Raman Spectra of Guest Molecules in β-Quinol Clathrates

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Summary The Raman spectra of SO_2, C_2H_2, H_2S, and HCl as guest molecules in β-quinol clathrates are reported; evidence is obtained for the rotational motion of the HCl guest molecule.

THE structures of β-quinol clathrate compounds containing such guest molecules as SO_2, C_2H_2, H_2S, and HCl have been reported by Palin and Powell.[1] Subsequent i.r. studies[2,3] (4000—650 cm^{-1}) failed to detect any vibrational band due to the HCl guest molecule or to the $\nu_1(a_1)$ and $\nu_3(b_2)$ modes of the H_2S guest molecule since the region of interest was obscured by the broad, intense absorption band of the hydrogen-bonded OH groups of the host lattice. Recent far-i.r. studies[4,5] (10—100 cm^{-1}) have provided evidence for the quantized rotation of the HCl and H_2S guest molecules within the cavities of the β-quinol host lattice.

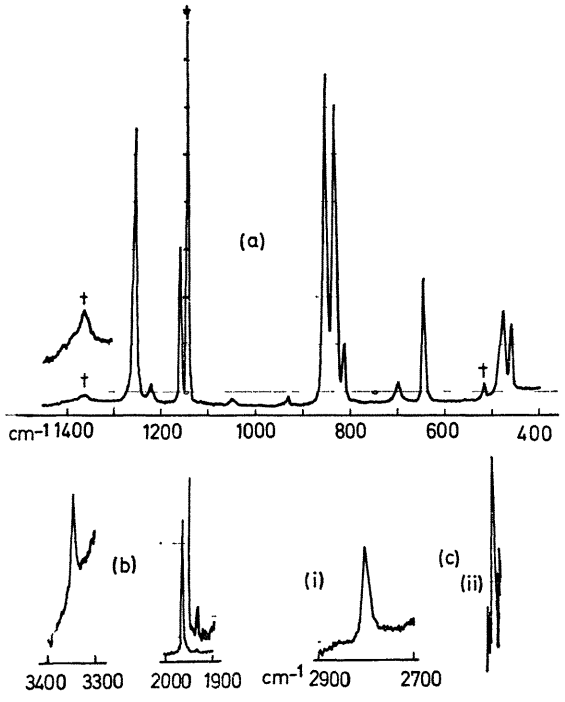

FIGURE. *Raman spectra of guest molecules in β-quinol clathrates* (a) SO_2, Kr 5682 Å *excitation*, 23 mW *at sample*, SO_2 *bands marked* †, (b) C_2H_2, (c) HCl, (i) *sample at room temperature*, (ii) *sample at* 77 K. *Spectra* (b) *and* (c) *used* Kr 5208 Å *excitation*, 30 mW *at sample. All spectra were recorded using* 3 cm^{-1} *slit width.*

We report here the Raman spectra of the guest molecules in β-quinol clathrates; SO_2, C_2H_2, H_2S, and HCl: apparently this is the first such report of the Raman spectra of clathrates. There are substantial differences between the Raman spectra of the β-quinol host lattice and of α-quinol, and these differences will be reported in detail elsewhere. Some of the spectra are illustrated in the Figure and the Raman frequencies of the guest molecules are compared with the gaseous, liquid, and solid-state Raman frequencies in the Table.

Three bands are observed for the SO_2 guest molecule at 521w, 1146vs, and 1363vw cm^{-1} in the room-temperature Raman spectrum [Figure (a)]. Four bands are observed for the C_2H_2 guest molecule [Figure (b)], the wavenumber value of the 620 cm^{-1} band being uncertain since it overlaps with a host band. The very weak band at 1938 cm^{-1} probably arises from a ^{13}C-containing molecule. No Raman-inactive bands were observed, indicating that acetylene retains its centrosymmetric structure in the clathrate.† Only one band is observed for the H_2S guest molecule, at 2588 cm^{-1}. The $\nu_2(a_1)$ and $\nu_3(b_2)$ bands are not observed, and these bands have also not been observed in the gaseous and liquid-phase Raman spectra.[6]

The room-temperature Raman spectrum of the HCl guest molecule‡ consists of a band at 2805 cm^{-1} with a half-width of 18 cm^{-1} [Figure c(i)] compared with a half-width of 7 cm^{-1} for the 2588 cm^{-1} band of H_2S. The width of the HCl band is probably due to a rotational motion within the host cavity, and a low-temperature (77 K) Raman spectrum [Figure c(ii)] supports this assumption. On cooling the sample from room temperature to 77 K, the half-width decreases from 18 to 7 cm^{-1}, while the H_2S band shows a corresponding decrease from 7 to 5 cm^{-1}. This

† However, a reduction in symmetry could cause activation of normally Raman inactive bands, but with an intensity too low to be detected.

‡ The room temperature results on the HCl clathrate agree with unpublished results by D. Ogden.

observation together with recent far-i.r. data[4,5] indicates a rotational motion of the HCl guest molecule within the β-quinol host cavity.

can be conveniently studied at room temperature whereas matrix-isolated molecules have to be studied at very low temperatures (*ca.* 20 K) to prevent solute diffusion.

TABLE. *Raman frequencies of molecules in the gaseous, liquid, and solid states, and as guest molecules in β-quinol clathrates (frequencies in cm^{-1})*

	Gas	Liquid	Solid	Clathrate Room temp.	Clathrate 77 K
SO_2	519[a] $\nu_2(a_1)$	524[b]	524[b]	521w	
			542		
	1151 $\nu_1(a_1)$	1145	1144	1146vs	
	1361 $\nu_3(b_2)$	1334	1311	1363vw	
			1323		
			1339		
			1349		
C_2H_2	612[c] ν_4		626m[d]	620vw	
			1956vs	1938vw	
	1974 ν_2		1960w	1968s	
	3374 ν_1		3324m	3350w	
			3332m		
H_2S	2611[c] $\nu_1(a_1)$	2574[e]	2559[e]	2588	2583
HCl	2886[c]	2758[f]	2706vs[g]	2805	2802
			2716m		
			2745s		
			2755m		

[a] I.r. values from ref. 6; [b] Ref. 7: liquid at 225 °K, solid at 77 °K; [c] Raman values from ref. 6; [d] Ref. 8: solid at 173 °K; [e] Ref. 9: solid at 138 °K; [f] Ref. 10: liquid at 168 °K; [g] Ref. 11: solid at 77 °K.

The data in the Table show that the clathrate frequencies are closer to the gas-phase frequencies than to the liquid or solid-state frequencies. This indicates that the guest molecules in the β-quinol clathrates are essentially isolated molecules, and the use of clathrates, like the matrix-isolation technique, enables one to study isolated molecules. One advantage of using clathrates is that the guest molecules Furthermore, guest molecules in clathrates can be studied over a very wide temperature range whereas matrix-isolated molecules can only be studied over a very narrow temperature range.

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