

Raman Spectra of Molecules Adsorbed on Porous Vycor Glass; Elimination of the Fluorescent Background

By T. A. EGERTON, A. H. HARDIN, Y. KOZIROVSKI, and N. SHEPPARD*

(School of Chemical Sciences, University of East Anglia, Norwich, NOR 88C)

Summary Adequate heating of porous Vycor glass in oxygen or in air completely eliminates the fluorescence background normally obtained in attempts to measure Raman spectra of adsorbed molecules; spectra of adsorbed pyridine and benzene are reported.

THE application of laser Raman spectroscopy to the study of adsorbed species has been reported by Hendra and his co-workers,^{1,2} and by Kagel.³ Unfortunately the use of

this method is limited by the strong background emission which for many adsorbents is found to extend over a wide range of wavelengths in the vicinity of all exciting lines. This phenomenon, usually termed "fluorescence", has been observed in many Raman studies of solids. The background emission is often found to decay when the sample is irradiated with the laser beam for extended periods of time. In such cases it is sometimes possible to reduce the background to reasonable proportions, and hence obtain satisfactory spectra. This technique was used by Hendra and

his co-workers in their study of pyridine adsorption on alumina.²

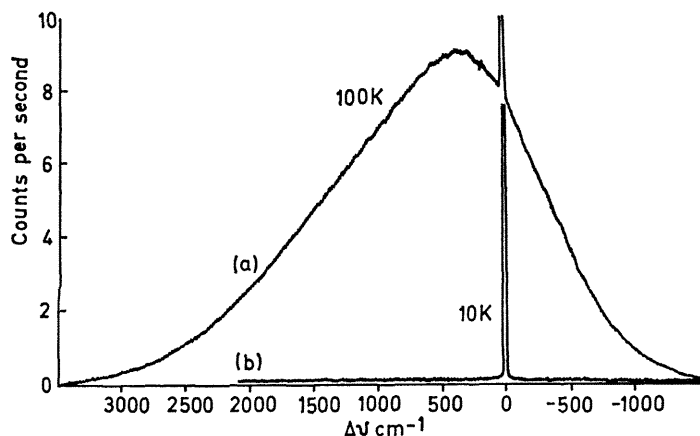


FIGURE 1. 'Fluorescence' spectra of porous Vycor after heating (a) in air at 100°, and (b) in oxygen at 550°. The spectra were run under the same conditions except that the amplification for (b) is ten times higher than for (a).

We report the adsorption of molecules on porous Vycor glass.⁴ Our choice of adsorbent was prompted by the fact that homogeneous glasses do not fluoresce strongly; therefore we might reasonably have expected to obtain good fluorescence-free spectra from a porous material.

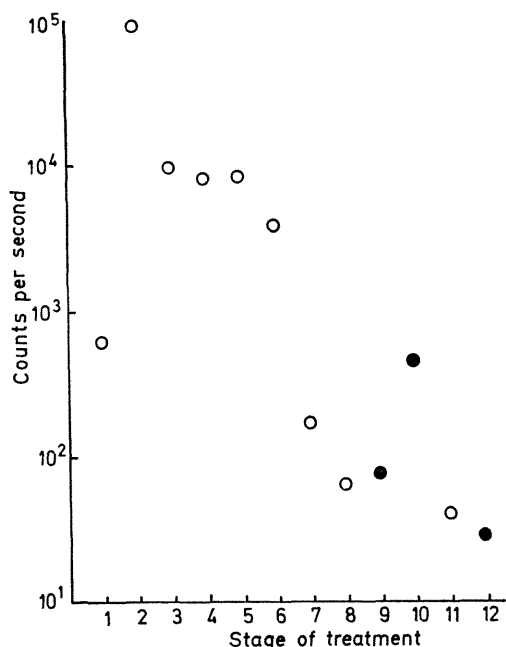


FIGURE 2. The relative intensities of the 'fluorescence' maxima at consecutive stages of clean-up treatment. Stage (1) corresponds to the untreated Vycor, whilst stages 2–12 correspond to Vycor heated at the following temperatures: 2, 100° in air for 15 h; 3, 200° in O₂ for 2 h; 4, 300° in O₂ for 3 h; 5, 400° in O₂ for 2 h; 6, 500° in O₂ for 1½ h; 7, 550° in O₂ for 1 h; 8, 550° in O₂ for 15 h; 9, 500° in vacuum for 1 h; 10, 500° in vacuum for 11 h; 11, 550° in O₂ for 1 h; 12, 500° in vacuum for 15 h; all greased joints were cooled for stage (12). Samples treated in vacuum are designated ●.

Spectra were recorded using a Spex Ramalog system equipped with a Spectra-Physics Model 125 He/Ne laser

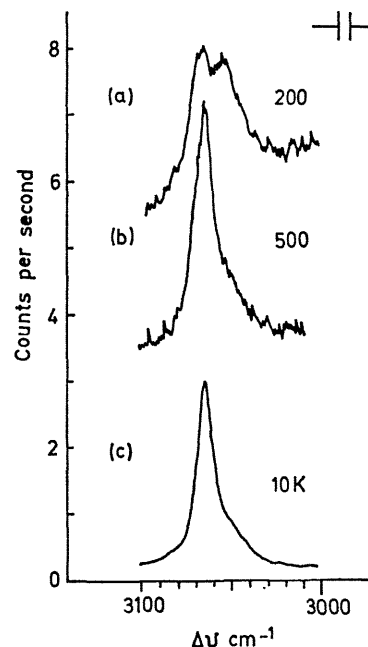


FIGURE 3. The C-H stretching region of the Raman spectrum of benzene adsorbed on Vycor: (a) the initial spectrum and (b) spectrum after standing for a further 12 days. (c) Spectrum of liquid benzene. The spectra were recorded with the same He-Ne laser and slit-widths but with different amplifications. Thus, for spectra (a), (b), and (c) 10 ordinate divisions correspond to 200, 500, and 10,000 counts per second, respectively.

and employing 90° illumination. A specially designed cell-holder allowed the position of the sample to be varied in a controlled manner and also enabled the Raman cell to be positioned reproducibly at an angle of 30° with respect to the laser beam after successive treatments of the Vycor. The Vycor discs, 5 mm thick and 25 mm in diameter, had to be freed from traces of organic matter by heating at increasing temperatures, initially in air and then in a slow stream of oxygen.

Prior to heating, the discs gave moderate fluorescence, but after heating in air at 100°C a marked increase in fluorescence occurred. A typical fluorescence spectrum at this stage of treatment is shown in Figure 1 (curve a). However heating at successively higher temperatures led to a progressive reduction of the fluorescence until it became negligible (Figure 1, curve b). The fluorescence maximum for this adsorbent always occurred in the region $\Delta\nu$ 300–500 cm⁻¹. Figure 2 shows the intensity at the fluorescence maximum as a function of the heat treatment. Other samples of Vycor gave similar results except for a somewhat variable height for the intensity plateau observed between stages 3 to 5 (Figure 2). Fluorescence was essentially eliminated by heating in oxygen at 500°C; the slight rise in fluorescence during subsequent heating and evacuation of the sample at 500°C could be minimised by cooling the greased joints and taps of the Raman cell, by using Apiezon T grease instead of Apiezon N, or by using a greaseless tap. The fluorescence is probably due to very

small amounts of surface species derived from the reaction of hydrocarbons at the surface of hot Vycor. In subsequent experiments the following procedure always eliminated fluorescence.† The sample was heated slowly to 500 °C; the temperature was then held at this value for several hours whilst a slow stream of oxygen was passed over the disc; and finally, the sample was evacuated overnight at the desired temperature. During the evacuation all greased joints were carefully cooled.

The spectrum of the clean Vycor disc *in vacuo* showed a broad, rather weak, band at 300–500 cm^{-1} with a maximum at *ca.* 460 cm^{-1} (not shown at the sensitivity used to obtain Figure 1b).

Initial adsorption of pyridine on Vycor outgassed at 500 °C led to the development of principal bands at 3072, 1031, and 1008 cm^{-1} . Further adsorption led to additional bands at 3056, 1595, 1576, 1221, 1070, 991, 654, and 606 cm^{-1} , plus intensification near 1030 cm^{-1} . These additional

bands fall close to Raman bands of liquid pyridine and are probably caused by physical adsorption. Similar Raman bands have previously been obtained on silica.^{2,3}

The position of the bands due to adsorbed benzene are close to those of the liquid but some marked changes in relative band intensities were observed. Figure 3 compares the relative intensities of the bands in the C–H stretching region after initial adsorption, and after keeping for 12 days without further addition of benzene to the cell. Additional adsorption from the gas phase could have occurred during this time. On desorbing the benzene the lower frequency band did not reappear with comparable strength. We shall investigate the nature of the initially adsorbed species from pyridine and benzene through parallel i.r. spectroscopic studies.

We thank Professor M. Folman for the samples of Vycor porous glass used in these studies.

(Received, May 10th, 1971; Com. 722.)

† The same procedure has been shown to eliminate fluorescence from B.D.H. chromatographic silica gel, γ -alumina, and a commercial silica-alumina catalyst.

¹ P. J. Hendra and E. J. Loader, *Nature*, 1967, **216**, 789; 1968, **217**, 637.

² P. J. Hendra, J. R. Horder, and E. J. Loader, *Chem. Comm.*, 1970, 563.

³ R. O. Kagel, *J. Phys. Chem.*, 1970, **74**, 4518.

⁴ M. E. Nordberg, *J. Amer. Ceram. Soc.*, 1944, **27**, 299.