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THE RAMAN SPECTRA OF ADSORBED MOLECULES ON POROUS VYCOR GLASS

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The Raman spectra of pyridine, triethylamine, dimethylsulfoxide and maleic anhydride adsorbed on porous Vycor glass were measured and compared with results on other silicas. The spectral changes upon adsorption are interpreted to be due to the hydrogen bond formation with the surface OH groups.

Raman spectroscopic study on adsorbed molecules has lately attracted considerable attention as one of the new application of laser Raman spectroscopy. Several reports on the Raman spectra of adsorbed molecules have recently been published, together with the experimental devices for obtaining them.1-4) The Raman spectra of pyridine, triethylamine, dimethylsulfoxide(DMSO) and maleic anhydride adsorbed on porous Vycor glass were clearly obtained. The spectra are compared with those for the molecules adsorbed on the other silicas. Porous Vycor glass was obtained from Corning Glass Works, No.7930; a plate 1 mm thick was cut to the size 10 x 20 mm. Other adsorbents used were (A) Silica gel (ca. 20 mesh, from Wako Chem. Co.), and (B) Aerosil 380 (Degussa) which was pressed to disks of 10^{ϕ}x 1 mm and then broken into small pieces.

All of the adsorbents gave off rather strong fluorescence due to impurities included when they were irradiated in the laser beam. In order to eliminate the fluorescence, the adsorbents were degassed for 4 hrs. at 400°C at 10^{-3} Torr, then heated at 500°C in oxygen at 500 Torr for 6 hrs., and finally evacuated for 2 hrs. at 550°C. The adsorbents thus prepared diminished in fluorescence remarkably, so that the Raman spectra could be measured. The surface areas of the adsorbents prepared were determined by use of the BET method; 140 m^2/g for the porous Vycor glass, 400 m^2/g for (A) and 250 m^2/g for (B).

A quartz vacuum cell supporting the sample was 12^{ϕ} x 150 mm with a stopcock at the top. By connection to a vacuum line, the heating and degassing processes for the adsorbents and also the adsorption process of gases on them could be carried out. After the sample preparation, the cell was moved to a Raman spectrophotometer.

Raman spectra were measured by use of a Jasco R-300 spectrophotometer or the four prism spectrophotometer constructed in our laboratory,5) with an Ar^+ ion laser (JEOL-04) source. The 4880 Å (less than 50 mW) beam was used as the exciting line. The sample cell was irradiated from the bottom and the scattered light was gathered in a direction perpendicular to the incident beam. The sample with the porous Vycor glass was irradiated parallel to the plane of the plate. The samples with (A) and (B) were irradiated at close proximity to the inner wall of the cell.

Pyridine When pyridine was adsorbed on the porous Vycor glass, the bands of pyridine at 993, 1033 and 3063 cm^{-1} were shifted to the higher frequency side. The Raman spectra in the 950～1050 cm^{-1} region are shown in Fig. 1. (a) shows that of the pure liquid, the peaks of which at 993 and 1033 cm^{-1} are assigned to the totally symmetric ring breathing and the trigonal ring breathing vibrations, respectively.6) (b) is for a sample in which the porous Vycor glass had been exposed for 0.5 hr. to pyridine vapor at 10 Torr, followed by a brief degassing at 25°C, where the peaks at 993, 1010 and 1038 cm^{-1} are observed, indicating the existence of two kinds of pyridine. (c) was obtained after evacuation of the sample (b) to 10^{-3} Torr for 0.5 hr. at 25°C, where the peak at 993 cm^{-1} disappears completely and the peaks at 1010 and 1038 cm^{-1}, however, remain with the intensity ratio of I(1010)/I(1038) = 2.5 while that for the pure liquid I(993)/(1033) = 1.2. The (c) spectrum may be identified as characteristic of the pyridine adsorbed on the porous Vycor glass.

The observed peak frequencies are listed in Table I, with those for the surface species adsorbed on the other silicas and also those of pyridine in liquid and in various solutions. In the last row the intensity ratios between the totally symmetric ring breathing band and the trigonal ring breathing band are given. The frequencies and the intensity ratios observed for the surface species adsorbed on the Silica gel and the Aerosil 380 are in good agreement with those in literature.1,3) The spectral changes upon adsorption are similar to those

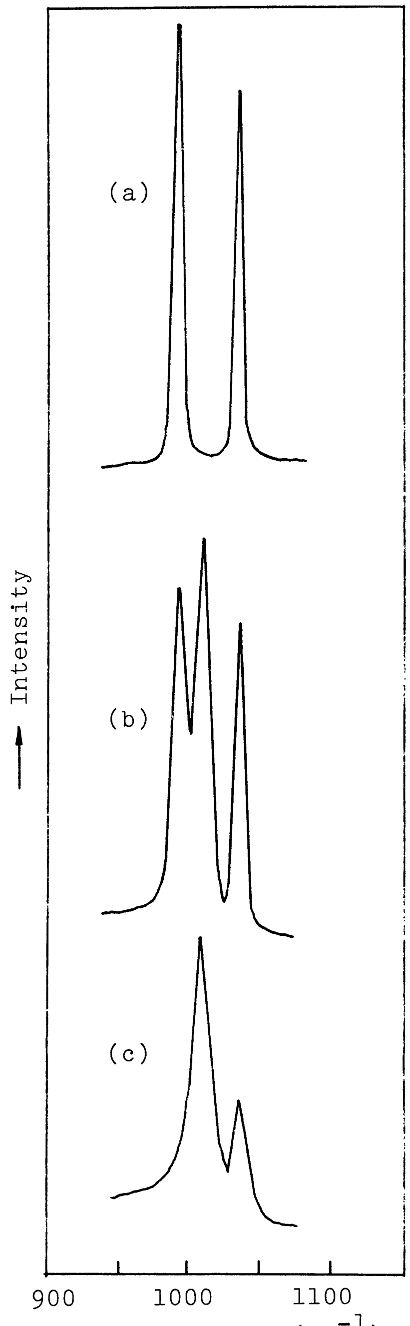

Fig.1. Raman spectra of pyridine;
(a) liquid,
(b) adsorbed on porous Vycor glass,
(c) adsorbed on porous Vycor glass after evacuation to 10^{-3} Torr.

observed for the pyridine-C_2H_5OH or pyridine-H_2O system, suggesting that the pyridine forms a hydrogen bond with the OH group on the adsorbent surface. Slightly larger changes are observed for the sample on the porous Vycor glass than those for the samples on the other silicas, due to the slightly larger polarity of the OH groups in the porous Vycor glass than those in the other silicas, because of the existence of small amount of surface BOH groups besides SiOH groups in porous Vycor glass. This is supported by the fact$^{7)}$ that the infrared OH stretching band observed for the porous Vycor glass (at 3730 cm^{-1}) is lower in frequency and broader than that for the other silicas (at 3749 cm^{-1}).

Triethylamine Triethylamine was adsorbed on the porous Vycor glass in the same way as pyridine. The band peaks observed for the triethylamine adsorbed on the porous Vycor glass are at 1460, 2886, 2945 and 2980 cm^{-1}, assigned to the CH deformation and CH stretching vibrations, showing blue shifts from those of the liquid, at 1455, 2877, 2938 and 2968 cm^{-1}. These shifts are similarly observed for the other silicas and interpreted to be due to the hydrogen bond formation with the surface OH groups. The relative intensities of the bands are slightly changed upon adsorption.

Dimethylsulfoxide Raman spectra of dimethylsulfoxide(DMSO) adsorbed on the porous Vycor glass and the Silica gel were obtained. The spectrum of the surface species was more clearly obtained for the porous Vycor glass than for

Table I. Raman frequencies of pyridine, for surface species, pure liquid and various solutions (ca. 0.5 mol/l)

Assignment	Surface species adsorbed on			Liquid	CCl_4 soln.	C_2H_5OH soln.	H_2O soln.
	Porous Vycor glass	Silica gel	Aerosil 380				
	$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$	$\tilde{\nu}$
Ring breathing totally sym. A_1 (α)	1010	1009	1008	993	993	1003	1006
Ring breathing trigonal A_1 (β)	1038	1035	1033	1033	1032	1035	1038
CH stretch A_1	3077	3072	3072	3063	3064	3073	3078
I(α)/I(β)	2.5	2.2	2.2	1.2	1.2	2.0	2.2

Table II. Raman frequencies and relative intensities of DMSO, for surface species, pure liquid and various solutions

Assignment *	Surface species adsorbed on				Liquid		C_6H_6 soln.		CH_3OH soln.		H_2O soln.	
	Porous Vycor glass		Silica gel									
	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I	$\tilde{\nu}$	I
δ(CSC)A'	302	3	not clear	not clear	307	1.5	302	2	308	2	307	2
γ(SO)A"	335	2.5			335	3	334	2.5	338	1.5	344	1.5
δ(SO)A'	386	1			384	1	383	1	387	0.5	390	0.5
ν_s(CSC)A'	675	10	674	13	671	10	669	8	676	9	679	10.5
ν_a(CSC)A"	708	5	705	6	700	4.5	697	4	709	3.5	715	4
$r_\perp(CH_3)$A'	—	—	—	—	956	<0.5	—	—	957	0.5	956	1.5
ν(SO)A'	1030	2.5 br.	1040	3 br.	1048	1.5	1068	1.5	—	—	1020	2
$\delta_s'(CH_3)$A', $\delta_a(CH_3)$A"	1428	3	1425	4	1423	1.5	—	—	1422	1	1422	2.5
$\nu_s(CH_3)$A', A"	2931	20	2928	20	2920	20	2924	20	2927	20	2934	20
ν_a, ν_s' (CH_3)A', A"	3010	8	3010	8	3003	5.5	3008	4	3007	4	3020	5

* M.-T. Forel and M. Tranquille, Spectrochim. Acta, 26A, 1023 (1970).

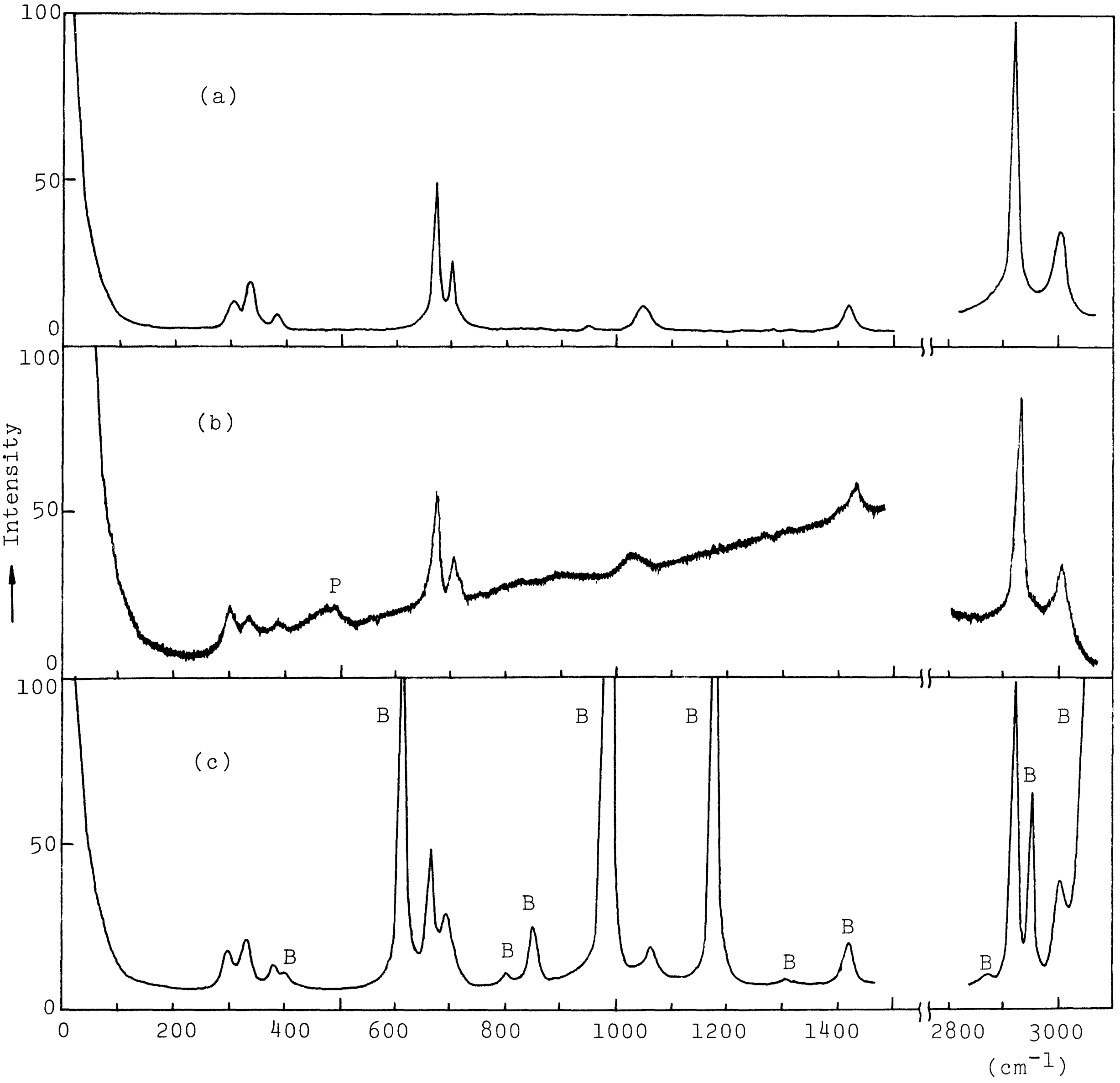

Fig.2. Raman spectra of DMSO; (a) in pure liquid,(b) adsorbed on porous Vycor glass after evacuation to 10^{-3} Torr,and (c) in C_6H_6 solution.
P; band of porous Vycor glass, B; band of benzene.

the Silica gel. The (b) spectrum in Fig. 2 was obtained for the sample in which the porous Vycor glass had been exposed for 2 hrs. to DMSO vapor at ca. 1 Torr, followed by 1 hr. evacuation at 25°C. Table II gives the frequencies and the relative intensities of the bands for the surface species on the adsorbents, together with those of DMSO in liquid and in various solutions (ca. 1 mol/l). Comparing the frequencies in Table II, it is found that the frequencies vary in the order——C_6H_6 solution, liquid, surface species on Silica gel, surface species on porous Vycor glass, CH_3OH solution and H_2O solution. The frequency of ν(SO) decreases while those of ν_a(CSC), ν_s(CSC) and γ(SO) increase in that order. The frequency shifts in ν(SO), ν(CSC) and γ(SO) for the CH_3OH or H_2O solution from those for the C_6H_6 solution (close to those for the free molecule) are interpreted to be due to the hydrogen bonding between the SO group and the CH_3OH or H_2O molecule. The frequencies for the surface species adsorbed on the porous Vycor glass correspond to values obtained in CH_3OH solution. This shows that the adsorption led to the hydrogen bond formation between the SO group and the surface OH group, similar to that in the DMSO-CH_3OH system. The relative intensities changed on adsorption considerably for the γ(SO) band and also for the δ(CSC) band.

Maleic anhydride Maleic anhydride was adsorbed on the porous Vycor glass and on the Silica gel, by sublimation in the vacuum line. The Raman bands for the maleic anhydride adsorbed on the porous Vycor glass are observed at 1070, 1595 and 1859 cm^{-1}, which correspond to those of maleic anhydride in $CHCl_3$ solution. This suggests that a weak hydrogen bond is formed between the maleic anhydide and the surface OH group.

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