Surface-Enhanced Raman Spectra of Isomeric Picolines Adsorbed on Silver Sols

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Raman spectra of 2-, 3-, and 4-methylpyridines (MePys) are obtained in the bulk phase, in aqueous solution and in the adsorbed state on silver sol. Addition of the MePys to Ag-sol results in aggregation of the Ag-particles showing characteristic charge transfer (CT) bands. Significant surface enhancement of Raman bands is observed. Both the estimated enhancement factor and the absorption maximum of CT band are in inverse parallel relationship with the electron density of the N atom as reflected by the Hammett σ value of the substituent. It is inferred that the charge transfer interaction between the absorbates and the metal particles contributes to the enhancement mechanism. SER spectra of MePys adsorbed on Ag-sol are compared with the reported spectra of these molecules adsorbed on Ag-electrode and the difference in the surface structure is discussed. Some new bands appear in the SER spectra and some vibrational modes show SERS selectivity. These experimental observations provide information about the orientation of the molecules on the metal surface.

Surface enhanced Raman scattering (SERS) is known to originate from the interaction of electromagnetic radiation with the metal surface. Two mechanisms have been shown to contribute to the effect:[1] (i) long range classical electromagnetic enhancement, (ii) short range 'first layer' contribution which is chemically specific and vibrationally selective. Several factors are reported to influence the effect including the shape of the surface[2] and the orientation of the molecules on the surface.[3,4] Three types of surfaces are mostly used (i) metal electrodes, (ii) colloidal metal particles, and (iii) cold deposited films. The electromagnetic model is based on the concept that the incident and the scattered field near the surface is enhanced through surface plasmon resonance while the other model involves Charge-Transfer (CT) interaction between the absorbed molecule and the metal surface.

Our present study on SERS from colloidal Ag-particles takes the concept of charge tranfer one step further. We observe SERS from 2-, 3-, and 4-methylpyridines (MePy) with different electron donating capabilities of the isomers as reflected from their Hammett σ values. The enhancement is observed to be related to the Hammett σ values suggesting thereby that the CT interaction contribute significantly in SERS of isomeric methylpyridines. The results are further compared with the reported SERS data of MePys obtained with Ag-elecrodes[5] and the differences between the two surfaces are discussed.

Experimental

Silver sol was prepared by the process described by Creighton et al.[6] Ice-cold 2×10^{-3} M $NaBH_4$ solution (15 ml) (1 M=1 mol dm^{-3}) was stirred vigorously and 5 ml of 1×10^{-3} M $AgNO_3$ solution was added rapidly. The yellowish sol thus prepared showed a single extinction maximum at 398 nm. The Ag-sol was stored at 5 °C. The methylpyridines were purchased from Fluka and were further purified by distillation under vacuum. Doubly distilled deionized water was used for the preparation of all solutions. Raman spectra were recorded by a Spex double monochromator (model 1403). The samples were taken in a quartz cell and were excited by the 514.5 nm line of Spectra Physics Ar$^+$ laser (model 2020-5). Spex datamate 1B was used for spectrometer control, data acquisition and analysis. The absorption spectra were recorded by a Shimadzu UV-vis spectrophotometer (model UV-VIS 210A).

Results and Discussion

Raman Spectra and Enhancement: Raman Spectra of 2-, 3-, and 4-MePys in aqueous solution (1 M) and the SER spectra adsorbed on Ag-sol (0.01 M) are shown in Figs. 1—3. Tables 1—3 summarize the observed fre-

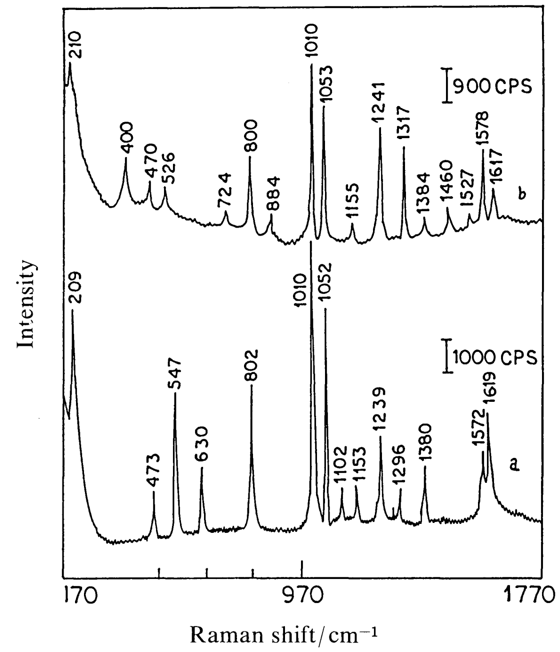

Fig. 1. Raman spectra of 2-methylpyridine, (a) in aqueous solution (1 M), (b) adsorbed on Ag-sol (0.01 M).

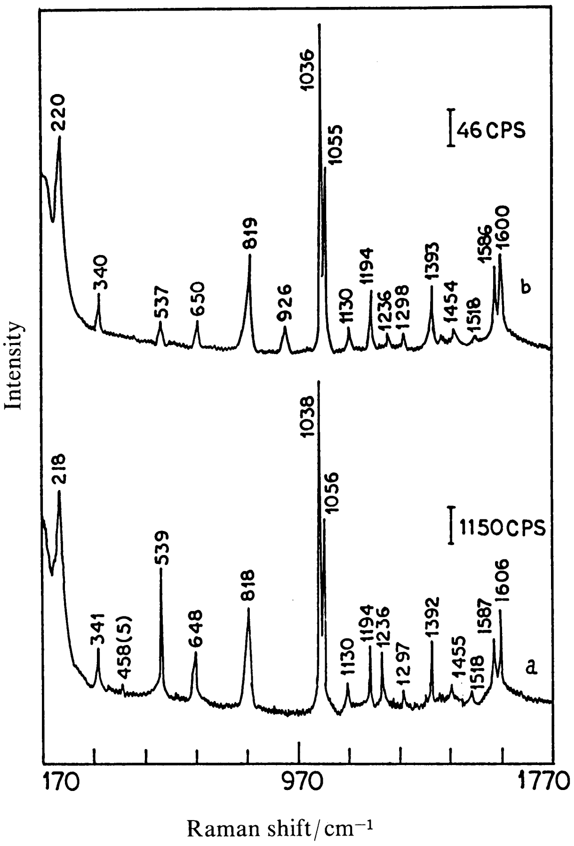

Fig. 2. Raman spectra of 3-methylpyridine, (a) in aqueous solution (1 M), (b) adsorbed on Ag-sol (0.01 M).

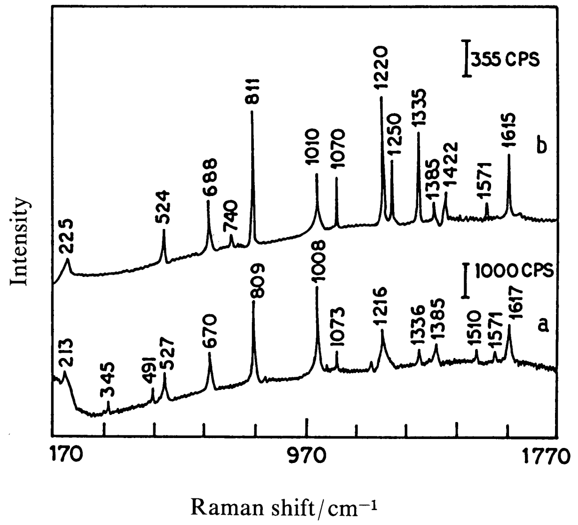

Fig. 3. Raman spectra of 4-methylpyridine, (a) in aqueous solution (1 M), (b) adsorbed on Ag-sol (0.01 M).

quency and intensities of Raman bands and compare the results with the existing SERS data of the molecules adsorbed on Ag-electrode (after Ref. 5). The intensities (figures in the parantheses) are measured in such a scale in which the ring breathing modes at 1010 cm^{-1}, 1038 cm^{-1}, and 1008 cm^{-1}, in 2-, 3-, and 4-MePys respectively, are of intensity value 100. An enhancement ratio is estimated assuming the ring breathing

Table 1. Raman Spectral Data of 2-Methylpyridine in Different Conditions and Comparison with Existing SERS Data

Bulk cm^{-1}	Aqueous solution cm^{-1}	Ag-sol cm^{-1}	Ag-electrode[a] cm^{-1}	E.R.[b]	E.F.[c] ×10^2	Assignment
212	219(55)	210(43)	225	0.78	43	16b, X sens
365			385			15, X sens
406		400(35)	399			16a, ϕ(CC)
474	473(21)	470(24)	478	1.14	63	11, ϕ(CC)
525						6a, X sens
550	547(53)	526(22)	568	0.4	22	
634	630(30)		645			6b, α(CCC)
732		724(14)	725			4, ϕ(CC)
			769			10b, γ(CH)
803	802(56)	800(47)	809	0.83	46	12, X sens
892		884(17)				10a, γ(CH)
1005	1010(100)	1010(100)	1017	1.0	55	1, ring
1054	1052(79)	1053(78)	1061	1.0	55	18a, β(CH)
1106	1102(21)		1110			18b, β(CH)
			1134			
1154	1153(22)	1155(17)	1160	0.77	42	9a, β(CH)
1240	1239(36)	1245(68)	1245	1.90	105	13, X sens
1300	1296(20)	1317(56)	1299	2.8	154	3, β(CH)
1382	1380(27)	1384(17)	1389	0.55	30	14, ν(CC, CN)
		1460(19)				
1572	1576(30)	1578(45)	1570	1.5	83	8b, ν(CC)
1597	1619(42)	1617(16)	1604	0.4	22	8a, ν(CC)
2928	2935(37)	2936(47)	2898	1.3	72	ν(CH) in CH_3 group
3056	3064(41)	3056(72)	3061	1.7	94	2, ν(CH)

a) After Ref. 5. b) E.R.=enhancement ratio. c) E.F.=enhancement factor.

Table 2. Raman Spectral Data of 3-Methylpyridine in Different Conditions and Comparison with Existing SERS Data

Bulk	Aqueous solution	Ag-sol	Ag-electrode a)	E.R. b)	E.F. c) ×10^2	Assignment
cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}			
221	218(37)	220(32)	222	0.86	3.5	16b, X sens
342	341(16)	340(14)	351	0.82	3.3	15, X sens
456	458(5)					
538	539(41)	537(10)	541	0.24	1.0	6a, X sens
632	648(17)	650(11)	649	0.64	2.5	6b, α(CCC)
807	819(32)	819(32)	813	1.0	4.0	12, X sens
		926(10)				10a, γ(CH)
1032	1038(100)	1036(100)	1037	1.0	4.0	1, ring
1043	1056(58)	1056(58)	1052	1.0	4.0	18a, β(CH)
1108						18b, β(CH)
1130	1130(5)	1130(9)	1126	1.8	7.2	
1192	1194(21)	1194(21)	1197	1.0	4.0	9a, β(CH)
1231	1236(20)	1236(7)	1235	0.35	1.4	13, X sens
	1297(8)	1298(7)		0.87	3.5	
1385	1392(22)	1393(20)	1387	0.90	3.6	14, ν(CC, CN)
			1417			
	1455(8)	1454(6)		0.75	3.0	
			1487			
	1518(4)	1518(4)				
1579	1587(19.5)	1586(24)	1585	1.23	5.0	8b, ν(CC)
1599	1605(29)	1609(28)	1604	0.96	4.0	8a, ν(CC)
2926	2919(11)	2922(5)	2923	0.5	2.0	ν(CH) (asym) in CH$_3$ group
3057	3055(15)	3054(21)	3060	1.5	6.0	20a, ν(CH)

a) After Ref. 5. b) E.R.=enhancement ratio. c) E.F.=enhancement factor.

Table 3. Raman Spectral Data of 4-Methylpyridine in Different Conditions and Comparison with Existing SERS Data

Bulk	Aqueous solution	Ag-sol	Ag-electrode a)	E.R. b)	E.F. c) ×10^2	Assignment
cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}			
216	213(28)	225(27)	225	1.0	23	16b, X sens
343	345(18)		352			15, X sens
375			390			16a, ϕ(CC)
487	491(23)		490			11, ϕ(CC)
518	527(36)	524(65)	538	1.8	41.5	6a, X sens
671	670(50)	668(96)	673	1.9	44	6b, α(CCC)
738		740(39)				4, ϕ(CC)
806	809(95)	813(215)	813	2.26	52	12, X sens
			980			17a, γ(CH)
998	1008(100)	1010(100)	1018	1.0	23	1, ring
1071	1073(23)	1070(96)	1068	4.17	96	18a, β(CH)
			1165			
1224	1216(49)	1220(211)	1218	4.30	99	13, X sens
		1250(112)	1233			9a, β(CH)
			1284			3, β(CH)
	1336(26)	1335(150)		5.77	133	
1384	1385(30)	1385(46)	1383	1.50	35	14, ν(CC, CN)
1439		1422(27)	1439			19b, ν(CC, CN)
1500	1510(26)		1503			19a ν(CC, CN)
1563	1561(20)	1571(30)	1564	1.5	35	8b, ν(CC)
1610	1617(46)	1615(111)	1618	2.41	56	8a, ν(CC)
2926	2932(12)	2943(17)	2921	1.4	32	ν(CH) (symm) in CH$_3$ group
2989		2979(25)	2988			ν(CH) (asym) in CH$_3$ group
3056	3058(23)	3053(43)	3058	1.9	4	2, ν(CH)

a) After Ref. 5. b) E.R.=enhancement ratio. c) E.F.=enhancement factor.

vibration to be of equal intensity both in aqueous solution and in SER spectra. Enhancement of ring breathing mode in the three molecules may be estimated (assuming all the experimental conditions identical) from the enhanced photon counts in Ag-sol from that in aqueous solution. For 2-, 3-, and 4-MePys the enhanced photon count is in the ratio of 55:4:23. True enhancement factor is difficult to estimate as the number of scattering molecules in the adsorbed state is not known. Also the intensity of the excitation laser light (514.5 nm) is significantly reduced in Ag-sol than in aqueous solution due to enhanced extinction for absorption (Fig. 4) and scattering by Ag-particles. The paticle size in this type of Ag-sol has been estimated to be 1—50 nm[6] which gives 10^2 times fewer Ag-particles than the available MePy molecules in the sol. Sllman et al.[7] estimated the amount of solute adsorbed on Ag-sol to be in the range of 35% to 6% depending on the concentration of the solute. In the concentration range of ours it is expected to be on the higher limit side. A factor 10^2—10^4 has often been used to estimate the enhancement factor[8] from the relative enhancement value in sol. This factor may be different for different molecules even for identical experimental condition. However, for a reasonable estimate we assume this factor to be the same for the ring breathing mode of these isomeric molecules. It is interesting to note that the enhancement factors of the ring breathing mode in the three isomeric methylpyridines are in the reverse order of their Hammett σ (σ_H) values namely in the order 2-MePy>4-MePy>3-MePy.

In Tables 1—3 the relative enhancement ratio implies the intensity of a Raman band in Ag-sol devided by that in aqueous solution. The enhancement ratios have been reduced to enhancement factors by multiplying with the estimated values for the three isomers. These enhancement factors give useful information about the enhancement mechanism involved and also about the orientation of the molecules on silver particle surface.

A closer look into the Tables 1—3 finds that for many Raman bands this enhancement factor is highest for 2-MePy and least for 3-MePy, 4-MePy has an intermediate value.

Absorption Spectra and Aggregation of Ag-Particles: Absorption spectra of Ag-sol are shown in Fig. 4 with and without adsorption of isomeric methylpyridines (MePys) onto it. Before using for SERS experiments the Ag-sol was aged for several hours. Absorption spectrum of the Ag-sol shows a single extinction maximum at 398 nm but a shoulder appears in the longer wavelength side (500—600 nm) with a decrease in absorbance of the 398 nm band as soon as the MePys are added to it and the yellowish sol undergoes a color change yellowish→orange→red→blue grey. The appearance of this type of shoulders has been ascribed to coagulation of the Ag-particle in presence of the adsorbed molecules.[6] However, this coagulation is too fast to record Raman spectra unless the concentration of the MePys are optimum which is found to be 0.01 M. At this concentration the particle coagulation takes place slowly and after about 30 minutes it reaches a stable condition. From the absorption spectra (Fig. 4) it is observed that the maxima of the shoulders, in stable condition, are not the same for the three isomers though the experimental conditions are identical. Creighton et al.[6] found aggregation of Ag-particles when pyridine was added to Ag-sol and the maximum of the excitation profile coincides with that of the shoulder. This resonance was explained in terms of Mie scattering. In our present investigation we find that the absorption maxima, characteristic of Ag-particle aggregation, bear a linear relationship with the Hammett σ value (σ_H) of the adsorbed molecules (Fig. 5). Indeed in absorption experiment one measures not only extinction due to absorption but also the extinction due to scattering. The scattering contribution increases as the dimension of the aggregated sols increases. Also the wavelengh dependence of the extinction due to scattering depends on the size of the aggregated sol particles. Blue part of

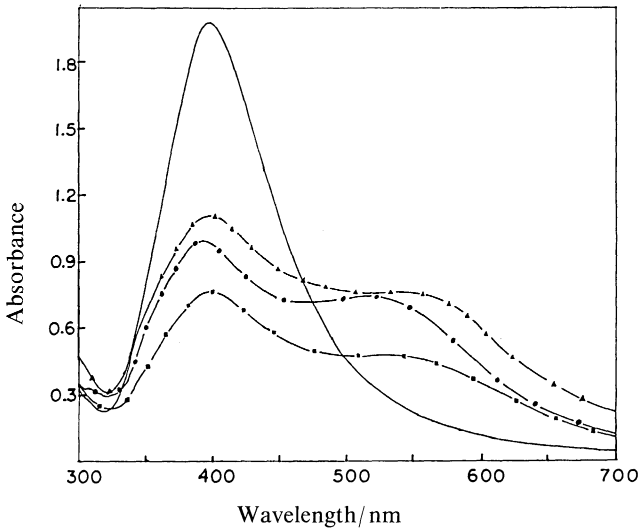

Fig. 4. Absorption spectra of Ag-sol with and without adsorbed methylpyridines: —— Ag-sol, —●— Ag-sol with 2-methylpyridine, —▲— Ag-sol with 3-methylpyridine, —■— Ag-sol with 4-methylpyridine.

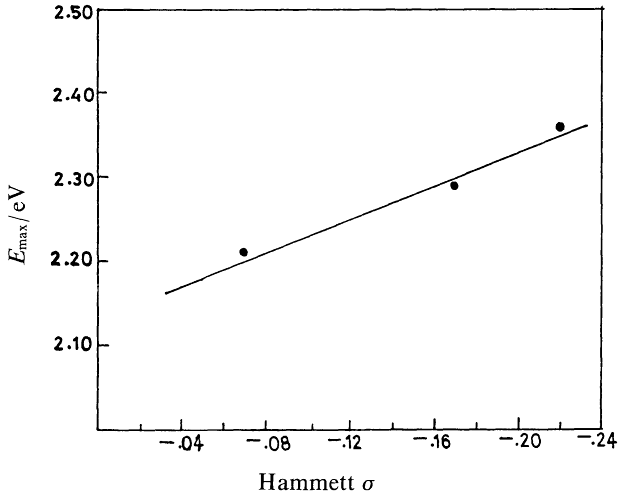

Fig. 5. Low energy absorption maxima versus Hammett σ value plot.

the absorption spectra is more scattered and as the particle size increases, the scattering increases. The absorption spectra will show an apparent red shift and this will be more for longer wavelength absorption spectra. However, for standard absorption set-up, this effect due to scattering is likely to be small and the relationship shown in Fig. 4 is likely to prevail. In the isomers the electron density on the N atom increases as σ_H changes from less to more negative value in the order 2-MePy>4-MePy>3-MePy and the new maxima appear at 525, 560, and 542 nm respectively for 2-, 3-, and 4-MePy. In the presence of the MePys with different electron densities on the N atom the Ag-particle may rush towards the molecules thereby resulting aggregates of different sizes which depends on the isomer.

Raman Spectra and Selective Enhancement: The enhancement is not the same for all the Raman bands of a molecule. There is considerable variation from band to band. The C–H in-plane bending modes are selectively enhanced at 1155 cm^{-1} (9a, β_{CH}) and 1317 cm^{-1} (3, β_{CH}) in 2-MePy and at 1070 cm^{-1} (18a, β_{CH}) in 4-MePy. Significant SERS selectively is also observed at 1384 cm^{-1} [14, $\nu_{CC,CN}$] in 2-MePy and at 1385 cm^{-1} [14, $\nu_{CC,CN}$] and 1422 cm^{-1} [19, $\nu_{CC,CN}$] in 4-MePy. C–C stretching modes are enhanced at 1578 cm^{-1} [8b, ν_{CC}] and 1617 cm^{-1} [8a, ν_{CC}] in 2-MePy and at 1571 cm^{-1} [8b, and ν_{CC}] and 1615 cm^{-1} [8a, ν_{CC}] in 4-MePy. In 3-MePy the C–C stretching mode is present in the SER spectrum at 1586 cm^{-1} [8b, ν_{CC}] and 1609 cm^{-1} [8a, ν_{CC}]. These have low enhancement factors. The C–H stretching mode is enhanced at 3056 cm^{-1} with a red shift of 8 cm^{-1} in 2-MePy. This mode is enhanced at 3054 cm^{-1} in 3-MePy and at 3053 cm^{-1} in 4-MePy.

Selective enhancement of the stretching modes associated with the C–N and C–C suggests that the molecules are adsorbed on the metal surface through their N atom. The C–C stretching mode and the C–H in-plane bending modes have dipole moments in the plane of the molecule. Enhancement of these vibrational modes can be explained in terms of the surface selection rules predicted by Creighton[9] coupled with the dipolar contribution from the electron localization on the N atom in different molecules. Electron localization at the N atom in these isomeric picolines being in the order 2-MePy>4-MePy>3-MePy, they will have dipolar contribution to the vibrational modes along the *z*-axis in the same order. A molecule being adsorbed on the surface of small isolated metal spheres with *z*-axis perpendicular to the metal surface and in the molecule's plane, the vibrations having larger component of polarizability component along the *z*-axis are expected to be enhanced more. Our observation agrees with this prediction and suggests that the molecule is adsorbed on the metal surface with its plane perpendicular to the metal surface. The C–H mode in the methyl group appears at 2935 cm^{-1} in the aqueous solution Raman spectrum of 2-MePy but at 2936 cm^{-1} in the SER spectrum. In 3-MePy the C–H stretching mode appears at 2919 cm^{-1} in solution Raman spectrum but at 2922 cm^{-1} in the SER spectrum. In 4-MePy the symmetric C–H stretching mode in CH_2 group is shifted from 2932 cm^{-1} (solution Raman spectrum) to 2943 cm^{-1} (SER spectrum) whereas the anti-symmetric C–H stretching mode appears at 2979 cm^{-1} in the SER spectrum. In 2-MePy Bunding et al.[5] noticed significant shift and broadening of the symmetric C–H stretching mode in the SER spectrum on Ag-electrode compared to that in solution Raman spectrum. They explained the broadening of this mode in the SER spectrum in terms of interaction of methyl group with the electrode surface. This interaction in the case of 3-MePy and 4-MePy is weak in Ag-electrode because the methyl group does not come near to the electrode surface in these molecules. In Ag-sol, on the other hand, we have observed significant shift (11 cm^{-1}) of this symmetric methyl C–H stretching from that in aqueous solution in 4-MePy only indicating that in this isomer the methyl group interact with a neighboring Ag-particle whereas such interaction is absent in other two isomers.

The C–H out-of-plane bending modes are generally weak in solution Raman spectrum. In SERS also these γ(CH) vibrations are generally not observed, only 884 cm^{-1} (10a, γ_{CH}) in 2-MePy and 926 cm^{-1} (10a, γ_{CH}) in 3-MePy are observed very weakly. These out-of-plane bending vibrations have larger component of dipole moment in the *x*-direction (which is considered to be parallel to the metal surface and perpendicular to the molecular plane). According to the "edge on" adsorption enhancement of these bands are indeed not expected. The observation of some out-of-plane modes with good enhancement in the SER spectra on Ag electrode[5] has been explained by assuming the molecules on the electrode surface to be tilted with respect to the *z*-axis. Complete absence or extremely weak appearance of a few of these modes in our SER spectra possibly points to the difference in the surface structures in the two cases. Colloidal particles which are stable at room temperature have smoother surfaces than in Ag electrode. In Ag-electrode surfaces are likely to have sharper features resulting in field gradient effects and consequent tilting of the molecule on the surface. Some bands not observed in aqueous solution appear in the SER spectra (Tables 1—3). These are in-plane C–C bending at 400 and 724 cm^{-1} and out-of-plane C–H bending at 884 cm^{-1} in 2-MePy, 926 cm^{-1} out-of-plane bending in 3-MePy and in-plane vibrations at 740 and 1422 cm^{-1} in 4-MePy. The appearance of these bands can not be rationalized immediately. Surface complex formation with the Ag-particles may somehow make these bands Raman active. Lombardi et al.[10] observed a charge transfer from the metal to molecule in substituted pyridines including methylpyridines. This charge transfer interaction depends on the electronic charge density on the nitrogen atom as shown in the electrode voltage maxima versus Hammett σ value plot by Lombardi et al.[10] Figure 5 illustrates a similar situation when the molecules are adsorbed on colloidal Ag-particles. A ground state charge transfer may be inferred from the aggregation of the Ag-particles on addition of the methylpyridines to the Ag-sol. The linearity of the plot of absorption energy maxima of the aggregated Ag-particles versus the Hammett σ values shows that the strength of the above mentioned charge transfer in the ground state, depends on the electron density on the N atom. Our estimated enhancement factors for the three methylpyridines also show similar trend though they do not fit in the linear plot of Fig. 5. This is understandable as there is large degree of uncertainty in our estimated enhancement factor values.

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