Clathrates and Inclusion Compounds. Part I. Infrared and Raman Studies of Several β-Quinol (Hydroquinone) Clathrates

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Infrared (4000—200 cm^{-1}) and Raman (3700—50 cm^{-1}) spectra are reported for α- and β-quinol, and for β-quinol clathrates containing the following guest molecules: N_2, O_2, HCl, HBr, CO_2, SO_2, H_2S, C_2H_2, HCO_2H, CH_3OH, CH_3CN, and CD_3CN. Comparison of the room-temperature and the low-temperature (77 K) Raman spectra of the HCl and HBr clathrates indicates a rotational motion of these guest molecules in the host lattice. The results are less conclusive for the N_2 and O_2 guest molecules due to the smaller values of their rotational constants. The guest-molecule vibrational frequencies are, in general, closer to the vapour-phase values than to the liquid- or solid-phase values. This is particularly true for the methanol and formic acid guest molecules, the spectra suggesting that these molecules are present as the *monomeric* species in the host cavities.

THE existence of compounds formed between quinol (hydroquinone) and molecules such as hydrogen sulphide[1] and formic acid[2] has been known for over a century. The precise nature of these compounds was not known until the crystallographic studies of Palin and Powell[3] showed that these compounds should be classified as a new class of compounds which were called clathrates. In these compounds the guest molecules (H_2S, HCO_2H, *etc.*) are trapped within an almost spherical cavity formed by hydrogen bonding of the quinol molecules and in which there is very little association between the guest molecules and the host lattice.

I.r. studies (4000—650 cm^{-1})[4-7] and more recently far-i.r. studies[8-12] of the guest molecules have been reported by several workers. In some cases the guest-molecule bands were obscured by the absorption bands of the host lattice but where guest-molecule bands were observed the spectra indicated that the guest molecules exist as essentially isolated molecules and also that some guest molecules can undergo rotation within the host cavity. In this paper the i.r. spectra (4000—200 cm^{-1}) of 12 quinol clathrates are reported. The Raman spectra (3700—50 cm^{-1}) are also reported for the first time. Preliminary reports of the Raman spectra have been published elsewhere.[13]

The Host Spectra.—During their crystallographic studies Palin and Powell[3] noted that the crystal structure of quinol when acting as a host lattice in a clathrate (β-quinol) differed from the ordinary crystal structure of quinol (α-quinol). The studies of Hexter and Goldfarb[4] and of Davies and Child[6] revealed minor differences between the i.r. spectra of the α and β modifications. The Raman spectra of the two forms show much more substantial differences (Figure 1). There are for example changes in the relative intensities of the bands centred at 480, 850, and 1610 cm^{-1}, the doublet at 1163/1169 cm^{-1} in the α spectrum appearing as a single band at 1163 cm^{-1} in the β spectrum, and the OH deformation band at around 1250 cm^{-1} is much simpler in both the i.r. and Raman spectra of the β-form than in the spectra of the α-form. An assignment has been proposed for α-quinol by Jakobsen and Brewer,[14] and the vibrational spectra support the crystallographic conclusion that the β-form has a more symmetrical structure than the α-form.

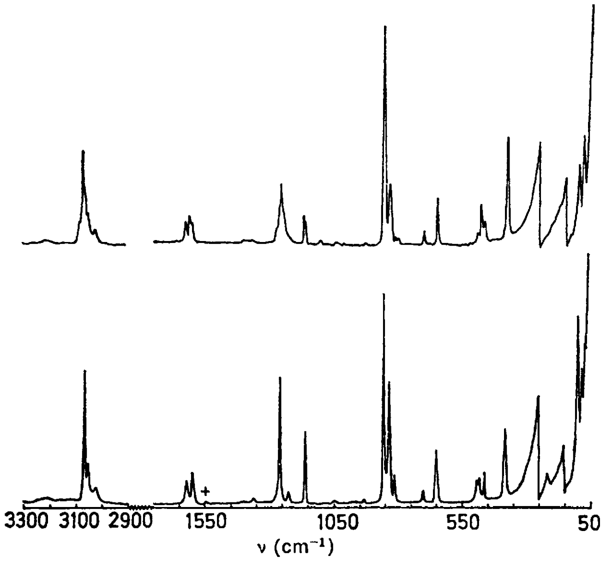

FIGURE 1 Raman spectra (3 cm^{-1} slits) of α-(upper trace) and β-(lower trace) quinol. Band due to included O_2 in β-quinol marked with a cross (see Experimental section).

The vibrational spectra of the host lattices of the clathrates are similar to that of β-quinol itself. The only exception is the host spectrum of the acetonitrile clathrate which contains many weak bands not found in the spectra of the other clathrates.

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[1] F. Wohler, *Annalen*, 1849, **69**, 294.

[2] F. Mylius, *Ber.*, 1886, **19**, 999.

[3] D. E. Palin and H. M. Powell, *J. Chem. Soc.*, 1947, 208; *ibid.*, 1948, 571, 815.

[4] R. H. Hexter and T. D. Goldfarb, *J. Inorg. Nuclear Chem.*, 1957, **4**, 171.

[5] D. F. Ball and D. C. McKean, *Spectrochim. Acta*, 1962, **18**, 933.

[6] M. Davies and W. C. Child, *Spectrochim. Acta*, 1965, **21**, 1195.

[7] R. K. Gosavi and C. N. R. Rao, *Indian J. Chem.*, 1967, **5**, 162.

[8] J. C. Burgiel, H. Meyer, and P. L. Richards, *J. Chem. Phys.*, 1965, **43**, 4291.

[9] S. J. Allen, *J. Chem. Phys.*, 1966, **44**, 394.

[10] P. R. Davies, *Discuss. Faraday Soc.*, 1969 (49), 181.

[11] C. Barthel, X. Gerbaux, and A. Hadni, *Spectrochim. Acta*, 1970, **26***A*, 1183.

[12] X. Gerbaux, C. Barthel, and A. Hadni, *Compt. rend.*, 1970, **271***B*, 888.

[13] (*a*) J. E. D. Davies, *Chem. Comm.*, 1971, 270; (*b*) *J. Mol. Struct.*, 1971, **9**, 483.

[14] R. J. Jakobsen and E. J. Brewer, *Appl. Spectroscopy.*, 1962, **16**, 32.

The far-i.r. spectrum[10,11] of the acetonitrile clathrate has also been found to be very different from the spectra of other quinol clathrates. The spectroscopic results are consistent with the crystallographic observation[15] that the quinol host lattice is more distorted in the acetonitrile clathrate than in other quinol clathrates. Further evidence for this distortion is obtained from differential thermal analysis.[16] Most quinol clathrates lose the guest molecule at a temperature in the region of 140 °C, but the acetonitrile guest molecule is lost at the much lower temperature of 96 °C.

The Guest Molecule Spectra.—One of the difficulties encountered in clathrate work is that some of the guest-molecule bands are obscured by the generally more intense host bands. The β-quinol host lattice is however centrosymmetric[3] resulting in the non-coincidence between i.r. and Raman bands. It is therefore advantageous to employ both i.r. and Raman spectroscopy in order to observe the maximum number of guest-molecule bands. The dependence of Raman band intensities on polarizability changes as opposed to the i.r. dependence on dipole-moment changes gives Raman spectroscopy an added advantage in the 2500—3300 cm^{-1} range.

The i.r. spectra of quinol clathrates in this region are dominated by the very broad and intense band arising from the hydrogen-bonded OH groups of the lattice. Previous i.r. studies[4,6] have found that this band obscures not only the CH stretching modes of the host lattice but also the CH stretching modes of guest molecules and also the vibrational bands of guest molecules such as HCl, HBr, and H_2S.

Raman bands arising from OH stretching modes are very much less intense than the corresponding i.r. bands. The use of Raman spectroscopy has consequently enabled us to observe for the first time the CH stretching modes of the formic acid, methanol, and acetonitrile guest molecules, and also the vibrational bands of the HCl, HBr, and H_2S guest molecules. In general more guest bands have been observed in the Raman spectra than in the i.r. spectra.

Diatomic guest molecules. As mentioned above, vibrational frequencies of diatomic guest molecules have not been reported previously and all the data reported in this section was obtained from Raman studies.

There are two main points of interest regarding diatomic guest molecules (i) the frequency of the band in comparison to the gaseous-, liquid-, and solid-state values and (ii) whether there is any evidence for a rotational motion of the guest molecules particularly in view of the result that HCl and HBr do rotate in a variety of low-temperature matrices.[17]

Previous far-i.r. studies[9-12] of the HCl guest molecule have obtained evidence for its rotation by direct observation of the $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ rotational transitions. No firm evidence could be obtained for the rotation of the HBr guest molecule since the $J = 0 \rightarrow 1$ transition could not be observed as it lay outside the range of the spectrometer, the gas-phase value being 16·7 cm^{-1}, and the value in an argon matrix[18] being 16·2 cm^{-1}.

There is an appreciable difference between the gaseous- and liquid-phase values for the vibrational frequencies of HCl and HBr (Table 1) and the guest-molecule frequencies lie between these two values. Comparison of the room-temperature and 77 K Raman spectra (Figure 2) give firm evidence for a rotational motion of *both* of these guest molecules within the host cavity. At room temperature the guest-molecule bands are broad with half-widths of 16 and 12 cm^{-1} for HCl and HBr respectively, which decrease to 7 and 6 cm^{-1} respectively when the sample is cooled to 77 K.

TABLE 1

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

				Clathrate	
	Gas	Liquid	Solid	Room temp.[a]	77 K[a]
HCl	2886[b]	2758[c]	2706vs[d] 2716m 2745s 2755m	2804(16)	2801(7)
HBr	2558[b]	2477[e]	2407vs 2417w 2442s 2454w	2492(12)	2487(6)
N_2	2331[b]	2329(4)[a]	2326[f] 2327	2323(4)	2328(4)
O_2	1556[g]	1552(2)[g]	1552(1·5)[g]	1547(6)	

Figures in parentheses give the half-width of bands in cm^{-1}.

[a] This work. [b] Ref. 21. [c] C. H. Wang and P. A. Fleury, *J. Chem. Phys.*, 1970, **53**, 2243; liquid at 168 K. [d] M. Ito, M. Suzuki, and T. Yokoyama, *J. Chem. Phys.*, 1969, **50**, 2949; solid at 77 K. [e] L. C. Brunel and M. Peyron, *Compt. rend.*, 1967, **264**C, 930; i.r. spectrum of liquid at 190 K. [f] A. Anderson, T. S. Sun, and M. C. A. Donkersloot, *Canad. J. Phys.*, 1970, **48**, 2265; solid at 18 K (α-phase). [g] J. E. Cahill and G. E. Leroi, *J. Chem. Phys.*, 1969, **51**, 97; liquid at 77 K; solid at 10 K (α-phase).

The present study of the N_2 and O_2 guest molecules provides less conclusive evidence for their rotation. The rotational constants of N_2 (1·99 cm^{-1})[19] and O_2 (1·44 cm^{-1})[19] are very much less than those of HCl (10·44 cm^{-1})[20] and HBr (8·34 cm^{-1})[20] resulting in much narrower vibrational bands whose half-widths do not change appreciably with temperature.

Triatomic and tetratomic guest molecules. Table 2 shows comparisons of the i.r. and Raman frequencies of the molecules SO_2, H_2S, CO_2, and C_2H_2 as guest molecules with the frequencies of these molecules in the gaseous-, liquid- and solid-states.

The Raman spectrum of the sulphur dioxide clathrate

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[15] S. C. Wallwork and H. M. Powell, *J. Chem. Soc.*, 1956, 4855.

[16] J. E. D. Davies and D. Stubley, unpublished observations.

[17] A. J. Barnes, H. E. Hallam, and G. F. Scrimshaw, *Trans. Faraday Soc.*, 1969, **65**, 3159.

[18] A. J. Barnes, J. B. Davies, H. E. Hallam, G. F. Scrimshaw, H. C. Hayward, and R. C. Milward, *Chem. Comm.*, 1969, 1089.

[19] R. J. Butcher, D. V. Willetts, and W. J. Jones, *Proc. Roy. Soc.*, 1971, *A*, **324**, 231.

[20] J. P. Perchard, W. F. Murphy, and H. J. Bernstein, *Chem. Phys. Letters*, 1971, **8**, 559.

displays all three vibrational bands expected for a guest molecule of C_{2v} point-group. The $\nu_3(b_2)$ band overlaps with a weak host band and there is consequently some uncertainty about its exact position in the Raman spectrum, but it can be easily identified in the i.r. spectrum. This is in fact the only band observed in the i.r. spectrum, since the two other guest-molecule bands coincide with strong host-lattice bands. Isotopic splitting of the $\nu_1(a_1)$ band is observed in the Raman spectrum.

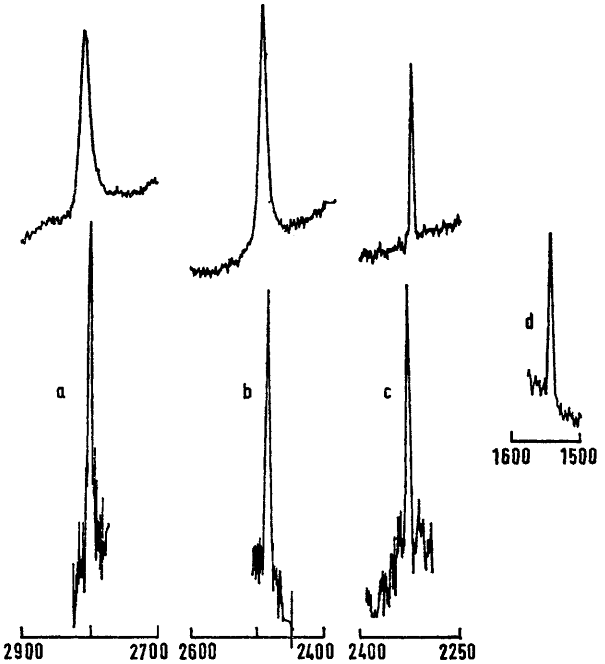

FIGURE 2 Raman spectra at room temperature (upper trace) and 77 K (lower trace) of the guest molecules (a) HCl, (b) HBr, (c) N_2, and (d) O_2 (room-temperature spectrum only). Slits of 3 cm^{-1} for a, b, and c, 4 cm^{-1} slit for d.

Only one band, arising from the $\nu_1(a_1)$ mode, has been observed in the gaseous-[21] and liquid-[21] phase Raman spectra of H_2S, but the $\nu_2(a_1)$ band has been observed as a weak band in the solid-phase Raman spectrum.[22] The H_2S guest molecule displays only one Raman band at 2587 cm^{-1}. No bands due to the guest molecule can be observed in the i.r. spectrum due to their coincidence with host-lattice bands.

The isolated carbon dioxide and acetylene molecules possess a centre of symmetry and the guest-molecule spectra indicate that the centrosymmetric structure is retained in the clathrate. The Fermi resonance doublet of ν_1 and $2\nu_2$ are the only bands observed in the Raman spectrum of the CO_2 guest molecule and the i.r.-active bands of the guest molecule are shown in Figure 3B.

No previous report of the i.r. and Raman spectra of the acetylene guest molecule has appeared. The present results indicate that the mutual-exclusion rule is operative, and isotopic splitting of the $\nu_2(\Sigma g)$ Raman band has been observed.

The formic acid and methanol guest molecules. These guest molecules are of interest since their vibrational spectra should indicate whether or not they are present as monomeric species in the host cavities. Previous i.r. studies of the formic acid[6,7] and methanol[6,23] guest molecules indicated that they do occur as the monomeric species and the present Raman study is in agreement with this conclusion.

The Raman frequencies of the formic acid guest molecule (Table 3, Figure 4) are much closer to the monomer vapour-phase i.r. values[24] than to the liquid-phase Raman values,[25] which have been interpreted in terms of a helical-chain polymeric structure. Of particular significance are the guest values for the ν(O–H) and ν(C=O) modes which are much closer to the vapour-phase values than to the liquid-phase values. The guest value for the ν(O–H) mode of methanol is also close to the vapour-phase value,[26] indicating the presence of a monomeric species in the host cavity.

During the present Raman study the bands due to the C–H stretching modes of methanol and formic acid have been observed. It has been pointed out earlier that these bands cannot be observed in the i.r. spectrum due to the presence of the strong, broad band due to the hydrogen-bonded O–H groups of the lattice. An indication of the

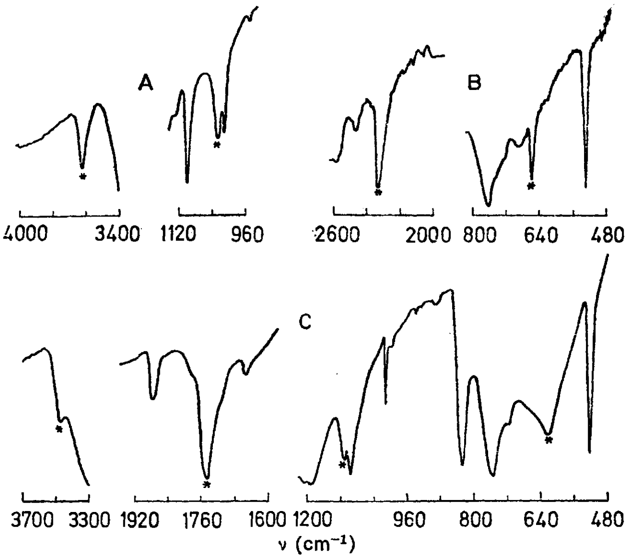

FIGURE 3 Infrared spectra of the β-quinol clathrates of (A) methanol, (B) carbon dioxide, and (C) formic acid. Bands due to the guest molecules marked *

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[21] G. Herzberg, 'Molecular Spectra and Molecular Structure,' Van Nostrand, New York, 1945.

[22] R. E. Miller and G. E. Leroi, *J. Chem. Phys.*, 1968, **49**, 2789.

[23] M. Jaffrain, J.-L. Siemons and A. Lebreton, *Compt. rend.*, 1969, **268C**, 2240.

[24] R. C. Millikan and K. S. Pitzer, *J. Chem. Phys.*, 1957, **27**, 1305.

[25] G. E. Tomlinson, B. Curnutte, and C. E. Hathaway, *J. Mol. Spectroscopy.*, 1970, **36**, 26.

[26] A. J. Barnes and H. E. Hallam, *Trans. Faraday Soc.*, 1970, **66**, 1920.

TABLE 2

Vibrational frequencies (in cm^{-1}) of triatomic and tetratomic molecules in the gaseous, liquid and solid states, and as guest molecules in β-quinol clathrates

					Clathrate	
	Gas		Liquid	Solid	Infrared[a]	Raman[a]
SO_2	519[b]	$\nu_2(a_1)$	524[c]	524[c] 542	†	521w
	1151	$\nu_1(a_1)$	1141$^{34}S^{16}O_2$ 1145$^{32}S^{16}O_2$	1141 1144 1148	†	1140vw$^{34}S^{16}O_2$ 1146vs$^{32}S^{16}O_2$
	1361	$\nu_3(b_2)$	1334	1312 1324 1341 1351	1340(1344)	1363vw †
H_2S		$\nu_2(a_1)$		1170[f]w	†	
	2611,[e] 2614[d]	$\nu_1(a_1)$	2574[e]	2559s	†	2587
	2627[d]	$\nu_3(b_2)$			†	
CO_2	667[g]	$\nu_2(\pi_u)$			654s	
	1285	$2\nu_2$		1277[h]		1272
	1388	$\nu_1(\Sigma_g)$		1385		1379
	2349	$\nu_3(\Sigma_u)$			2335s(2340)	
C_2H_2	613[g]	$\nu_4(\pi_g)$		626[i] 637 656		620w †
	729	$\nu_5(\pi_u)$		747[j] 761 769	729	
	1974	$\nu_2(\Sigma_g)$		1927[i] 1948 1959		1938vw$^{13}C_2H_2$ 1967s$^{12}C_2H_2$
	3285	$\nu_3(\Sigma_u)$		3226[j]	†	
	3373	$\nu_1(\Sigma_g)$		3314[i] 3324		3349w

Figures in parentheses give the i.r. values obtained in previous studies.[4,7]

† Host band in this region.

[a] This work. [b] I.r. values from ref. 21; [c] A. Anderson and R. Savoie, *Canad. J. Chem.*, 1965, **43**, 2271. Raman of liquid at 225 K, solid at 77 K. [d] I.r. value from A. J. Tursi and E. R. Nixon, *J. Chem. Phys.*, 1970, **53**, 518. [e] Raman value from ref. **21.** [f] Ref. 22. Raman of solid at 138 K. [g] I.r. and Raman values from W. J. Jones, 'Infrared Spectroscopy and Molecular Structure,' (ed. M. Davies), Elsevier, Amsterdam, 1963. [h] J. E. Cahill and G. E. Leroi, *J. Chem. Phys.*, 1969, **51**, 1324; Raman of solid at 88 K. [i] M. Ito, T. Yokoyama, and M. Suzuki, *Spectrochim. Acta.*, 1970, **26A**, 695; Raman of solid at 77 K. [j] G. L. Bottger and D. F. Eggers, *J. Chem. Phys.*, 1964, **40**, 2010; i.r. of solid at 63 K.

TABLE 3

The vibrational frequencies (in cm^{-1}) of methanol and formic acid in various phases, and as guest molecules in β-quinol clathrates

					Quinol clathrate	
Species		Mode	Vapour I.r.	Liquid Raman	I.r.[c]	Raman[c]
HCOOH	$\nu_1(a')$	OH stretch	3570[a]	3110 w,b[b]	3470(3473)	3480(3·4)
	$\nu_2(a')$	CH stretch	2943	2960vs	†	2946(10·0)
	$\nu_3(a')$	C=O stretch	1770	1654s	1741(1744)	1747(6·0)
	$\nu_5(a')$	CH bend	1387	1398s		1385
	$\nu_6(a')$	OH bend	1229	1333w	†	†
	$\nu_4(a')$	C–O stretch	1105	1208m	1108(1109)	1111(2·3)
	$\nu_8(a'')$	CH bend	1033	1060w		
	$\nu_7(a')$	OCO bend	625	679m	625vb	†
	$\nu_9(a'')$	OH bend	625			†
CH_3OH		OH stretch (a')	3682[d]	3340 (0·4)vb[c]	3620(3623)	3628(4·2)
		CH_3 asym. stretch $(a' + a'')$	2977	2946(7·6) 2985(2·4)sh	†	2944(6·9)
		CH_3 sym. stretch (a')	2844	2837(10·0)	†	2839(10·0)
		CH_3 asym. bend $(a' + a'')$	1477	1470(1·6)sh	†	1460vb
		CH_3 sym. bend (a')	1455	1455(1·7)	†	
		OH bend (a')	1340		1331	
		CH_3 rock (a'')	1150	1160(0·4)	†	†
		CH_3 rock (a')	1100	1112(0·6)		
		CO stretch (a')	1034	1038(4·6)	1022(1022)	1028
		OH bend (a'')	232			

Figures in parentheses after the Raman frequencies indicate the relative intensities of the bands. In Tables 3 and 4 relative intensities of the guest bands are given only where it was felt that reasonable values could be obtained. Figures in parentheses after the i.r. values are the results of a previous infrared study (ref. 6).

[a] Ref. 24. [b] Ref. 25. [c] This work. [d] Ref. 26.

† Host band in this region.

breadth and intensity of this band can be obtained from Figure 3C where the ν(O–H) band of formic acid guest molecule at 3470 cm^{-1} is only just resolved.

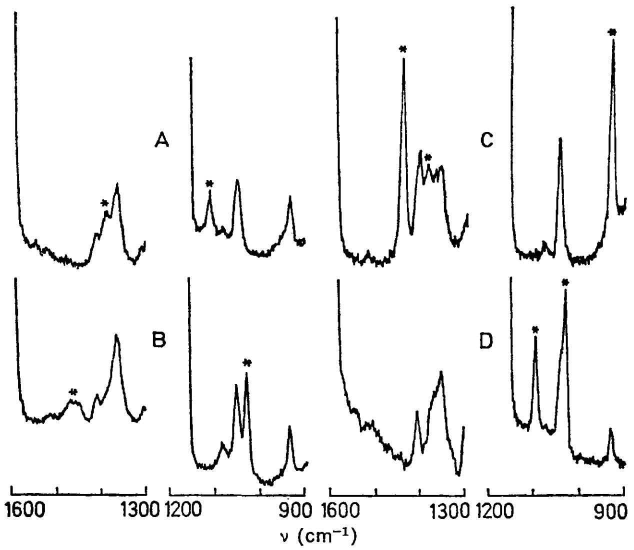

FIGURE 4 The Raman spectra (6 cm^{-1} slits) of the clathrates of (A) formic acid, (B) methanol, (C) acetonitrile, and (D) acetonitrile-d$_3$. Bands due to guest molecules marked *

*The acetonitrile and acetonitrile-*d$_3$ *guest molecules.* The acetonitrile clathrate is of interest since it is known to have a distorted host lattice compared to other quinol clathrates,[15] giving rise to some differences between the spectra of the acetonitrile host lattice compared to the host-lattice spectra of other clathrates as mentioned previously.

TABLE 4

Vibrational frequencies (in cm^{-1}) of CH_3CN and CD_3CN in the vapour and liquid states, and as guest molecules in β-quinol clathrates

	CH_3CN				CD_3CN			
	Vapour	Liquid	Quinol clathrate		Vapour	Liquid	Quinol clathrate	
	I.r. [a]	Raman [b]	I.r. [b]	Raman [b]	I.r. [a]	Raman [b]	I.r. [b]	Raman [b]
$\nu_5(e)$ CX_3 asym. stretch	3009	3005(0·6)	†	3007(0·2)	2257	2262(7·2)		2254(3·6)
$\nu_1(a_1)$ CX_3 sym. stretch	2954	2945(10·0)	†	2944(10·0)	2126	2116(10·0)		2115(10·0)
$\nu_3(a_1) + \nu_4(a_1)$	2305	2295(0·6)		2297(0·7)				
$\nu_2(a_1)$ CN stretch	2268	2255(6·2)	2258(2261)	2261(2·8)	2278	2262(7·2)	2270	2270(7·7)
$\nu_6(e)$ CX_3 asym. bend	1454	1445(0·2)	†	1442	1046	1040(0·3)	1032	1036
$\nu_3(a_1)$ CX_3 sym. bend	1389	1376(0·7)	†	1385	1110	1103(0·4)		1102
$\nu_7(e)$ CX_3 rock	1041	1045(0·1)	(1036?)	†	846		†	†
$\nu_4(a_1)$ CC stretch	920	922(2·2)	924(928?)	931 †	831	833(2·8)	†	†
ν_8 (e) CCN bend	361	381(1·5)	†	†	331	350(1·9)	345	348

Figures in parentheses after the Raman values indicate the relative peak-heights of bands. Figures in parentheses after the i.r. values are taken from ref. 6.

[a] E. L. Pace and L. J. Noe, *J. Chem. Phys.*, 1968, **49**, 5317. [b] This work.

† Host band in this region.

The bands of the acetonitrile, methanol, and formic acid guest molecules are very much weaker than the host-lattice bands. An indication of their relative intensities can be obtained from the illustration in ref. 13*b*. Several of the guest molecule bands occur in the regions 900—1150 cm^{-1} and 1300—1550 cm^{-1}, and the Raman spectra of the clathrates in these regions are compared in Figure 4. Comparison of the spectra of the formic acid and methanol clathrates clearly distinguishes the guest-molecule bands, whose assignment has been given in Table 3.

Due to its distorted structure the acetonitrile clathrate gives a different spectrum in the 1300—1550 cm^{-1} region, and comparison of this spectrum with that of the formic acid and methanol clathrate is not sufficient to identify the guest-molecule bands. Consequently the [$^2H_3$]acetonitrile clathrate was prepared on the assumption that the CH_3CN and CD_3CN clathrates have a similar structure.

Comparison of the spectra of these two clathrates gives the assignment shown in Table 4. In the 900—1150 cm^{-1} region it is evident that the $\nu_4(a_1)$ band of CH_3CN coincides with the host-lattice band at 931 cm^{-1}, and that bands due to CD_3CN occur at 1036 and 1102 cm^{-1}. Comparison of the CH_3CN and CD_3CN spectra in the 1300—1550 cm^{-1} region would suggest that the CH_3 deformation modes give rise to the bands at 1442 and 1385 cm^{-1}, since CD_3CN has no bands in this region. A significant difference between the liquid-phase and guest-molecule spectra of CH_3CN is that whilst the $\nu_3(a_1)$ CH_3 symmetric deformation mode gives rise to a more intense band than the $\nu_6(e)$ asymmetric mode in the liquid phase, the relative intensities seem to be in the reverse order for the guest molecule.

This change in relative intensities (as measured by peak-heights rather than areas) might well be associated with a reduction of rotational freedom about the three-fold axis of the guest molecule.

Another interesting difference is observed between the liquid-phase and guest-molecule Raman spectra of CD_3CN in the 2000—2400 cm^{-1} region (Figure 5). The liquid-phase Raman spectrum of CD_3CN has been reported and assigned by Evans and Bernstein,[27] and the wavenumber values reported in Table 4 are in moderate agreement

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[27] J. C. Evans and H. J. Bernstein, *Canad. J. Chem.*, 1955, **33**, 1746.

with their values. In the liquid-phase spectrum the band at 2060 cm^{-1} is due to the overtone $2\nu_6(a_1 + e)$, the 2116 cm^{-1} band to $\nu_1(a_1)$, the 2213 cm^{-1} band to the overtone $2\nu_3(a_1)$, and the $\nu_2(a_1)$ and $\nu_5(e)$ modes overlap in the 2262 cm^{-1} band, the a_1 modes in this region being in Fermi resonance. The weak band at 2177 cm^{-1} was not reported by Evans and Bernstein and could well be due to an impurity such as CD_2HCN, since a very weak band is also observed at 2981 cm^{-1}. The CD_3CN guest-molecule Raman spectrum is very similar to the liquid-phase spectrum except that in place of the single liquid band at 2262 cm^{-1}, two guest-molecule bands are observed at 2254 and 2270 cm^{-1}. These are tentatively assigned to the $\nu_5(e)$ and $\nu_2(a_1)$ modes respectively, on the assumption that the most intense band arises from an a_1 mode.

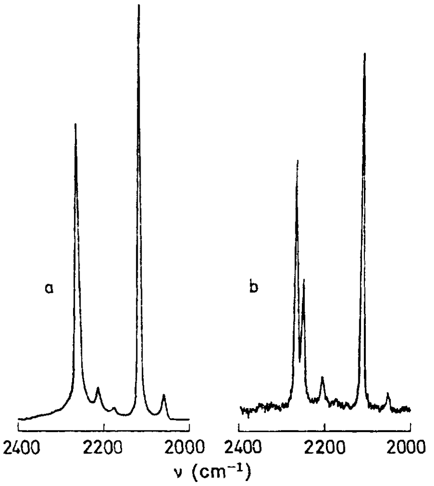

FIGURE 5 The Raman spectra (3 cm^{-1} slits) of CD_3CN (a) in the liquid state (b) as a guest molecule in the β-quinol clathrate

The $\nu_1(a_1)$ 2115 cm^{-1} band has a similar half band-width in both the liquid- and guest-molecule spectra whereas the two guest-molecule components at 2254 and 2270 cm^{-1} are very much sharper than the liquid-phase 2262 cm^{-1} band. These differences may also be associated with a reduction in the rotational freedom of the guest molecule about the three-fold axis. This is supported by the observation that there is a difference in the relative intensities of the $\nu_6(e)$ and $\nu_3(a_1)$ bands in the liquid- and guest-molecule spectra similar to the effect observed for CH_3CN.

The present vibrational study indicates that for clathrates with a centrosymmetric host lattice it is essential to obtain both the i.r. and Raman spectra in order to observe the maximum number of guest-molecule bands. For clathrates without a centrosymmetric host lattice (*e.g.* Dianin's compound [28]) the i.r. and Raman spectra will be very similar, and it is consequently necessary to rely on the differences in the i.r. and Raman band intensities in order to observe the maximum number of guest-molecule bands. Raman spectroscopy affords an additional advantage for studying the 2500—3300 cm^{-1} region of quinol clathrates, since bands arising from O–H stretching modes are very much less intense in the Raman than in the i.r. spectrum.

The use of clathrates, like the matrix-isolation technique, enables one to study the spectra of isolated molecules. One advantage of using clathrates is that the guest molecules can be conveniently studied at room temperature whereas matrix-isolated molecules have to be studied at temperatures as low as 4 K to prevent solute diffusion. 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. An obvious disadvantage of the use of clathrates is that the host-lattice bands can obscure many of the guest-molecule bands, but the present study would seem to indicate that the use of both i.r. and Raman spectroscopy can largely overcome this disadvantage for clathrates with a centrosymmetric host lattice.

EXPERIMENTAL

The clathrates of HCO_2H, CH_3OH, CH_3CN, and CD_3CN were prepared by the method of Palin and Powell [3] by cooling a saturated solution of quinol in these solvents. The clathrates of HCl, HBr, SO_2, H_2S, and C_2H_2 were prepared by bubbling the gas into a saturated solution of quinol in water (SO_2, H_2S) or ether (HCl, HBr, C_2H_2). The clathrate then precipitated out of solution. The carbon dioxide clathrate was prepared by slowly cooling a saturated aqueous solution of quinol from 70 °C to room temperature in a bomb containing CO_2 at a pressure of *ca.* 30 atm.

The clathrates of N_2 and O_2 were prepared by slowly cooling a saturated solution of quinol in n-propanol from 70 °C to room temperature in a bomb containing the gas at a pressure of *ca.* 100 atm as described by Burgiel *et al.*[8] The preparation of the oxygen clathrate was not entirely successful. Several preparations gave the quinol/quinone complex, quinhydrone, rather than the oxygen clathrate. A small quantity of the clathrate, sufficient to obtain a room-temperature Raman spectrum, but insufficient to obtain a low-temperature spectrum, was obtained from one preparation.

Attempts to prepare the hydrogen clathrate by the method of Burgiel *et al.*[8] were unsuccessful. The preparation gave β-quinol containing empty cavities. The far-i.r. spectra reported by Burgiel *et al.*[8] would not have distinguished between the hydrogen clathrate and an empty β-quinol lattice.

Samples of β-quinol were prepared by slow recrystallization of quinol from n-propanol as described by Evans and Richards.[29] These samples did in fact contain a very small quantity of included oxygen and nitrogen, the oxygen band at 1547 cm^{-1} being marked with a cross in Figure 1.

Raman Spectra.—The Raman spectra were excited by means of a CRL Model 52K krypton laser and recorded on a Cary 81 spectrometer. The majority of the spectra were obtained using 5208 Å excitation with a power of about 30 mW at the sample. The spectra of the yellow SO_2 and HBr clathrates were obtained using 5682 Å excitation with a power of 23 mW at the sample. The spectrometer was

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[28] J. E. D. Davies, unpublished results.

[29] D. F. Evans and R. E. Richards, *J. Chem. Soc.*, 1952, 3295, 3932.

calibrated using krypton emission lines. Most spectra were recorded using 2 or 3 cm^{-1} slits; the spectra shown in Figure 4 were obtained using 6 cm^{-1} slits. The low-temperature spectra were obtained by immersing a sample sealed under nitrogen in a dewar vessel of liquid nitrogen.

Infrared Spectra.—The i.r. spectra of mulls (Nujol and Kel-F) held between CsI plates were obtained in the range 4000—200 cm^{-1} on a PE 225 spectrometer.

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