The Raman Spectra of Some Guest Molecules in β -Quinol Clathrates

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The Raman spectra of some β -quinol clathrates together with "empty" β -quinol and α -quinol have been recorded at low-temperature in the range ~ 20 – 3300 cm^{-1} . The spectra indicates, that some of the enclosed molecular species are able to rotate in the host cavities. Bands below 200 cm^{-1} due to the guest molecules are tentatively assigned to translational motions.

In continuation of an earlier investigation on the clathrate compounds of HCHO , CH_3CHO , CH_3OH , CH_2CH_2 , HCOOH , and HCl together with "empty" β -quinol and α -quinol at room temperature,¹ is here reported an investigation of the same compounds at low temperature. Furthermore the Raman spectra of the guest molecules H_2S and HCN have been recorded both at room temperature and low temperature in the region ~ 20 – 3300 cm^{-1} .

EXPERIMENTAL

The preparation of all compounds except hydrogen cyanide clathrate has been described before.^{1,2} The clathrate of hydrogen cyanide was prepared by adding liquid hydrogen cyanide to a saturated solution of quinol in diethylether. The compound precipitated out of solution as the volatile components evaporated.

The Raman spectra were recorded with a spectrometer equipped with a Jarrell-Ash model 25–101 double grating monochromator. The exciting lines used were 4880 and 5145 Å obtained from a Spectra-Physics model 165–00 Argon-ion laser and 6471 and 6764 Å from a Spectra-Physics model 165–01 Krypton-ion laser.

The spectral resolution in any scan is better than 2.7 cm^{-1} below 200 cm^{-1} and above 1000 cm^{-1} better than 4.2 cm^{-1} depending on the exciting line used. The wavenumbers are believed to be accurate to within $\pm 1.5\text{ cm}^{-1}$.

THE GUEST SPECTRA ABOVE 200 cm^{-1}

The wavenumbers, half-widths and relative intensities of the bands assigned to the guest molecules in the eight clathrate compounds at room-temperature and approximately 93 K are given in Table 1. Furthermore the wavenumbers of the liquid- and gas-phase are given for comparison. The Raman spectra at room temperature of all the compounds except hydrogen cyanide have been previously reported.^{1–4} It should be mentioned that all observed bands except 2948 cm^{-1} in methanol and 2970 cm^{-1} in acetaldehyde belong to the totally symmetric species in the point groups of the free molecules.

At low temperature the population in the higher rotational energy levels is diminished, which will give rise to reduced half-widths of the bands in the Raman spectrum.

If the trapped guest molecules are able to rotate more or less hindered in the cavities, it will be expected, that bands with a big half-width at room-temperature must have a considerably diminished half-width at 93 K.

In the clathrates of hydrogen chloride, formaldehyde, methanol, formic acid, and acetaldehyde several relatively broad bands are observed at room temperature. At low temperature there is observed a considerable decrease in the half-widths of the broad bands of the three first mentioned compounds, which indicates that these molecules can rotate in the host cavities. Davies and Child¹⁷ have investigated the infrared spectrum of methanol clathrate and suggested that the enclosed molecules rotate in the cavities. This suggestion is supported by the Raman spectrum. It is also

Table 1. Guest bands in the Raman spectra above 200 cm⁻¹.

Guest Species	<i>T</i> ~ 300 K Wave-number cm ⁻¹	Rel. int. ^a	Half-width cm ⁻¹	<i>T</i> ~ 93 K Wave-number cm ⁻¹	Rel. int. ^a	Half-width cm ⁻¹	(Gas) Wave-number cm ⁻¹	(Liquid) Wave-number cm ⁻¹
HCl	2806	w	16	2804	m	8	2886 ⁵	2758 ⁶
HCN	2091	m	3	2093	m	3	2095 ⁷	2096 ⁸
H ₂ S	2585	w	5	2582	w	5	2611 ⁵	2574 ⁵
CH ₂ CH ₂	1350	w	8	1354	vw	8	1342 ⁹	1339 ¹⁰
CH ₃ OH	3630	w	13	3619	m	7	3682 ¹¹	3340 ²
	2948	w	14	2948	w	8	2977	2946
	2839	w	14	2844	m	10	2844	2837
	1033	w	11	1030	w	7	1034	1038
HCOOH	3484	vw	—	3470	w	13	3570 ¹²	3110 ¹³
	2948	w	8	2949	m	7	2943	2960
	1747	vw	—	1747	vw	—	1770	1654
	—	—	—	1379	vw	19	1387	1398
	1111	w	28	1116	m	25	1105	1208
HCHO	2790	w	17	2790	m	8	2780 ¹⁴	—
	1732	w	8	1728	m	7	1748	—
	1499	w	9	1500	vw	—	1507	—
CH ₃ CHO	2970	w	23	2976	w	—	2971 ¹⁵	— ¹⁶
	2922	m	12	2926	m	10	2918	2918
	2859	w	18	2866	vw	18	2844	—
	1729	m	9	1733	m	8	1721	1721

^a w = weak; vw = very weak; m = medium.

possible that the formic acid molecules rotate in the cavities because a new band, not observed at room temperature, is observed at low temperature and because the band at 3470 cm⁻¹ has sharpened so much that the half-width has become measurable. The half-widths of the bands in the acetaldehyde compound do not change essentially, which indicates stronger interaction in this case. In the other clathrates, where the half-widths of the bands at room temperature are small, there is, as expected, not observed any essential changes and it is not possible in these cases to conclude anything about rotation from these experiments.

The observed bands in the clathrate compounds do not show any regular shift relative to the gas-phase wavenumbers as a function of temperature.

THE SPECTRA BELOW 200 cm⁻¹

(i) *The quinol spectra.* The bands assigned to the β -quinol lattice vibrations are observed at approximately 69, 80, and 99 cm⁻¹ at room temperature; furthermore a weak band at approximately 186 cm⁻¹ is observed in most of the compounds. The intensity and wavenumber of each line vary from compound to compound. This is believed to be caused by different interaction between the host and the guest molecules. The variation in intensity could also be caused by overlap with bands due to the enclosed molecules.

In a recent communication Fukushima¹⁸ has reported the Raman spectrum of the acetonitrile clathrate. The three bands below 100 cm⁻¹ mentioned above are also observed by Fukushima, but he has assigned the band at highest wavenumber (96 cm⁻¹) to the guest molecules. Fukushima has not investigated further clath-

Fig. 1. The Raman spectra below 150 cm^{-1} of (1) "empty" β -quinol, (2) HCl-, (3) HCN-, (4) H₂S-, (5) CH₃CH₃-, (6) CH₃OH-, (7) HCOOH-, (8) HCHO-, and (9) CH₃CHO clathrate. (+): Bands assigned to the guest molecules. Abscissa unit: cm^{-1} .

rates nor "empty" β -quinol. In the present investigation it has become apparent that this band is observed in all clathrate compounds and in "empty" β -quinol. It is therefore most likely that the band should be assigned as a host lattice vibration and not to a rotational motion of the guest molecules.

In "empty" β -quinol at approximately 93 K the following bands are observed: 75(m), 86(s), 102(vs), 121(w), and 190 cm^{-1} (w). Those bands, which also are observed at room-temperature, show a shift towards higher wavenumber at low-temperature as expected. The bands mentioned above are also observed in the clathrates and show variation in intensity and wavenumber from compound to compound just as at room temperature. The spectra below 150 cm^{-1} are sketched in Fig. 1.

At room temperature the α -quinol spectrum is far more complex than the β -quinol spectrum as mentioned in Ref. 1. The bands of the former observed at room-temperature are given in Ref. 1. At 93 K the following ten bands are observed:

33(w), 48(w), 57(w), 67(s), 88(vs), 96(w), 107(vs), 124(w), 140(w), and 161 cm^{-1} (vw). This complex spectrum in comparison with the β -quinol spectrum reflects the lower symmetry of the α -modification.¹⁹

(ii) *The guest spectra.* In the region below 200 cm^{-1} bands due to translational and hindered rotational motions of the molecules enclosed in the cavities are expected.

As mentioned in Ref. 1 no bands due to the enclosed molecules are observed below 200 cm^{-1} at room temperature in the six investigated clathrates. The same is valid for the hydrogen sulfide and hydrogen cyanide clathrates.

At 93 K the population will be considerable in not only the rotational level $J=0$, but in several of the lower levels. Transitions from these levels will be comparable in intensity and it is expected that this will give rise to very broad bands, which cannot be discerned.

According to the point group symmetry of the free guest molecules the translational motions should be active in the Raman spectrum of all

Table 2. Guest bands below 200 cm^{-1} .

Guest Species	Raman ^a wave-number cm^{-1}	Temp. K	FIR wave-number cm^{-1}	Temp. K	Assignment ^b
HCl	51	93	52	1.2 ²²	trans.
	—	—	39	90–300 ²⁰	rot.
	—	—	25	1.2 ²²	rot.
HCN	—	—	20–90	90 ²⁰	rot.
	55	93	—	—	trans.
H ₂ S	—	—	74	18 ²³	trans.
	—	—	57	18 ²³	trans.
	45	93	—	—	trans.
CH ₂ CH ₂	52	93	—	—	trans.
	43	93	—	—	trans.
CH ₃ OH	—	—	73	80 ²³	trans.
	49	93	—	—	trans.
HCOOH	—	—	—	— ²⁴	—
HCHO	55	93	—	—	trans.
	29	93	—	—	trans.
CH ₃ CHO	43	93	—	—	trans.
	27	93	—	—	trans.

^a This work. ^b trans.=translational motion; rot.=rotational motion.

compounds except ethylene.

The bands observed below 200 cm^{-1} at 93 K, which are assigned to the guest molecules, are given in Table 2. For comparison FIR data, found in the literature, are also given. The spectra below 150 cm^{-1} are sketched in Fig. 1. The bands assigned to the enclosed molecules are all very weak and may possibly in some cases be questionable.

Because the rotational motions are believed to give rise to very broad bands, all observed bands are tentatively assigned as translational motions. It should be noted that also the bands observed in the ethylene compound have been assigned as translational motions, as it is likely that interaction with the host lattice may break down the selection rules.

When the mass of the enclosed molecules increases, one would expect that the wavenumber of the translational motions decreases. By comparing the wavenumbers of the translational motions given in Table 2 with the wavenumbers of the translational motions for a larger number of clathrate compounds found in the literature (N_2 , O_2 , NO , CO , SO_2 , CO_2)^{20,21} it can be seen, that such a dependence does not appear to exist.

As for the clathrates of ethylene, formaldehyde, and acetaldehyde no comparison between FIR and Raman data can be made because FIR investigations are lacking.

The FIR spectrum of hydrogen chloride clathrate was first investigated by Allen.²² He observed two bands at 52 cm^{-1} and approximately 25 cm^{-1} due to the enclosed molecules. The wavenumber of the latter band was found to be dependent on temperature and HCl concentration. It was shown that the band at 52 cm^{-1} was not altered by isotopic substitution (DCl) whereas the band at 25 cm^{-1} was considerably diminished. On the basis of these observations Allen assigned the band at 52 cm^{-1} to a translational and the band at 25 cm^{-1} to a rotational motion. A weak shoulder observed at 51 cm^{-1} in the Raman spectrum is in agreement with the FIR investigation assigned to a translational motion of the trapped molecules.

No bands due to the enclosed molecules are observed neither in the FIR nor Raman spectrum of formic acid clathrate.

Davies²⁰ has reported that the FIR spectrum

of hydrogen cyanide clathrate is very complex. In the Raman spectrum only one band at 55 cm^{-1} , assigned to the enclosed molecules, is observed in this region.

Barthel *et al.*²³ have observed two bands at 74 and 57 cm^{-1} due to the enclosed molecules in the FIR spectrum of hydrogen sulfide clathrate. Both bands are assigned to translational motions. In the Raman spectrum none of these bands have been observed, the former presumably because of overlap with a quinol band. Only one band at 45 cm^{-1} , assigned to the guest molecules, has been observed in the Raman spectrum.

The band at 49 cm^{-1} in the Raman spectrum of methanol clathrate has not been observed in the FIR spectrum.²³ The band at 73 cm^{-1} in the FIR spectrum cannot be found in the Raman spectrum possibly because of overlap with a quinol band. Fukushima²⁴ has also recorded the FIR spectrum of methanol clathrate, but he has not reported any band at all due to the guest molecules in the range below 100 cm^{-1} .

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