Contribution of hydrogen bonding to charge-transfer induced surface-enhanced Raman scattering of an intermolecular system comprising \( p \)-aminothiophenol and benzoic acid†

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We investigated the influence of hydrogen bonds (H-bonds) on the intermolecular interactions of a system comprising \( p \)-aminothiophenol (PATP) and benzoic acid (BA) using surface-enhanced Raman scattering (SERS) for the first time. In this system, H-bonds form through intermolecular interactions between the \( \equiv \text{NH}_2 \) and \( \equiv \text{COOH} \) groups and promote the charge-transfer (CT) transition from the Ag substrate to the adsorbed PATP molecules. Accordingly, the intensities of the non-totally symmetric vibrations (the \( b_2 \)-type bands) of PATP are influenced through the Herzberg–Teller contribution. This is clearly a BA concentration-dependent phenomenon. This behaviour can be attributed to an increase in the degree of conjugation of the system, which facilitates the CT process in the system with H-bonds. Furthermore, temperature-dependent SERS experiments and their two-dimensional (2D) correlation analysis confirmed that the formation of H-bonds facilitated the CT transition between the adsorbed molecules and substrate. The degree of CT was reduced by H-bond breakage that occurred with increasing temperature. An additional SERS experiment involving substituted BA molecules yielded similar conclusions.

Introduction

A hydrogen bond (H-bond) is a bond between an electron-deficient hydrogen atom and a region of high electron density and is of continuing interest to chemists. H-bonds play a key role in determining molecular conformation, molecular aggregation, and the function of a vast number of chemical systems ranging from inorganic to biological.1–3 In supramolecular chemistry, they are important particularly with respect to intermolecular interactions.4,5 Unlike covalent bonds, which involve massive shifts of electron density, the rearrangements that occur as a consequence of H-bonding are much more subtle. The development of an effective technique for exploring H-bonding has always been a goal in the field of chemistry. In recent years, there have been extensive and in-depth studies on H-bonding that include the use of techniques such as infrared spectroscopy and X-ray crystallography.6–9 In addition, new techniques, such as near-infrared and terahertz spectroscopy, have recently been introduced in the field of H-bond research.

Surface-enhanced Raman scattering (SERS) has also been proven to be very useful for studying H-bonding. Here, we report a detailed SERS study of intermolecular H-bonding in a system.

SERS has proved to be a powerful analytical technique with the advantages of high sensitivity, high selectivity, non-destructive trace detection, and no strict requirements for the measurement conditions of the sample. It has been extensively applied to various fields including chemical and industrial fields, bioscience, medical diagnosis, and sensor technology.10–13 Currently, it is widely accepted that the electromagnetic (EM) mechanism is responsible for its most important contribution, which is a long-range effect from a large, local electrical field generated by collective oscillations of surface plasmons in noble metal particles.14,15 An additional contribution to the SERS phenomenon is the charge transfer (CT) mechanism, which involves the transfer of an electron from the Fermi level of the metal to an unoccupied molecular orbital of the adsorbate or vice versa depending on the energy of the photon and electric potential of the interphase.16,17 It has long been believed that the two enhancement mechanisms simultaneously contribute to SERS; it can amplify the Raman signals of adsorbed resonant molecules by as much as \( 10^{14} \) under suitable conditions, even allowing single-molecule detection.18,19 The CT contribution...

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continues to be of great importance to SERS. Our group has focused on investigating chemical mechanisms using SERS and revealed several important results, in particular, CT enhancement in the semiconductor field.\textsuperscript{20–24} Recently, we investigated the pH-response mechanism of \( p \)-aminobenzonethiol based on the CT contribution.\textsuperscript{23}

\( p \)-Aminothiophenol (PATP), which contains an amino group, has been used as a unique probe molecule for SERS.\textsuperscript{25–29} Notably, some of the characteristic peaks of PATP occur at around 1076, 1141, 1390, and 1435 cm\(^{-1}\). These are attributed to non-totally symmetric vibrations, which predominate in the SERS spectrum with \( \text{b}_2 \) symmetry. The relative intensity of these peaks with respect to the \( \text{a}_1 \)-type bands (totally symmetric vibrations) is dependent not only on the type of SERS substrate but also on the relevant measurement conditions. The intensities of the \( \text{b}_2 \)-type bands are usually dependent on the pH of the solution because of the sensitivity of the amine group. Here, we chose a series of carboxyl derivatives. The system under study contains amine and carboxyl groups that form H-bonds and resembles biological molecules, such as proteins and DNA, which contain abundant amine and carboxylic acid groups and mainly interact by aromatic-aromatic, edge-to-face, CH–π, and H-bonding interactions, etc.\textsuperscript{23,30,31}

In this work, we explore the effect of H-bonding on systems with intermolecular interactions by employing the SERS technique using a system composed of PATP and BA molecules. There are few reports in the literature on the application of SERS technology. This study represents an innovative based on the influence of intermolecular interaction in the study of H-bonds via SERS technology combined with the CT mechanism. The effect of H-bonding on the adsorbed molecules can be elucidated by SERS because of its high sensitivity, applicability to samples in any physical state and condition, and ability to be investigated simultaneously with the degree of CT in the system. These aspects facilitate the study of slight changes in the spectra of adsorbed molecules caused by intermolecular interactions. Moreover, the influence of H-bonding in systems cannot be elucidated as conveniently or effectively using other methods, such as NMR and infrared spectroscopy. This study considers the susceptibility of PATP to the surrounding conditions. Note that the intensities of the \( \text{b}_2 \)-type bands of PATP are significantly enhanced by the presence of BA in a Ag–PATP–BA system fabricated by self-assembly. Furthermore, varying the concentrations of BA enables elucidation of the effect of different amounts of carboxyl groups on the PATP interactions in this system via the SERS spectra. The corresponding results confirm that the intensities of the \( \text{b}_2 \)-type bands of PATP are dependent on the concentration of BA. The phenomenon is due to the increase in the conjugation of the system caused by the introduction of BA molecules and the consequent formation of H-bonds, which promotes the CT process through the Herzberg–Teller contribution. Using a temperature-dependent SERS experiment on the intermolecular interactions of PATP and BA, we obtain the following conclusions. The formation of H-bonds facilitates the CT process between the adsorbed PATP molecules and the Ag substrate. With increasing temperature, some of the H-bonds in the system break, resulting in reduced CT. Furthermore, the same conclusion is reached using two-dimensional (2D) correlation SERS spectra. We also discuss experiments using substituted BA molecules, such as \( p \)-cyanobenzoic acid (CBA) and \( p \)-hydroxybenzoic acid (HBA), in place of BA. In these systems, the formation of H-bonds similarly promotes the CT process in the intermolecular system.

**Experimental section**

**Chemicals**

\( p \)-Aminothiophenol (PATP) and benzoic acid (BA) were purchased from Sigma Aldrich and J&K Chemical Co., respectively. \( p \)-Cyanobenzoic acid (CBA), \( p \)-hydroxybenzoic acid (HBA), and other chemicals (analytic grade) were obtained from Beijing Chemical Reagent Factory. All chemicals were used without further purification. Highly purified water with a resistivity greater than 18.0 M\( \Omega \) cm (Millipore Milli-Q System) was used to prepare aqueous solutions of the above reagents.

**Preparation of a silver substrate**

A Ag hydrosol was prepared using the following procedures reported by Lee and Meisel.\textsuperscript{32} Briefly, 36 mg of AgNO\(_3\) was dissolved in 200 mL of water under vigorous stirring. A 4 mL aliquot of 1% trisodium citrate was added to the AgNO\(_3\) solution as it began to boil, and the temperature was held at 85 °C for 40 min. A Ag hydrosol with a narrow surface plasmon absorption at 416 nm, as shown in Fig. 2A, was prepared. Subsequently, a layer of Ag nanoparticles was assembled via electrostatic interaction on glass slides that were modified with a positively charged polyelectrolyte after hydroxylation. A scanning electron microscopy (SEM) image of the surface morphology of the assembled Ag nanoparticles is presented in Fig. 2B. It is evident that the silver nanoparticles are spherical and have an average diameter of \( \sim 70 \) nm.

**Preparation of the system**

Initially, the prepared substrates were soaked overnight in a PATP ethanol solution to absorb the PATP molecules onto the surface of the assembled Ag substrate through the formation of Ag–S bonds. After thorough rinsing with ethanol and drying with nitrogen, the substrates containing the adsorbed PATP were immersed in different concentrations of BA for 24 h before the SERS measurements, and measured without taking out the substrates from BA ethanol solutions. Thus, Ag–PATP–BA systems were generated and could be detected directly. The scheme indicating the formation of the system is shown in Fig. 1. The preparation of the other systems is similar to that of the Ag–PATP–BA system.

To avoid the interference of other uncertainties, the pH values of the BA and other ethanolic solutions of oxycids were adjusted to the same value of \( \sim 5.1 \), which is the pH value of a 10\(^{-3}\) M PATP ethanol solution under the experimental conditions, using aqueous solutions of NaOH and HCl before forming the intermolecular system.
Sample characterization

UV-Vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer, and TEM images were taken using a JEOL JSM-6700F field-emission scanning electron microscope (FE-SEM) operating at 3.0 kV. SERS spectra were obtained using a Horiba-Jobin Yvon LabRAM ARAMIS system with 633 nm radiation from a 17 mW He/Ne laser excitation source. The laser beam was focused on a spot approximately 1 μm in diameter using an objective microscope with 50× magnification. The data acquisition time was 5 s for all systems. The holographic grating and slit allowed a spectral resolution of ~4 cm⁻¹. The Raman band of the silicon wafer at 520.7 cm⁻¹ was used to calibrate the spectrometer. The laser power at the sample position was typically 7 mW.

Analysis of 2D SERS correlation spectra

All calculations were performed using MATLAB software; during the calculations, the generalized 2D correlation approach was employed. In the synchronous spectrum, positive and negative peaks at (ν₁, ν₂) indicate that the intensity changes at these two bands occur in the same and opposite directions, respectively. In the asynchronous spectrum, Ψ(ν₁, ν₂) × Ψ(ν₁, ν₂) > 0 means that the spectral change at ν₁ occurs earlier, as a function of perturbation, than ν₂; if Ψ(ν₁, ν₂) × Ψ(ν₁, ν₂) < 0, the spectral change order is reversed.

Results and discussion

Measurements of UV-Vis spectra

Fig. 2A shows the absorption spectrum of colloidal silver. The Ag nanoparticles yield a narrow surface plasmon absorption band at 416 nm. An SEM image of the surface morphology of the assembled Ag nanoparticles is presented in Fig. 2B; it is evident that the Ag nanoparticles are spherical and have an average diameter of ~70 nm. As a result of the dipole–dipole EM interactions of the particles, the surface plasmon resonance (SPR) of the silver nanoparticles shifts from 416 nm for the particles in the colloid (Fig. 2A) to 392 nm for the particles immobilized on the surface of the glass slide (Fig. 3, black line). After the PATP molecules are absorbed and immersed in BA solution, the SPR absorption spectrum further shifts to 396 and 399 nm (Fig. 3). The spectrum shows a slight red-shift and broadening after adsorption of the PATP molecules onto the assembled Ag nanoparticle substrate. This is mainly due to CT from the substrate to the linked PATP molecules, which further reduces the surface electron density of the Ag nanoparticles. Additionally, introduction of BA molecules into the system to
form the Ag–PATP–BA intermolecular system results in further red-shifting and broadening of the SPR peak, although the changes are not significant, as shown in Fig. 3. This phenomenon results from weak interactions between the carboxyl group of BA and the amino group of PATP, which further increase the CT transition of the adsorbed PATP molecules on the substrate because of the degree of molecule–molecule conjugation in the system.

SERS spectra of PATP in an Ag–PATP–BA system

It is generally known that the PATP and BA molecular geometries in solution are sensitive to pH owing to protonation and deprotonation reactions. The pH values of all solutions in the experiment were adjusted to ~5.1 using NaOH and HCl aqueous solutions to ensure uniform configuration of the PATP and BA molecules. Fig. 4A(a–g) show SERS spectra of PATP adsorbed on the assembled silver substrate and PATP in the Ag–PATP–BA system with BA concentrations of 10^−3, 10^−7, 10^−9, 10^−4, 10^−3, and 10^−2 M, respectively. For comparison, all the spectra were normalized with respect to the peak at 1076 cm^−1 (ν_{\text{CS,7a}}). The relative intensities of the SERS spectrum of PATP adsorbed onto the assembled substrate (Fig. 4A(a)) differ from those of the other spectra. However, the spectrum is consistent with previously reported SERS spectra of PATP. All the spectra are dominated by four strong bands at about 1076, 1141, 1390, and 1435 cm^−1, which were assigned to ν_{\text{CS,7a}}, ν_{\text{NH,9a}}, ν_{\text{NH,3}}, and ν_{\text{CS,15a}} vibrations, respectively. The characteristic bands at 1141, 1390, and 1435 cm^−1 can be attributed to the b_2-type vibration bands of PATP, while the remaining one at 1076 cm^−1 is due to the a_1-type band. As shown in Fig. 4A, there are many peaks, which are not well-resolved, in the region of 1550 to 1650 cm^−1. This region contains important information. At least three bands can be clearly identified at 1577, 1588, and 1620 cm^−1, which are attributed to the b_2-type band, the a_1-type band, and characteristic rocking vibrations of the NH_2 group, respectively. We will discuss the effect of H-bonding on the bands in this region in detail further in the paper. The band assignments for PATP are shown in Table 1 and are consistent with literature reports. The Raman spectra of PATP and BA and the SERS spectrum of 10^−2 M BA are shown in the ESI† (Fig. S1).

The introduction of the BA molecules results in no obvious shift of the characteristic SERS peaks of PATP (Fig. 4A(b–g)). Meanwhile, no conspicuous bands corresponding to BA are observed. This phenomenon can be explained as follows. The SERS signal intensity is dependent on the distance between the substrate and adsorbed molecules. The intensity of the SERS signal of molecules reduces with increasing distance between the Ag nanoparticle substrate and the molecules. In addition, the formation of H-bonds is impaired by the orientation of the BA molecules. The optimized intermolecular geometry of BA molecules interacting with PATP molecules involves a tilt angle. In this case, the coverage of BA molecules on the Ag nanoparticle substrate is significantly less than the coverage of PATP. Another factor is that the Raman scatter cross-section of BA is much smaller than that of PATP, resulting in a relatively

![SERS spectrum of PATP in an Ag–PATP–BA system](image)

**Fig. 4** (A) SERS spectrum of (a) PATP molecules adsorbed on the assembled Ag film and PATP molecules in the Ag–PATP–BA system with a BA concentration of (b) 10^−3, (c) 10^−7, (d) 10^−5, (e) 10^−4, (f) 10^−3, and (g) 10^−2 M. All spectra were measured with 633 nm excitation and normalized to the band at 1076 cm^−1. (B) Degree of charge transfer (p_C) for PATP versus negative log of the concentration of BA of the characteristic b_2 bands, including 1141 (squares), 1390 (dots), and 1435 cm^−1 (triangles) bands, which are the bands identified with asterisks in Fig. 4A.

### Table 1  Wavenumbers and assignment of bands in a SERS spectrum of the PATP-modified SERS substrate

<table>
<thead>
<tr>
<th>Wavenumber (cm^−1)</th>
<th>Band assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1007</td>
<td>υ(CCC) + υ(CC), 18a (a_1)</td>
</tr>
<tr>
<td>1077</td>
<td>υ(CS), 7a (a_1)</td>
</tr>
<tr>
<td>1141</td>
<td>δ(CH), 9b (b_2)</td>
</tr>
<tr>
<td>1190</td>
<td>δ(CH), 9a (a_1)</td>
</tr>
<tr>
<td>1307</td>
<td>υ(CC) + υ(CH), 14 (b_1)</td>
</tr>
<tr>
<td>1390</td>
<td>υ(CC) + υ(CH), 3 (b_1)</td>
</tr>
<tr>
<td>1435</td>
<td>υ(CC) + υ(CH), 19 (b_2)</td>
</tr>
<tr>
<td>1577</td>
<td>υ(CC), 8a (b_2)</td>
</tr>
<tr>
<td>1588</td>
<td>υ(CC), 8a (a_1)</td>
</tr>
<tr>
<td>1618</td>
<td>υ(NH_2)</td>
</tr>
</tbody>
</table>

*a υ, stretching; ρ, rocking; δ and γ, bending. For ring vibrations, the corresponding vibrational modes of benzene and the symmetry species under C\_2v symmetry are indicated.*
small enhancement factor (as shown in Fig. S1, ESI†). Consequently, the SERS bands corresponding to BA are not easily observed. It is noteworthy that the intensities of the b2-type bands of PATP increase considerably. Furthermore, enhancement of these b2-type bands is dependent on the concentration of BA. The intensities of the b2-type modes increased with increasing concentration of BA.

**Degree of charge transfer**

In the PATP Raman spectra, some characteristic bands are assigned to b2-type vibrations that are only observed in SERS spectra. Lombardi and Birke explained this phenomenon using the Herzberg–Teller surface selection rules. Moreover, they proposed a new concept for quantitatively estimating the CT contribution to SERS. Herein, the degree of charge transfer \( p_{(CT)}(k) \) is used for investigating the CT contribution to the SERS intensity. The \( p_{(CT)}(k) \) of a \( k \)-bond can be determined using the following equation:

\[
p_{(CT)}(k) = \frac{I^\ddagger(CT) - I^\ddagger(SPR)}{I^\ddagger(CT) + I^\ddagger(SPR)}
\]

where the index “\( k \)” represents individual lines in the SERS spectra. Here, the \( k \)-line may be either a totally symmetric or non-totally symmetric. To better understand this equation, we chose the intensities of two reference lines in the spectral region. One line is totally symmetric with the SERS signal produced by contributions from SPR (intensity denoted \( I^\ddagger( SPR) \)) and the other line is non-totally symmetric (intensity denoted \( I^\ddagger( CT) \)). \( I^\ddagger( CT) \) is the measured intensity of the \( k \)-line in the region of the spectrum where CT resonance makes an additional contribution to the SERS intensity excluding the contribution of SPR. Notably, for a totally symmetric line, \( I^\ddagger( SPR) = I^\ddagger( CT) \); while for a non-totally symmetric line, \( I^\ddagger( SPR) \) is usually quite small or zero, therefore, the SERS intensity is primarily derived from CT contributions.

Since the laser wavelength we used can excite the CT state in these systems, there is no band that is completely derived from SPR. However, the CT contribution to the totally symmetric band is small and does not significantly impact its overall intensity. We defined \( I^\ddagger( SPR) \) as the intensity of the 1076 cm\(^{-1} \) band \( a_1 \) mode) and \( I^\ddagger( CT) \) as the intensities of the bands at 1141, 1390, and 1435 cm\(^{-1} \)(b2 mode), which are derived from non-totally symmetric contributions. The degrees of CT for PATP in the Ag–PATP–BA system at 1141, 1390, and 1435 cm\(^{-1} \) as a function of the negative log of the BA concentration with excitation at 633 nm are listed in Table S2 (ESI†). As is evident from the values of \( p_{(CT)}(k) \), the phenomenon is BA concentration dependent.

Fig. 4B shows the degree of CT of PATP in the Ag–PATP–BA system versus the concentration of BA. Clearly, the \( p_{(CT)} \) values increase with increasing concentration of BA, which is consistent with the obtained SERS spectra. These bands are enhanced by the CT process through Herzberg–Teller contributions.

Introduction of the BA molecules affects the electronic conjugation of the whole system, resulting in increased conjugation and formation of H-bonds between the carboxyl groups of BA and amine groups of PATP. Therefore, the energy-level between the Fermi level of the silver and dimer formed by BA and PATP becomes small. It should be considered that there are more excited states that match the required resonance to promote CT from the Ag nanoparticles to adsorbed PATP. Upon the formation of H-bonds, more dimers appear in the intermolecular system. Therefore, the degree of conjugation of the system further increases, which is more conducive to the CT transition. Accordingly, the intensities of the b2-type bands of PATP are enhanced as the concentration of BA increases. However, at lower concentrations, the amount of BA is insufficient to interact with the PATP molecules adsorbed onto the Ag nanoparticles and there are fewer dimer interactions involving H-bonds between PATP and BA in the system than at higher concentrations. Therefore, the intensities of the b2-type bands of PATP and the degree of CT of the system are concentration dependent.

In the system, when a BA molecule is introduced, it is likely that the formation of H-bonds enhances the b2-type bands of PATP, as they facilitate CT from the substrate to the adsorbed PATP molecules. Further evidence to support this perspective is provided by density functional calculations, which were performed using Beck’s three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP). Here, we focused on the interactions between BA and PATP in the intermolecular system (ESI†).

**Temperature-dependent SERS spectra of the system**

Generally, the formation and strength of H-bonds are affected by temperature. To demonstrate the effect of temperature on H-bond formation in the intermolecular system, a temperature-dependent SERS measurement was performed and the degree of CT was plotted as a function of temperature (Fig. 5). Here, the PATP molecules absorbed onto the inner wall of the capillary after assembly of a layer of Ag nanoparticles. The capillary tube was then filled with \( 10^{-3} \) M BA solution by capillary action and sintered at both ends. In a control experiment, ethanol was used instead of BA. All the SERS spectra were measured using 633 nm excitation at 25–75 °C with increments of 5 °C. For the purposes of our discussion, both the temperature-dependent and control-experiment SERS spectra were normalized to the intensity of the band at 1076 cm\(^{-1} \). The results revealed that the relative intensities of the b2-bands of PATP decreased remarkably with increasing temperature. In contrast, there was no consistent change in the control experiment spectrum (Fig. 5A). These changes in the b2-bands have been ascribed to the formation of H-bonds between PATP and BA molecules, which promote CT from the substrate to absorbed PATP molecules. Since the H-bond is an unstable interaction, it should break with increasing temperature, resulting in a change in the relative intensities of the SERS spectra, as shown in Fig. 5A. The degrees of CT in the system at different temperatures were calculated and decline as the temperatures rise (Fig. 5B). However, there was no significant consistent trend of either ascent or declination in the control experiment (Fig. 6). The effect of the changing temperature on the b2-type
bonds of PATP was not observed. These variations in the SERS spectra of PATP further support the presence of H-bonds in the intermolecular system, which is consistent with our previous results: the formation of intermolecular H-bonds facilitates CT. Accordingly, the degree of CT can be used to determine the extent of H-bonding in the system.

Two-dimensional (2D) correlation spectroscopy is one of the most powerful and versatile spectral analysis methods for investigating perturbation-induced variations in dynamic data.23,46 To further elucidate the effect of H-bonds on the temperature-dependent SERS spectra, 2D SERS correlation analysis was applied to this intermolecular system. The synchronous and asynchronous 2D SERS correlation spectra from the temperature-dependent SERS data shown in Fig. 5A are displayed in Fig. 7. The synchronous map (Fig. 7A) shows five domain-positive auto-correlation peaks at $\nu_1 = \nu_2 = 1076$, 1141, 1390, 1435, and 1588 cm$^{-1}$, which are characteristic benzene ring vibrational peaks for PATP. Note that a weak auto-correlation was observed at $\nu_1 = \nu_2 = 1380$ cm$^{-1}$, which was not clearly assigned to any vibration of PATP but rather to $\nu_2$(COO$^-$) of BA, which was introduced into the system. Since both molecules contain benzene rings, there is overlap in the spectral region of benzene-ring vibrations. Moreover, the SERS signal of BA is much weaker than that of PATP, as discussed above, which impairs the ability to discern information concerning the BA molecules. In the 2D SERS correlation analysis, these details can be well amplified. Several positive correlation peaks centred at (1076, 1141), (1076, 1390), (1076, 1435), (1588, 1577), and (1618, 1380) suggest that the changes in SERS spectra of the two molecules are synchronous with the rise in temperature. However, the corresponding correlation peaks on the asynchronous map are negative (Fig. 7B). According to Noda’s rules, the band at 1380 cm$^{-1}$ appeared before that at 1618 cm$^{-1}$. This indicated that the variation of BA takes place before PATP due to the breaking of the H-bond with increasing temperature. This indirectly confirms the presence of H-bonds in the intermolecular system. Further confirmation was derived from the different
signs of the corresponding synchronous and asynchronous correlation features that indicate that changes in the $b_2$ (1141, 1390, 1435, and 1577 cm$^{-1}$) bands are delayed relative to changes in the $a_1$ (1076 and 1588 cm$^{-1}$) bands with increasing temperature and corresponding H-bond breakage in this intermolecular system. The effects of H-bonding on the $b_2$ bands appear before those on the $a_1$ bands. It can be considered that the $b_2$ bands are more susceptible to the effects of the H-bonds. This indicates that increasing the temperature results in breakage of the H-bonds, which influences the CT in the system.

**Contribution of other substituted BA molecules to PATP**

To further demonstrate this point, we proposed that the carbonyl group of the BA molecule promotes CT from the Ag nanoparticles to adsorbed PATP molecules. We selected two substituted BA molecules, $p$-cyanobenzoic acid (CBA) and $p$-hydroxybenzoic acid (HBA), as references. All the molecules here were used with ethanol solution as solvent with the concentration of $10^{-3}$ M. CBA contains a cyanogen moiety, which is an electron-withdrawing group, opposite the carbonyl group, while HBA contains a hydroxyl group, which is an electron-donating group and has an opposite effect on the electron-cloud density of the carbonyl groups with respect to CBA. The order of electron density on the carbonyl group in these three molecules is CBA < BA < HBA. Accordingly, the order of the interactions between the PATP and Ag nanoparticles should be CBA < BA < HBA. Fig. 8A confirms this: the intensities of the $b_2$-type bands of PATP increase in the proposed order.

We also calculated the degree of CT of PATP in systems with the substituted BA molecules with 633 nm excitation (Table S3, ESI†). Note that the $p_{(CT)}$ values obtained in the system including HBA are considerably larger than those obtained for the CBA system. Since the hydroxyl group of HBA can significantly enhance electron density of the carbonyl group, it can further facilitate the interaction between the amino group of PATP to the carbonyl-group of the HBA molecule, as shown in Fig. 8B.
Conclusions

In this work, we investigated the interactions in an intermolecular system composed of PATP and BA using SERS. It is worth noting that the degree of CT between the substrate and adsorbed PATP molecules is enhanced with the existence of BA. The phenomenon that b2-type bands of PATP are significantly affected by BA can be observed. This is attributed to the contribution of the carbonyl group of BA, which can form a large conjugated system and promote CT from the substrate to the adsorbed PATP. The degree of CT was evidently dependent on the concentration of BA, which significantly increased the intensity of the b2-type bands of PATP. Furthermore, we performed temperature-dependent SERS experiments on the intermolecular interactions of Ag–PATP–BA and a two-dimensional correlation analysis, which further confirmed our proposal. The results indicate that H-bond formation in the system affects CT and contributes markedly to SERS.

The authors declare no competing financial interest.

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