

SERS spectrum of pyrazinamide in silver colloid

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Abstract : SERS spectrum of pyrazinamide is recorded in silver colloid. In the low frequency metal-molecule stretching mode region, two bands are observed which correspond to Ag–N and Ag–O stretching modes indicating the silver surface involved in coordination with the pyrazinamide molecule through ring nitrogen and amide oxygen atoms. Further, enhancements in intensity of the bands due to both in-plane and out-of-plane pyrazine ring modes are observed which indicate the inclined orientation of the ring with respect to the silver surface. Some of the amide bands are also enhanced in intensity.

Keywords : Pyrazinamide, SERS spectrum, silver colloid

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1. Introduction

Detailed study on the Raman and IR spectra of pyrazinamide has been reported by Kalkar *et al* [1]. They found considerable perturbations on the vibrational energy levels of the aromatic pyrazine moiety due to the presence of the strong electron accepting amide group and intermolecular hydrogen bonding. The results of their low frequency vibrational analysis [2] suggest a planar structure for the pyrazinamide dimer. In the present communication, the results of the analysis of the Surface Enhanced Raman Scattering (SERS) spectrum of pyrazinamide is reported as it could give information regarding the silver-molecule coordination and orientation of the molecule on the silver surface [3]. For comparison, the SERS spectrum of pyrazine in silver colloid is also recorded though it is already reported in the literature [4–6].

2. Experimental

Greenish yellow silver colloid is prepared from AgNO_3 and NaBH_4 by the method described by Creighton *et al* [7]. It has a sharp absorption band at 390 nm and is stable for

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several weeks. Sample for SERS measurement is prepared by mixing equal volumes of colloid and 10^{-3} M aqueous solution of pyrazinamide/pyrazine. All the chemicals are procured from Sigma, U.S.A. Raman spectra [Figures (1–5)] are recorded using a

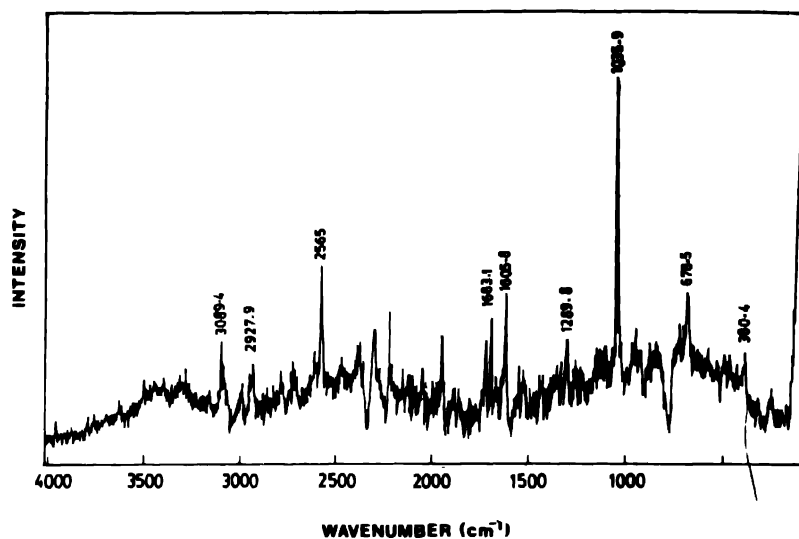


Figure 1. Normal Raman spectrum of pyrazine.

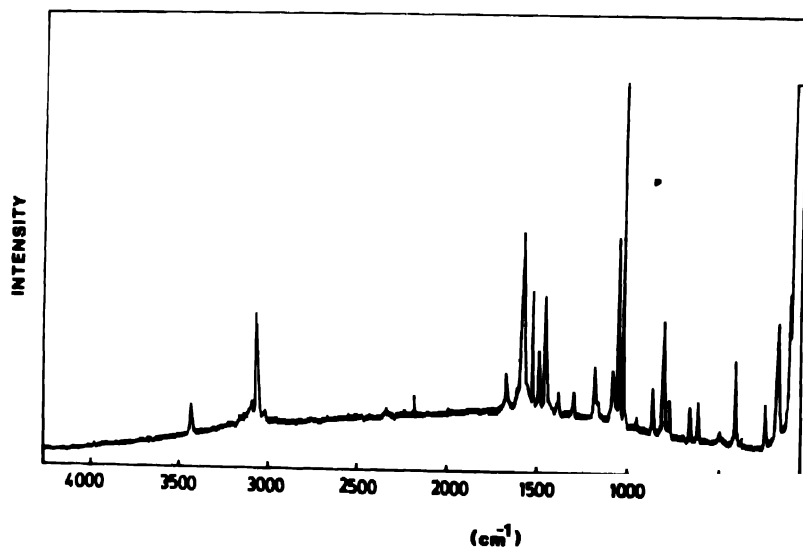


Figure 2. Normal Raman spectrum of pyrazinamide.

Dilor GMBH Z24 spectrometer equipped with a Spectra Physics model 165 Ar⁺ laser. The 514.5 nm radiation with a power of 200 mW is used as the source of excitation.

Electronic absorption spectra are obtained using a UV-240 Shimadzu UV-Visible recording spectrophotometer. Addition of pyrazinamide gives light pink colour to the

colloid showing aggregation of particles. The sharp absorption band at 390 nm broadens with centre around 400 nm and an additional very broad band appears around 560 nm.

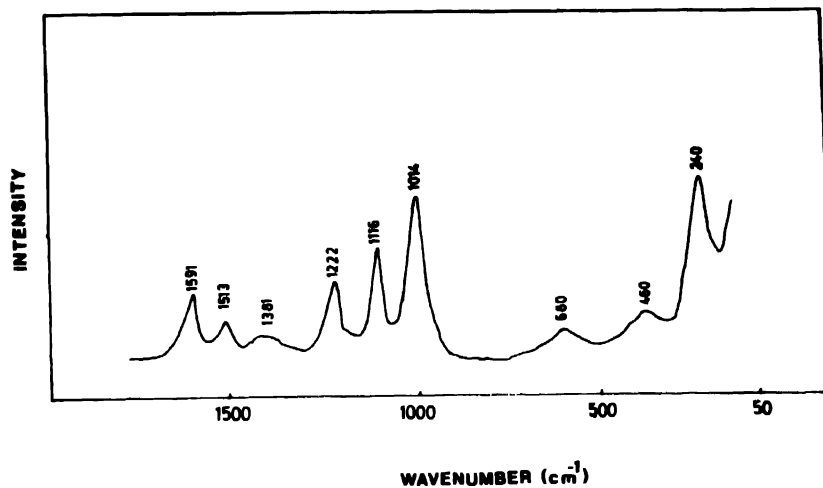


Figure 3. SERS spectrum of pyrazine in silver colloid

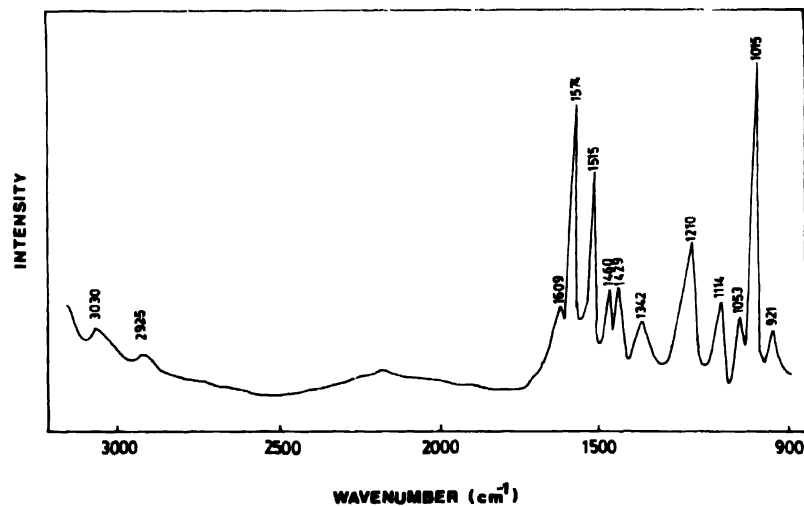


Figure 4. SERS spectrum of pyrazinamide in silver colloid (900–3000 cm^{-1} region)

3. Results and discussion

It is reported [5] that pyrazine molecule adsorbed on the silver surface has an end-on orientation. No appreciable shift is noticed for the SERS bands from the normal Raman bands [4–6]. This observation along with the Ag–N stretching mode at 240 cm^{-1} (Figure 3) and the enhancement in intensity of the in-plane CH bending modes ν_3 and ν_6 indicate that pyrazine gets adsorbed onto the silver surface through the ring nitrogen and its plane is perpendicular to the silver surface [8, 9].

The intensity distribution in the SERS spectrum of pyrazinamide is similar to that of its solution spectrum [1,10] except for some additional bands. In the SERS spectrum of pyrazinamide (Figure 4), bands corresponding to the vibrational modes 8a, 8b, 9a and 14

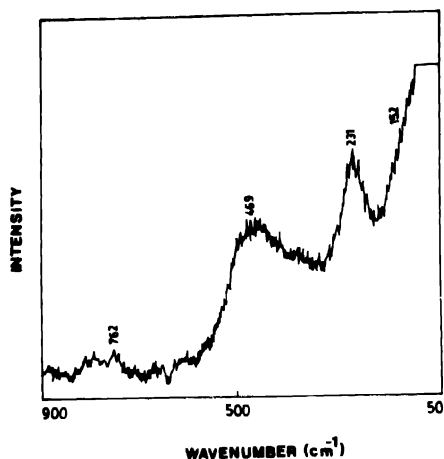


Figure 5. SERS spectrum of pyrazinamide in the 50–900 cm^{-1} region.

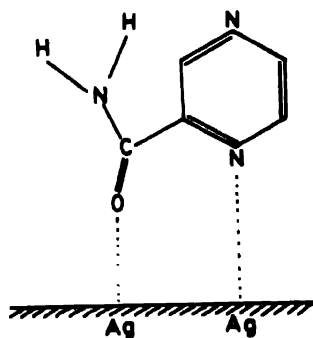


Figure 6. Orientation of the pyrazinamide molecule on the silver surface

are enhanced with frequencies almost close to those of pyrazine (Table 1). But, there is slight variation in the intensity distribution. In addition, the 19a and 19b modes are also

Table 1. SERS spectral data (cm^{-1}) and band assignments

Pyrazinamide	Pyrazine	Assignment
2925 wbr		Combination
1609 m		$\delta \text{NH}_2 / \nu \text{C}=\text{O}$
1574 vs	1591 m	8a ring
1515 s	1513 w	8b ring
1460 m		19a ring
1429 m		19b ring
1342 mbr	1381 wbr	3H bend/ $\nu \text{C}-\text{NH}_2$
1210 s	1222 s	9a H bend
1114 m	1116 s	14 ring
1053 m		18a H bend
1015 vs	1014 vs	ν_1 / ν_{12}
921 w		10a H wag
762 m		$\text{C}=\text{O}$ ipb
	680 wbr	6 ring
	460 wbr	16 ring
469 sbr		$\text{C}=\text{O}$ opb/ $\text{C}-\text{NH}_2$ ipb
231 sbr	240 s	$\nu \text{Ag}-\text{N}$
152 sh		$\nu \text{Ag}-\text{O}$

v-very, s-strong, m-medium, br-broad, sh-shoulder.

enhanced. The band at 1381 cm^{-1} in pyrazine corresponds to CH in-plane bend (vibration 3). In pyrazinamide, a medium broad band is seen around 1342 cm^{-1} . This is assigned to C–NH₂ stretching mode as a similar band is observed in maleimide [3]. The bands at 921 cm^{-1} corresponds to the vibration 10a (CH out-of-plane bend). The 18a (CH out-of-plane bend) is observed without appreciable shift from the normal Raman spectral wavenumber [1].

There is a shift of about 10 cm^{-1} for the totally symmetric ring vibration 1 while going from the normal Raman to SERS (1025 to 1015 cm^{-1}). This indicates the involvement of ring nitrogen in coordination with the silver surface [4]. This result is further supported by the observation of a strong broad band around 231 cm^{-1} for the low frequency Ag–N stretching mode similar to that in pyrazine. The observation of an additional low frequency band around 152 cm^{-1} and the enhancement of the bands due to C=O *ipb* (762 cm^{-1}), C=O *opb*/C–NH₂ *ipb* (469 cm^{-1}), ν C–NH₂ (1342 cm^{-1}) and ν C=O/ δ NH₂ (1609 cm^{-1}) indicate the coordination of oxygen atom of amide group to the silver surface.

The vibrational modes involving the atoms bound directly to the metal surface are more affected than others. In the case of mono-substituted benzenes, the ring breathing modes are known to undergo a red-shift of more than 10 cm^{-1} with substantial band broadening when adsorbed flat on the surface with surface-ring π -orbital interaction [11]. In the present case, the frequency and band width of the 1014 cm^{-1} band are not changed appreciably and hence discards the flat orientation of the pyrazinamide molecule on the silver surface. As both in-plane and out-of-plane bending modes are enhanced, it may be inferred that the pyrazine ring is inclined to the silver surface as in the case of benzoic acid [12]. As the vibrational bands of both pyrazine ring and the amide group are enhanced in intensity (Table 1) and both Ag–N and Ag–O stretching modes are observed, it is possible that the molecule coordinates with the silver surface through two atoms as in the case of maleimide [3] : the ring nitrogen and amide oxygen. The possible orientation is as shown in Figure 6. The plane of the pyrazine ring is not perpendicular to the silver surface, but it is inclined.

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References

- [1] A K Kalkar, N M Bhosekar and S T Kshirsagar *Spectrochim. Acta*, **45A** 635 (1989)
- [2] A K Kalkar, N M Bhosekar and S T Kshirsagar *Proc. Indian Acad. Sci. (Chem. Sci.)* **102** 653 (1990)
- [3] R Aroca and M Scraba *Spectrochim. Acta* **47A** 263 (1991)
- [4] M Muniz-Miranda, N Neto and G Sbrana *J. Phys. Chem.* **92** 954 (1988)

- [5] Yi Huang and Guozhen Wu *Spectrochim. Acta* **46A** 177 (1990)
- [6] R Bhattacharjee *J. Raman Spectrosc* **21** 301 (1990)
- [7] J A Creighton, C G Batchford and M G Albrecht *J. Chem. Soc. Faraday Trans. 2* **75** 790 (1979)
- [8] M Moskovits *Rev. Modern Phys.* **57** 783 (1985)
- [9] A Otto, I Mrozek, H Grabhorn and W Akemann *J. Phys. Condens. Matter* **4** 1143 (1992)
- [10] M J Martin Delgado, F Marquez, M I Suero and J I Marcos *Spectrosc. Lett* **21** 841 (1988)
- [11] T W Lee, K Kim and M S Kim *J. Mol. Struct.* **274** 59 (1992)
- [12] M Pagannone, B Fornari and G Mattei *Spectrochim. Acta* **43A** 621 (1987)