# The Laser Raman Spectra of Pyridine adsorbed on to Oxide Surfaces

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*Summary* The Raman spectra of pyridine adsorbed on to alumina, titanium dioxide, magnesium oxide, and silica gel are used to distinguish between physical and chemical adsorption and to indicate the nature of the bonding of pyridine to these surfaces.

THE i.r. spectra of adsorbed species have been extensively studied in order to determine the nature of bonding of molecules to active surfaces. There is some limitation to the use of the technique, owing to strong i.r. adsorption by the adsorbents themselves. Raman spectroscopy is relatively free of this limitation, and two of us have previously described the application of laser Raman spectroscopy to the study of adsorbed species.[1] We now report the use of this technique to study the vibrational spectra of pyridine adsorbed on to several oxide surfaces.

A thin disc of "cab-o-sil" silica was exposed to pyridine vapour, when reversible adsorption occurred. It is assumed, therefore, that the sorption was solely physical. The laser Raman spectrum clearly showed bands due to pyridine. In particular, bands at 991 and 1031 cm$^{-1}$, assigned as ring stretching-modes, were quite intense. This spectrum was identical with that of liquid pyridine with the exception of the appearance of weak bands at

1006 and 1034 cm$^{-1}$. At low coverage there would seem to be little perturbation of the pyridine molecule on physical adsorption.

Pyridine was similarly physically adsorbed on to magnesium oxide. At a low coverage (1 molecule of pyridine per 20 Å$^2$ of surface) the Raman spectrum was practically identical with that of liquid pyridine, but showed in addition very weak bands at 1007 and 1016 cm$^{-1}$ which were found to remain after prolonged pumping.

Alumina ($\eta$-type, surface area 250 m$^2$g$^{-1}$) was exposed to pyridine vapour at room temperature for 30 min and the Raman spectrum recorded. The sample was then successively evacuated to remove adsorbed pyridine and the spectrum recorded after each period of evacuation. Finally, the alumina was heated to 90° for 1 hr under high vacuum, then cooled, and its Raman spectrum recorded. The spectra obtained at various concentrations of pyridine are shown in the Figure.

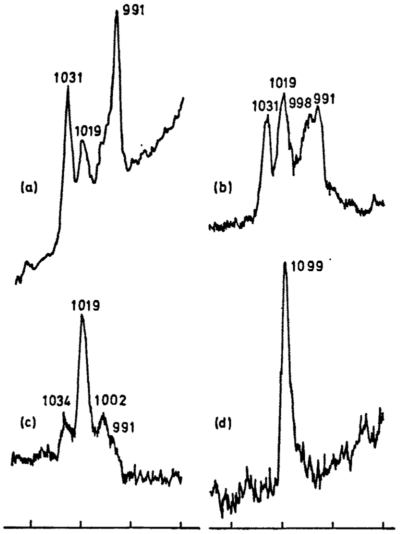

FIGURE. *The Raman spectrum of pyridine adsorbed on to $\eta$-alumina* (a) 0·217 g, (b) 0·147 g, (c) 0·111 g *pyridine on* 1·19 g *alumina*, (d) *after evacuation at* 90°.

The spectrum recorded at the highest coverage shows bands at 991, 1019, and 1031 cm$^{-1}$. The feature at 991 cm$^{-1}$ has a shoulder to higher frequency [Figure (a)]. The 991 and 1031 cm$^{-1}$ bands are assigned to physically adsorbed pyridine. Evacuation at 90° removes all weakly adsorbed pyridine, leaving only co-ordinated pyridine, identified by a band at 1019 cm$^{-1}$ [Figure (d)]. At intermediate coverages, the 991 and 1031 cm$^{-1}$ bands are reduced in intensity relative to that at 1019 cm$^{-1}$ indicating a loss of physically adsorbed pyridine [Figure (b)]. In addition, a band at 998 cm$^{-1}$ becomes distinct. On further evacuation, but without heating of the adsorbent, all bands are again reduced in intensity relative to that at 1019 cm$^{-1}$. The Figure (c) shows that the 991 cm$^{-1}$ feature has virtually disappeared, indicating loss of all physically adsorbed pyridine. The 1031 cm$^{-1}$ band has not reduced in intensity to the same extent, and appears shifted to slightly higher frequency. Accordingly, the remaining bands (at 1002 and 1034 cm$^{-1}$) are assigned to hydrogen-bonded pyridine. Assignments were made by reference to model compounds. Thus, pyridine co-ordination compounds [*e.g.* $SiCl_4(py)_2$] show bands near 1020 cm$^{-1}$, pyridinium salts at 1010 and 1028 cm$^{-1}$, and hydrogen-bonded pyridine species (*e.g.* pyridine in water) near 1003 and 1036 cm$^{-1}$.

A second sample of alumina (Actal A-$\gamma$ type) was also exposed to an atmosphere of pyridine at room temperature. The material was found to be highly fluorescent, but exposure to the laser beam for an extended period prior to recording spectra reduces this to manageable proportions. The Raman spectrum clearly contains bands due to physically adsorbed pyridine. The appearance of a pair of bands near 1050 and 1020 cm$^{-1}$ would be characteristic of co-ordinated pyridine but the origin of the feature at 958 cm$^{-1}$ is obscure. It is noteworthy that no emission occurs near $\Delta\nu = 1050$ cm$^{-1}$ for the $\eta$-alumina system. It appears from preliminary measurements that a sample of $\beta$-alumina (Bayerite) behaves similarly to the $\eta$-alumina in its adsorption of pyridine.

Titanium dioxide shows similar behaviour. Pyridine is both physically adsorbed (Raman bands at 991 and 1031 cm$^{-1}$) and co-ordinated (Raman band at 1016 cm$^{-1}$).

Chromatographic grade silica gel was used in some initial adsorption experiments with pyridine. After removal of physically adsorbed pyridine by evacuation, a residue of the adsorbate hydrogen-bonded to OH groups of the gel remained. The spectrum of the surface showed bands at 1007(s) and 1037(m). The spectrum of pyridine adsorbed on to a sample of silica gel contained added $Al^{3+}$ ions showed an additional band at 1020(w) due to co-ordinated pyridine.

These conclusions are in good agreement with those made in earlier i.r. studies on pyridine adsorbed on to "cab-o-sil" and on $\eta$-alumina.[2] The data accumulated in this work are in the Table.

TABLE

| Adsorbent | Raman band frequencies (cm$^{-1}$) |
|---|---|
| "Cab-o-sil" | 991 (10), 1006 (0), 1031 (8·4), 1034 (0) |
| Magnesium oxide | 991 (10), 1007 (0), 1016 (0), 1031 (8) |
| $\eta$-Alumina | See Figure |
| Alumina (Actal-A) | 957 (4), 991 (10), 1019 (3), 1031 (6), 1052 (3) |
| Titanium dioxide | 991 (10), 1016 (4), 1031 (8) |
| Silica gel | 1007 (10), 1037 (4) |
| Silica with an excess of $Al^{3+}$ ions | 1007 (10), 1020 (2·5), 1037 (5) |
| Compound: | |
| Pyridine (liquid) | 991 (10), 1031 (8) |
| Pyridine in water | 1003 (10), 1036 (5) |
| $(C_5H_5N)^+ Br^-$ in water | 1010 (10), 1028 (3·8), 1060 (0·7) |
| $SiCl_4(py)_2$ (solid) (ref. 3) | 1021 (vs), 1048 (s) |

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