

Raman spectra of solids*

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Abstract—The Raman spectra of solid inorganic, organic, biological and polymeric substances were obtained with the Cary model 81 spectrophotometer§, using the same optics and source of the instrument that are employed for liquid samples. To study the quality of the spectra obtained, several types of sample tubes were tried and the effects of crystal size, sample thickness, sample position and method of solid preparation were investigated. In all cases studied the spectral data were obtained in periods of 1–2 hr, and the results agreed with those reported in the literature.

Introduction

THERE is great interest in Raman spectroscopy of solid materials. Solid Raman spectra are very helpful in studying materials that are generally insoluble or that can change in dissolution in solvents (e.g. depolymerization, solute-solvent interaction), such as polymers. In addition, such problems as solid crystal defects, solid solutions, surface reactions and solid catalysts can be considerably aided by solid Raman studies.

Most of the Raman work reported in the literature has been done on liquids or solutions. In India [1] some work has been done on solids, but generally the field has been neglected. This has been due to the extreme difficulty in obtaining solid spectra. Many investigators have reported the long exposures necessary, and the problems inherent in using photographic plates. In addition, realignment of the optics and changing the source in going from liquid operation to solid operation is very time-consuming. TOBIN [2] has discussed the versatility of using an ideal instrument employing the same optical alignment and source for both solids and liquids. The availability of a commercial recording Raman spectrophotometer has reduced exposure times, and eliminated the problem of photographic plates. This paper deals with the study made on obtaining the Raman spectra of solid substances using the spectrophotometer as it is used in obtaining liquid spectra.

Our interest in obtaining solid Raman spectra was motivated by the fact that the state of aggregation of several compounds of interest to us was changed on dissolution in solvents. We are unaware of any reported solid Raman investigation using the Cary model 81 spectrophotometer. It is the purpose of this paper to discuss the factors involved in obtaining these spectra, and as a result of our experiences, to outline the most advantageous operating procedure to be used.

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§ The operating features and design of the Cary model 81 spectrophotometer were presented at the Symposium on Molecular Spectroscopy in Columbus, Ohio in 1953 and 1955 by HOWARD CARY.

[1] R. ANANTHAKRISHNAN, *Proc. Indian. Acad. Sci.* **5**, 200 (1937).

[2] M. C. TOBIN, *J. Opt. Soc. Am.* **49**, 850 (1959).

Experimental

All spectra were obtained using a Cary model 81 spectrophotometer. The sample tubes of Pyrex glass were 457 mm in length (7 mm and 19 mm in diameter) and had a flat Pyrex glass window at one end. The tubes were capable of being mounted on one end at the conical slot of the instrument, and held on the other end by the tube holder bracket.

Results and discussion

The Raman spectra for various classes of solids were obtained. Observed Raman displacements are presented in Table 1 and compared with those from the literature wherever these are available. In obtaining these spectra the following factors, of varying degree of importance, were considered.

Sample tube

In the course of this study it was found that the 19-mm Raman tube gave a Raman spectrum with less background than the 7-mm tube. If the wall of the 7-mm tube is masked with tape or black paint from the end of the sample to a point about 150 mm up the tube, the background is reduced. Masking was not helpful in the case of the 19-mm tube. Other 7-mm tubes were tested, such as a rounded, a conical and a tube with a glass lens on the end. None of these tubes appeared to offer any improvement over the flat window tube, and in fact were less satisfactory.

The solid sample holding assembly, as manufactured by Applied Physics Corporation, can also be used. However, this holder is intended for use with a large crystal. The holder can be modified for use with polycrystalline material by replacing the solid sample holder with a 15-mm Pyrex glass tube, which will fit snugly in the assembly. In addition, the solid sample holder can be used to hold a KBr disk of the material of interest with satisfactory results.

Sample crystal size

Various particle sizes of naphthalene for a given volume of sample were considered. It was found that the larger the size of the particles the greater the intensity (see Fig. 1). Single crystals always gave better spectra.

Sample thickness

For a given particle size the effect of the crystalline volume on the spectrum of naphthalene was studied. It was found that a 2-mm thickness gave the best results when the 7-mm Raman tube was employed. The 3-mm thickness appeared to be better than a 1-mm thickness, but not as good as the 2-mm thickness (see Fig. 2). It must be emphasized that this finding applies to naphthalene, and it is quite likely that the sample thickness is related in part to the scattering power of the solid, and is therefore different for each solid used. It appears necessary to determine experimentally the maximum thickness which gives a satisfactory spectrum for each individual solid.

Table 1. Observed Raman frequencies for inorganic, organic, biological and polymeric materials (cm^{-1})—solids
Inorganic Compounds

[1]	KNO_3 This paper	NH_4NO_3 [1] This paper	$\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}^*$ This paper	$\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}^*$ This paper	NaClO_3^\dagger [2] This paper	$\text{Cd}(\text{SCN})_2$ This paper
715	248 (vw)	716	760 (vw)	810 (m)	130	448 (sh)
	308 (vw)	1051	810 (vw)	1042 (s)	173	467 (m)
	525 (vw)	1291	1044 (vs)	1225 (w)	486	770 (w)
	718 (w)	1360	1104 (vw)		625	2139 (vs)
1050.5	825 (vw)	1423	1213 (w)		787	
	1055 (s)	1455			877	
	1075 (sh)				935	937 (vs)
	1112 (w)				968	968 (sh)
1343	1213 (w)				987	987 (w)
	1350 (m)				1030	1030 (m)
	1362 (sh)					
1360	1687 (vw)					
	1887 (vw)	3150				

vs, very strong. s, strong. m, medium. w, weak. vw, very weak. vvw, very very weak. sh, shoulder.

* Range between 500–1500 cm^{-1} run.

† Range between 0–1200 cm^{-1} run.

Table 1—(contd.)
Organic Compounds

Naphthalene		Acetamide		Phenyl hydrogen phenyl phosphonate	Diphenyl phosphoric acid	Maleic anhydride	Succino- nitrile	Oxalic acid	
[1]	This paper	[1]	This paper	This paper	This paper	This paper	This paper	[1]	This paper
	398 (vw)	455	460 (m)	525 (w)	333 (vw)	287 (vw)	820 (vw)	485	865 (s)
511	515 (s)		577 (m)		373 (vw)	573 (vw)	1220 (vw)	854	1177 (w)
764	767 (s)	875	878 (s)	585 (w)	436 (vw)	650 (s)	1330 (vw)	1360	1360 (w)
1019	1022 (s)	1147	1156 (m)	660 (w)	460 (vw)	775 (vw)	1675 (vw)	1486	1487 (w)
1144	1148 (m)		1225 (vw)		602 (vw)	875 (m)	1755 (vw)		1750 (vw)
1168	1169 (sh)	1354	1352 (w)	875 (m)	623 (vw)	948 (vw)	1875 (vw)		3400 (vw)
1240	1240 (w)	1397	1399 (w)	1010 (s)	728 (m)	1070 (s)	2250 (s)	3432	3432 (vw)
1280	1275 (vw)	1594	1595 (vw)	1075 (w)	775 (vw)	1247 (w)	2785 (vw)	3467	
1328	1325 (w)	2933	2936 (s)	1120 (w)	791 (vw)	1600 (s)	2950 (s)		
1379	1380 (vs)	2970		1139 (vw)	1012 (vs)	1630 (vw)	2987 (vw)		
1440	1448 (sh)	3020	3012 (vw)	1175 (vw)	1026 (sh)	1800 (sh)			
1460	1463 (s)	3150	3162 (s)	1225 (w)	1102 (vw)	1850 (vs)			
1573	1577 (s)		3270 (w)	1360 (w)	1160 (m)	3135 (s)			
1623	1627 (m)	3286	3287 (w)	1505 (w)	1198 (sh)				
	1675 (w)			1537 (w)	1220 (s)				
	1770 (w)	3351	3330 (w)	1605 (m)	1405 (vw)				
	1885 (w)			1685 (m)	1452 (vw)				
	2975 (vw)			1775 (m)	1597 (m)				
3001	3015 (m)			2775 (sh)	1650 (vw)				
3025				2800 (m)	1770 (vw)				
3054	3060 (vs)			3070 (s)	2725 (vw)				
					2777 (w)				
					3025 (sh)				
					3050 (vs)				

Table 1—(contd.)
Biological Compounds

Sucrose* This paper	[1]	Urea This paper
540 (w)		550 (s)
637 (vw)		820 (m)
850 (m)	1012	1016 (vs)
925 (vw)	1171	1170 (vw)
950 (vw)		1225 (vw)
1049 (w)		1380 (vw)
1100 (vw)	1465	1465 (w)
1130 (w)	1537	1537 (m)
1175 (w)	1576	1580 (vw)
1237 (w)		1650 (w)
1275 (vw)	3243	3243 (w)
1350 (w)		3328 (sh)
1375 (w)		3361 (s)
1430 (vw)		3437 (m)
1467 (w)		
2912 (m)		
2947 (m)		
2997 (w)		
3012 (vw)		

* Range between 500–3200 cm^{-1} run.

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Table 1—(contd.)

Polymers

Poly-3-methyl-1-butene This paper	Polypropylene [2, 3] This paper		Lucite This paper	Polystyrene [4-6] This paper	
337 (vw)		375 (vw)	230 (vw)	152 (vw)	
395 (vw)		420 (vw)	250 (vw)	196 (w)	
425 (vw)	808 (m)	812 (w)	280 (vw)	210 (w)	220 (m)
					410 (w)
780 (w)	1155 (s)	1148 (w)	290 (w)	558 (w)	550 (vw)
				621 (m)	622 (m)
800 (vw)		1160 (w)	366 (m)		700 (vw)
				722 (vww)	722 (vw)
900 (w)		1225 (w)	480 (m)	757 (vw)	752 (w)
1137 (w)	1333 (s)	1333 (w)	600 (s)		
1225 (m)		1352 (w)	748 (vw)	791 (vww)	786 (m)
1270 (w)	1457 (s)	1457 (m)	817 (vs)	833 (vww)	844 (w)
1320 (w)		1530 (m)	914 (vw)	908 (vw)	908 (w)
1375 (w)	2831 (s)	2840 (w)	972 (s)	952 (vw)	947 (vw)
1388 (w)	2884 (s)	2884 (s)	980 (sh)	999 (vvs)	1000 (vs)
1470 (m)	2921 (s)	2921 (w)	1070 (w)	1011 (vw)	
1540 (vw)	2968 (s)	2968 (m)	1164 (m)	1031 (m)	1032 (s)
1760 (vw)			1166 (vw)	1058 (vww)	1072 (vw)
1780 (vw)			1195 (w)	1094 (vww)	1098 (vw)
1900 (vw)			1247 (m)	1110 (w)	
2887 (s)			1334 (m)	1165 (w)	1158 (m)
2960 (s)			1398 (m)	1177 (vw)	1185 (sh)
3025 (vw)			1456 (vs)	1200 (m)	1199 (m)
3040 (vw)			1732 (s)	1269 (vww)	1280 (vw)
3110 (vw)			2848 (s)	1298 (w)	
3130 (vw)			2955 (vs)	1326 (vww)	1328 (w)
			3003 (vs)		1370 (vw)
				1449 (vw)	1450 (w)
				1470 (vww)	
				1588 (vw)	1585 (sh)
				1606 (m)	1604 (vs)
				1634 (vw)	1630 (vw)
				2886 (mw)	2852 (m)
				2933 (w)	2908 (s)
					2978 (w)
					3004 (w)
				3056 (s)	3043 (sh)
				3066 (vw)	3058 (vs)
				3138 (m)	3162 (vw)
					3200 (vw)

vs. very strong. s, strong. m, medium. w, weak. vw, very weak. vww, very very weak. sh, shoulder

[3] M. C. TOBIN, *J. Phys. Chem.* **64**, 216 (1960).

[4] A. PALM, *J. Phys. & Colloid Chem.* **55**, 1320 (1951).

[5] R. SIGNER and J. WEILER, *Helv. Chim. Acta* **15**, 649 (1932).

[6] S. KRIMM, *Fortschr. Hochpolym-Forsch.* (Advances in Polymer Sci.) **2**, Band 2, 51-172 (1960).

Sample position

The solid sample was generally placed at the end of the sample tube, and packed gently with a solid rod so that the sample remained upright. For most experiments the position of the solid was at the end of the tube. In the 19-mm tube, some experiments were made by placing the sample about 150 mm from the

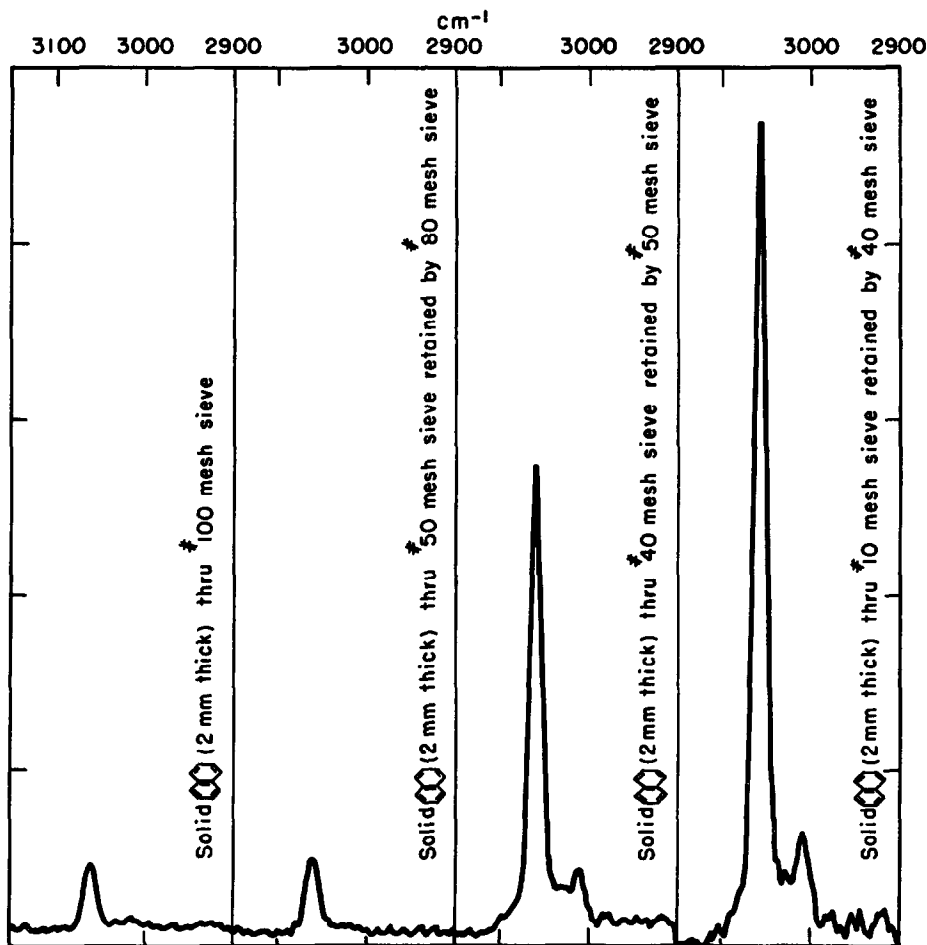


Fig. 1. Solid naphthalene spectra illustrating effect of crystal size.

end of the tube with satisfactory results. This did not help with the 7-mm tube, and spectra were less satisfactory than those obtained with the sample at the end.

Sample preparation

The solids used were C.P. or Reagent Grade from the Chemistry storeroom without further purification. In some cases, single crystals were prepared (e.g. bis-(diphenyl)-phosphoric acid). For low-melting solids, some cooled liquid films were run. The spectra were adequate, and better than those of fine powders but

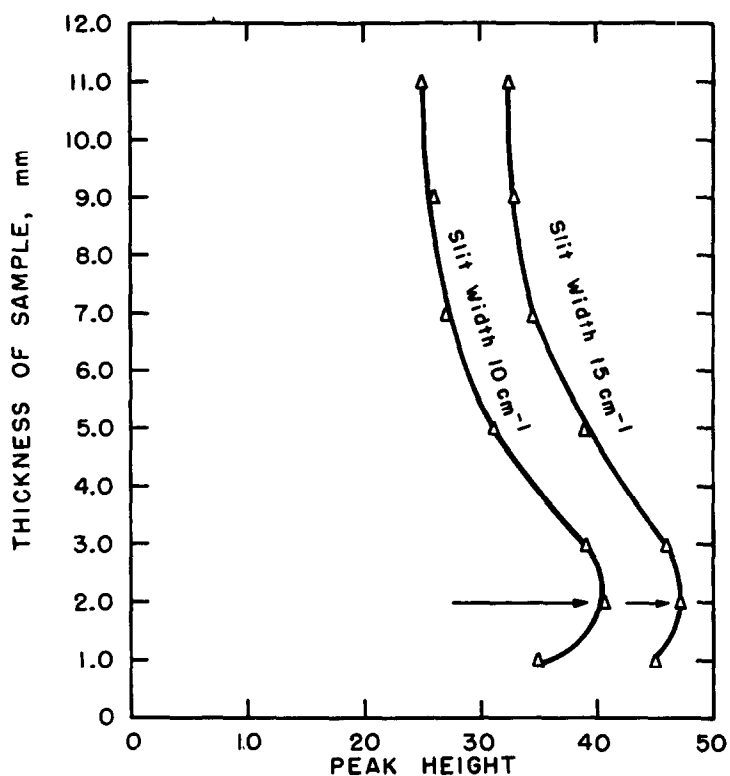


Fig. 2. Relation of peak height with sample thickness for solid naphthalene (region of 3057.5 cm^{-1}).

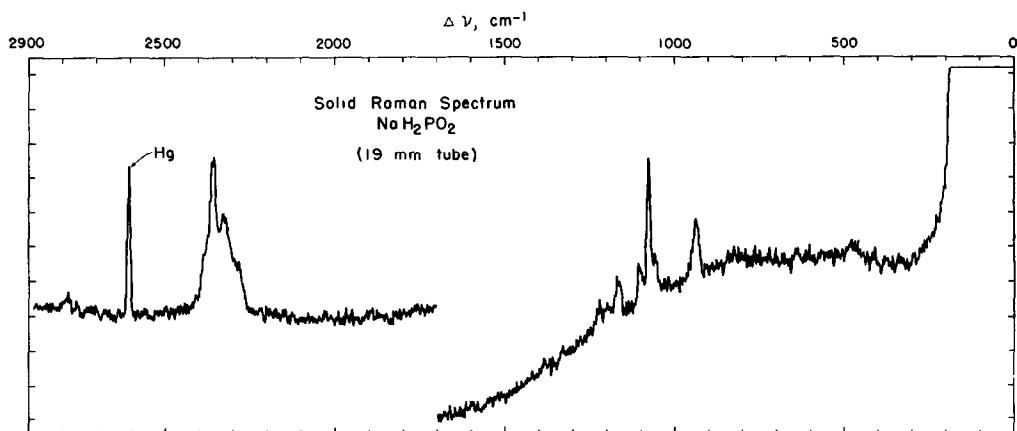


Fig. 3. Solid Raman spectrum NaH_2PO_2 .

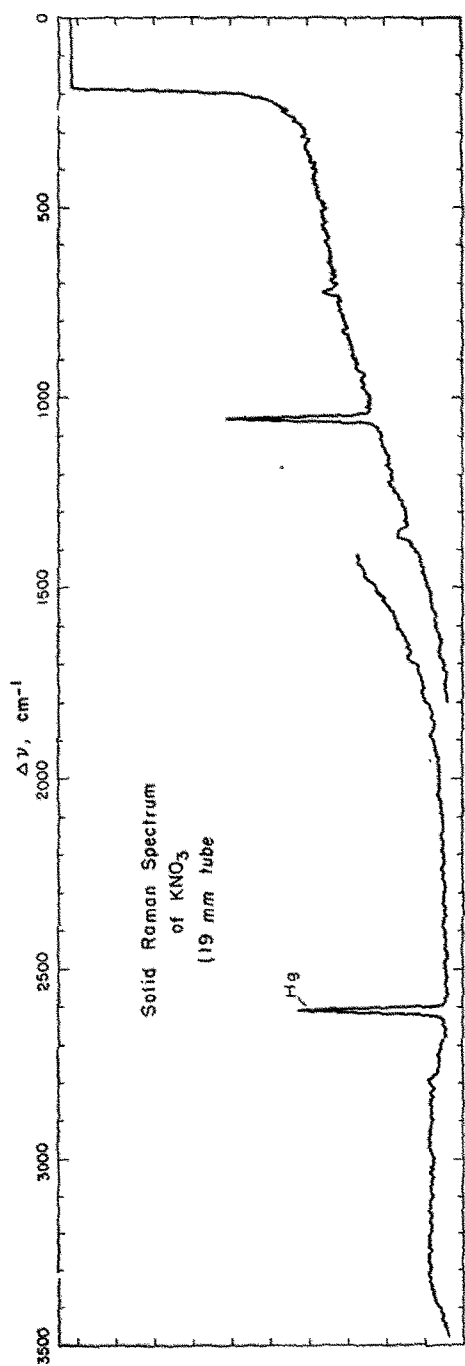


Fig. 4. Solid Raman spectrum KNO_3 .

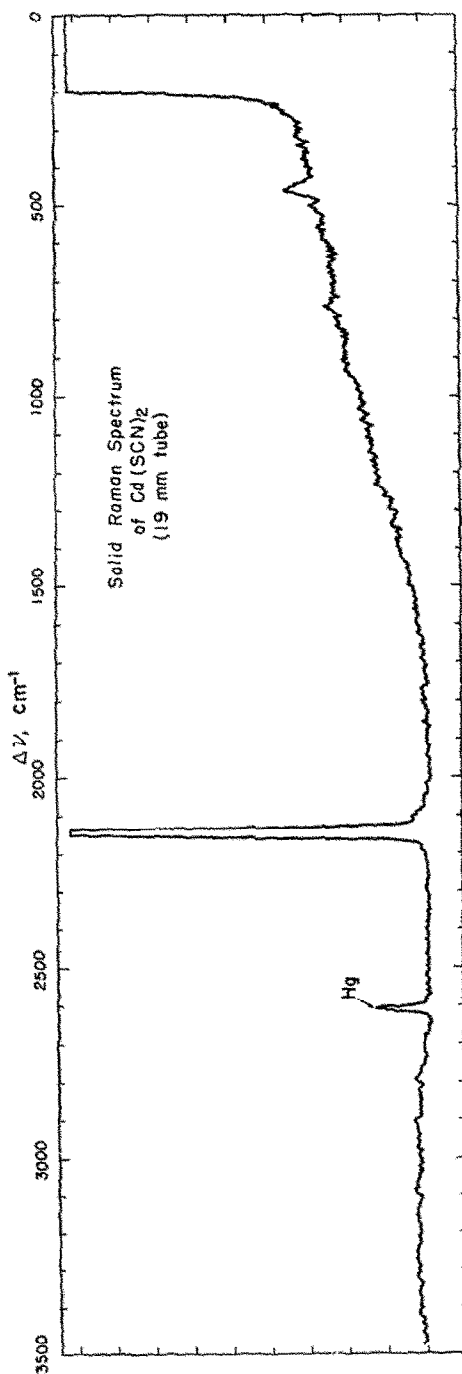


Fig. 5. Solid Raman spectrum $\text{Cd}(\text{SCN})_2$.

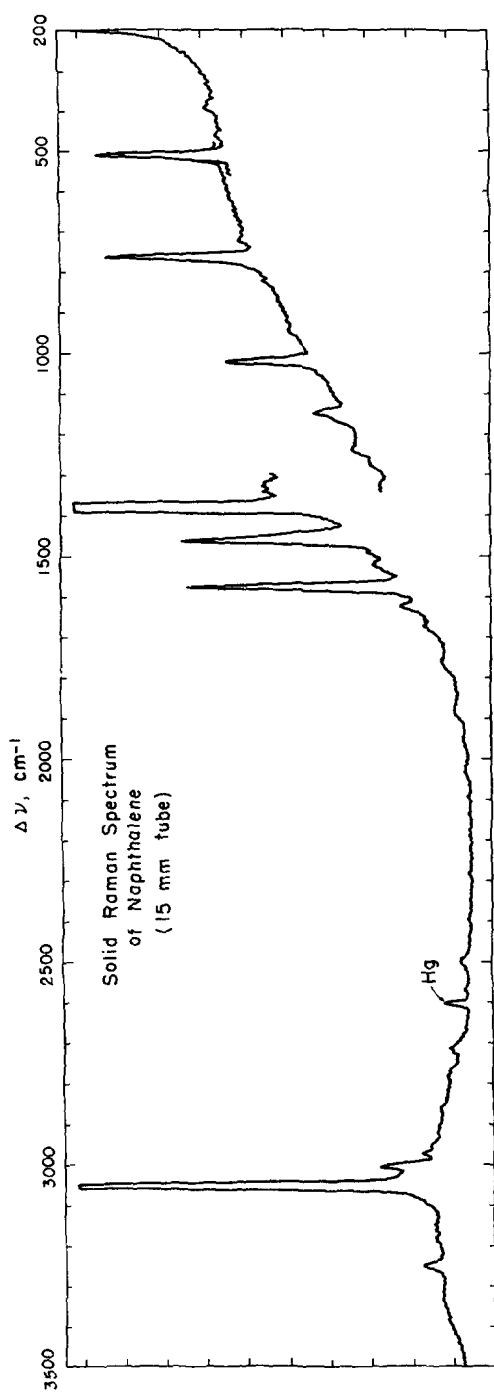


Fig. 6. Solid Raman spectrum naphthalene.

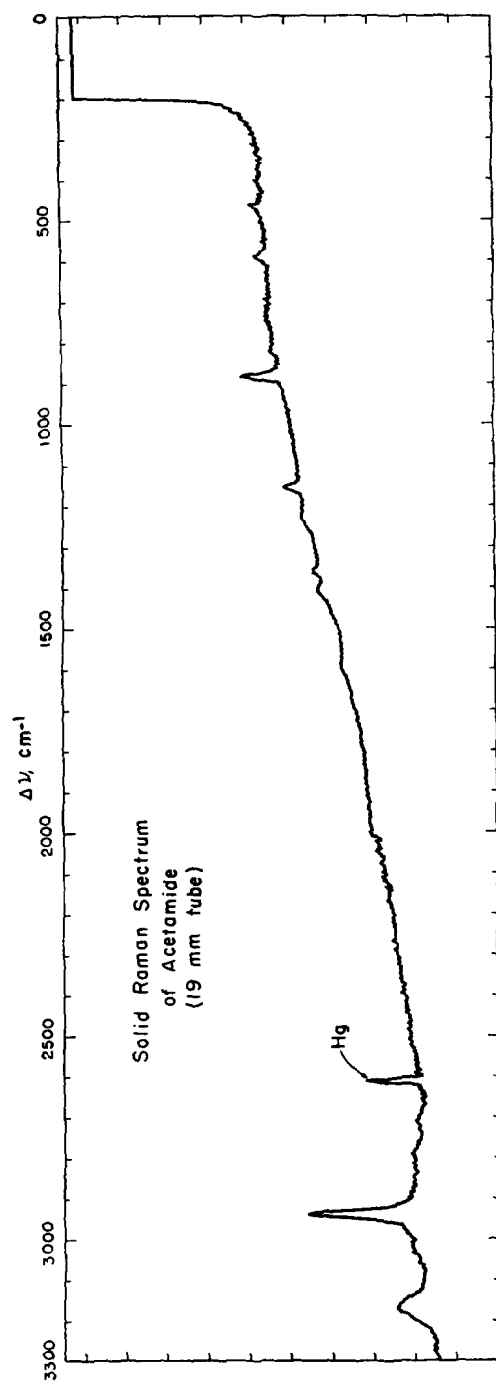


Fig. 7. Solid Raman spectrum acetamide.

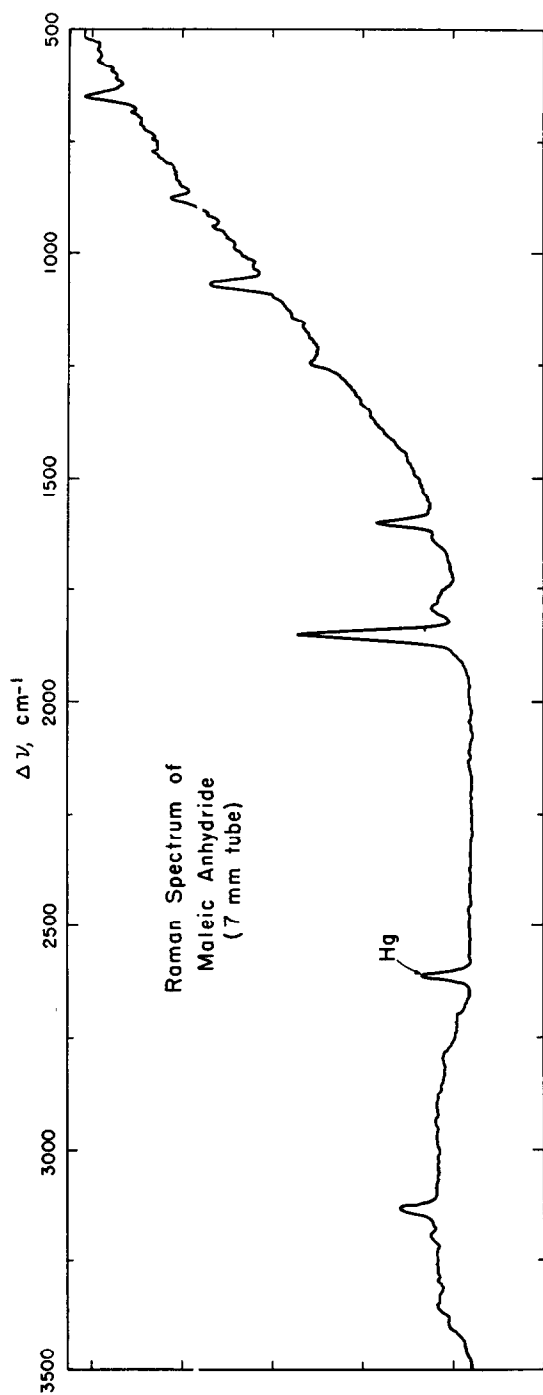


Fig. 8. Solid Raman spectrum maleic anhydride.

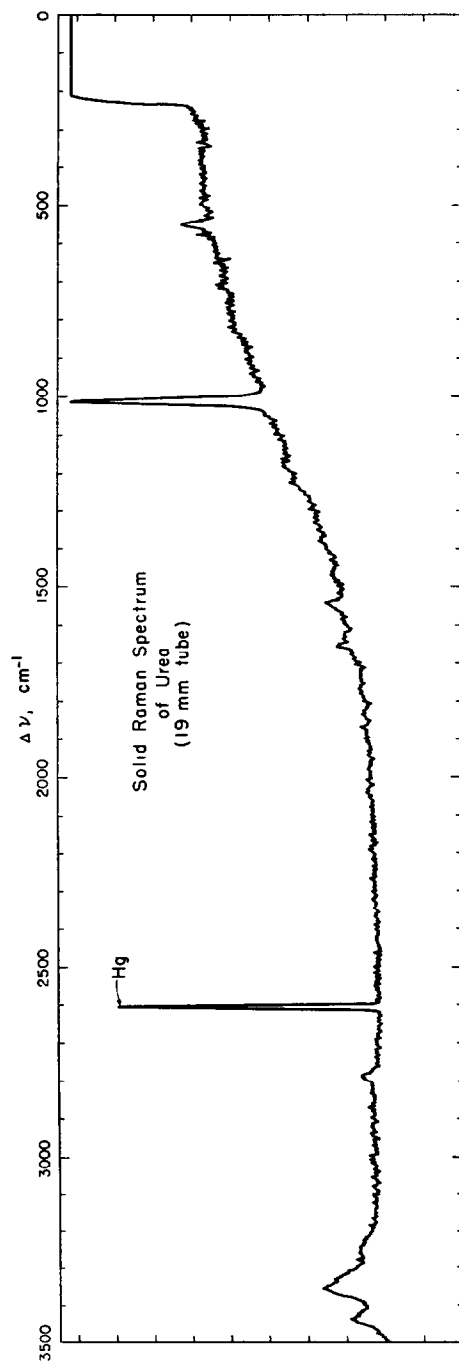


Fig. 9. Solid Raman spectrum urea.

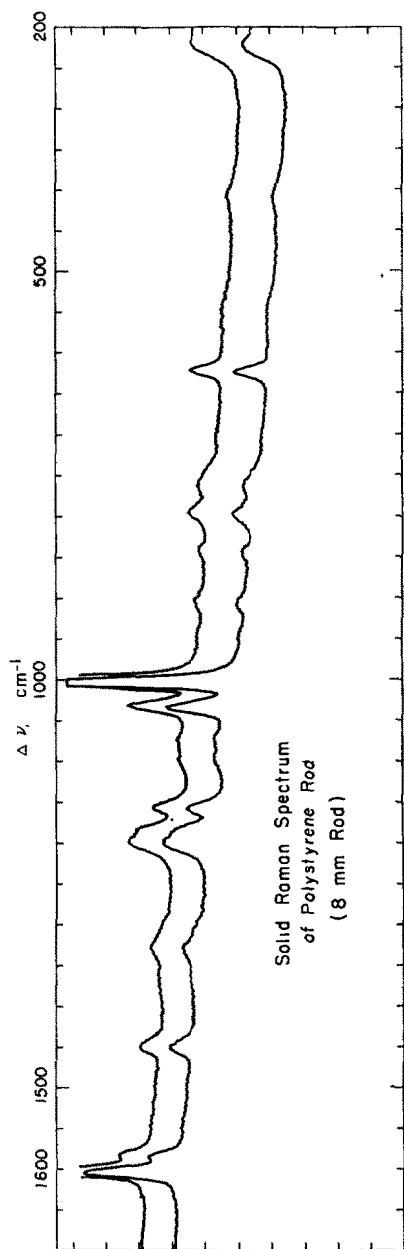


Fig. 10(a). Solid Raman spectrum polystyrene rod 200–1700 cm^{-1} .

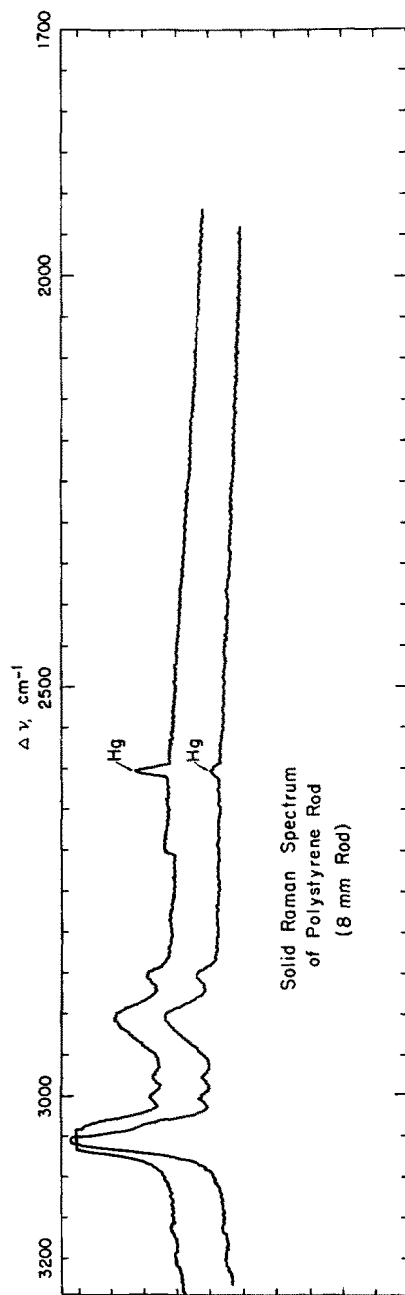


Fig. 10(b). Solid Raman spectrum polystyrene rod 1700–3200 cm^{-1}

not as good as those of crystalline material. The use of pressed pellet samples was also investigated. Satisfactory spectra were obtained for KBr-naphthalene and KBr-KNO₃ mixtures. These experiments must be approached with caution because of possible solid state effects.

In the case of polystyrene and lucite, which are transparent or nearly so, 7-mm and 19-mm rods (457 mm in length) of the plastic were placed in the spectrophotometer in place of the sample tube, and excellent spectra were obtained.

Summary

Several typical solid spectra are shown in Figs. 3–10. It is recommended that the 19-mm sample tube be used in obtaining solid spectra with the Cary model 81 spectrophotometer wherever sufficient solid sample is available. The 19-mm tube is more satisfactory than the 7-mm tube because of its lowered background for scattered radiation. In addition, the continuum from the Hg source is much reduced and Raman scattering from 200–500 cm⁻¹ can be observed even with double slit operation. In cases where the solid can be pressed into a transparent rod (e.g. some polymers), the rod can be used directly in place of the sample tube.