

# Hydration of pyridine-4-carbaldehyde at the silver-water interface: a pH-dependent surface enhanced Raman study

PERKIN  
2

Kana M. Mukherjee and Tridibendra N. Misra \*

Department of Spectroscopy, Indian Association For The Cultivation of Science,  
Calcutta-700032, India

Surface enhanced Raman (SER) spectra of samples in silver sols have been used to monitor the relative concentration of protonated and neutral pyridine-4-carbaldehyde (4PCA) on the silver surface, which is shown to depend on the solution pH. At low pH, the relative amount of adsorbed free aldehyde decreases as the molecule becomes hydrated.

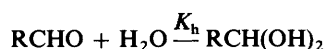
When the pH value is in the range  $5 < \text{pH} < 6$ , most of the aldehyde is protonated and consequently the presence of free aldehyde is not shown in the SER spectrum. As the pH increases further, the neutral hydrate becomes the adsorbed species. The identical nature of the SER spectra of 4-PCA and 4-pyridylmethanol at pH 6.45 confirms the complete hydration of surface adsorbed 4-PCA molecules.

## Introduction

Surface enhanced Raman spectroscopy (SERS) has been used as a suitable technique for the *in-situ* investigation of molecular structure and conformation on the interfacial environment. This technique has been successfully used by Allen and Van Duyne, Hallmark and Campion and Creighton to determine the adsorbate orientation with respect to the metal surface.<sup>1-3</sup>

The surface-adsorbed molecule may exist in variety of forms related to one another by means of acid-base reactions, complexation, tautomerisation, *etc.* We have shown in our earlier report that SER spectroscopy can efficiently identify the tautomeric form<sup>4</sup> of such molecules adsorbed on a metal surface.

In this paper we characterise the conformation and structure of pyridine-4-carbaldehyde (4-PCA) adsorbed on silver surfaces as a function of solution pH with the aid of SER spectra. In aqueous solution many aldehydes exist in two forms, the free aldehyde and the hydrate or *gem*-diol related by a hydration equilibrium constant  $K_h$ .<sup>5</sup>



$$K_h = \frac{[\text{RCH}(\text{OH})_2]}{[\text{RCHO}]}, \text{ in a large excess of water}$$

where R denotes the pyridyl ring.

We show that the presence of metal surface modifies the extent of hydration significantly and that if the pH of the solution is then varied,  $K_h$  reaches an optimum value for which the adsorbate molecule is completely hydrated showing an SER spectrum identical with that of 4-pyridyl-methanol.

## Experimental

4-PCA (Aldrich) was purified by vacuum distillation. Milli-Q-plus de-ionised water was used to prepare the aqueous solutions. The silver sol was prepared following the method of Creighton,<sup>6</sup> and showed a sharp extinction maximum at 398 nm and contained spherical silver particles of diameter 1-50 nm. Acetate buffers were used to maintain pH values at  $< 5.5$  while phosphate buffers were used for pH values  $> 5.5$ .

All normal Raman (NR) and SER spectra were recorded with the laser line of 514.5 nm of a Spectra Physics Model 2020-05 Ar<sup>+</sup> laser with an incident laser power of 0.2 W. The

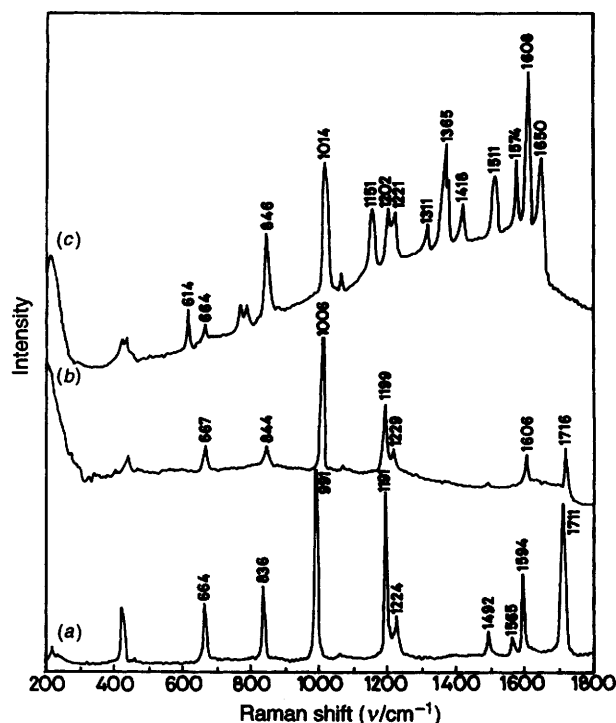


Fig. 1 Normal Raman spectra of pyridine-4-carbaldehyde: (a) pure liquid; (b) 0.01 mol dm<sup>-3</sup> aqueous solution; (c) 8 × 10<sup>-3</sup> mol dm<sup>-3</sup> silver sol

scattered light passing normal to the incoming radiation was focussed on the entrance slit of width 4 cm<sup>-1</sup> of a Spex Model 1403, 0.85 m double monochromator fitted with a holographic grating with 1800 groove per mm and a cooled Hamamatsu Photonics photomultiplier tube model R 928/115, for detection. A Spex Datamate 1B was used for monochromator control and data acquisition. pH values of all the solutions were measured by means of a Systronics μ<sub>pH</sub> system Model 361, the relative accuracy of which is 0.001 pH unit.

## Results and discussion

NRS of neat liquid 4PCA and of its aqueous solution (concentration 0.01 mol dm<sup>-3</sup>) and its SER spectrum in Ag-sol at a concentration of 8 × 10<sup>-3</sup> mol dm<sup>-3</sup>, are shown in Fig. 1. In

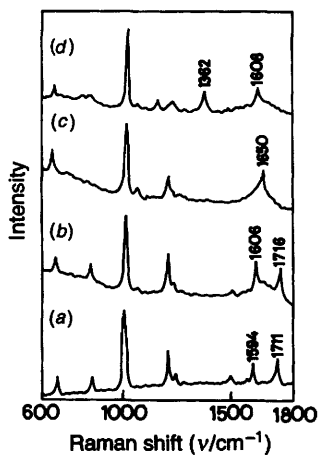


Fig. 2 Normal Raman spectra of pyridine-4-carbaldehyde: (a) pure liquid; (b)  $0.01 \text{ mol dm}^{-3}$  aqueous solution; (c)  $0.01 \text{ mol dm}^{-3}$  in  $0.5 \text{ mol dm}^{-3}$  HCl; (d)  $0.01 \text{ mol dm}^{-3}$  in  $0.5 \text{ mol dm}^{-3}$  NaOH

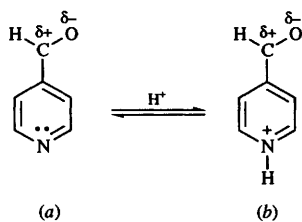


Fig. 3 Pyridine-4-carbaldehyde: (a) normal form; (b) protonated form

the SER spectrum the carbonyl stretching frequency at  $1711 \text{ cm}^{-1}$  is completely absent and three new bands at  $1650$ ,  $1365$  and  $1420 \text{ cm}^{-1}$  develop. Also the ring mode at  $1608 \text{ cm}^{-1}$  is greatly enhanced and the ring breathing mode which is at  $991 \text{ cm}^{-1}$  in the pure liquid undergoes a largely hypsochromic shift. From a previous study<sup>7</sup> we inferred that in basic or acidic solution the ring breathing mode and the trigonal mode appear around  $1010 \text{ cm}^{-1}$  and  $1050 \text{ cm}^{-1}$  but in neutral solution of concentration  $0.05 \text{ mol dm}^{-3}$  these modes appear at  $1003 \text{ cm}^{-1}$  and  $1036 \text{ cm}^{-1}$ , respectively.

It was therefore interesting to examine the acid-base equilibrium of 4-PCA. The NRS of this molecule in neutral, acidic and also in basic media is shown in Fig. 2 where we observe that the carbonyl band at about  $1711 \text{ cm}^{-1}$  is prominent in the neat liquid and in aqueous solution but is observed in neither acidic nor strong base medium. Another notable feature is the behaviour of the ring mode near  $1600 \text{ cm}^{-1}$  seen in the neat liquid and also in aqueous solution. In the NRS of the acidic solution this ring mode is absent and is replaced by a new band at about  $1650 \text{ cm}^{-1}$ . In acidic media, owing to the availability of  $\text{H}^+$  ions, the pyridine nitrogen becomes protonated<sup>8,9</sup> [Fig. 3(b)] causing the ring mode to shift to higher frequency. In the NRS of the basic solution such a ring mode is present, as is a new band around  $1360 \text{ cm}^{-1}$ . The appearance of this band, assigned as asymmetric C–O stretching<sup>10–12</sup> mode, instead of  $\nu_{\text{C=O}}$  mode, indicates that the absorbate molecules do not exist as the aldehyde form. The band at  $1365 \text{ cm}^{-1}$  in the SER spectrum [Fig. 1(c)], which is totally absent in neutral solution [Fig. 1(b)] and also in the neat liquid [Fig. 1(a)], is assigned to the  $\nu_{\text{C(OH)}}$  mode, which arises on conversion of the aldehyde into the hydrate.

Hydration of the aldehyde group is an addition reaction caused by the nucleophilic attack<sup>13</sup> of a water molecule on the positively charged carbon atom of the polarised carbonyl group (Fig. 3). When the 4PCA molecule is adsorbed onto the metal surface, this positivity increases. As a result nucleophilic attack by water also increases and hydration of the aldehyde group occurs. Formation of the hydrate is evidenced by the appearance of C–OH in-plane bending mode<sup>10,11–15</sup> at  $1420$

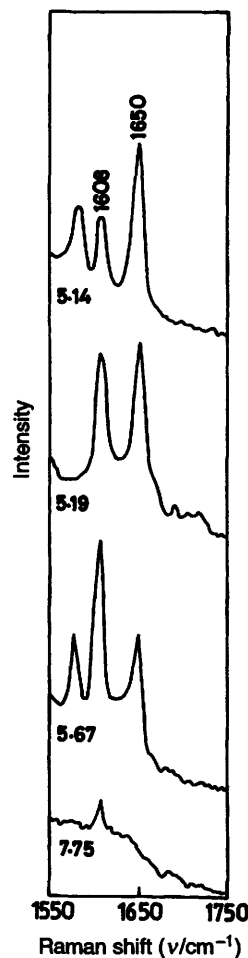


Fig. 4 SER spectra of  $0.04 \text{ mol dm}^{-3}$  pyridine-4-carbaldehyde at different pH at fixed laser power  $200 \text{ mW}$

$\text{cm}^{-1}$  in the SER spectrum [Fig. 1(c)]. Although because of large fluorescence background  $\nu_{\text{OH}}$  region could not be observed. That hydration of the surface species is responsible for the disappearance of the carbonyl band has previously been reported for metal electrodes.<sup>8,16</sup>

#### Spectroscopic behaviour of 4-PCA in Ag sol as a function of solution pH

The SER spectra of 4PCA molecule in the range  $1550$ – $1750 \text{ cm}^{-1}$  at different pH (shown in Fig. 4) indicate that at pH 5.19 the ring mode is slightly enhanced compared with the protonated mode. At lower pH, 5.14, the SER intensity of the normal ring mode decreases whereas the band due to the protonated species is observed to be greatly enhanced. This implies that as the pH value of the sol decreases, *i.e.* the sol becomes more acidic, the relative intensity of the band at  $1650 \text{ cm}^{-1}$  (protonated) increases and the pyridyl ring is protonated. In comparison at higher pH, 5.67, the protonated band is weak, while ring mode becomes stronger and it follows that, as the pH of sol increases, protonation decreases. Such protonation occurs up to pH 5.98; above this value the pyridyl ring is not protonated. At higher pH, 7.75, *i.e.* in the basic region, only the normal ring mode is observed. Thus by studying the SER spectra of 4PCA molecule at various pH values of the sol the extent of protonation can be monitored. The relative population of protonated and neutral hydrate on the silver surface can be estimated by calculating the intensity ratio  $I_{1650}/(I_{1608} + I_{1650})$ , assuming this to be equal to the mole fraction of pyridine species on the surface that is protonated, if the scattering cross section is assumed to be same. Using this relationship the estimated fraction of protonated hydrate is 40–

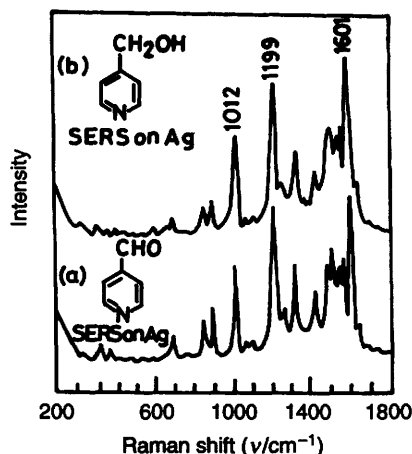


Fig. 5 SER spectra in Ag-sol at pH 6.45: (a) pyridine-4-carbaldehyde; (b) 4-pyridylmethanol

60% in the pH region  $5 < \text{pH} < 6$ , more than 60% at  $\text{pH} < 5$  and for pH value  $> 6$ , only normal hydrate is present.

The fraction of aldehyde that is completely hydrated, may be rapidly and efficiently converted into the alcohol, 4-pyridylmethanol,<sup>17</sup> as is also reflected from the resemblance of the SER spectrum of 4-PCA and 4PC (Fig. 5) at pH 6.45, under identical conditions. Thus SER spectroscopy allows us properly to identify surface species, which may often be quite different from that found in the bulk solution.

#### Acknowledgements

The authors gratefully acknowledge financial support from the Department of Science & Technology, Govt. of India (through

project No. SP/INC/L06/93). One of the authors (K. M. M.) thanks CSIR for a NET fellowship.

#### References

- 1 C. Allen and R. P. Van Duyne, *Chem. Phys. Lett.*, 1979, **63**, 455.
- 2 V. M. Hallmark and A. Campion, *J. Chem. Phys.*, 1986, **84**, 2933.
- 3 J. A. Creighton, *Surf. Sci.*, 1983, **124**, 209.
- 4 K. Mukherjee and T. N. Misra, *J. Raman Spectrosc.*, in the press.
- 5 K. Abe, E. Hiroko and M. Hirota, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 466.
- 6 J. A. Creighton, *J. Chem. Soc., Faraday Trans. 2*, 1979, 75.
- 7 H. Chang and Kuo-Chu Hwang, *J. Am. Chem. Soc.*, 1984, **106**, 6586.
- 8 Mark R. Anderson and H. Evans, *J. Am. Chem. Soc.*, 1988, **110**, 6612.
- 9 G. Profahl, J. Barthelines and W. Plieth, *J. Electroanal. Chem.*, 1992, **329**, 329.
- 10 N. B. Colthup, L. H. Daly and S. E. Wiberly, *Introduction to IR and Raman Spectroscopy*, Academic Press, New York, 1964.
- 11 W. Kemp, *Organic Spectroscopy*, ELBS, Hong Kong, 1986.
- 12 M. Paris, G. Thomas and J. C. Merlin, *Bull. Soc. Chem. Fr.*, 1961, 707.
- 13 K. Abe and M. Hirota, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2028.
- 14 G. Varsanyi, *Vibrational Spectra of Benzene Derivatives*, Academic Press, New York, London, 1969.
- 15 R. M. Silverstein and C. C. Basseler, *Spectrophotometric Identification of Organic Compounds*, 2nd edn., Wiley, New York, 1964.
- 16 K. A. Bunding and M. I. Bell, *Surf. Sci.*, 1983, **118**, 329.
- 17 T. Nonaka, T. Kato, T. Fuchigami and T. Sekine, *Electrochim. Acta*, 1981, **26**, 887.

Paper 6/00196C

Received 22nd May 1996

Accepted 30th May 1996