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LASER EXCITED RAMAN SPECTRA OF β-HYDROQUINONE CONTAINING THE GUEST MOLECULE OF ACETONITRILE

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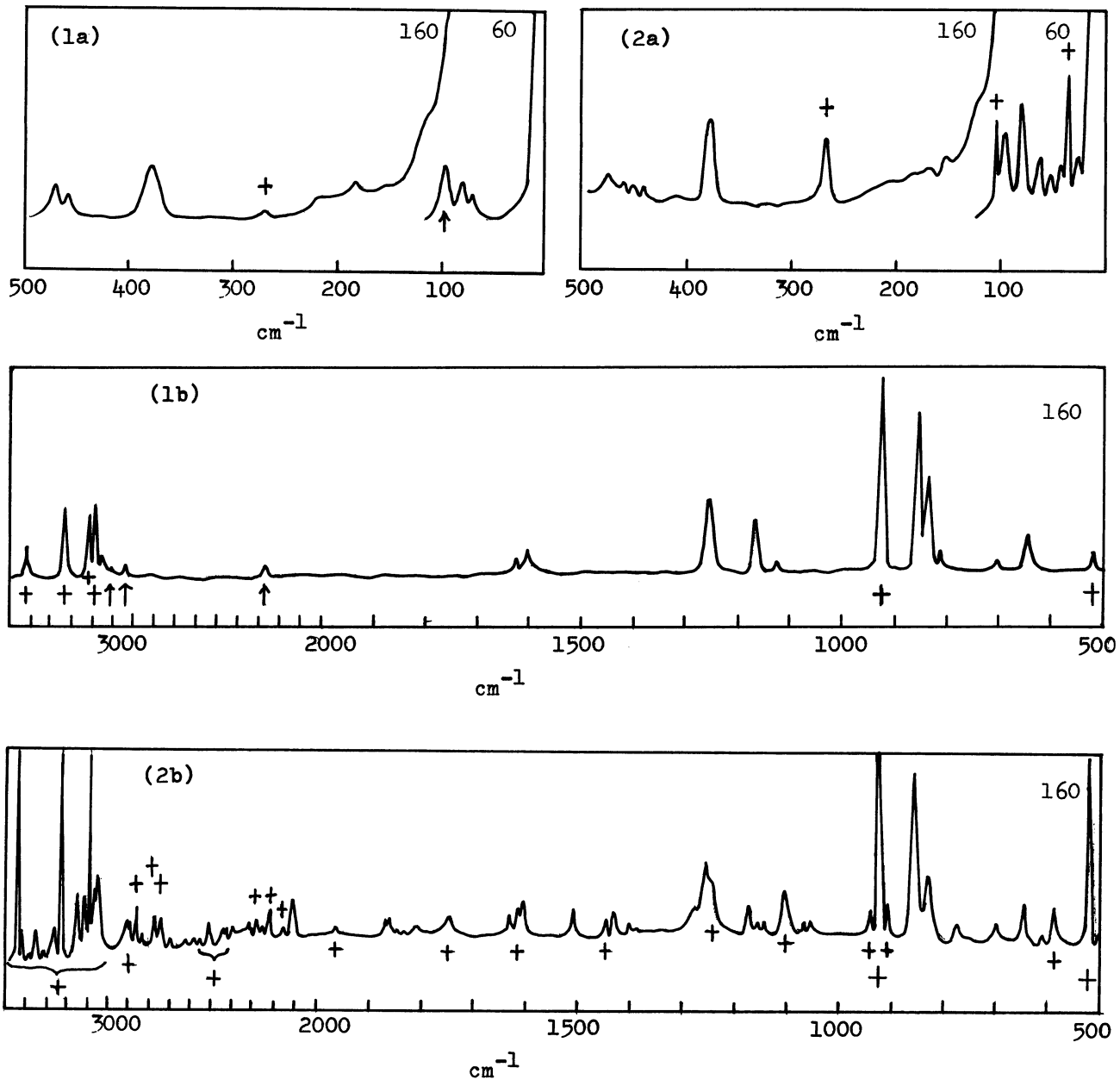
Laser excited Raman spectra of β-hydroquinone clathrate of acetonitrile and α-hydroquinone in their crystalline state were observed. The Raman band at 96 cm^{-1} for the β-hydroquinone was assigned to the rotational vibration of the guest molecule, and remarkable difference was found between the Raman spectra of the β-hydroquinone and α-hydroquinone.

During the measurements of far-infrared spectra of β-hydroquinone clathrate of acetonitrile and acetonitrile-d_3 for study of the bound state of the occluded guest molecules in the β-hydroquinone clathrates, it was found that the far-infrared spectra of the β-hydroquinone clathrates are different from those of α-hydroquinone, corresponding to their difference in the lattice structure, and that several infrared bands due to the translational and the rotational vibrations of the occluded guest molecule appear. Only available laser Raman spectra of α and β-hydroquinones are those by Davies.[1),2)] The following two points found in the literatures prompted me to measure the laser Raman spectra of β-hydroquinone clathrate of acetonitrile and α-hydroquinone by use of more powerful laser. 1) In Davies' measurements, 5208 Å Kr^+ laser line of rather weak power (~30 mW) was used. 2) In the Raman spectra obtained by Davies, the difference of the host lattice spectra between α and β-hydroquinones are not remarkable even in low frequency region.

In the present study, laser Raman spectra of powder and pellets of α-hydroquinone (JIS Special Grade, Wako Pure Chemical Industries, Ltd.) and β-hydroquinone clathrate of acetonitrile made from the α-hydroquinone and acetonitrile (JIS Special Grade, Wako Pure Chemical Industries, Ltd.) were measured by use of Ar^+ 4880 Å and 5145 Å excitation with a JRS-02AS Laser Raman Spectrometer. The obtained spectra are shown in Figures 1a, 1b, 2a and 2b and in Table 1.

Difference of spectra between α and β-hydroquinones. The complete Raman spectra of α-hydroquinone and β-hydroquinone clathrate of acetonitrile in the region below 100 cm^{-1} were obtained clearly for the first time by the present study. Difference of the spectra between the two hydroquinones is remarkable in the region as shown in Figures 1a and 2a. This is not consistent with the results described in Davies' papers. The inconsistency is in short that Davies reported the Raman spectra of β-hydroquinone clathrate of acetonitrile in the region below 150 cm^{-1} are similar to those of α-hydroquinone while in Figures 1a and 2a the spectra are very much different. The change of β-hydroquinone clathrate of acetonitrile into α-hydroquinone was confirmed by measurement of far-infrared spectra by the present author.[3)]



Figures (1a) and (1b) Laser Raman spectra of a pellet of β-hydroquinone clathrate of acetonitrile (Ar^+ 5145 Å excitation; figures represent slit width in μ).

(2a) and (2b) Laser Raman spectra of powder of α-hydroquinone (Ar^+ 5145 Å excitation; Ar^+ 4880 Å excitation for the region below 110 cm^{-1}; figures represent slit width in μ).

(the lines marked with + are spontaneous emission lines, and the bands marked with arrows are due to the guest molecule; ordinate represents Raman intensity.)

Table 1. Frequencies of Raman bands of β-hydroquinone clathrate of acetonitrile and α-hydroquinone (in cm^{-1}).

β-hydroquinone clathrate of acetonitrile		α-hydroquinone	
69		29	2583
77		43	2636
96	guest	52	2709
151		62	2848
182		79	2902
218		98	2909
378	guest	152	3392
459		377	
470		440	
646		450	
702		461	
812		477	
834		503	
853		610	
1126		646	
1164		700	
1255		772	
1602		831	
1611		853	
1625		1054	
2264	guest	1065	
2947	guest	1142	
3022	guest	1153	
3053		1170	
3068		1257	
		1275	
		1401	
		1431	
		1509	
		1602	
		1627	
		1809	
		1832	
		1846	
		1861	
		1868	
		2250	
		2283	
		2326	
		2403	
		2437	

Therefore, a possible explanation for the inconsistency is that "β-hydroquinone clathrate of acetonitrile" in Davies' work might be the changed sample and a mixture of α and β-hydroquinones.

Raman bands of guest molecule. Raman bands of intramolecular vibrations of the guest molecule in β-hydroquinone clathrate of acetonitrile have been already found by Davies,[1),2)] and the bands exist in the spectra shown in Fig. 1b. The lower frequency Raman spectra of β-hydroquinone clathrate of acetonitrile show a Raman band at 96 cm^{-1}. Although α-hydroquinone has a corresponding band at 98 cm^{-1}, the relative intensity of the band compared with the band at 79 cm^{-1}, is weaker than the corresponding relative intensity for the β-hydroquinone. Moreover, the band at 96 cm^{-1} corresponds to the far-infrared band of β-hydroquinone clathrate of acetonitrile at 98 cm^{-1}, which was clearly assigned to the rotational vibration of the guest molecule on the basis of a comparison of spectra with those of β-hydroquinone clathrate of acetonitrile-d_3.[3)] These facts lead us to a conclusion that the Raman band at 96 cm^{-1} is due to the guest molecule. Another Raman band, which is also due to the guest molecule and corresponds to the infrared band at 380 cm^{-1} [3)], is masked by the Raman band at 378 cm^{-1}.

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References

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