Raman Spectral Studies of Aqueous Acidic Pyrazine Solutions

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

Raman spectra of aqueous pyrazine have been investigated in acidic media: HCl from pH = 4 up to 11 M; $HClO_4$ from 0.1 M to 12 M; H_2SO_4 form 0.1 M to 18 M. From observation of the shifts of the bands from neutral solutions, it has been possible to identify bands uniquely characteristic of unprotonated pyrazine and its two protonated forms. The diprotonated form was only observed for high concentrations of $HClO_4$ and H_2SO_4. From bandfitting of the spectral contours it has been possible to construct the species distribution diagram and estimate the pK values. Raman bands of the three species have been identified and assigned. The results are used to explain an unassigned band at 1235 cm^{-1}, reported by several authors, in SERS from pyrazine on silver and gold electrodes.

Key words: Pyrazine, Pyrazinium, SERS, Raman spectroscopy.

Introduction

This study of the vibrational spectra of pyrazine (pz) and its protonated forms has been motivated by our interest in the surface enhanced Raman scattering (SERS) of pyrazine adsorbed on gold electrodes [1]. Some thermodyamic properties of this system, such as the Gibbs free energy of adsorption, the Gibbs surface excess, and the electrosorption valence, have been measured in our Centre [2] using electrochemical techniques. A goal of this work is to extend the understanding of the relationship between the SER intensity and surface coverage and orientation at a given potential. An extensive study of this matter, involving the adsorption of pyridine on a gold electrode was conducted in our laboratory [3, 4]. In that work it was demonstrated that the SER intensity is directly proportional to surface coverage to about 60% of a monolayer for "smooth" electrodes. In preliminary studies of pyrazine, no spectra were obtained from "smooth" electrodes; following one oxidation-reduction cycle, enhanced intensity from pyrazine was observed [1]. A band at ca. 1220 cm^{-1} was significantly enhanced, as reported by Erdheim et al. [5], but this band was not assigned by them; progress in understanding the SERS is dependent on knowledge of the origin of all pyrazine bands.

Pyrazine is a non-polar, planar molecule with D_{2h} symmetry. Dornhaus et al. [6] suggested that the selection rules for symmetry D_{2h} break down at the electrode surface; C_{2v} symmetry would result from the removal of the inversion operation. Such symmetry lowering, if true, makes this system very attractive for the study of selection rules at surfaces [7, 8].

On the other hand, this simplistic interpretation (symmetry lowering) has been contested by Moskovits et al. [9]. They suggest that the observed small shifts of bands of adsorbed pyrazine, compared to the spectrum of liquid pyrazine, are not compatible with a pyrazine-surface complex strong enough to justify the symmetry lowering. They showed that the presence of forbidden bands can be explained based on electromagnetic considerations. Face-on, end-on or edge-on orientations are possible for pyrazine adsorbed to a metal surface. For cold deposited silver films it was suggested that the pyrazine molecules lie flat at low coverage and stand up as the surface concentration increases [9]. From the calculated bond polarizabilities an end-on configuration [10] is predictable at a silver electrode. The same result (pyrazine molecules perpendicular to the electrode surface) was observed at high coverage on positively charged gold electrodes [2].

The assignment of the new bands that appear in the spectrum of pyrazine at the electrode surface is a very important step. One can attempt to lower the symme-

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try of pyrazine in solution and compare the new bands to those from adsorbed pyrazine. In order to break down the symmetry of pyrazine in aqueous solution the molecule can be protonated. However, pyrazine is a very weak base [11] ($pK_{a1} = 0.65$ and $pK_{a2} = -5.8$) and protonation can be accomplished only in a very acidic medium. Figure 1 shows the calculated fractional composition of the pyrazine species using the pK_a values given above. The acidity function [12] (H_0) was used to replace the simple pH function for high acidic concentrations.

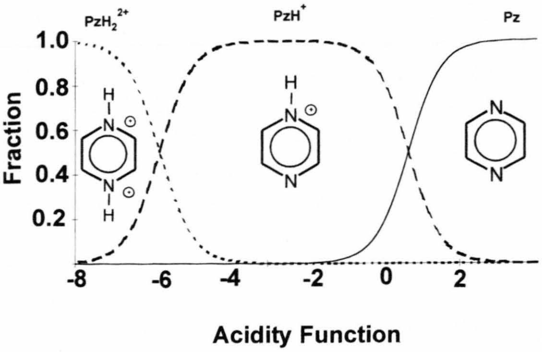


Fig. 1. Calculated fractional distribution of 1 M pyrazine species in solutions of varying acidity.

Symmetry analysis leads to the following vibrational representation for free pyrazine with D_{2h} symmetry:

$$\Gamma^{vib} = 5A_g + 1B_{1g} + 4B_{2g} + 2B_{3g} + 2A_u + 4B_{1u} + 2B_{2u} + 4B_{3u}.$$

The Raman selection rules for a centrosymmetric molecule establish that only the symmetrical normal modes have allowed transitions. Therefore only the "*g*" species are Raman active.

For monoprotonated pyrazine (C_{2v} symmetry), the vibrational modes span

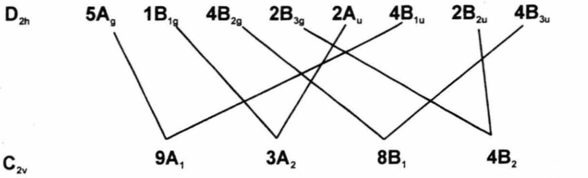
$$\Gamma^{vib} = 10A_1 + 3A_2 + 9B_1 + 5B_2.$$

In this case, all modes are Raman allowed. Therefore, the number of bands in the Raman spectrum should change from 12 to 27 with protonation.

For a diprotonated pyrazine (D_{2h}), we have

$$\Gamma^{vib} = 6A_g + 1B_{1g} + 5B_{2g} + 3B_{3g} + 2A_u + 5B_{1u} + 3B_{2u} + 5B_{3u}.$$

The centre of symmetry is regenerated and the exclusion rule for active modes in Raman and IR is valid again. Hence, 15 bands are expected in the Raman spectrum. The correlation table between D_{2h} and C_{2v} symmetries is given in Figure 2. The symmetries of modes generated by protonation are also given.



PzH^+ additional modes = $1A_1 + 1B_1 + 1B_2$

PzH_2^{2+} additional modes = $1A_g + 1B_{2g} + 1B_{3g} + 1B_{1u} + 1B_{2u} + 1B_{3u}$

Fig. 2. Correlation table between D_{2h} and C_{2v} symmetries, with reference to pz and its protonated forms.

Therefore, to place the interpretation of SERS on a firm basis there is a need to understand the vibrational spectrum of pyrazine and its protonated forms in solution. Raman and IR spectra of pyrazinium halides were reported by Foglizzo and Novak [13]. The spectra of diprotonated pyrazine have not been reported before. The new features from the protonated pyrazine will be related to the spectrum from the surface adsorbed species. It is evident that the SERS from pyrazine adsorbed on Ag and Au electrodes deserves further investigation in order to clarify fundamental questions, such as orientation, coverage, and predominant enhancement mechanisms. Furthermore, it is surprising to notice that, when compared to pyridine, little work has been done so far on the SERS from pyrazine on gold electrodes. Some of our preliminary results were presented at the last ICORS conference [14].

Experimental

Raman spectra were measured with a Jarrell-Ash 25–100 spectrometer (1-m double Czerny-Turner monochromator) with an RCA 31034 photomultiplier tube and an SSR Model 1105/1120 photon counting system. Spectra were excited by the 514.5 nm (1.5 W at the head) line of a Coherent Innova 300 argon ion laser. For data acquisition the spectrometer is interfaced to an IBM PC-AT 286 computer. The spectra were treated with an IBM PC-AT 486 computer on which baseline correction, band-fitting, and plotting programs were available. Pyrazine 99+% from Aldrich, H_2SO_4 96% ($d = 1.84$ g/mL) from BDH, HCl 37% ($d = 1.19$ g/mL) from BDH and $HClO_4$ 71% ($d = 1.76$ g/mL) from Baker were used. All solutions were prepared with Milli-Q water. The solutions were injected into capillary tubes and sealed. All spectra were recorded of samples at a controlled temperature of 25 °C.

Results and Discussion

Studies of Pyrazine in Solution with Several Solvents

In order to obtain information about possible interactions between pyrazine and the solvent, spectra of aqueous solutions of pyrazine at several concentrations were measured. Some small shifts were observed, mainly in the 1500 cm^{-1} region (ν-ring modes), as shown in Figure 3. These shifts are surely related to a pyrazine-water interaction. As the water concentration increases from liquid pz to 0.3 M aqueous solution the B_{2g} and A_g ring vibrations rise in frequency (1525 and 1580 to 1530 and 1594 cm^{-1}, respectively). A summary for the most sensitive bands of these systems is given in Table 1.

Figure 4, regions 1 to 4, shows the spectra of pyrazine in water (H_2O), in heavy water (D_2O) and in carbon tetrachloride (CCl_4). Almost no peak shifts are

Table 1. Vibrational frequencies (cm^{-1}) of liquid pyrazine, aqueous pyrazine at several concentrations, and 1 M pyrazine in CCl_4.

pz liquid (from [15])	pz 1 M in CCl_4	pz 5 M in H_2O	pz 0.3 M in H_2O
602 (w)[a]	610 (w)	617 (w)	620 (w)
704 (s)	704 (m)	702 (m)	703 (m)
927 (w)	918 (w)	921 (w)	923 (w)
	1006 (sh)	1010 (sh)	1010 (sh)
1016 (vs)	1014 (vs)	1018 (vs)	1020 (vs)
1208 (m)	1201 (w)	1217 (sh)	1220 (sh)
1233 (s)	1232 (m)	1237 (m)	1238 (m)
1346 (w)	1345 (w)	1346 (w)	1349 (w)
1525 (m)	1527 (m)	1528 (m)	1530 (m)
1580 (s)	1579 (m)	1591 (m)	1594 (m)
2820 (w)	2820 (w)		
2865 (w)	2865 (w)		
2883 (w)	2883 (w)		
2959 (w)	2960 (w)	2969 (w)	2972 (w)
3040 (sh)	3045 (sh)	3057 (sh)	3063 (sh)
3055 (s)	3058 (s)	3071 (s)	3077 (s)
3152 (vw)	3152 (w)		

[a] w – weak; m – medium; s – strong; v – very; sh – shoulder.

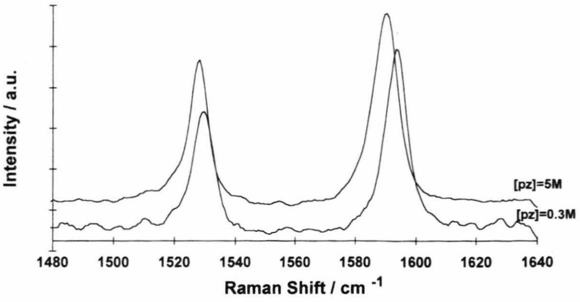


Fig. 3. Raman-spectra of two aqueous pyrazine solutions in the 1480–1640 cm^{-1} region.

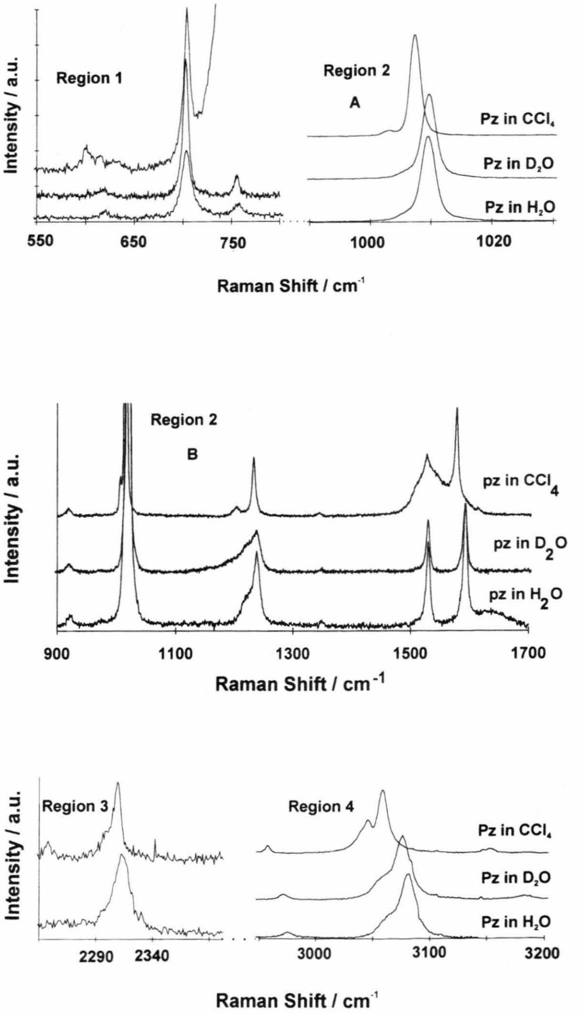


Fig. 4. Spectra of solutions of 1 M pyrazine in three different solvents.

observed when the spectra of pyrazine in water and in heavy water are compared. On the other hand, both are different from the spectrum of pz in CCl_4. The frequencies are in good agreement with the literature [15–20]. Some of these bands are summarized in Table 1 and compared to the liquid pyrazine spectrum. It is interesting to notice, from Table 1 and Fig. 4, that the shoulders in the aqueous pyrazine spectrum at around 1010, 1220 and 3060 cm^{-1} appear as very well resolved bands in the spectrum of pyrazine in CCl_4 at ca. 1006, 1202, and 3045 cm^{-1}, respectively. In addition, significant shifts occur for the bands of pyrazine in H_2O, compared to the bands of pyrazine in CCl_4. For instance, the bands of aqueous pyrazine at ca. 620, 921, 1019, 1237, 1590, 2970, and 3076 cm^{-1} shift to 610, 918, 1014, 1232, 1579, 2960, and 3058 cm^{-1} for pyrazine in CCl_4. Also, it is clear from Table 1 that the spectrum of pz in CCl_4 has more similarity to the spectrum of liquid pz.

Close examination of the spectra in Fig. 4, region 2 B, reveals differences between the spectra of aqueous pyrazine and pyrazine in heavy water in the 1220 cm^{-1} region. The bandfitting program indicated two bands from the aqueous pz, coincident with two bands of pz in heavy water, at 1220 (sh) and 1237 cm^{-1}; however, in the spectrum of pz in heavy water, an additional band at 1200 cm^{-1} was found. This band arises from the bending mode of heavy water [21]. A curious background shows up under the 1527 cm^{-1} band in the spectrum of pz in CCl_4; it arises from a combination band of the solvent.

Pyrazine can interact with water by hydrogen bonding, either via the lone pairs of electrons of nitrogen or by the π cloud of the aromatic ring. The intermolecular pz interaction (present in liquid pz) and the interaction between pyrazine and CCl_4 have the same nature, and mainly can be attributed to London forces. The hydrogen bond interaction between pz and water is stronger than London forces causing broadening and band shifts that result in overlap. This can explain the better resolution in the spectrum of pyrazine in CCl_4. The absence of pz-water complexes in the pz/CCl_4 solutions leaves the pyrazine molecules more isolated, leading to sharper bands and, consequently, to better resolution. The band positions of pz in CCl_4 are similar to those of liquid pyrazine, due to the weaker intermolecular interactions, compared to aqueous pz solutions.

One can notice that the majority of the shifts in the spectrum of pyrazine in CCl_4 are to lower frequency, when compared to the spectrum of aqueous pyrazine. This is also good evidence of the presence of a pyrazine-solvent complex. For an aqueous pyrazine complex the nature of the hydrogen bonding is similar for both water and heavy water, and thus small or no shifts are expected in their vibrational spectrum. However, when water is replaced by the inert solvent CCl_4, significant shifts occur, mainly to lower frequencies.

Another interesting point is the nature of the shoulder at 1225 cm^{-1} in the spectrum of aqueous pyrazine. As observed by Erdheim et al. [5], this band suffers a very significant enhancement when pz is on the electrode surface, and its intensity becomes greater than that of the 1235 cm^{-1} band. Erdheim et al. [5] did not assign this band. We will delay the explanation for these two bands (1225 and 1235 cm^{-1}), which appear in the pz spectrum from the electrode surface, until the next section. A survey of the pyrazine SERS studies [1, 5, 6, 9], shows that the bands at 615, 1020, 1220, 1235, 1590, and 3074 cm^{-1} are the predominant features. These same bands suffer the major shifts when the solvent is changed from CCl_4 to water. These coincidences suggest that the interaction of pyrazine with water and with the electrode surface occurs via the same molecular site.

Studies of Pyrazine in Aqueous HCl Solutions

In Fig. 5 (regions 1 to 4) spectra of 1 M pyrazine in several concentrations of aqueous HCl are presented. One can notice that practically all bands shift and new features show up in the spectrum as the HCl concentration increases.

At pH values higher than 1.5 the predominant species in solution are the aquated pyrazine molecules (accurately, a pyrazine-water complex, as shown in the section above). When the pH is around 0.5 the spectrum includes bands due to both pz and pzH^+. At HCl concentrations greater than 5.4 M, the aquated pzH^+ is the only species present in the solution. Therefore it is possible to identify and assign specific bands related to each species. These new bands can be related to bands that appear on the electrode surface. These results are summarized in Table 2; the modes are numbered according to the Wilson scheme [22].

Using computer bandfitting techniques, two bands were isolated under the envelope around 1025 cm^{-1} in the pzH^+ spectrum. One band is at 1020 cm^{-1} and is due to the symmetrical ring breathing mode. The other one is located at 1030 cm^{-1} and is assigned to

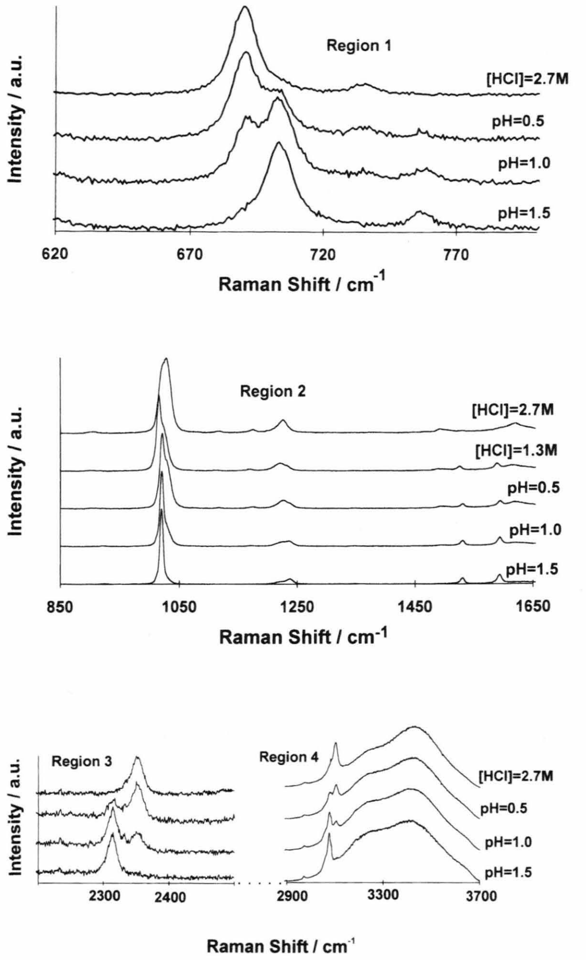


Fig. 5. Spectra of solutions of 1 M pyrazine in HCl.

a ring deformation mode; both are A_1 modes Although this 1030 cm^{-1} band is very strong for aqueous solutions, it is a very weak band from the electrode surface [1, 5–9].

The shoulder in the aquated pz spectrum at 1220 cm^{-1} disappears and the band at 1235 shifts to the 1225 cm^{-1} position as the solution becomes more acidic. The new 1225 cm^{-1} band can be assigned to a symmetrical CH bending (A_1–9a).

A relatively intense band was always oberved in the SER spectrum of pyrazine due to this 9a mode [1, 5, 6, 9]. This band was detected by both Moskovits et al. [9], at 1233 cm^{-1} in the pz spectrum from silver in UHV, and Dornhaus et al. [6], at 1242 cm^{-1} in the pz spectrum from a silver electrode in KCl aqueous solution. However, Erdheim et al. [5] reported two bands in the SER spectrum of pz from a silver electrode in that region, one at 1220 and another at 1237 cm^{-1}. The same two bands were also observed in our laboratory in a preliminary study of the pz spectrum from gold electrodes [1], one at 1213 and another at 1233 cm^{-1}. In both cases, the former band is stronger than the latter. Assuming that the SER spectrum of pz should be similar to the spectrum of monoprotonated pz (considering the simplistic argument that both monoprotonated pzH^+ and pz adsorbed at the electrode surface have the same symmetry – C_{2v}), one would expect just one band in the SER spectrum in that region at ca. 1225 cm^{-1} (small shifts are expected when a species in solution is adsorbed at a surface). In order to explain these two bands in the spectrum from the electrode surface, one must look back and analyze this region in the spectrum of aquated pz. In the latter case, two bands were observed: a shoulder at ca. 1220 cm^{-1} and a medium intensity band at ca. 1230 cm^{-1}. All authors [15–20] agree that the assignment of the ca. 1230 cm^{-1} band is to the fundamental 9a mode. Sbrana et al. [18] assigned the 1201 cm^{-1} band of pz in CCl_4 (recall that the 1220 cm^{-1} aquated pz band shifts when the solvent is changed to CCl_4 – see Table 1) to an overtone of the 6a ring deformation mode at 600 cm^{-1} (δ ring). Despite the fact this assignment is suitable to explain the 1208 cm^{-1} band of liquid pz, Zarembowitch et al. [20] chose an alternative possibility; they assigned that band to the combination B_{2u} (11 γCH 785 cm^{-1})$\otimes B_{2u}$(16b γ ring 418 cm^{-1}) $= A_g$ 1203 cm^{-1}. This latter assignment was supported by Arenas et al. [15] from the study of the spectrum of d_4-pz.

However, from Tables 1 and 2, it may be noticed that the A_g 6a (δ ring) mode of pyrazine in aqueous solution occurs at ca. 618 cm^{-1}. This band would give an overtone of A_g symmetry at 1236 cm^{-1}, which is very close to the fundamental A_g at 1235 cm^{-1} (9a–δCH). These coincidences suggest a Fermi resonance involving the 9a fundamental mode and a combination with A_g symmetry. Fermi resonance occurs when two modes of the same symmetry are accidentally degenerate. The result is usually a doublet, in which the bands share their energy and intensity [23]. Both modes 11 and 16b were observed in the pzH^+ spectra as weak bands [13] at 780 and 418 cm^{-1}, respectively. The fundamental 6a shifts down to 605 cm^{-1} in the aquated monoprotonated pz spectrum. These shifts of the fundamental bands could be

Table 2. Vibrational frequencies (cm^{-1}) for 1 M pyrazine in aqueous HCl solutions[a]: Comparison to the literature and assignments[b].

This work						Literature[c]				
Assign. for pz	pH = 4	pH = 1.1	pH = 0.5	[HCl] = 8.1 M	Assign. for pzH$^+$	solution ref. [9]	SERS ref. [9]	liquid ref. [17]	solution ref. [15]	solution ref. [20]
		606 w	605 w	606 w (p)	A_1 (6a) δ ring	600 vw	615 m	596	602	602
A_g (6a) δ ring	620 w (p)	617 w						641		
		691 m	690 m	688 m (dp)	B_1 (6b) δ ring					
B_{2g} (6b) δ ring	702 m (dp)	702 m	702 sh			699 m	700 w	703	704	704
		735 w	735 w	732 w (dp)	B_2 (4) γ ring					
B_{3g} (4) γ ring	758 w (dp)	757 w	754 vw			756 w	753 w	757	756	754
B_{2u} (11) γ CH						(785)	792 m	(804)	(785)	(784)
		906 vw	911 w	898 w (dp)	A_2 (10a) γ CH					
B_{1g} (10a) γ CH	922 w (dp)	921 w				(927)	922 w	919	927	
	973 vw	973 vw		970 vw	B_2 (5) γ CH	(960)	972 w			975
B_{3g} (5) γ CH						(983)			983	997
A_g (1) ν ring	1019 vs (p)	1019 vs	1020 vs	1020 sh (p)	A_1 (1) ν ring	1015 s	1015 s	1015	1016	1014
B_{1u} (12) δ ring			1031 sh	1031 vs (p)	A_1 (12) δ ring	(1018)	1031 w	(1021)	(1018)	(1018)
B_{3u} (15) δ CH						(1063)	1088 m	(1063)	(1063)	(1061)
		1119 w	1117 w	1112 w (p)	A_1 (18a) δ CH			1118		
B_{1u} (18a) δ CH						(1130)		(1135)	(1130)	(1130)
B_{3u} (14) ν ring		1172 w	1175 w	1173 w (dp)	B_1 (14) ν ring				(1149)	(1150)
A_g (11 + 16b)	1218 sh (p)									
		1225 m	1226 m	1223 m (p)	A_1 (9a) δ CH					
A_g (9a) δ CH	1238 m (p)	1235 m	1235 sh			1239	1233 m	1230	1233	1248
B_{2g} (3) δ CH	1348 vw	1347 vw				(1347)	1347 w	(1346)	1346	
				1372 vw	B_1 (3) δ CH	(1360)	1360 w			1358
B_{3u} (19b) ν ring						(1411)	1410 m	(1418)	(1411)	(1411)
				1464 vw	B_1 (19b) ν ring					
B_{1u} (19a) ν ring		1498 vw	1495 w	1488 w (dp)	A_1 (19a) ν ring	(1483)	1484 m	(1484)	(1483)	(1482)
B_{2g} (8b) ν ring	1530 m (dp)	1530 m	1528 w			1524	1522 m	1524	1525	1521
A_g (8a) ν ring	1593 m (p)	1594 m	1594 m	1594 m	B_1 (8b) ν ring	1583	1578 s	1578	1580	1581
A_g (1 + 6a)		1618 w	1619 m	1618 m (p)	A_1 (8a) ν ring				1615	
A_g (2 × 14)	2312 m (p)	2314 m	2317 w						2304	
		2350 w	2350 m	2346 m (p)	A_1 (2 × 14)					
A_g (2 × 19a)	2970 w (p)	2970 w	2970 w	2962 w	A_1 (2 × 19a)				2955	
B_{1u} (13) ν CH						(3012)			(3012)	(3011)
						(3013)				
B_{2g} (7b) ν CH	3061 sh					(3040)		3041	3040	3030
A_g (2) ν CH	3077 s (p)	3077 s	3079 m	3080 sh	B_1 (7b) ν CH	3055 s	3055 w	3054	3055	3046
		3105 m	3103 s	3092 s (p)	A_1 (2) ν CH			(3066)	3063	(3061)

[a] Intensities – see Table 1; p – polarized; dp – depolarized.

[b] Assignments are made with consideration of references [9], [13] and [15–20]; the Wilson numbering scheme [22] is presented in parentheses following the species symbol.

[c] Values in parentheses are calculated or infrared values.

enough to take the combination out of the resonance condition. This could explain only one band at 1225 cm^{-1} in the aquated pyrazinium spectrum. This hypothesis is supported by the higher intensity of the 1225 cm^{-1} pzH^+ band when compared to the 1235 cm^{-1} band from "free" aqueous pyrazine (see Fig. 5, region 2). At the electrode, the surface perturbation might be enough to provoke shifts in the frequencies of the fundamental modes that put these in Fermi resonance again. Changes in Fermi resonance conditions due to shifts induced by the surface have been invoked previously [24]. The 6a vibrational mode was reported at 636 cm^{-1} by both Erdheim et al. [5] and us [1] when pz is adsorbed on a metallic surface. It would give an overtone at ca. 1272 cm^{-1}. On the other hand, for pz at the electrode surface, the 11 and 16b modes show up at 800 and 440 cm^{-1}, which would give an overtone at 1240 cm^{-1}. Hence, we suggest that the band of pz at the electrode surface at ca. 1235 cm^{-1} can be assigned as the combination 11 + 16b.

The 2312 cm^{-1} band in the pz spectra shifts to 2350 cm^{-1} for pzH^+. While no fundamental vibrations of pz are expected in this region, we follow Arenas et al. [15] and assign these bands as an overtone from the ν_{14} (B_{3u}) mode which appears at ca. 1148 cm^{-1} in the liquid pz and at ca. 1175 cm^{-1} in the aquated pyrazinium spectrum.

The 702 cm^{-1} band in the pz spectrum (symmetrical ring deformation) shifts to 690 cm^{-1} in the pzH^+ spectrum. Using a band fitting program, it was possible to isolate each band for a mixture of both species. Figure 6 shows an example of this procedure. The 702 cm^{-1} band intensity (I_{720}) is proportional to the amount of pz in solution and the 735 cm^{-1} band intensity (I_{735}) is proportional to the amount of pzH^+ in solution. Therefore, the fractional amount of both pz and pzH^+ is given by the expressions

$$I_{720} \propto [\mathrm{pz}], \quad I_{735} \propto [\mathrm{pzH}^+],$$

so

$$X_{\mathrm{pz}} \propto \frac{I_{720}}{I_{720} + I_{735}}, \quad X_{\mathrm{pzH}^+} = (1 - X_{\mathrm{pz}}).$$

The fractional distribution calculated in this way is presented in Figure 7. The pK_{a1} value obtained from the intersection is 0.70. This is in surprisingly good agreement with the literature value 0.65 [11]. We didn't expect such good agreement, because the Raman intensity does not depend only on the concentration, but also on the Raman polarizability, which can differ considerably for the two species. A 5% error is not unreasonable from the bandfitting procedure.

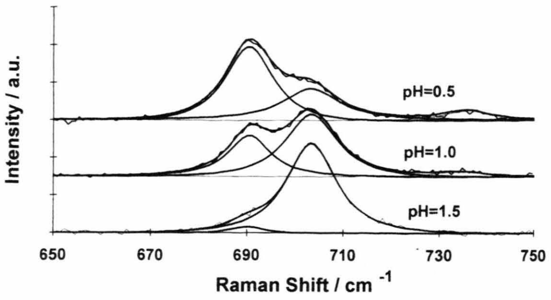


Fig. 6. Sample of the bandfitting procedure. Solutions are 1 M pyrazine in HCl at three concentrations. The component bands, their sum and the original spectra are shown.

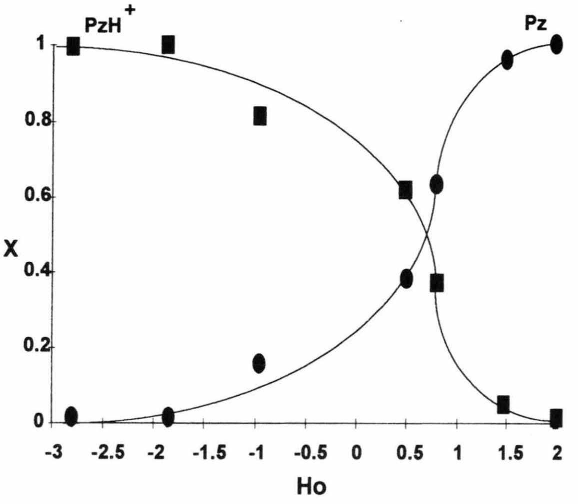


Fig. 7. Experimental fractional distribution of 1 M pyrazine and its monoprotonated form in HCl. The fraction of pyrazine species has been calculated as explained in the text.

It was not possible to observe the spectrum of the diprotonated pyrazine, even in the most concentrated HCl solution (37%). The spectrum of diprotonated pyrazine can be useful in order to identify bands which arise from protonation of the "free" N of an eventually end-on adsorbed pyrazine molecule at very acidic interfacial conditions. Therefore we measured some spectra of more acidic media and these results are presented in the next section.

Table 3. Frequencies (cm^{-1}) of vibrational modes for all three pyrazine species in aqueous sulfuric, perchloric and hydrochloric acid media.

Pyrazine-pz				Monoprotonated pyrazine				Diprotonated pyrazine		
H_2SO_4	$HClO_4$	HCl	assign	H_2SO_4	$HClO_4$	HCl	assign	H_2SO_4	$HClO_4$	assign
		620	A_g (6a)		609	606	A_1 (6a)	614		A_g (6a)
702	701	702	B_{2g} (6b)	689	689	688	B_1 (6b)	671	675	B_{2g} (6b)
756	755	758	B_{3g} (4)	734	734	732	B_2 (4)			
921	922	922	B_{1g} (10a)							
1019	1019	1019	A_g (1)	1015	1015	1020	A_1 (1)			
				1030	1030	1031	A_1 (12)	1034	1032	A_g (1)
				1114		1117	A_1 (18a)			
					1173	1173	B_1 (14)			
								1208	1214	A_g (9a)
1222	1217	1218	A_g (11+16b)	1224	1225	1223	A_1 (9a)			
1237	1237	1238	A_g (9a)							
1348	1347	1348	B_{2g} (3)					1376		B_{2g} (3)
				1491	1491	1495	A_1 (19a)			
1529	1529	1530	B_{2g} (8b)			1594	A_1 (8b)			
1593	1593	1593	A_g (8a)	1621	1619	1618	A_1 (8a)	1612	1609	A_g (8a)
								1661	1660	B_{2g} (8b)
2312	2312	2312	A_g (2 × 14)	2350	2350	2350	A_1 (2 × 14)	2345	2364	A_g (2 × 14)
2972	2967	2970	A_g (2 × 19a)	2969	2971	2970	A_1 (2 × 19a)		2982	A_g (2 × 19a)
3075	3074	3077	A_g (2)	3105	3104	3103	A_1 (2)	3125	3110	A_g (2)

Studies of Pyrazine in $HClO_4$ and H_2SO_4 Solutions

The biggest problem found with these acids was the overlap between bands due to the acids and those due to the protonated pyrazine. In spite of these problems, some bands due to the diprotonated pyrazine are apparent. Figure 8 shows spectra in the 970–1100 cm^{-1} spectral region, of pyrazine in $HClO_4$ at different concentrations. Bands due to pz, pzH^+ and pzH_2^{2+} can be identified. At a concentration 0.3 M of $HClO_4$ the aquated pz is the predominant species, and just one sharp band is observed at 1019 cm^{-1}. As the $HClO_4$ concentration increases to 4 M a broad envelope containing two intense bands at 1020 and 1030 cm^{-1} appears, which is characteristic of aquated pyrazinium ion. The broad feature completely disappears at a $HClO_4$ concentration of 12 M, and in this condition just one band is observed at 1034 cm^{-1}; it is attributed to the aquated diprotonated pzH_2^{2+} species.

The fractional distribution of pyrazine in H_2SO_4 was obtained in a manner similar to that described for HCl. Spectra shown in Fig. 9 were used and the curve, with the H_0 values from Tickle et al. [25], is presented in Figure 10. The points of intersection give $pK_{a1} = 0.5$ and $pK_{a2} = -7$. These results differ from the literature values (0.65 and -5.8) [11]. The difference can be attributed to the change of polarizability of the protonated species, to the overlap of the 700 cm^{-1} band of pyrazine and a broad sulfuric acid band at 570 cm^{-1} (mainly at elevated acid concentrations) and to the

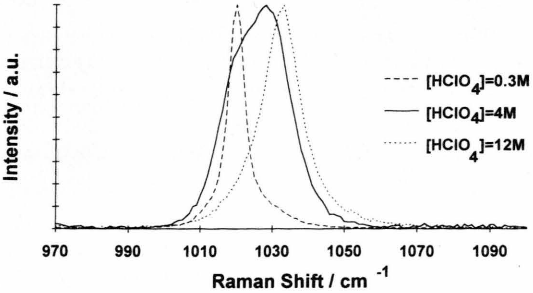


Fig. 8. Spectra of solutions of 1 M pyrazine in $HClO_4$.

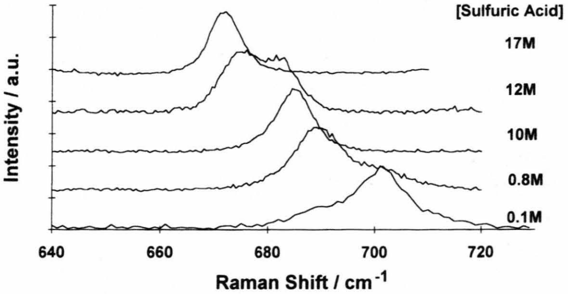


Fig. 9. Spectra of solutions of 1 M pyrazine in H_2SO_4.

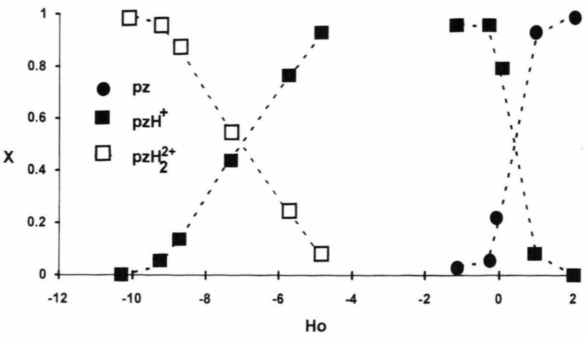


Fig. 10. Experimental fractional distribution of 1 M pyrazine and its mono and diprotonated forms in H_2SO_4.

ambiguity in the precise definition of various acidity scales. Bands due to all pyrazine species in these acidic media are presented and assigned in Table 3.

Conclusions

Raman spectra of pyrazine solutions are presented for various acidic media. From these spectra, bands due to 3 different pyrazine species, pz, pzH$^+$ and pzH$_2^{2+}$, have been identified. The spectra also suggest an interaction between pyrazine and water; the specific geometry and stoichiometry of this interaction cannot be deduced from the spectral changes alone.

An approximate fractional distribution of these pyrazine species was obtained through the relation between band intensity and species concentration. The estimated pyrazine pK_a values are reasonably consistent with the literature.

The new bands can be related to those observed when pyrazine adsorbs to an electrode surface. Therefore, these results should prove useful when interpreting the SERS spectrum of adsorbed pyrazine – a study now in progress. Insight may thus be gleaned into the nature of surface acidity.

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