(3) There is a possibility that a volatile impurity in the molybdenum is responsible for the new diffraction pattern. The last suggestion seems to be excluded for the following reasons. The molybdenum sheet (from Murex Ltd.) contained 0·01 per cent iron as the only detectable impurity. Of the possible compounds which could be formed under the experimental conditions, the symmetry of the diffraction pattern is consistent only with cubic ferrous oxide. However, the lattice parameter of ferrous oxide is larger than that found for the phase. In any event the furnace was preheated at 1,500° C for 15 min to clean it up.

There is, therefore, reasonably good evidence that a face-centred cubic molybdenum carbide with a lattice constant of 4·26Å was formed at 1,200° C as a thin film phase in the experiments now reported. This is to be contrasted with the extreme condition of 40–70 kb and 2,000° C used by Clougherty, Lothrop and Kafalas[2] to produce the same structure in bulk.

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[1] Pearson, W. B., *A Handbook of Lattice Spacings and the Structure of Metals and Alloys* (Pergamon Press, London, 1954).
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Raman Spectra of Adsorbed Molecules : Quenching of Fluorescence by Adsorption

IT is well known that the infra-red spectra of molecules go through changes in position and intensity by their adsorption on solid surfaces[1-8]. In earlier communications we have shown[9] that the infra-red spectra of organic molecules spread in molecular layers over the surfaces of inorganic salts show differences in position and intensity of the bands compared with the spectra of the bulk substances. The observed differences are greater the more the atomic distances of the vibrating groups coincide with the lattice distances of the salt surfaces. The distortion of molecules with a centre of symmetry by the local fields of the lattice surface causes the appearances of Raman active vibrations in the infra-red.

In this communication we wish to describe some results obtained on the Raman spectra of organic molecules in the adsorbed state. As adsorbing material, aerosil (spec. surface 175 m²/g), porous glass or potassium bromide powder of great specific surface was used. The Raman spectra were obtained by Brandmüller's method[10] for crystal powders, which has been modified by introduction of an interference filter with great transparency for the Raman lines and a maximum of reflexion for the exciting frequency (4356 Å.). The scattered light was allowed to traverse this filter so that the exciting light could by reflexion pass again through the scattering sample increasing the intensity of Raman lines. Registration was made either photographically or with the aid of a photomultiplier and electronic amplification (*Steinheil*).

The thickness of the scattering powder is critical for the observed intensity of the Raman lines. Changes in that thickness by only 0·05 mm causes the maximum intensity to be passed over. The optimum

Table 1

Substance	New Raman lines shown by adsorption on SiO₂ (cm⁻¹)	Infra-red frequencies (cm⁻¹)
Naphthaline	1,310	1,302
	1,360	1,364
	1,410	1,391 or 1,431
	1,500	1,506
Biphenyl	1,308	1,307
	1,380	1,386
	1,480	1,481
Trans-stilbene	1,220	1,255
	1,609	1,502
Terphenyl	1,112	1,121
Anthracene	960	957
	1,100	1,149

thickness lies around 0·32 mm, varying from sample to sample. With the aid of a cuvette of variable length in intervals of 0·01 mm it was possible to work at the maximum intensity for the Raman lines.

The spectra of biphenyl, naphthaline, anthracene, phenanthrene, terphenyl, trans-stilbene, p-nitrophenol, and p-nitrotoluol were registered in the state of monomolecular ($n = 1$) and polymolecular (up to $n = 10$) layers. Figs. 1 and 2 illustrate a comparison between the Raman spectra of adsorbed molecules and their spectra in the crystal state. It can be stated generally that the intensities of the lines are very much equalized by the adsorption and that new lines appear (indicated by arrows in the figures) in the case of molecules possessing a centre of symmetry. Table 1 shows that the frequencies of the new Raman lines almost coincide with well-known infra-red bands of the molecules.

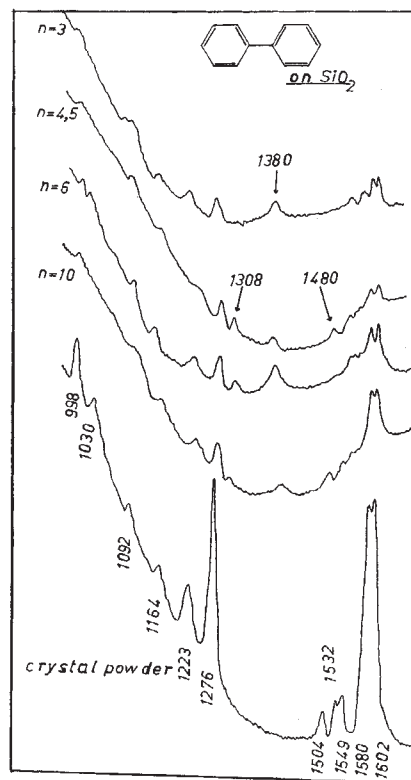It is then possible to register Raman lines of adsorbed molecules only if the adsorbing material has

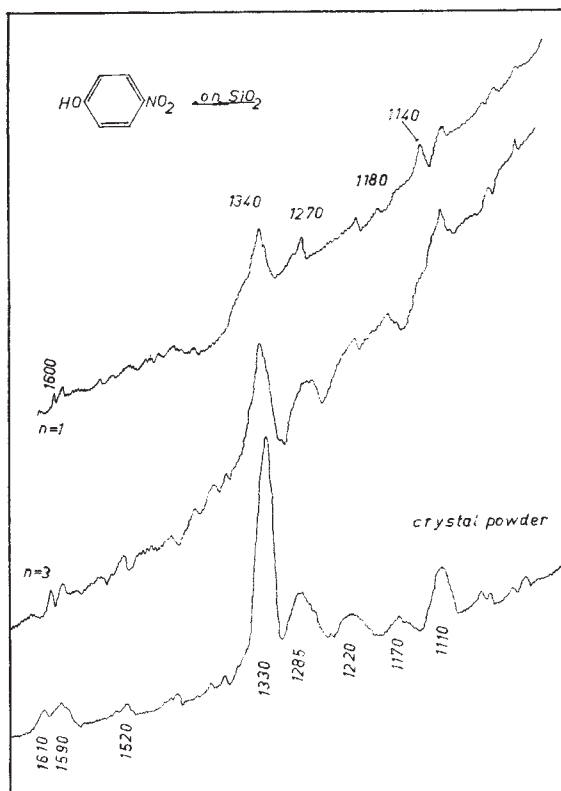Fig. 1. Raman spectra of biphenyl as crystal powder and adsorbed on silica

Fig. 2. Raman spectra of *p*-nitrophenol as crystal powder and adsorbed on silica

a sufficiently great specific surface. In the case of coloured substances detectable intensities of Raman lines are even observable below a monomolecular coverage of the surface, probably due to an increase of intensities by a resonance Raman effect.

Another observation made on this occasion is that the fluorescence of molecules is completely quenched by adsorption at a monomolecular coverage. The measurement of Raman spectra of fluorescent molecules is possible, using the substances in adsorbed
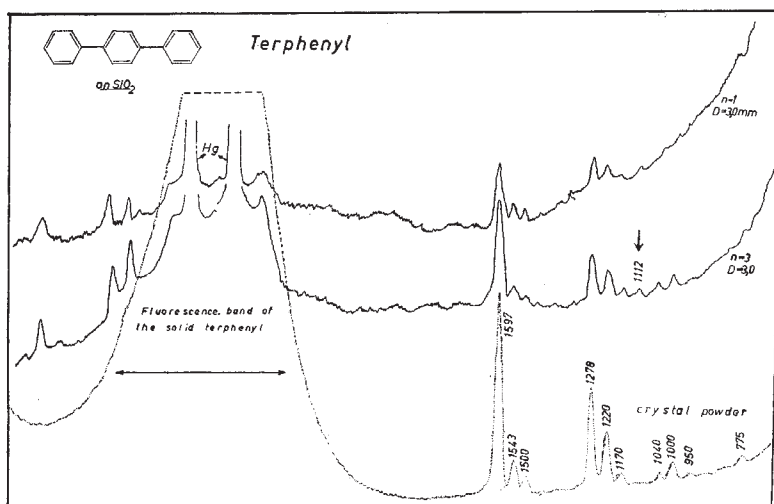

Fig. 3. Quenching of fluorescence of terphenyl by adsorption

state. Fig. 3 illustrates, for example, terphenyl, that the fluorescence disappears for $n = 1$, and the covered Raman lines appear.

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Water as a Chain-transferring Agent in Vinyl Polymerization

IN a previous communication[1] the chain-transfer constant (C_s) of a solvent in a mixed solvent system was determined. This opens up the possibility of determining the chain-transfer constant of solvents which are immiscible with the monomer. By a suitable choice of a common solvent the heterogeneous mixture of the monomer and the immiscible solvent can be kept in a homogeneous medium, and the C_s value of the latter can be determined. An attempt is reported here to determine the chain-transferring capacity of water with the growing radical of poly-(methyl methacrylate) on the above principle.

Tert-butyl alcohol was selected as the solvent to keep the mixture of water and methyl methacrylate in a homogeneous phase. 1 : 1 ratio of *tert*-butyl alcohol and methyl methacrylate was taken and different weighed amount of water was added to the ampoule. Polymerization was carried out at 60° ± 0·05° C in nitrogen-flushed vacuum-sealed ampoules[1,4]. The polymer was precipitated by ethanol followed by reprecipitation from benzene solution. The samples were dried *in vacuo* and the viscosity determined by Ostwald viscometer of flow-time 232 sec with benzene. The results are shown in Table 1 and Fig. 1. The arrow point in Fig. 1 indicates the onset of precipitation.

The most remarkable feature of the result is that addition of water even in small quantity brings about an almost monotonous increase in molecular weight instead of the expected decrease due to chain transfer and dilution.

A plot of the results, that is $1/\bar{P} - R_p\delta^2/M^2$ against $[H_2O]/[M]$, shows the peculiar nature of the curve. Instead of the usual straight line with a positive slope, the curve takes a reverse course, finally becoming almost parallel with the H_2O/M axis. This undoubtedly indicates that water has no chain-transferring capacity. Jenkins and