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The Raman Spectra of Diazines Adsorbed on Silicas

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Synopsis. The Raman spectra of three diazines adsorbed on silicas have been measured. Spectra changes upon adsorption are interpreted as the result of hydrogen-bond formation between the surface OH group and the N atom of diazine. The order of the shifts of the Raman bands between three diazines is: 1,3-diazine>1,4-diazine>1,2-diazine.

Raman spectroscopy has recently been applied to the study of adsorbed species on solids, and the spectra of adsorbed pyridine have been measured considerably.[1-4] For the elucidation of the adsorption sites and the interactions between adsorbents and adsorbates, it is desirable to study the Raman spectra of several types of basic molecules in comparison with those of adsorbed pyridine. The present work will report on the Raman spectra of three diazines, 1,2-diazine (pyridazine), 1,3-diazine (pyrimidine), and 1,4-diazine (pyrazine), adsorbed on silicas.

Guaranteed reagents of 1,2-diazine and 1,3-diazine were obtained from the Tokyo Kasei Co. and a guaranteed reagent of 1,4-diazine, from the Nakarai Chem. Co. Silica gel (*ca.* 20 mesh) was obtained from the Wako Chem. Co., and porous Vycor glass plate (Corning Glass No. 7930; 1 mm thick), from the Corning Glass Works. They were used after degassing, heating, and oxygen treatment, as has been described previously.[4,5] The surface area after the pretreatment was 620 m^2/g for the silica gel and 170 m^2/g for the porous Vycor glass. Gaseous diazine was adsorbed on the pretreated silica, and then the sample was evacuated for 0.5—30 min.

The Raman spectra were measured with a Jasco R-300 spectrophotometer equipped with an argon ion laser JEOL-04. The 488.0 nm excitation line and the 90° sample illumination were employed.[4]

The observed Raman spectra are shown in Fig. 1. The peak frequencies, with the relative intensities, are listed in Table 1, together with those of the liquids and CCl_4 solution (this work). The Raman spectrum of 1,3-diazine adsorbed on the silica gel is quite similar to that of pyridine adsorbed on the silica gel. The ring-stretching band at 993 cm^{-1} shifts by 17 cm^{-1} to a higher frequency side from that of the liquid 1,3-diazine, while the CH stretching band at 3060 cm^{-1} shifts by 15 cm^{-1}. These shifts are a little larger than those observed for the pyridine adsorbed on the silica gel, 16 and 9 cm^{-1} respectively, and are interpreted as representing the hydrogen-bond formation between the surface OH group and the N atom of 1,3-diazine.

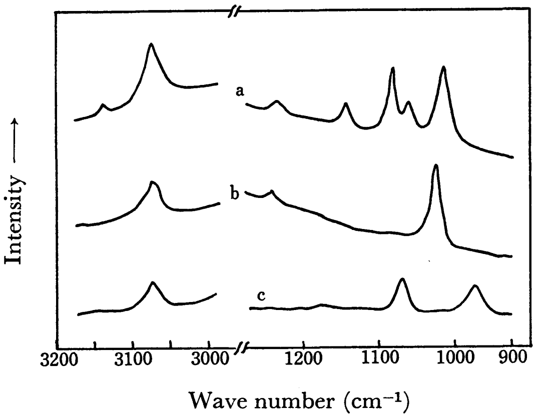

Fig. 1. Raman spectra of diazines adsorbed on silica gel; (a) 1,3-diazine, (b) 1,4-diazine, and (c) 1,2-diazine.

The shifts observed for 1,4-diazine and 1,2-diazine are smaller than those for 1,3-diazine. The spectra observed on the porous Vycor glass are almost the same as those observed on the silica gel. The Raman shifts observed, upon adsorption, on the silica gel are in the order of:

1,3-diazine > pyridine > 1,4-diazine > 1,2-diazine,

in agreement with the order of adsorption strength based on the upper limit temperatures of adsorption reported by Pichat:[6] 1,3-diazine 1,4-diazine 1,2-diazine. This

TABLE 1. RAMAN SPECTRA OF DIAZINES ADSORBED ON SILICA GEL (cm^{-1})

Assignment[a]	1,3-Diazine		1,4-Diazine		1,2-Diazine	
	Adsorbed	Liquid	Adsorbed	CCl_4 soln	Adsorbed	Liquid
Ring deform	681 (16)	680 (11)	703 (14)	708 (17)		670 (22)
Ring stretch	1010 (100)	993 (100)	1021 (100)	1019 (100)	968 (100)	968 (100)
Ring stretch	1056 (56)	1057 (36)				
CH deform	1078 (86)	1077 (35)			1068 (100)	1068 (103)
CH deform	1140 (18)	1142 (12)				1165 (62)
CH deform	1230 (21)	1231 (9)	1240 (10)	1235 (9)		1290 (10)
Ring stretch	1570 (12)	1570 (15)	1532 (14)	1531 (5)		
Ring stretch			1580 (9)	1580 (14)		1570 (23)
CH stretch	3075 (63)	3060 (53)	3075 (46)	3063 (50)	3075 (86)	3062 (118)

a) F. R. Dollish, W. G. Fateley, and F. F. Bentley, "Characteristic Raman Frequencies of Organic Compounds," Wiley Interscience, New York (1974), p. 274.

also corresponds to the order of the π-electron density of the N atom for the basic molecules,[7] but differs from the order of the first ionization potentials or the pK_a:[8]

pyridine > 1,2-diazine > 1,3-diazine > 1,4-diazine.

Consequently, 1,3-diazine may be used, instead of pyridine, as a basic molecule for the study of adsorption on solid surfaces.

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