

Article

Surface Enhanced Vibrational Spectroscopy of 1,2-Bis(4-Pyridyl) Ethane

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São reportados os espectros vibracionais intensificados pela superfície do composto 1,2(4-piridil) etano (BPA). A atribuição das frequências fundamentais é proposta com base nos espectros Raman e infravermelho de BPA sólido e em cálculos AM1 dos modos vibracionais. Foram obtidos espectros Raman e infravermelho intensificados pela superfície (SERS e SEIR) de filmes de BPA preparados sobre filmes de ilhas de prata. Foi obtido também o espectro de reflexão - absorção no infravermelho (RAIR) de um filme fino de BPA depositado sobre um filme liso de prata. As propriedades do processo de intensificação da absorção no infravermelho foram analisadas e comparadas com as do SERS, sendo discutidas as condições para a intensificação eletromagnética no infravermelho. A partir da comparação dos espectros FTIR de transmissão em pastilha de KBr com os resultados SEIR e RAIR, a geometria de adsorção da molécula de BPA na superfície da prata é também discutida.

The surface enhanced vibrational spectra of 1,2(4-pyridyl) ethane (BPA) is reported. The Raman and infrared spectra of solid BPA and AM1 calculations of vibrational modes are used to propose an assignment of characteristic fundamental frequencies. The surface enhanced Raman scattering (SERS) and the surface enhanced infrared (SEIR) spectra have been obtained for samples prepared by vacuum evaporation and dipping from BPA solution onto rough silver island films. Reflection absorption FTIR (RAIR) spectra of a thin solid film deposited on smooth silver were also recorded. The nature and properties of surface enhanced infrared spectra obtained by transmission in two different substrates are examined and compared with those of SERS. The requirements for electromagnetic enhancement in the infrared region are discussed. Based on the comparison of the FTIR transmission spectra in the KBr pellet with the SEIR and RAIR results, the adsorption geometry of the BPA molecule on the silver surface is also discussed.

Keywords: *surface enhanced infrared, surface enhanced Raman scattering*

Introduction

Vibrational spectroscopy plays a central role in the investigation of the structure, bonding and reactivity of matter in gas, liquid and solid phases. Modern vibrational spectroscopy includes a powerful group of **vibrational enhanced spectroscopic techniques** that allow the observation of adsorbed species on surfaces, most commonly metal surfaces. The two complementary experimental techniques **infrared and Raman**, are thereby termed Surface Enhanced Raman Scat-

tering (SERS), now an established analytical technique for adsorbates on surfaces and interfaces^{1,2}, and Surface Enhanced Infrared (SEIR) spectroscopy, first observed and investigated by Hartstein³ using gold or silver island films. The initial work on SEIR was carried out using attenuated total reflection techniques. SEIR has now been reported using reflection absorption geometry (SEIRRA)^{4,5} and transmission geometry (SEIR)^{6,7}.

The coordination chemistry of polynuclear polypyridil complexes has been widely studied in order to develop

possible applications as light harvesting units^{8,9}. The metal to ligand back bonding plays an important role in the stability of these compounds¹⁰. It has been shown that bridging ligands derived from 4,4' bipyridine, like BPA, can either mediate intermolecular charge transfer reactions or electronically insulate the metal centers, depending on the conjugation between the two pyridine rings^{11,12}. In the present work, we have investigated the SEIR and SERS spectra of the molecule BPA adsorbed on silver island films and compared the results with the unenhanced FTIR and Raman spectra. All the SEIR spectra were recorded using transmission geometry. Two very different infrared transparent substrates, CaF₂ and ZnS, were coated with 5 nm thick silver island film and used in the SEIR experiment to compare reproducibility and the possible effect of the substrate on the SEIR signals. SERS spectra obtained from the same samples are reported to complete the vibrational-enhanced analysis of adsorbed BPA on silver.

Experimental

The BPA ligand (Aldrich Chemical Co.) was recrystallized from water and ethanol. The substrate for SEIR spectroscopy in transmission geometry was prepared by vacuum evaporation of 5 nm (mass thickness) of silver onto polished CaF₂ or ZnS windows (from Wilmad). Substrates used for reflection/absorption spectroscopy (smooth metal films) were similarly prepared by the evaporation of 100 nm of silver onto Corning 7059 glass slides held at 200 °C. The silver was heated under a base pressure of 3×10^{-6} mbars and the film thickness was monitored using a XTC Inficon quartz crystal oscillator. In addition, silver coated glass slides were used to investigate the SERS spectra of BPA.

Infrared spectra were recorded using a Bomen DA3 interferometer equipped with a MCT wide range detector. All spectra resulted from the coaddition of 1000 scans at a 4 cm⁻¹ resolution with a sample box pressure of 1 torr. A Spectra-tech variable angle reflectance accessory was used to record the reflection absorption infrared spectra (RAIRS).

A THR-1000 spectrograph equipped with a liquid nitrogen cooled CCD detector and a microscope accessory was used to record SERS spectra in the back scattering configuration. Laser excitation at 514.5 nm was provided by an argon ion laser.

Results and Discussion

The vibrational assignment of characteristic frequencies of BPA

For materials characterization and structural research, the knowledge of characteristic vibrational modes of a molecule is, in many cases, the starting point. An assignment of the characteristic fundamental vibrational frequen-

cies of BPA is presented here first. The computation of normal modes was carried out using the AM1 method found in HyperChem 4.5, and the aim was to interpret the observed IR bands that are studied by SEIR and RAIR. The main spectral region for which the assignment is discussed can be seen in Fig. 1. In all of the figures, the y axis is in arbitrary units. Ring vibrations and structure can be compared with pyridine. A complete vibrational analysis of pyridine carried out using *ab initio* methods has been reported by Wiberg *et al.*¹³. The minimisation routine gave a BPA geometry which is not the staggered conformation, and the dihedral angle formed by the four carbons connecting the two rings is 94°. The calculated C-C single bond was 1.521 Å. The pyridine bond lengths and angles, and the AM1 calculated values for BPA rings are in good agreement, and are given here for comparison.

Coordinate	Calculated Pyridine	Observed Pyridine	Calculated BPA
C-N	1.329	1.338	1.346
C-C	1.382	1.392	1.406
C-H	1.070	1.082	1.098
C-N-C	119.0	116.7	117.0
C-C-C	118.6	118.5	118.8
N-C-C	122.4	123.8	123.6
C-C-H	120.3	120.1	120.2

There are 72 fundamentals of BPA, all of which are infrared and Raman active. Of the 27 stretching vibrations, there are 12 high frequency C-H modes that are assigned without difficulty. The AM1 calculations give vibrational frequencies with nearly degenerate energy in groups of two or four. The CH₂ stretches are calculated at 2850-2856 cm⁻¹ for the symmetrical stretch, and 2918-2928 cm⁻¹ for the anti-symmetrical stretching vibrations (scaling factor used = 0.95). The symmetrical stretch is observed at 2859 cm⁻¹ in the IR spectrum of the KBr pellet, as shown in Figure 2. Also in Fig. 2, two bands with medium relative intensity are clearly seen in the IR spectrum at 2925 and 2947 cm⁻¹, and are assigned to anti-symmetrical CH stretching vibrations. Notably, the C-H stretches in RAIRS follow the same pattern observed in the KBr pellet spectrum. However, the relative intensity and the frequencies are slightly different in the SEIR spectrum of the CH stretching modes. The small frequency shifts and changes in the relative intensity confirm the chemical adsorption of BPA on the rough silver surface. Using the same scaling factor, two groups of four frequencies are clustered between 2989-2993 cm⁻¹ and 3030-3034 cm⁻¹ for the aromatic C-H stretching fundamentals. The frequencies recorded in the IR were at 3030 cm⁻¹ and 3067 cm⁻¹. The corresponding frequencies in pyridine are 3030 cm⁻¹ and 3072 cm⁻¹¹³. Other weak bands in this region have been identified as combinations, and the over-

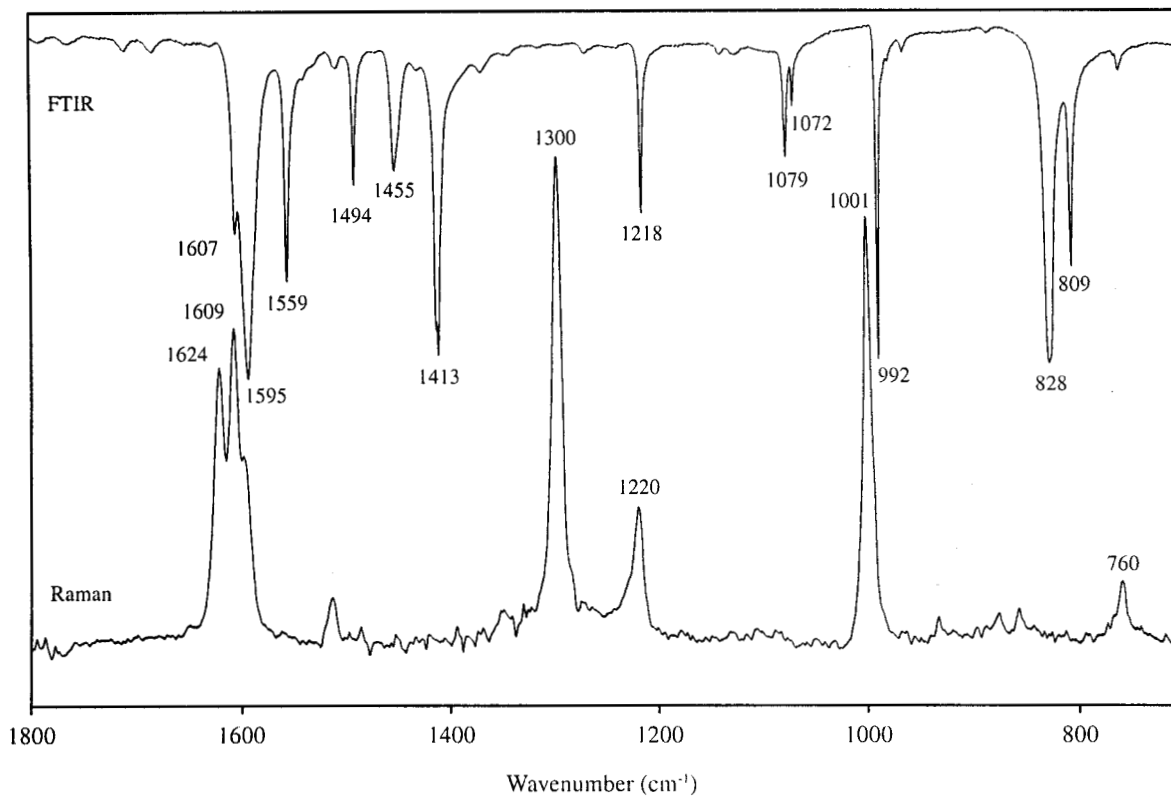


Figure 1. Spontaneous Raman spectrum of solid BPA ($\lambda_{\text{exc}} = 514.5 \text{ nm}$) and transmission FTIR spectra of BPA in a KBr pellet.

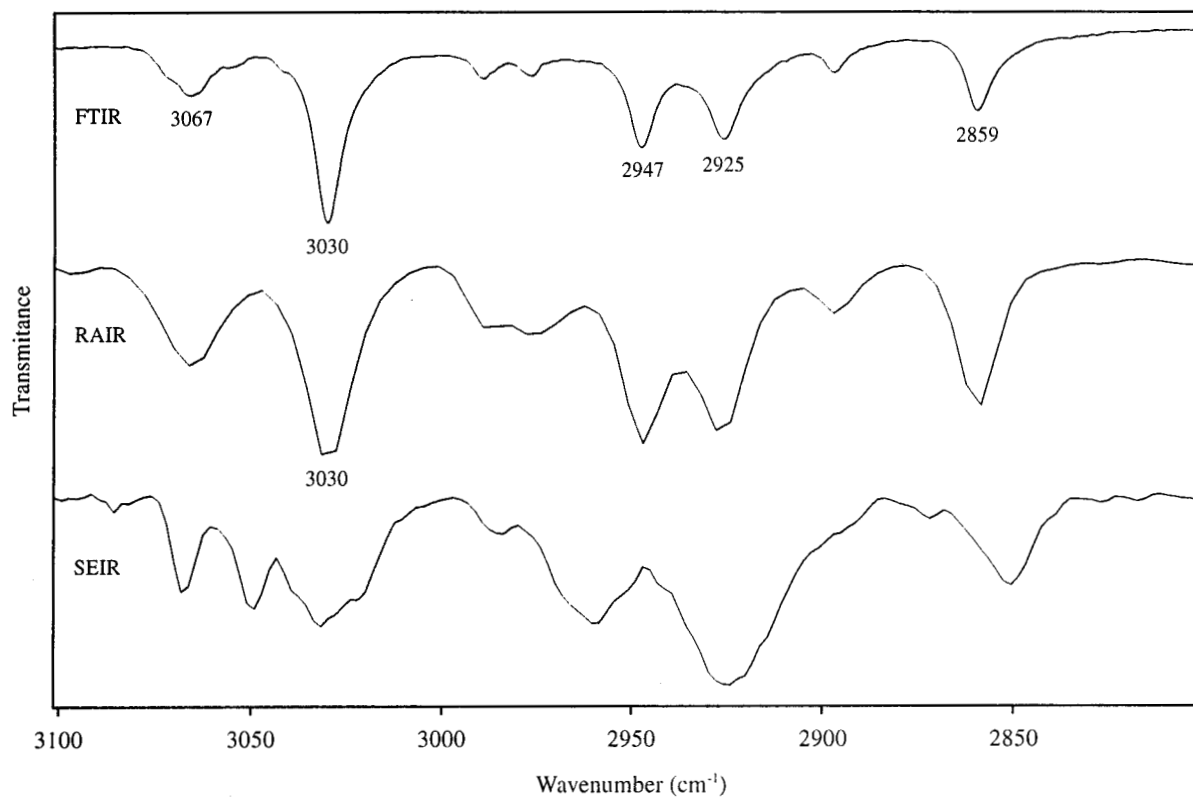


Figure 2. C-H stretching vibrations of BPA in a KBr pellet, transmission SEIR spectrum and reflection absorption FTIR on smooth silver.

tone of the band at 1494 cm^{-1} (2988). The AM1 results lead to the conclusion that each band may contain as many as four nearly degenerate C-H modes.

The remaining 15 stretches include 12 ring modes, some of which are highly coupled to C-H bending modes, and 3 C-C stretching of the alkyl groups. All compounds derived from benzene have four characteristic in-plane ring vibrations which are IR active in the region between $1600\text{--}1300\text{ cm}^{-1}$. In pyridine, these frequencies are observed at 1580 , 1572 , 1482 , and 1410 cm^{-1} ¹⁴. The BPA molecule shows 5 strong features in this region, suggesting that while four of them correspond to in-plane ring vibrations, the 1455 cm^{-1} mode should be related to the aliphatic C-C inter-ring group. In fact, the CH_2 scissoring modes of alkanes are found to be in this region¹⁵. Two of these calculated frequencies, mainly related to ring stretches in the plane of the pyridil ring, can be seen in Fig. 3. Here, the infrared vectors have been added to illustrate the vibrational modes occurring in the plane of the pyridil ring. The experimentally assigned vibrations are observed at 1595 , 1553 , 1494 , and 1413 cm^{-1} . Calculated frequencies (0.9 scaling factor) in descending order contained a pair at 1324 and 1314 cm^{-1} , which is described by an in-phase motion of the rings with a large displacement of the C-N coordinates. The strong band at 1300 cm^{-1} in the Raman spectrum is assigned to one of these vibrations. A weak band at 1272 cm^{-1} could be the second ring mode. The scissoring and wagging vibrations of the CH_2 groups have characteristic atomic displacements, as illustrated in Fig. 4. Using the same scaling factor of 0.9,

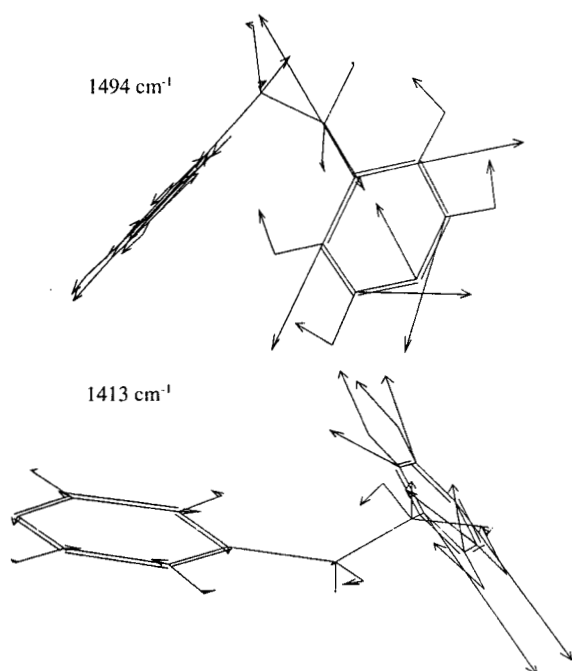


Figure 3. Infrared vectors for two ring stretching vibrations. The drawings illustrate that the atomic displacements take place in the plane of the two aromatic rings.

the wagging vibrations are calculated at $1098\text{--}1086\text{ cm}^{-1}$, which permits the assignment of the IR bands at 1079 and 1072 cm^{-1} to these modes of the alkyl group.

Surface-enhanced infrared and RAIRS spectra

The enhancement of the infrared absorption of molecules adsorbed onto silver islands can be attributed to the ability of the infrared radiation, ω_v , at which the molecules absorb, to excite electromagnetic resonances. This electromagnetic enhancement (EM) corresponds to the local field term $|A(\omega_L)|^2$ in the well known expression for SERS^{1,2}. The EM enhancement is a function of the dielectric constants of the metal and metal particle size and shape. Experimentally, the enhancement produced by silver island films of different thicknesses has been clearly demonstrated by Osawa and Ikeda¹⁶, using cast films of p-nitrobenzoic acid. The typical distance dependence of the EM in SEIR has also been determined⁵. In fact, a calculation of the $|A(\omega_L)|^2$ factor for the middle infrared region of a prolate spheroid (3:1) of silver gives an enhancement factor of 29. The SEIR intensities are then proportional to:

$$I_{\text{SEIR}} \propto |A(\omega_L)|^2 \left| \frac{\partial \mu}{\partial Q} \right|^2$$

where $|\partial \mu / \partial Q|^2$ represents the value of the optical constant for the vibrational mode Q of the surface complex.

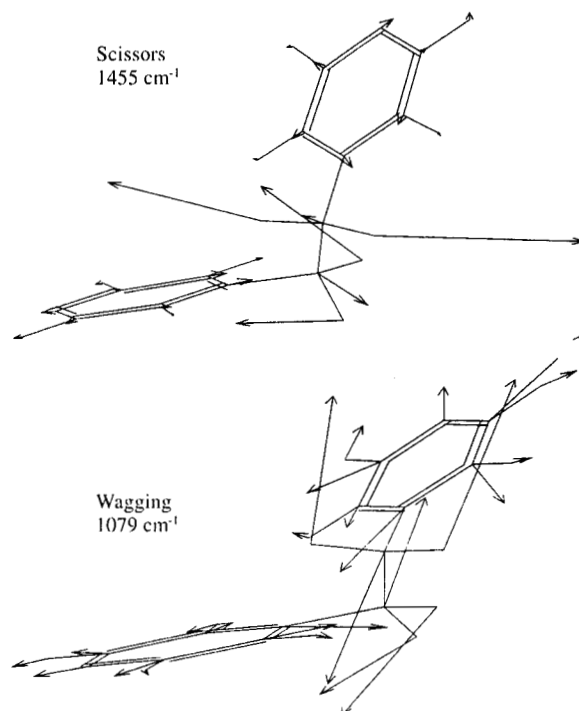


Figure 4. Infrared vectors for CH_2 scissor and CH_2 wagging vibrations of the alkyl group in BPA.

Figure 5 shows the SEIR spectrum of a film of BPA obtained by dipping a CaF_2 window coated with 5 nm Ag on a 10^{-3} M BPA solution, as well as the FTIR spectrum of the KBr pellet, which will be used as a reference for discussion. It is assumed that in the KBr pellet, the BPA molecules are randomly dispersed, and do not show any orientation. The SEIR spectrum shows changes in the relative intensities and a minor frequency shift for some modes. This result suggests the existence of a preferential orientation in the BPA film formed. For an experiment in the transmission geometry, the electrical field of the incident radiation lies in the plane of the substrate. Therefore, only vibrational modes with a component of the variation of the electrical dipole moment parallel to the substrate surface will be enhanced. The SEIR spectra shows that while the 1595 cm^{-1} vibrational mode is highly enhanced, the 1455 cm^{-1} mode is completely absent. This indicates that the 1595 cm^{-1} vibrational mode should involve a change in the electrical dipole moment, with a large component parallel to the surface, while the 1455 cm^{-1} mode should involve a change in the electrical dipole moment almost completely perpendicular to the metallic surface.

Figure 6 shows the RAIR spectra of a BPA film also obtained by dipping of a glass slide coated with 100 nm Ag on the 10^{-3} M BPA solution, as well as the FTIR spectrum

of the KBr pellet. In the RAIR experiment, the surface selection rules are operative^{17,18}. When the infrared light is reflected by the metal surface, a phase inversion takes place, resulting in a constructive interference for the p polarized light and in a destructive interference for the s polarized light. As a result, the electrical field perpendicular to the surface is enhanced, while the electrical field parallel to the surface is cancelled. Therefore, only vibrational modes with a component of the variation of the electrical dipole moment perpendicular to the substrate surface can be probed in the RAIR experiment. The frequencies of the RAIR spectrum are seen unchanged with respect to the KBr reference spectrum, but there are marked changes in the relative intensities of the bands. In this case, however, the tendency is the opposite of that observed in the SEIR spectra. The vibrational modes in 1455 and 1079 cm^{-1} seem to be enhanced at the reflection absorption geometry, while the 1595 cm^{-1} mode is relatively less intense.

The comparison of the FTIR transmission spectra in the KBr pellet with the SEIR and RAIR spectra gives information regarding the adsorption geometry of the BPA molecule on the metallic films. If the molecule were adsorbed through its π electrons with its aromatic rings parallel to the surface, the in-plane ring modes would be especially en-

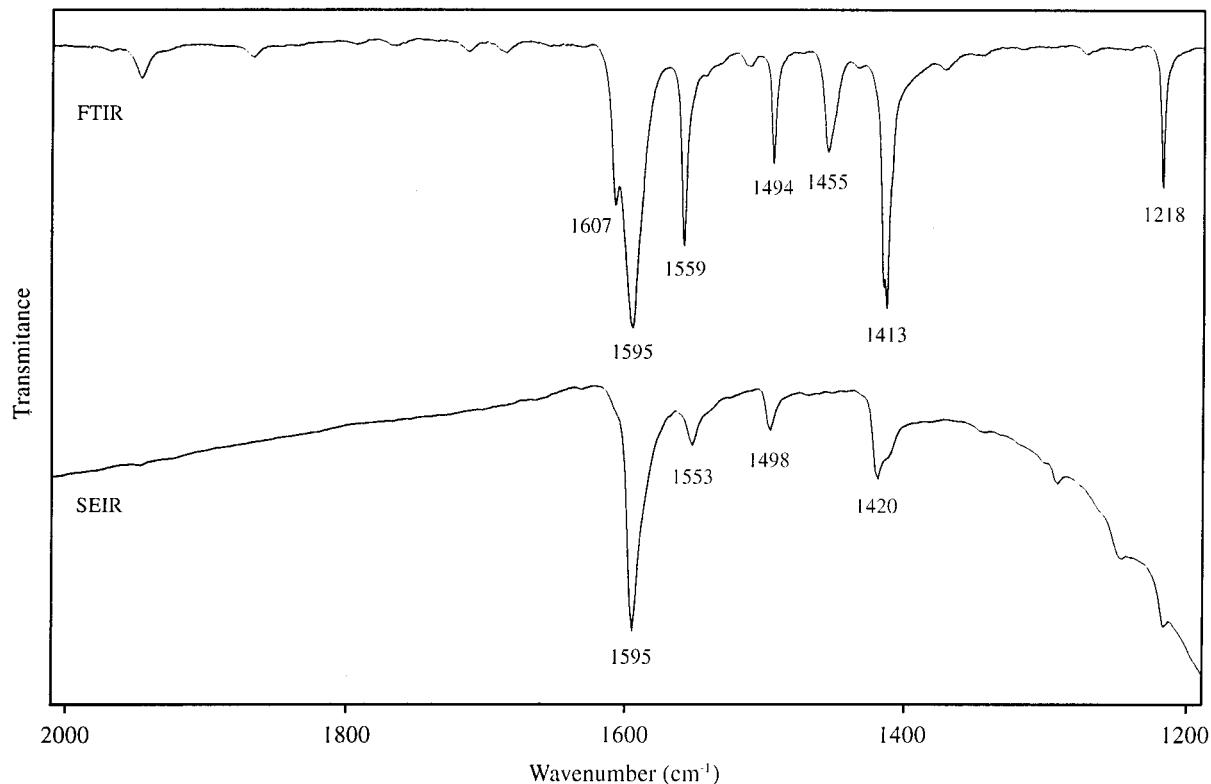


Figure 5. SEIR transmission spectra of BPA adsorbed on 5 nm silver island film on a CaF_2 window and transmission FTIR spectra of BPA in a KBr pellet.

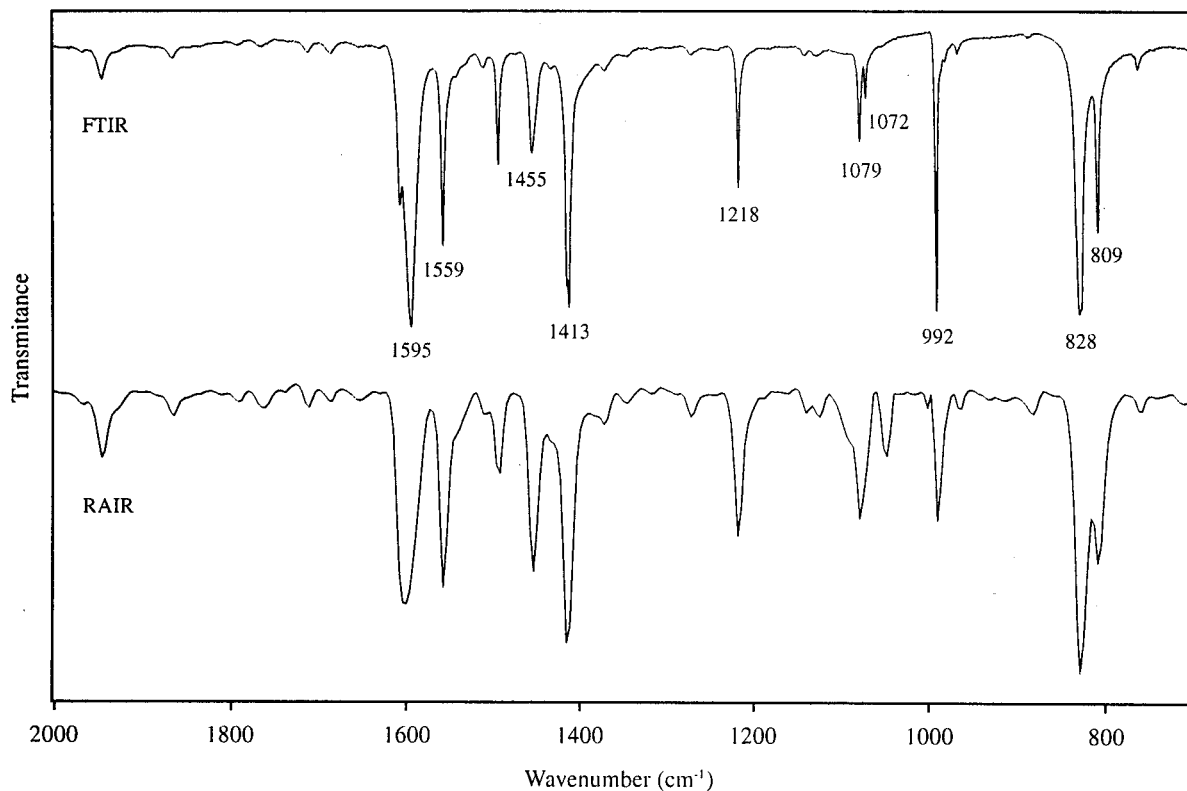


Figure 6. RAIR spectra of BPA on smooth (100 nm) silver film and transmission FTIR spectra of BPA in a KBr pellet.

hanced in the SEIR spectra, and the out-of-plane modes would be enhanced in the RAIR spectra. However, the behavior observed shows the opposite trend, suggesting that the molecule is adsorbed with its rings more perpendicular to the surface. The behavior of the 1455 cm^{-1} mode, assigned to the CH_2 aliphatic scissors, enhanced in the RAIR spectrum and absent in the SEIR one indicates that the variation of the electrical dipole moment involved in this vibration is almost perpendicular to the surface. This indicates that the geometry of the BPA molecule on the surface should be slightly different from that in the solution, allowing an interaction with the surface which would involve the 2 N atoms, and the molecule would be adsorbed with its aromatic rings almost perpendicular to the substrate, as shown in Fig. 7. In this adsorption geometry, the change in the dipole moment for CH_2 scissors would be almost perpendicular to the surface, explaining its absence in the SEIR and enhancement in the RAIR spectra.

Surface-enhanced Raman spectra

The spontaneous Raman scattering and the SERS spectra of BPA on a silver metal island film on glass are shown in Fig. 8. In general, the vibrational bands in the SERS spectrum are broadened and slightly shifted with respect to the normal Raman spectrum. Broadening and shifting of vibrational frequencies are characteristic indicators of

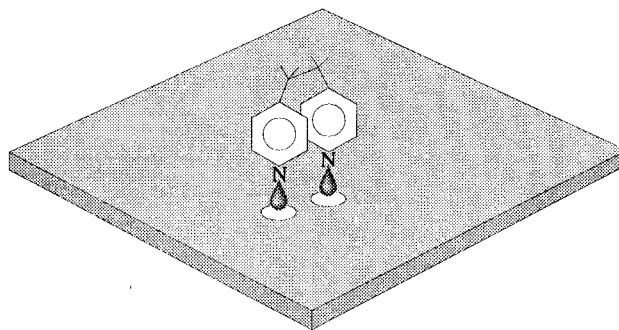


Figure 7. Adsorption geometry of BPA chemisorbed on silver island films.

chemisorption of BPA on the silver islands. The most prominent band in the SER spectrum at 514.5 nm excitation is the ring stretching vibration, with a high $\text{C}=\text{C}$ character at 1604 cm^{-1} . This vibration is associated with a change in polarizability along the long axis of the pyridil ring, is locally symmetric, and is observed at 1609 cm^{-1} in the Raman spectrum. The intensity of the SERS vibrational bands is determined by an enhancement factor (EF) given by¹⁹:

$$\text{EF} = |A(\omega_L)|^2 |A(\omega_E)|^2 \left| \frac{\partial \mu}{\partial Q} \right|^2$$

where $|A(\omega_L)|^2$ and $|A(\omega_E)|^2$ are the local field and emission enhancements due to the presence of the metal islands.

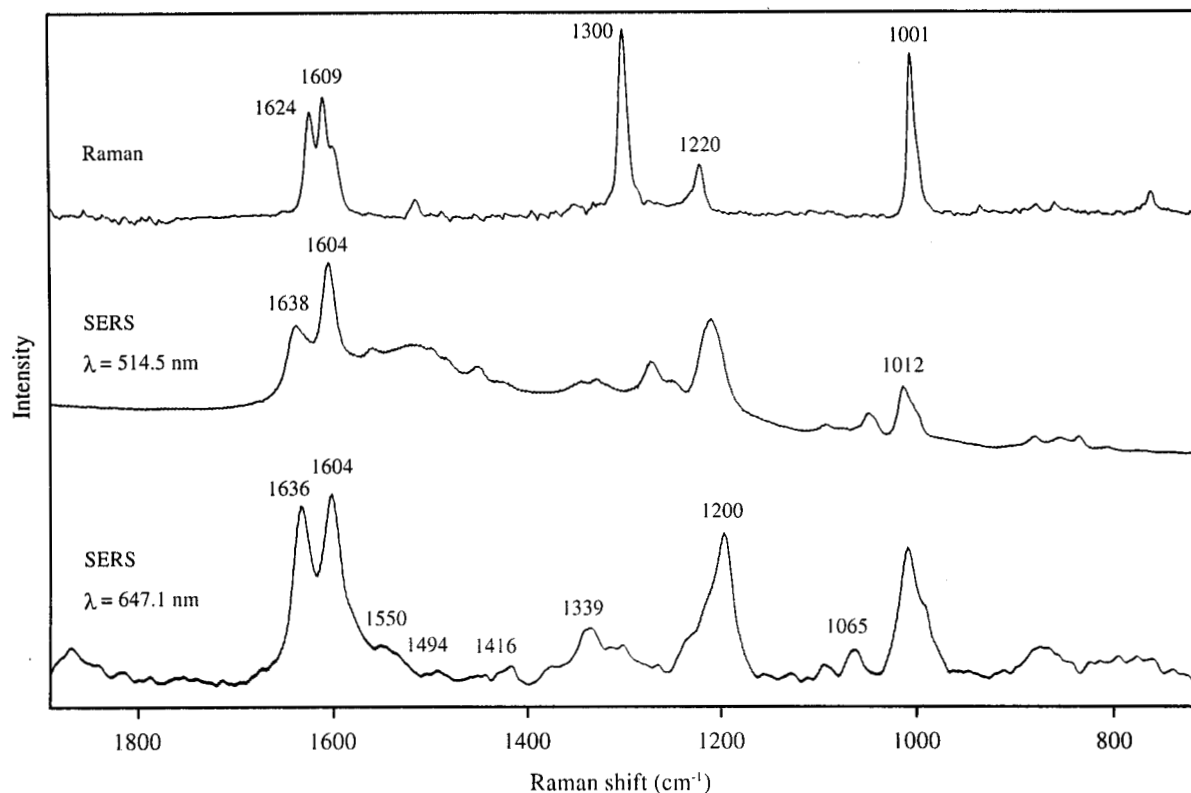


Figure 8. Spontaneous Raman spectrum of solid BPA ($\lambda_{\text{exc}} = 514.5$ nm) and SERS spectrum of BPA on 5 nm silver islands film obtained with the 514.5 nm and 647.1 nm laser lines.

Here, $|\hat{\alpha}_{\mu, \nu}^{\alpha}|^2$ represents the ratio of the molecular polarizability derivative tensor (α') elements and the corresponding elements of the adsorbed molecule. Changes in the relative intensity could be associated with a variation in the α' tensor due to chemisorption. However, it should be pointed out that relative intensities are also strongly affected by molecular orientation and the position of the excitation frequency with respect to the plasmon absorption²⁰. To illustrate the effect of the laser line, the SERS spectrum obtained with 647.1 nm is also given on Fig. 8. The 647.1 nm laser line is on the red side of the main plasmon absorption of the silver island film, which is shown on Fig. 9. It can be observed that locally symmetrical vibrations are seen with high relative intensity, in agreement with the assumption of the BPA rings chemisorbed through the N atoms. The SERS spectra also show the bands at 1550, 1494, 1416 and 1065 cm^{-1} , which are not observed in the normal Raman spectrum. These modes are also enhanced in the RAIR spectra (Fig. 6). Since the electromagnetic model for the SERS effect predicts an enhancement of the electrical field perpendicular to the metal surface, it can be concluded that this mechanism is the one responsible for the SERS spectra of BPA adsorbed on metal island films. The chemisorption is observed in both SERS and SEIR. The 1624 cm^{-1} band is shifted in the

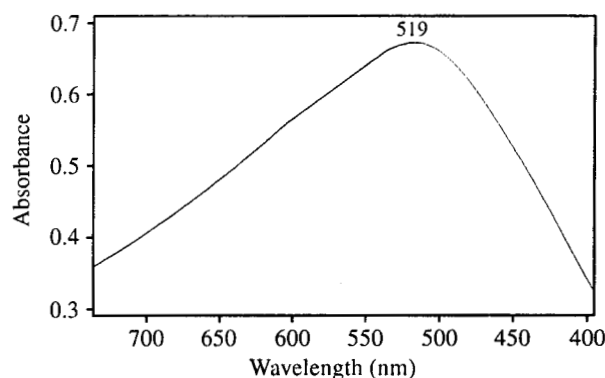


Figure 9. Absorption spectra of a 5 nm silver island film on glass in the visible region (surface plasmon absorption spectra).

SERS spectra, being observed at 1636 cm^{-1} . The ring breathing modes are observed in the SEIR spectrum at 995 cm^{-1} (992 cm^{-1} in the normal FTIR spectrum), and at 1012 cm^{-1} in the SERS spectrum (1001 cm^{-1} in the NR spectrum). These are two independent, nearly degenerate ring modes. The surface-modified vibrational frequencies, with a significant contribution from the C-N internal coordinate, are strongly affected by chemisorption. The ring mode with a high C-N character at 1300 cm^{-1} is shifted to 1328 cm^{-1} , forming a broad band in the surface complex, while other

Table 1. Characteristic Vibrational Frequencies of BPA.

Infrared	SEIR	Raman	SERS	Assignment
		1624 s	1638 s	i. p. ring stretch
1607 sh		1609 s	1604 s	i. p. ring stretch
1595 vs	1595 vs		1595 sh	i. p. ring stretch
1559 s	1553 m	1559 w	1550 w	i. p. ring stretch
1494 m	1498 m		1494 w	i. p. ring stretch + C-H bend
1455 m		1451 w	1451 m	CH ₂ scissors
1413 vs	1420 s	1415 w	1416 w	i. p. ring stretch + C-H bend
1371 w	1364 w			i. p. ring stretch
		1300 vs	1328 w	i. p. ring stretch
1218 s	1218 m	1220 m	1200 vs	C-H bend (aromatic)
1079 s	1076 w			C-H wag (alk)
1072 m			1065 m	C-H wag (alk)
992 vs	995 s	1001 vs	1012 s	Ring breathing
		854 w	855 w	C-H wag (alk)
828 vs	818 s	835 w	835 w	C-H wag (aromatic)
809 s	803 s		805 w	C-H wag (aromatic)
547 vs				Ring def.
517 s				Ring def.

frequencies show a surface-induced shift, $\Delta\omega < 15 \text{ cm}^{-1}$, confirming the strong interaction of the N ring atoms with the silver surface.

Conclusions

The attainment of surface-enhanced vibrational spectroscopy using the complementary SERS and SEIR spectra is demonstrated for a common organic ligand. The surface-enhanced infrared and reflection absorption infrared spectra of BPA are reported here for the first time. The SEIR effect was studied and obtained on 5 nm Ag silver films evaporated onto two different substrates: ZnS and CaF₂. Frequency shifts in the SEIR and SERS spectra of BPA indicate chemisorption of the adsorbate molecules on the silver islands. The comparison of the FTIR transmission spectra in the KBr pellet with the SEIR and RAIR spectra indicates that the geometry of the chemisorbed BPA molecule on the surface is slightly different from that in the solution, allowing an interaction with the surface that involves the 2 N ring atoms.

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