}$  and of the form III Ag–bpy surface complex. In particular, both the frequencies and relative band intensities in the SERRS spectrum of  $[\text{Fe}(\text{bpy})_3]^{2+}$  excited by  $514.5\text{ nm}$ <sup>10</sup> closely match those in the SERRS spectra of  $[\text{Ru}(\text{bpy})_3]^{2+}$  (457.9 nm excitation) and in the SERS spectra of form III Ag–bpy (541 nm excitation). Both  $[\text{Os}(\text{bpy})_3]^{2+}$  and  $[\text{Fe}(\text{bpy})_3]^{2+}$  possess MLCT transitions at ca. 500 and at 524 nm, respectively. We thus propose that the typical frequency pattern of coordinated bpy in the RR and SERRS in the above-mentioned tris(bpy) complexes as well as in SERS of Ag–bpy originates from a stronger metal–ligand bonding interaction than that encountered in both form I Ag–bpy surface complex and in  $[\text{Ag}(\text{bpy})_2]^+$ . Both the stronger bonding interaction and the existence of the Ag metal to bpy CT in form III of Ag–bpy are incompatible with coordination of bpy to a single (isolated)  $\text{Ag}^+$  cation and indicate that form III is the actual surface complex of bpy in which bonding of bpy to Ag metal surface enables an interaction of the bpy orbitals with the Ag metal surface states. Furthermore, the results presented in this paper indicate that HCl plays a dual role in Ag colloid/HCl/bpy systems: (I) as an aggregation agent, for which addition of the  $10^{-2}\text{ M}$  acid into the system is sufficient to produce large fractal aggregates, and (II) as the agent that modifies the surface of Ag colloidal particles. The surface modification is dependent on HCl concentration, while the addition of  $10^{-2}\text{ M}$  HCl promotes adsorption of cations, i.e.,  $[\text{Ag}(\text{bpy})_2]^+$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$ , most probably via their interaction with adsorbed chlorides, and addition of 1 M acid induces a more severe surface modification that enables formation of the Ag–bpy surface complex. A detailed elucidation of the mechanism of this surface modification will be provided elsewhere.<sup>31</sup>

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(29) The only band that was not assigned in the NCA in ref 20 and that is actually very weak in the RR at 457.9 nm (presented both in this paper and in ref 20) is that at  $1040\text{ cm}^{-1}$ . This band, however, is clearly observed in the SERRS spectra (both in those presented in this paper and in ref 10). In ref 21, the  $1040\text{ cm}^{-1}$  band was assigned to  $\nu_{15}$  instead of the  $1028\text{ cm}^{-1}$  band assigned to this mode in ref 20. The comparison of the resonance and off-resonance Raman spectra presented in this paper indicates a strong resonance enhancement of the  $1028\text{ cm}^{-1}$  upon resonance and thus favors the original assignment in ref 20.

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**CT Mechanism Contribution to SERS.** Finally, we conclude that manifestation of the chemical mechanism contribution to SERS of form III of Ag–bpy is analogous to RR scattering. While this conclusion is generally in accord with that achieved for the chemical mechanism of SERS of the pyromellitic dianhydride chemisorbed on Cu single-crystal surfaces,<sup>3</sup> observation of overtones and combination bands in SERS of form III Ag–bpy surface complex provides a new piece of evidence for the analogy between the chemical mechanism of SERS and RR scattering. According to our knowledge, observation of overtones in SERS of adsorbates, which are nonchromophoric as free species, has not been reported up to now. On the other hand, overtones are known to appear in SERRS of chromophoric adsorbates<sup>10</sup> and in SERRS of chromophores formed by a redox process accompanying adsorption.<sup>33</sup> Observation of overtones and combination bands in SERS of form III Ag–bpy surface complex also indicates operation of the Franck–Condon type

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of the resonance enhancement mechanism. Finally, we would like to emphasize that in SERS of form III Ag–bpy surface complex formed on the surface of Ag colloidal (nanoparticle) aggregates, the CT resonance mechanism operates in addition to the EM mechanism. While the EM mechanism contribution to the overall SERS enhancement of Ag–bpy is estimated to reach a factor of  $10^4$ , the additional enhancement by the resonance CT mechanism is found to contribute by a factor of ca. 30 for the most enhanced fundamental and by ca. 150 for the combination band. Our results show that the magnitude of the CT resonance enhancement in a system in which the CT and the EM mechanism operate simultaneously (1–2 orders of magnitude) is comparable to that achieved in a system in which the CT resonance is the only enhancement mechanism.<sup>3</sup>

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