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Laser Raman Spectra of Styrene Adsorbed on Silica

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The laser Raman spectra of styrene adsorbed on 18–30 mesh chromatographic grade silica gel, Cab-o-sil, and Aerosil 380 are described. In the latter two cases, the styrene is only physically adsorbed. In the former case, the molecule is chemisorbed, and Raman lines recorded at 1277 and 1456 cm^{-1} are assigned to vibrations of the vinyl group modified by the surface.

INTRODUCTION

Infrared spectroscopy has been widely used to study surface-adsorbed species, but Raman spectroscopy has been, until recently, a little used technique. The use of conventional Raman spectroscopic methods, using mercury arc excitation, has been described by Karagounis and Issa (*1*) and Pershina and Raskin (*2*). Although the quality of the spectra recorded by the latter workers was good and many useful data were obtained, the technique is not easy, and it was not taken up by other research groups. Raman spectra of adsorbed species recorded using helium–neon laser excitation have been described by Hendra and Loader (*3–5*). Hendra, Horder and Loader (*6*) have shown that laser Raman spectral studies of adsorbed pyridine can also be used to determine the nature of surface sites. They showed that interference from the spectrum of many oxide adsorbents was virtually nonexistent, making the technique applicable to a larger number of surfaces than infrared methods, but it was also less sensitive, and sample 'fluorescence' could prevent observation of the spectrum of the adsorbed species.

The origin of the so-called 'fluorescence' has not been satisfactorily explained as yet. The phenomenon takes the form of a broad emission band with a half-width of about 2000 cm^{-1} centered to the Stokes side of the laser line, but it has a measurable intensity to the anti-Stokes side (higher energy). The Raman lines due to the adsorbed species appear as weak lines on top of the 'fluorescence', and can be obscured by the noise associated with it. The intensity of the 'fluorescence' does, however, decrease with exposure to the laser, and in cases where the adsorbed species spectrum cannot be recorded immediately on placing the sample in the instrument, it may be possible to obtain it by waiting for some hours. In some cases, exposures of 18 hr have been necessary (*6*). In the case of styrene adsorbed on silica 'fluorescence' is not a severe problem, as the decay is virtually complete in a few minutes. The Silica Gel Ltd. 18–30 mesh silica gel (silica gel 1, described in the next section), showed the strongest 'fluorescence' of any of the samples used in this study, but the problem was minimized by cleaning the gel at a lower temperature than the other silicas. It had to be accepted that the state of dehydroxylation of silica gel 1 would be different to the other two silicas.

Silica gel 1 has been shown by previous studies (*5, 7*) to exhibit slightly unusual characteristics for a silica gel, and it was

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for this reason that the adsorption of styrene, a substituted olefin, was studied. It was hoped that adsorption would occur through the double bond of the vinyl group, and the phenyl group would be relatively unaffected and would act as an internal vibrational standard. In addition, the presence of the latter group, a good Raman scatterer, would make the detection of the adsorbed species spectrum easier at low coverages.

EXPERIMENTAL

Materials

Silica Gel Ltd. 18–30 mesh silica gel (silica gel 1) was cleaned prior to use by evacuating at 160°C until the static pressure in the cell was better than 10^{-4} Torr. The gel had a surface area of 775 m^2 g^{-1} and a typical analysis of SiO_2, 99.6%, Fe_2O_3, 0.01%, Al_2O_3, 0.03%, Na_2O, 0.2%, and CaO, 0.04%.

Cab-o-sil and Aerosil 380 were cleaned by igniting at 600°C in air followed by evacuation in the Raman cell at 290°C. The surface areas of these silicas were 325 m^2 g^{-1} and 380 m^2 g^{-1}, respectively. The analysis of Aerosil given by the manufacturer was $SiO_2 > 99.8\%$, $Al_2O_3 < 0.03\%$, $Fe_2O_3 < 0.001\%$, $TiO_2 < 0.02\%$, and $HCl < 0.025\%$. The Cab-o-sil was used in two forms; viz., pressed discs and lightly pressed pellets. The discs were pressed at 12t in.$^{-2}$, using an 1⅛-in. stainless steel die and had a thickness of 247 mg cm^{-2}. These discs were broken up into smaller pieces which would lie against the end of the Raman cell. The lightly pressed pellets were produced by a ⅜ in. stainless steel die with pressures ranging from hand pressure to that developed by a bench mounted vice. Aerosil 380 was used only in the form of pressed pellets.

Styrene was B. D. H. reagent grade and was purified before use by vacuum distillation. During the course of the experiments, the sample was stored under vacuum at —78°C to prevent polymerization.

Apparatus

A conventional high vacuum system, having facilities for the cleaning of adsorbents at up to 1000°C, for adsorbate handling, and for measuring adsorption isotherms, was employed. The Raman cells were constructed from 14-mm diameter Pyrex tubing having a 1.5-mm thick optical flat at one end and a right angled high vacuum tap at the other. The adsorbent was inserted by removing the tap key and sliding the adsorbent into the cell where it was retained by a pad of silica wool.

Instrumentation

The spectra of styrene adsorbed on silica gel 1 were recorded using 180° illumination on a Cary 81 laser Raman spectrometer fitted with a Spectra Physics Model 125A helium–neon laser. The other spectra were recorded using 90° illumination on the Spex laser Raman system and the Spectra Physics Model 140 argon-ion laser operating on the 514.5-nm line.

The frequency calibration of the instruments was checked using the neon-emission spectrum (*7*), and individual spectra were calibrated using the Raman spectrum of indene (*8*).

An ICL 1907 computer was used for special accumulation, and the spectra processed by the computer were drawn by a Benson-Lehner Electroplotter.

General Procedure

Following the cleaning of the silica, styrene was distilled into the cell by cooling it in liquid nitrogen. It was then allowed to return to room temperature, and the excess styrene was pumped off. The quantity of styrene adsorbed was estimated by weighing the cell before and after adsorption. As fairly large samples of silica were used (0.5–2.5 g) the method is fairly accurate even at low coverages. The coverages were expressed as grams of adsorbate per gram of adsorbent or as Å^2 molecule^{-1}, the area available to one adsorbate molecule assuming a monolayer coverage.

Spectra were recorded as the coverage was progressively reduced until a point was reached, where the intensity of the Raman lines was of the same order as the background noise.

All the absorbed species spectra were recorded at room temperature.

RESULTS AND DISCUSSION

In the case of the silica gel 1 sample, the slight 'fluorescence' caused the spectrum of the adsorbed species to have a sloping background. The spectrum of the clean gel was run over the range 70–1700 cm^{-1}, and with the aid of a least-squares computer program, two polynomial equations were obtained which described it. The first equation covered the range from 70 to 700 cm^{-1} and the second 700–1700 cm^{-1}. For reasons described below, the spectrum of the adsorbed species was only recorded over the latter range, and the equation was used to calculate the contribution of the gel to the recorded spectrum. The contribution of the gel, after correction for changes in the instrumental settings, was then subtracted from the recorded spectrum to give the spectrum of the adsorbed species alone. The application of the above method only became necessary at low coverages, and it was used in conjunction with the accumulation of four spectra at the lowest coverage investigated. Because of the time-consuming nature of spectral accumulation, the study had to be restricted to the smallest area of the spectrum which contained the largest quantity of information. The range investigated was 700–1700 cm^{-1}, as below 700 cm^{-1} the vibrations of the styrene molecule give rise only to weak Raman lines which would not be readily detectable in the adsorbed state. There are no Raman lines between 1700 and 2900 cm^{-1}, and above the latter frequency, the sensitivity of the instrument is very low when helium–neon excitation is being used.

The problem of low instrumental sensitivity can in theory be surmounted by the use of an argon–ion laser to excite the spectrum, but the stability of the Spectra Physics Model 140 is usually too poor to be of use for adsorbed species studies. Many attempts were made to record the spectrum of styrene on Cab-o-sil in one scan in a form suitable for reproduction, before the spectrum shown in Fig. 2 was obtained.

The Raman spectrum of solid and liquid styrene, toluene, and ethylbenzene were obtained using the Cary 81 spectrometer to assist in the interpretation of the adsorbed species spectrum. Attempts to obtain the vapor-phase spectrum of styrene failed, due to its low vapor pressure at room temperature and the ease with which it polymerizes at temperatures where the vapor pressure would have been sufficient to allow the spectrum to be recorded. The details of the four spectra are shown in Table 1. The mode numbering is due to Wilson (*9*), and the assignments were derived from a number of papers on these and related compounds 10–14. The assignments in the literature are by no means consistent: Table 1 correlates them to give maximum agreement. The intensities are referred to the totally symmetric phenyl group vibration near 1000 cm^{-1} having an intensity of 100.

There are considerable similarities in the spectra of the three compounds due to the phenyl group common to them all. Phenyl group vibrations account for sixteen of the observed Raman lines, and four of these lines of particular interest occur close to 775, 1000, 1200, and 1600 cm^{-1}. The first and third of these lines are assigned to totally symmetric ring vibrations which are known to be particularly sensitive to changes in the nature of the substituent, X. The second and fourth are the most intense lines due to totally symmetric ring vibrations, and it will be seen from the table that their positions are not particularly sensitive to changes in the substituent. They should thus be relatively unaffected by adsorption, provided that the ring does not interact directly with the surface and should act as an internal vibrational standard.

It has been shown (*3–5*) that when a

TABLE 1

THE RAMAN SPECTRUM OF TOLUENE, ETHYLBENZENE, AND STYRENE IN THE LIQUID PHASE AND OF STYRENE IN THE SOLID PHASE

Toluene	Ethylbenzene	Styrene		
Liquid $\Delta\nu$ (cm^{-1})	Liquid $\Delta\nu$ (cm^{-1})	Liquid $\Delta\nu$ (cm^{-1})	Solid $\Delta\nu$ (cm^{-1})	Assignment
788 (53)	769 (48)	775 (25)	775 (46)	X sens A′ 12a
			793 (7)	γ (CH) A″ 11
814 (1)				464 + 350 = 814
845 ($\frac{1}{2}$)	840 (2)	842 ($\frac{1}{2}$)	842 (2)	γ (CH) A″ 10a
	910 (0)			γ (CH) A′ 17b
		911 (3)	905 (17)	Vinyl $=CH_2$ wag A″
	965 (9)			C—C stretch
988 ($\frac{1}{2}$)				464 + 522 = 986
		989 (6)	988 (7)	Vinyl C=C twist A″
1004 (100)	1003 (100)	999 (100)	999 (100)	Ring A′ 1
1031 (25)	1030 (42)	1023 (4)	1021 (6)	β (CH) A′ 18a
		1034 (10)	1037 (11)	Vinyl $=CH_2$ rock A′
1080 (0)	1064 (5)	1088 ($\frac{1}{2}$)	1087 (2)	β (CH) A′ 15
1159 (4)	1154 (6)	1157 (7)	1157 (23)	β (CH) A′ 9b
1182 (3)	1180 (5)	1182 (10)	1184 (17)	β (CH) A′ 9a
1213 (23)	1201 (19)	1204 (30)	1206 (28)	X sens A′ 7a
	1248 (2)			$—CH_2$ wag and twist
		1305 (5)	1313 (9)	Vinyl =CH rock A′
1312 (0)				464 + 845 = 1310
		1318 (11)	1326 (28)	ν (CC) A′ 14
1330 (0)	1332 (3)	1336 (3)	1342 (4)	β (CH) A′ 3
1382 (4)				δ CH_3
		1413 (16)	1419 (59)	Vinyl $=CH_2$ def. A′
	1448 (5)			$—CH_2$ bend, $—CH_3$ assym def.
1444 (1)		1452 ($1\frac{1}{2}$)	1452 (4)	ν (CC) A′ 19b
1500 (0)		1495 (5)		ν (CC) A′ 19a
1590 (4)	1584 (4)	1577 (6)	1576 (13)	ν (CC) A′ 8b
1607 (6)	1605 (12)	1602 (42)	1601 (113)	ν (CC) A′ 8a
			1619 (9)	
		1631 (73)	1633 (110)	Vinyl C=C stretch A′

molecule is physically adsorbed, there will be a broadening of the Raman lines accompanied, in some cases, by a frequency shift. If the molecule is chemisorbed, we may expect that there will be marked changes in the spectrum. In the case of styrene, chemisorption could occur either via the carbon–carbon double bond or via the π orbitals of the aromatic ring. In the former case, a marked decrease in the relative intensity of the Raman line at 1632 cm^{-1}, assigned to the carbon–carbon double-bond stretching vibration, would be expected. If the interaction was fairly strong, major changes in the other Raman lines arising from vinyl group vibrations might be observed, possibly accompanied by the appearance of a line or lines due to the vibrations of the modified group. In addition, changes in the frequencies of the substituent sensitive vibrations and in the relative intensities of the 1000 and 1600 cm^{-1} lines could occur if the changes in the vinyl group affected the electron density in the ring.

In the latter case, major changes in the frequencies and relative intensities of the ring modes should occur, while the frequencies of modes associated with the vinyl group and the intensity of the line due to the carbon–carbon double bond should be little affected unless that group is also interacting with the surface.

Styrene–Silica Gel I

The spectrum of the adsorbed species was recorded at nineteen coverages ranging from 0.2299 g g^{-1} to 0.1036 g g^{-1} (58.2 Å^2 mol^{-1} to 129.3 Å^2 mol^{-1} respectively). The adsorption isotherm for the system was measured at 30°C on another sample of silica gel I cleaned in an identical manner. The monolayer coverage was calculated to be 41.6 Å^2 mol^{-1} by the BET method, and it is therefore concluded that all the spectra were recorded at a coverage of less than a monolayer.

At the higher coverages, the majority of the Raman lines arising from the adsorbed species could be recorded, but as the coverage was reduced, the weaker lines became obscured by the noise associated with the background. Spectral accumulation was used at the lowest coverage to improve the quality of the spectrum to a level where the weaker lines were again visible above the noise. Four spectra were averaged to produce the composite spectrum shown in Fig. 1 (upper spectrum) together with the spectrum of liquid styrene (lower spectrum) drawn by the computer.

The full details of the adsorbed-species spectrum are shown in Table 2, with the results obtained from styrene adsorbed on the other silicas. The majority of the Raman lines broadened and moved to higher frequency on adsorption; in particular, the half-width of the line, centered at 775 cm^{-1} in the liquid, doubled. However, the most marked change in the spectrum, as the coverage was reduced, was the gradual reduction in the intensity of the line at 1631 cm^{-1} $\nu_{(C=C)}$ relative to the two most intense ring modes (999 and 1602 cm^{-1}). The relative intensity of the latter two lines remained constant throughout the experiment. In the liquid phase, the intensity ratio $I\nu_{(CC)8a}/I\nu_{(C=C)}$ was 0.56, while in the adsorbed species, it ranged from 0.78 at the highest coverage to 2.0 at the lowest.

The very marked decrease in the intensity of the Raman line due to the carbon–carbon double bond between the spectrum of the liquid and of the adsorbed species at low coverage is indicative of an interaction between that bond and the silica surface. Other lines assigned to vibrations of the vinyl group occurred at 911, 989, 1934, 1305, and 1413 cm^{-1}. The first, second, and fourth of the lines were weak in the spectrum of the liquid and could not be located with any certainty in the adsorbed species spectrum. The more intense line occurring at 1413 cm^{-1} in the liquid was absent from the spectrum of the adsorbed species, while the line found at 1034 cm^{-1} in the former spectrum

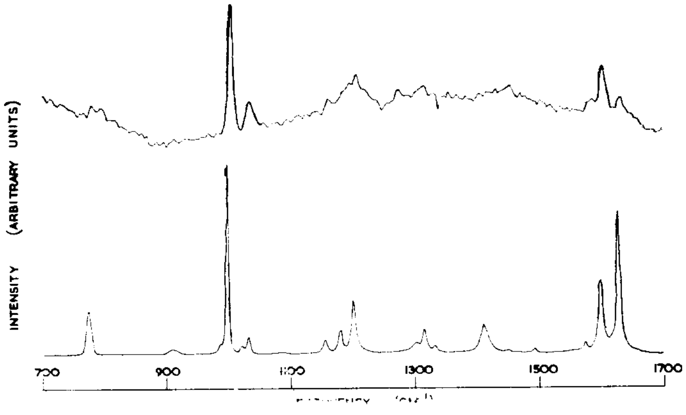

FIG. 1. The Raman spectrum of styrene in the liquid state and adsorbed on silica gel 1.

TABLE 2
The Raman Spectrum of Styrene Adsorbed on Silica Gel 1, Cab-o-sil and Aerosil 380

Silica gel 1		Cab-o-sil		Aerosil 380	
Frequency $\Delta\nu$ (cm^{-1})	Relative intensity	Frequency $\Delta\nu$ (cm^{-1})	Relative intensity	Frequency $\Delta\nu$ (cm^{-1})	Relative intensity
780	8	778	18	777	23
795	10				
1005	100	1003	100	1001	100
		1024	14	1027	4
1035	20	1037	18	1036	8
1162	12	1161	10	1160	7
		1186	20	1186	16
1209	28	1208	32	1205	39
1277	12				
1318	14	1321	20	1320	11
				1337	5
		1417	22	1416	20
1456	16				
1589	12	1582	10	1580	7
1606	40	1605	48	1602	57
1636	20	1634	76	1633	90
		3015	12		
		3068	24		

appeared to have increased in intensity in the latter.

That this latter line was due to the vinyl group —CH_2 rock is not completely certain, due to the presence at 1023 cm^{-1} of a weaker line assigned by Fateley, Carlson, and Dickson (*12*) to the aromatic ring —CH in-plane bending mode 18a. Both the modes are totally symmetric, and an investigation of the liquid spectrum showed that both the lines are polarized to the same extent. The assignment of the two lines could be reversed without materially affecting the overall conclusions, and as a result of the uncertainty, it is difficult to decide on exactly what has occurred on adsorption, but it is clear that there was no line at 1021 cm^{-1} in the adsorbed species spectrum.

An examination of the changes which occurred on adsorption in the Raman lines assigned to the ring modes showed that there was usually a shift to higher frequency accompanied in general by a line broadening. At the lowest coverage, the Raman line occurring at 775 cm^{-1} in the liquid and assigned both to the totally symmetric substituent sensitive mode 12a and the out-of-plane ring —CH bending mode 11, split into two lines at positions close to those found in the spectrum of the solid. The doublet found in the solid-phase spectrum is assigned in the way shown in Table 1, because it is expected that an A′ mode would be more intense in the Raman effect than an A″, because there is only a small change in frequency in the other substituent sensitive vibrations between the solid and liquid phases, and because the depolarization ratio of the composite line is 0.125. If it is assumed that the A′ line has a zero depolarization ratio, then the 0.125 is due solely to the depolarized A″ line. Multiplication by 4/3 gives the intensity of the line in the ordinary liquid-phase spectrum, and the intensity ratio of the two components can then be calculated as $A'/A'' = 7:1$, which is (fortuitously) of the same order as that found for the two lines in the solid. However, if the depolarization ratio of the A′ line is not zero, the A″ line will be weaker, and so the assignment is still justified. In the adsorbed state, the shift of 5 cm^{-1} in the lower of the two components would indicate that there had only been a small change in the nature of the substituent as far as the aromatic ring is concerned. This is confirmed by the intensity ratio of the lines due to the two strongest ring modes (1 and 8a) which is the same as in the liquid-phase spectrum. Examination of the data on toluene and ethylbenzene shows that the intensity ratio is fairly sensitive to changes in the substituent.

It is concluded that there was no spectral evidence for the presence of an unmodified vinyl group in the chemisorbed species, while at the same time, the ring has been only slightly perturbed. The interaction between the styrene and the surface must thus have occurred through the carbon–carbon double bond, and have led to a change in the bond strength, and hence to the vibrational frequencies of the whole vinyl group. A careful study of the adsorbed species spectrum showed that there were two weak lines present not accounted for in the previous discussion. The Raman line observed at 1277 cm^{-1} was definitely absent from the liquid-phase spectrum, but in the case of the line observed at 1456 cm^{-1}, there was a line of very low intensity at 1452 cm^{-1} in the spectrum of the liquid. The latter line had been assigned to the ring mode 19b by Fateley, Carlson, and Dickson (*12*). None of the other ring carbon–carbon stretching modes showed any dramatic changes in frequency or intensity on adsorption, and it is considered unlikely that adsorption could have caused an 11-fold increase in the intensity of the 1452 cm^{-1} line. It is inferred that the lines at 1277 and 1456 cm^{-1} were due to vibrations of the modified vinyl group.

The observation that the line due to the unmodified carbon–carbon double bond still had a measurable intensity at a coverage of a third of a monolayer can be explained by assuming the presence of a small number of styrene molecules physically adsorbed on top of the chemisorbed species while more than two thirds of the surface was unoccupied.

Styrene–Cab-o-sil

The Cab-o-sil was used in the form of a pressed disc and a lightly pressed pellet. Part of the disc was used in an experiment to measure the adsorption isotherm for styrene at 30°C, and the monolayer coverage was found to be 0.152 g g^{-1}. Styrene was adsorbed on the sample until the coverage was very slightly over a monolayer, and the spectrum was recorded by the Cary 81 spectrometer using helium–neon excitation.

In the case of the lightly pressed pellet, the coverages investigated were 1.6 and

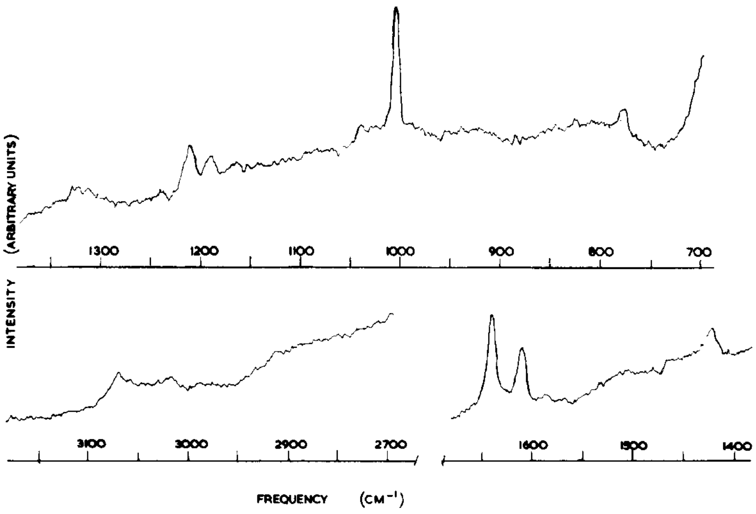

FIG. 2. The Raman spectrum of styrene adsorbed on Cab-o-sil.

1.25 layers, and the spectra were recorded by the Spex spectrometer using excitation by the 5145 Å line of the argon-ion laser. The spectra obtained from the two samples in the range 700–1700 cm^{-1} were identical, except for relative intensities due to the different excitation sources, and the results from the latter sample at the lowest coverage are included in Table 2. The spectrum is shown in Fig. 2.

The results will be discussed together with those from styrene-aerosil 380 in the next section.

Styrene-Aerosil 380

The Aerosil 380 sample was in the form of a pressed pellet. The spectra were excited by the argon ion laser operating at 5145 Å and were recorded on the Spex spectrometer at coverages ranging from 3.75 to 1.4 layers. There were no dramatic changes in the spectrum as the coverage was reduced and the details of the lowest coverage spectrum are given in Table 2.

There were no significant differences between the spectrum of the adsorbed styrene obtained in this experiment and those obtained in the previous one. In all cases the intensity ratio $I\nu_{(CC)8a}/I\nu_{(C=C)}$ was 0.63, close to the value found for the liquid. This observation, taken in conjunction with the relatively small changes in the frequencies of Raman lines, leads to the conclusion that the styrene was physically adsorbed in both cases.

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