Clathrate and Inclusion Compounds. Part III.[1] The Infrared and Raman Spectra of Some β-Quinol (Hydroquinone) Clathrates

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The i.r. (4000—200 cm^{-1}) and Raman (3200—50 cm^{-1}) spectra of the β-quinol clathrates containing the following guest molecules are reported: Ar, COS, CH_3Cl, CH_3Br, CH_3NC, CH_3SH, CH_4, C_2H_6, and C_2H_4. The preparations of the COS, CH_3NC, and CH_3SH clathrates have not been reported previously. The Raman spectrum of the CH_3NC guest molecule has been interpreted as indicating the loss of the rotational freedom of the guest molecule around the C_3 axis. The ν(C–Br) mode of the CH_3Br guest molecule gives rise to a Raman band which has a value 9 cm^{-1} *higher* than the corresponding gas-phase value. This has been interpreted as indicating a compression of the C–Br bond. An interesting correlation has been observed between the size of the guest molecule (and hence the extent of the distortion of the host lattice) and the splitting pattern of the host-lattice Raman bands in the 400—550 cm^{-1} region.

A PREVIOUS publication[2] reported the i.r. and Raman spectra of α- and β-quinol and of 12 β-quinol clathrates. Here we report similar studies on a further 9 clathrates with the aim of obtaining information on possible guest-molecule motions and any host–guest interactions. A further aim was to extend the range of size and type of guest molecule and to this end we can report the successful preparations of the COS, CH_3NC, and CH_3SH clathrates for the first time. The spectroscopic results are summarised in the Table for the guest-molecule bands which were not obscured by host-lattice bands.

The Methyl Chloride and Methyl Bromide Clathrates.—The i.r. spectrum of the methyl chloride clathrate has been reported previously.[3] The band arising from the ν(C–Cl) mode was observed at 728 cm^{-1} when the clathrate sample was cooled to 123 K. The present study confirms the existence of a very weak band in this region in the low-temperature i.r. spectrum.

There have been no previous spectroscopic studies of the methyl bromide clathrate. This clathrate was found to be rather unstable and great care was required when preparing mulls and discs. If the sample was ground too vigorously it decomposed to give α-quinol. This was not a problem in Raman spectroscopy since no preparation of the sample was required. The low-temperature (123 K) i.r. spectrum of the clathrate gave a very weak band at 612 cm^{-1} which was assigned to the ν(C–Br) mode. This value differs by 7 cm^{-1} from the Raman value, which is considered to be the more accurate value since this mode gives rise to a strong Raman band but a very weak i.r. band which overlaps with host-lattice bands.

The interesting feature of these two clathrates arises from a comparison of the gas-phase and guest-molecule values of the $\nu_3(a_1)$ (C–X) stretching mode. The methyl chloride guest-molecule value of 732 cm^{-1} is close to the i.r. † gas-phase value[4] of 733 cm^{-1} although the matrix isolated value[5] is 10 cm^{-1} lower than the gas-phase value. For methyl bromide, the guest-molecule value of 619 cm^{-1} is 9 cm^{-1} *higher* than the average gas-phase i.r. value.[6] Upward shifts from gas-phase values have been reported previously for some matrix isolated species,[7] and these upward shifts have been interpreted as indicating the tight fit of the species in the matrix.

An interesting trend becomes apparent when the difference between the gaseous-phase and guest-molecule values of $\nu_3(a_1)$ reported for methyl fluoride[3] is compared with the values given here for methyl chloride and methyl bromide. The magnitude of this difference ($\nu_{gas} - \nu_{guest}$) decreases markedly on going from CH_3F (33·6 cm^{-1}, 3·2% shift) to CH_3Cl (1 cm^{-1}, 0·1% shift) to CH_3Br (−8·5 cm^{-1}, −1·4% shift). This trend is attributed to the increasing size of the guest molecule which thus becomes increasingly difficult to fit into the host-lattice cavity. In the case of the methyl bromide clathrate the spectroscopic data would seem to suggest that the C–Br bond is actually compressed. Evidence will also be presented later which shows that the host lattice itself is also distorted.

The Methyl Isocyanide Clathrate.—The crystallographic work of Palin and Powell[8] indicated that the host lattice of the methyl cyanide clathrate was distorted, and a later detailed crystal-structure determination[9] bore out this conclusion. The host-lattice spectrum of the methyl cyanide clathrate has also been shown to be different from the spectra of other clathrates in recent far-i.r.[10,11] and Raman[12] studies. The preparation of the methyl isocyanide clathrate has not been reported previously, and it was felt worthwhile to attempt this preparation to see whether the host-lattice spectra indicated any distortions of the host lattice.

The Raman spectrum of the host lattice was very similar to that of the methyl cyanide host lattice indicating that both host lattices are distorted. Figure 1 compares the liquid-phase and guest-molecule Raman spectra of CH_3CN, CD_3CN, and CH_3NC in the region of the symmetric and asymmetric methyl deformation modes. All

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† The i.r. value is considered to be more accurate than the Raman value since the i.r. band has been resolved into its isotopic components.

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I.r. and Raman results (in cm^{-1}) for β-quinol clathrates

Guest	Vibration	Raman		Infrared		
		Vapour	Guest [a]	Vapour	Matrix isolated	Guest [a]
CH_3Cl	$\nu_3(a_1)$ CCl stretch	725 [b]	732	727·2 (^{35}Cl) [c]	717·0 [d]	731
				732·9 (^{37}Cl)	720·7	
	$\nu_5(e)$ CH_3 asym bend	1473	~1454	1452·1	1445·4	†
	$\nu_1(a_1)$ CH_3 sym stretch	2965	2963	2967·8	2965·4	†
				609·9 (^{81}Br) [e]		
CH_3Br	$\nu_3(a_1)$ CBr stretch	609 [b]	619	611·1 (^{79}Br)		612
	$\nu_2(a_1)$ CH_3 sym bend	1309	1303	1305·9	1300·4 [d]	†
	$\nu_5(e)$ CH_3 asym bend	1456	1454	1442·7	1436·0	†
	$\nu_1(a_1)$ CH_3 sym stretch	2972	2969	2973	2967·4	†
CH_3NC	$\nu_8(e)$ CNC bend	288 [f]	290	263 [g]	277 [h]	*
	$\nu_4(a_1)$ CN stretch	928	940	945	938	†
	$\nu_3(a_1)$ CH_3 asym bend	1419	1418	1427	1421	†
	$\nu_6(e)$ CH_3 sym bend	1456	1455	1463	1457	†
	$\nu_2(a_1)$ NC stretch	2165	2177	2166	2161	~2150
	$\nu_1(a_1)$ CH_3 sym stretch	2954	2950	2966	2959	†
CH_3SH	CS stretch (a')	704p [i]	725	710	704 [j]	*k*
	CH_3 asym bend (a'')	1444dp	~1440	1444	1435	*k*
	CH_3 asym bend (a')			1453	1445	*k*
	SH stretch (a')	2575p	2591	2605	2603	*k*
	CH_3 sym stretch (a')	2933p	2945	2948	2948	*k*
C_2H_6	$\nu_3(a_{1g})$ CC stretch	995 [l]	1013			
	$\nu_{11}(e_g)$ CH_3 asym bend	1468	1466			
	$2\nu_8$	2898	2893			
	$\nu_1(a_{1g})$ CH sym stretch	2954	2951			
	$\nu_{10}(e_g)$ CH asym stretch	2968	~2974			
C_2H_4	$\nu_7(b_{1u})$ out of plane bend			949 [m]		942
	$\nu_3(a_g)$ CH_2 deform	1342 [n]	1349			
	$\nu_2(a_g)$ C=C stretch	1623	1623 [o]			
	$\nu_1(a_g)$ CH sym stretch	3026	3018			

[a] This work. [b] H. L. Welsh, M. F. Crawford, T. R. Thomas, and G. R. Love, *Canad. J. Phys.*, 1952, **30**, 577. [c] Ref. 4. [d] Ref. 5. [e] Ref. 6. [f] Liquid-state values from J. E. D. Davies and W. J. Wood, *J. Raman Spectroscopy*, 1973, **1**, 383. [g] R. K. Thomas, E. C. Leisegang, and H. Thompson, *Proc. Roy. Soc.*, 1972, **330A**, 15. [h] T. B. Freedman and E. R. Nixon, *Spectrochim. Acta*, 1972, **28A**, 1375. [i] Liquid-state values from I. W. May and E. L. Pace, *Spectrochim. Acta*, 1968, **24A**, 1605. [j] A. J. Barnes, H. E. Hallam, and J. D. R. Howells, *J.C.S. Faraday II*, 1972, **68**, 737. [k] The clathrate decomposed on grinding. [l] D. W. Lepard, D. E. Shaw, and H. L. Welsh, *Canad. J. Phys.*, 1966, **44**, 2353. [m] J. L. Duncan, D. C. McKean, and P. D. Mallinson, *J. Mol. Spectroscopy*, 1973, **45**, 221. [n] T. Feldman, J. Romanko, and H. L. Welsh, *Canad. J. Phys.*, 1956, **34**, 737. [o] Overlaps with a host-lattice band.

* Not observed. † Obscured by host-lattice band.

three guest molecules show the same trend, *viz* there is a marked reduction in the half-band width of the band arising from the asymmetric mode, $\nu_6(e)$, on going from the liquid phase to the guest molecule. This dramatic change in half-band width could well be due to a reduction of the rotational freedom of the guest molecule about the three-fold axis.

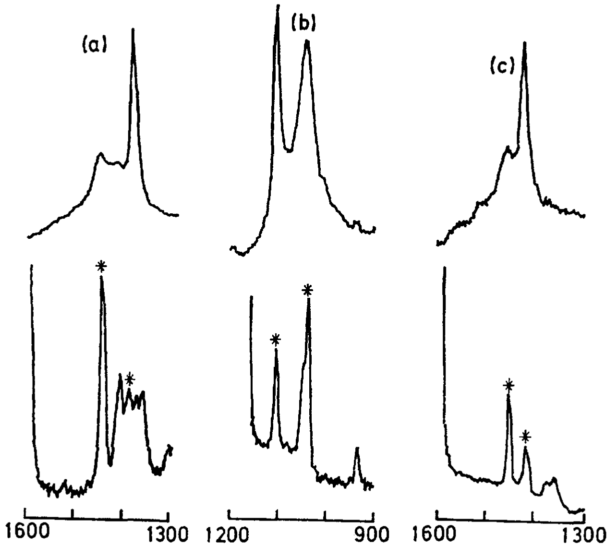

FIGURE 1 The liquid-phase (upper trace) and guest-molecule (lower trace) Raman spectra (in cm^{-1}) of (a) CH_3CN, (b) CD_3CN, and (c) CH_3NC. The guest-molecule Raman bands arising from the symmetric and asymmetric CX_3 deformation modes are marked with asterisks

The Methanethiol Clathrate.—It is well known that β-quinol forms a clathrate with methanol but not with ethanol, and this has been attributed to the fact that the ethanol molecule is too large to fit into the quinol cavity. It was thus thought worth while to attempt the preparation of a clathrate with a guest molecule similar to methanol and ethanol, but of intermediate size. We report the first successful preparation of the methanethiol clathrate.

There are two interesting features in the Raman spectrum of the clathrate: the value of the ν_8(C–S) stretching mode is 15 cm^{-1} *higher* than the gas-phase value, an *upward* shift of 2·1%, and the value of the ν_3(S–H) stretching mode is 14 cm^{-1} lower than the gas-phase value, a downward shift of 0·5%.

These changes are very different from the corresponding changes observed for the methanol clathrate.[2] In the methanol clathrate ν(O–H) showed a downward shift of 54 cm^{-1} (1·5%) from the gas-phase value, and ν(C–O) showed a downward shift of 6 cm^{-1} (0·6%). The small percentage shift of ν(S–H) and the large upward shift of ν(C–S) can be interpreted as indicating two competing effects occurring in the host cavity: hydrogen bonding between the guest molecule and the host lattice and a compression of the C–S bond. The host-lattice Raman spectrum also indicates a distorted host-lattice structure.

The Methane Clathrate.—The methane clathrate is of considerable interest since a study of its heat capacity over the temperature range 13—298 K has shown that the rotation of the guest molecule within the cavity is almost unrestricted.[13] Infrared [14] and Raman [15] studies of methane trapped in noble-gas matrices have also given evidence of near free rotation of methane in the matrices.

In the gas-phase Raman spectrum of methane,[16] $\nu_1(a_1)$ occurs as a sharp *Q* branch with no rotational fine structure, but the $\nu_3(f_2)$ band displays considerable rotational fine structure. Any information about guest-molecule rotation would therefore be obtained from the $\nu_3(f_2)$ band, but this band was unfortunately obscured by a host-lattice band. The only band observed in the Raman spectrum was the $\nu_1(a_1)$ band at 2905 cm^{-1}, which gave no information about guest-molecule rotation.

The Ethane and Ethylene Clathrates.—The preparations of these two clathrates have been reported,[17] but there have been no previous spectroscopic studies. Five guest-molecule Raman bands were observed for the ethane clathrate but all the i.r. bands were obscured by host-lattice bands. Because of the lack of i.r. data it was not possible to determine whether the guest molecule retains the staggered D_{3d} configuration found in the gaseous phase. The i.r. data on the ethylene guest molecule was also very sparse which made it impossible to test whether the rule of mutual exclusion was still valid for the guest molecule. The host-lattice Raman spectra of both clathrates indicate distorted host lattices.

The Carbonyl Sulphide Clathrate.—Since quinol is known to form a clathrate with carbon dioxide, it was thought worth while to attempt the preparations of the COS and CS_2 clathrates to see whether the host-lattice cavity can accommodate these larger molecules. The attempt with CS_2 was unsuccessful, but a product was obtained from the COS preparation.

The Raman spectrum of the COS product showed that the lattice had the β-quinol structure, but no guest-molecule bands could be observed. The i.r. spectrum was also consistent with the presence of the β-quinol structure, and an additional weak band was observed at 2045 cm^{-1} which could be the band arising from the $\nu_3(\Sigma)$ mode of the COS guest molecule, the gas-phase value [18] being 2062 cm^{-1}.

Further evidence that the product was the COS clathrate was obtained by its analysis which showed that 17% of the cavities were occupied. The DSC trace of the clathrate also contained an endotherm with a peak-maximum value of 106 °C arising from loss of the COS guest molecule.

The Argon Clathrate.—The i.r. and Raman spectra of the argon clathrate were identical in every respect to the spectra [2] of β-quinol.

DISCUSSION

During the course of our work on quinol clathrates we have recorded the Raman spectra of 21 clathrates and we have observed that whilst most of the host-lattice bands remain unchanged in relative intensities for a wide range of clathrates, the group of bands centred around 470 cm^{-1} do show marked changes. The Raman spectra (400—550 cm^{-1}) of seven clathrates are compared with the spectrum of β-quinol in Figure 2. The Raman band at 471 cm^{-1} observed in the solution spectrum of quinol has been assigned to an in-plane ring-deformation mode.[19]

The host-lattice Raman spectra can be divided into three types according to the splitting pattern of the bands in the 470 cm^{-1} region. All the Raman spectra shown in Figure 2 were obtained from solid samples and recorded using 3 cm^{-1} slit widths.

The Raman spectra obtained from β-quinol itself and from the HCl clathrate (Figure 2) are typical of the first type of spectrum. In these spectra three bands are observed at 460, 478, and 488 cm^{-1} with the relative intensity decreasing with increasing wavenumber value. This pattern is typical of clathrates having an undistorted host-lattice structure and has been obtained from clathrates containing the following guest molecules: Ar, N_2, O_2, HCl, HBr, and H_2S.

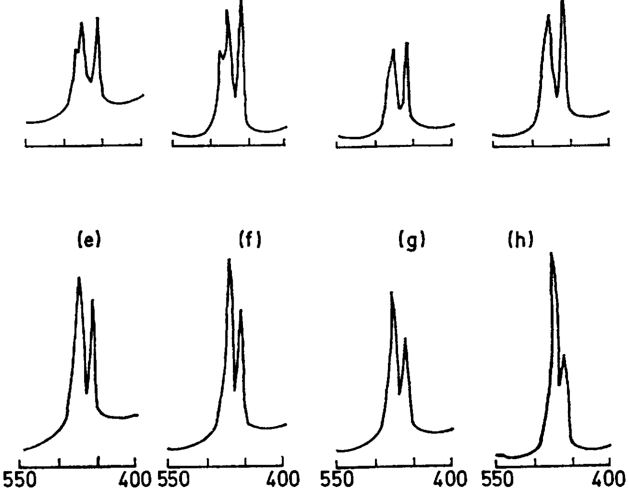

FIGURE 2 The host-lattice Raman spectra (400—550 cm^{-1}) of (a) β-quinol and the clathrates with (b) HCl, (c) CO_2, (d) CH_3OH, (e) SO_2, (f) CH_3SH, (g) CH_3Br, and (h) CH_3CN.

The second type of host-lattice Raman spectrum is exemplified by the CO_2 and CH_3OH clathrates (Figure 2). The 460 cm^{-1} band is still more intense than the 478 cm^{-1} band, but the 488 cm^{-1} band is no longer completely resolved and appears as a shoulder. This pattern has been observed for clathrates containing the following guest molecules: CO_2, COS, HCO_2H, CH_3OH, CH_4, and C_2H_2.

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The final type of Raman spectrum is illustrated in Figure 2 for the SO_2, CH_3SH, CH_3Br, and CH_3CN clathrates. Only two Raman bands, at 460 and 478 cm^{-1}, are observed with the 478 cm^{-1} band being more intense than the 460 cm^{-1} band, but the relative intensity of these two bands varies considerably. The clathrates which give this type of spectrum can be placed in a series in which the value of the ratio of peak heights of the 478/460 bands increases. The value of the ratio is given in parenthesis: C_2H_4 (1·2), SO_2 (1·2), CH_3SH (1·4), C_2H_6 (1·5), CH_3Cl (1·5), CH_3Br (1·7), CH_3NC (1·8), and CH_3CN, CD_3CN (2·1).

The only clathrates in this series for which unit-cell dimensions have been reported are the SO_2 and CH_3CN clathrates.[8] Both of these clathrates have c dimensions greater than 580 pm (*cf.* HCl clathrate with $c = 546$ pm) and the CH_3CN clathrate has been shown to have a distorted host-lattice structure.[9] It would thus appear that the clathrates giving rise to a two-band Raman spectrum in the 470 cm^{-1} region all have distorted host-lattice structures. Furthermore, for the CH_3Cl, CH_3Br, and CH_3CN clathrates there is a correlation between the length of the molecule and the value of the 478/460 peak-height ratio. It is thus possible that the value of this ratio can be used to indicate the degree of distortion of the host lattice.

EXPERIMENTAL

The clathrates of CH_3Cl and CH_3Br were prepared [3] by bubbling the gaseous guest molecule through a solution of quinol in ethanol saturated at 0 °C. The clathrates precipitated out of solution. The methanethiol clathrate, whose preparation has not been reported previously, was prepared by bubbling CH_3SH through a solution of quinol in ethanol saturated at room temperature. The clathrate of CH_3NC was prepared by cooling a saturated solution of quinol in CH_3NC. The methyl isocyanide was prepared using the literature method.[20]

The clathrates of Ar, CH_4, C_2H_6, C_2H_4, and COS were prepared by slowly cooling a saturated solution of quinol in ethanol from 70 °C to room temperature in a bomb containing the gas at high pressure.[17,21] The pressures were the maximum obtainable from a cylinder of the gas. Repeated attempts to prepare the propane clathrate using this method as described by Peyronel and Barbieri [22] were unsuccessful.

The clathrates were filtered and dried thoroughly in a desiccator. They were analysed using the method of Davies and Child.[3]

Raman Spectra.—The Raman spectra were excited by means of the 568·2 nm line from a CRL model 52K krypton laser and recorded on a Cary 81 spectrometer. The spectra of the solid samples were recorded using 3 cm^{-1} slit widths with a power of 30 mW at the sample. The spectrometer was calibrated using krypton emission lines.

Infrared Spectra.—The i.r. spectra of mulls held between CsI plates were recorded over the range 4000—200 cm^{-1} on a PE 225 spectrometer. The spectrometer was calibrated using a polystyrene film. The low-temperature spectra were obtained using a Beckmann-RIIC VLT-2 Variable Temperature Unit.

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