

Clathrate and Inclusion Compounds. Part 8 [1]. An Investigation of the Usefulness of the Spectral Subtraction Technique in Analysing the Infrared Spectra of Clathrates★

J. ERIC D. DAVIES

Department of Chemistry, University of Lancaster, Lancaster, Lancs, LA1 4YA, Great Britain

(Received: 11 September 1984)

Abstract. An investigation has been carried out into the usefulness of the spectral subtraction technique in analyzing the infrared spectra of the clathrates of quinol and of Dianin's compound. Due to the flexibility of the quinol host lattice, it is not advisable to use guest-free β -quinol as the reference if the host lattice in the clathrate is considerably distorted, as it is in the CH_3CN clathrate. In this case it is advisable to use another clathrate as the reference provided that the spectrum of the new reference does not contain guest bands in the region of interest. The Dianin's compound host lattice is less flexible than that of quinol, and guest-free Dianin's compound can be used as the reference irrespective of the size of the guest molecule. With both clathrates the spectral subtraction technique has revealed guest molecule bands which were previously obscured by host lattice bands.

Key words: Quinol clathrates, Dianin's compound clathrates, infrared spectra, spectral subtraction technique, difference spectra.

1. Introduction

The study of the infrared spectra of inclusion compounds can provide useful information such as (i) the state of aggregation and configuration of the guest molecule, (ii) the vibrational, rotational and translational motions of the guest molecule, (iii) the restricted internal rotations (torsions) of the guest molecule, (iv) host lattice – guest molecule interactions, and (v) the spectra of host lattices and guest molecules in unusual configurations [2, 3].

The main limitation to the usefulness of the technique arises from the fact that *both* components of the inclusion compound give a spectrum, with the guest molecule bands generally being weaker than the host lattice bands. There can therefore be extensive overlapping of the host lattice and guest molecule bands with some of the guest molecule bands being obscured by the host lattice bands (see Figure 1).

Considerable information can thus be lost by this overlap and this paper investigates the usefulness of the spectral subtraction technique in analyzing the infrared spectra of inclusion compounds.

Since this issue of the *Journal* is dedicated to Professor H. M. Powell it is appropriate that the subject of this investigation are two of the clathrate systems which he first characterized – those formed by quinol and by Dianin's compound.

★ Dedicated to Professor H. M. Powell.

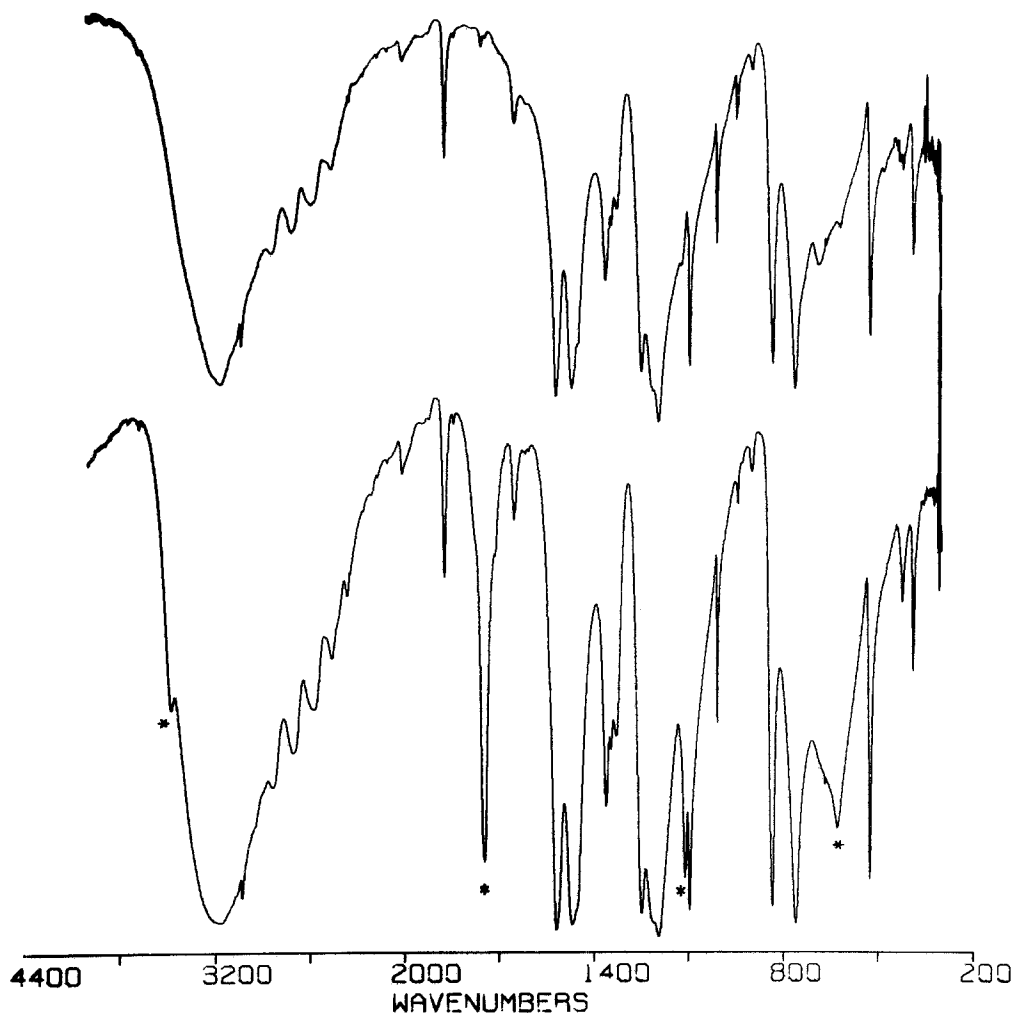


Fig. 1. The infrared spectra of KBr discs of β -quinol (upper trace) and of its formic acid clathrate (lower trace). Guest molecule bands marked*.

2. Experimental

The clathrates of quinol [4] and of Dianin's compound [5] were prepared by recrystallization from the liquid guest or by bubbling the gas through a saturated ethanol solution in the case of gaseous guests such as SO_2 and H_2S . The quinol clathrates were analyzed by determining the weight loss on melting the clathrate at 190°C .

The infrared spectra were recorded over the range $4000\text{--}225\text{ cm}^{-1}$ using a Nicolet MX-1 interferometer, and a Fourier transformation performed at 2 cm^{-1} resolution. Liquids were examined as thin films between CsI plates, and solids were examined as either KBr discs or HCBD mulls. The difference spectra were obtained using the Nicolet's spectral subtraction facility in which a *reference spectrum* is subtracted from a *sample spectrum* to give the *difference spectrum*.

3. Results and Discussion

3.1. THE QUINOL CLATHRATES

3.1.1. *The Choice of Reference*

It would seem that there can be only one choice of reference material *viz.* the β -polymorph of quinol containing empty cavities, which can be prepared by slow recrystallization of quinol from *n*-propanol [6]. The host lattice in the quinol clathrates can however display some flexibility depending on the size of the guest molecule, as illustrated by the variation in the unit cell dimensions on going from β -quinol ($a = 1655$, $c = 546$ pm) to the HCO_2H clathrate ($a = 1642$, $c = 565$ pm), to the SO_2 clathrate ($a = 1629$, $c = 581$ pm), to the CH_3CN clathrate ($a = 1595$, $c = 624$ pm) [4].

The variation in the unit cell dimensions gives rise to small differences in the vibrational spectra of the host lattice, and this is illustrated in Figure 2 where the residual intensity of the band at 3370 cm^{-1} increases as the mismatch between the sample and reference unit cell dimensions increases.

The quality of the difference spectrum can therefore be improved by using as a reference, not β -quinol, but another quinol clathrate whose unit cell dimensions are similar to those of the sample, with the added proviso that the guest molecule in the reference material does not give infrared bands in the region of interest.

This improvement is illustrated in Figure 3 where the mismatch between the unit cell dimensions is gradually reduced as the reference is changed from β -quinol (Figure 3a), to the SO_2 clathrate (Figure 3b), to the CD_3CN clathrate (Figure 3c). Note that the intensity of the residual OH peak at 3370 cm^{-1} decreases as the mismatch decreases.

3.1.2. *The Identification of the Guest Molecule Bands*

It is evident from Figures 2 and 3 that perfect subtractions remain a spectroscopist's dream and it is thus necessary to identify from the numerous weak bands in, e.g., Figure 2b the two bands arising from the two $\nu(\text{CH}_3)$ modes of guest CH_3CN . One possibility is to compare the subtracted spectrum with the Raman spectrum of the clathrate (Figure 4) since the Raman spectrum, unlike the infrared spectrum, is not dominated by the broad, intense band arising from the hydrogen-bonded OH groups of the host lattice [2]. This comparison leads to easy identification of the methyl bands in the difference spectrum (Figure 4c). Notice how difficult it is to identify the bands in the original spectrum, Figure 4b. Other illustrations of the usefulness of the comparison with Raman spectra can be found in [3] (Figure 7) and in [7] (Figure 4d).

The spectral subtraction technique can thus reveal guest molecule bands which are overlapped by the more intense host lattice bands.

Listed in Table I are the positions of guest molecule bands which have been revealed by the spectral subtraction technique and which were not observed in a previous infrared study [8].

3.2. CLATHRATES OF DIANIN'S COMPOUND

3.2.1. *The Choice of Reference*

The Dianin's compound host lattice does not show the wide variation in unit cell dimensions displayed by the β -quinol host lattice [9, 10], and is consequently more rigid than the latter.

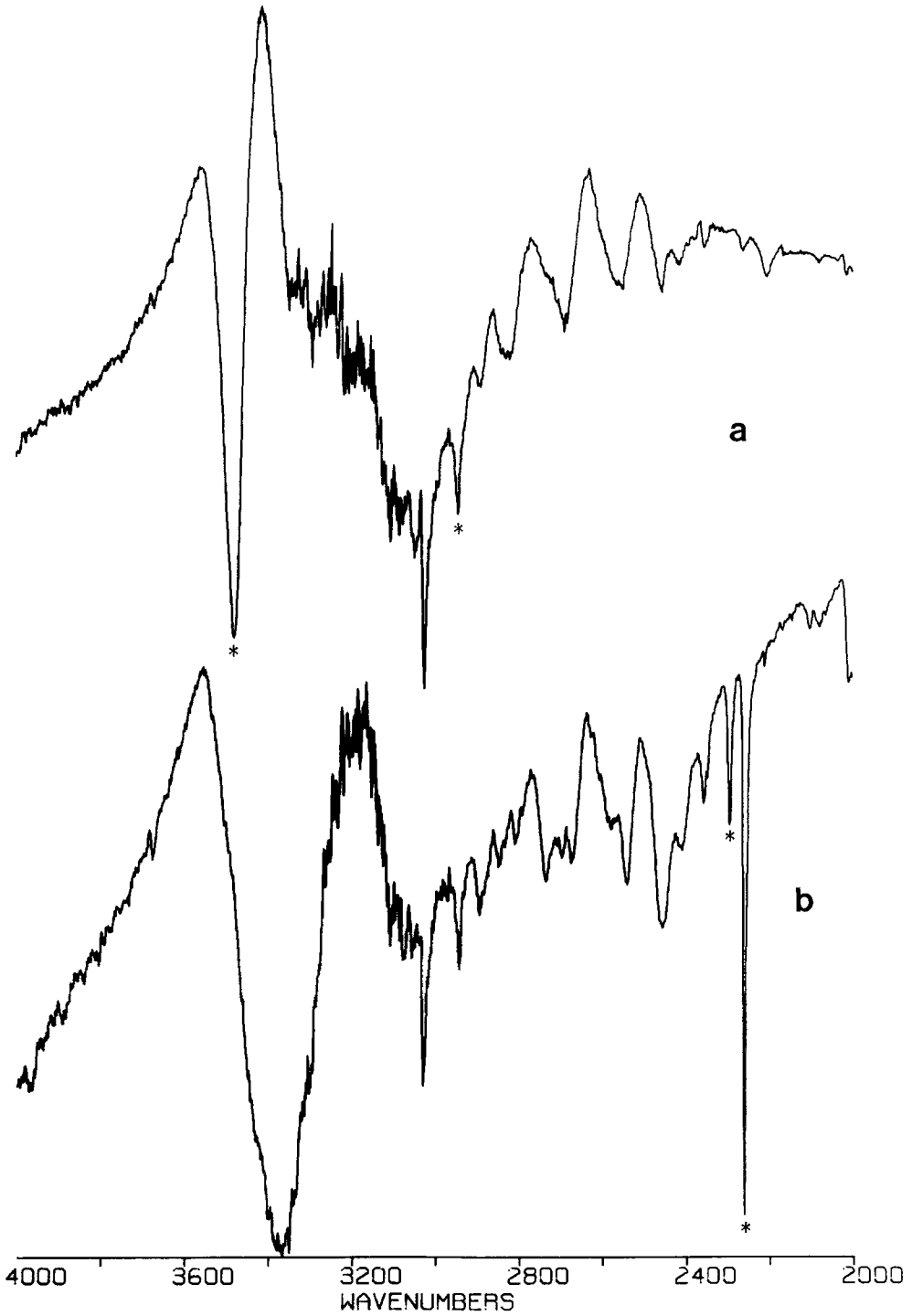


Fig. 2. Difference spectra, using β -quinol as the reference, of (a) the quinol/formic acid clathrate, (b) the quinol methyl cyanide clathrate. Guest molecule bands marked*.

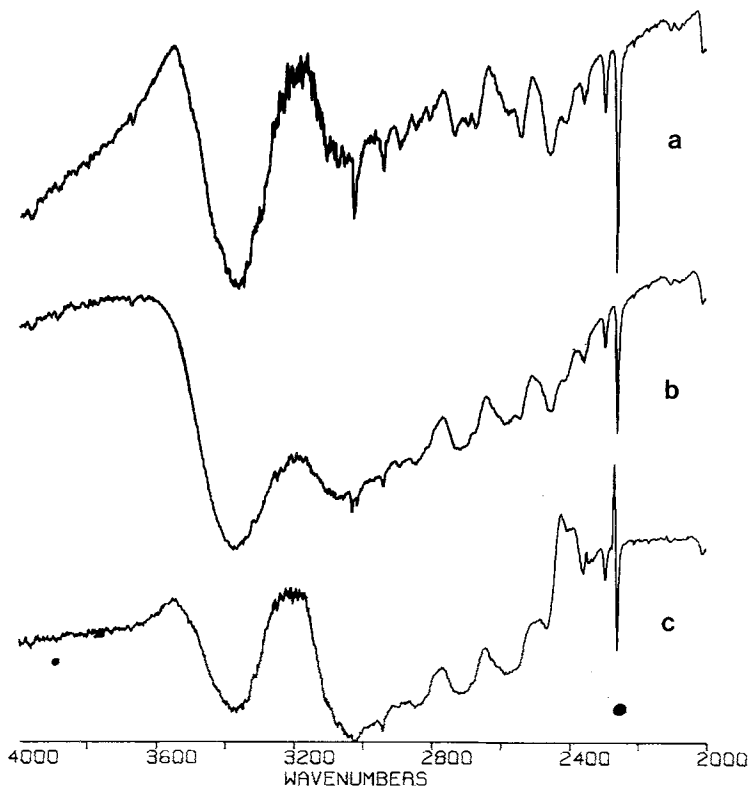


Fig. 3. Difference spectra using the quinol/ CH_3CN clathrate as the sample and (a) β -quinol, (b) the quinol/ SO_2 clathrate and (c) the quinol/ CD_3CN clathrate as the reference.

The empty host lattice can thus be used as the reference and, despite the complexity of its spectrum (Figure 5a), gives more satisfactory difference spectra than those given by β -quinol. The empty host lattice can thus be used as the reference in all the subtractions.

3.2.2. The Identification of Guest Molecule Bands

Despite the complexity of the infrared spectrum of Dianin's compound (Figure 5a), the difference spectrum (Figure 5c) readily reveals the $\nu(\text{C}-\text{O})$ band of the methanol guest molecule, a band which is not apparent as an additional band in the spectrum of the clathrate (Figure 5b).

The Dianin host lattice forms clathrates with a wide range of guest molecules [5] and this paper concentrates on brief discussions of the infrared spectra of two classes of guests: alcohols and carboxylic acids.

Alcohol Guest Molecules

The cavity in the Dianin host is larger than the cavity in the quinol host and it is thus possible to accommodate more than the single guest molecule per cavity found in the quinol clathrates.

Previous analytical [5, 11] and crystallographic [12] studies have shown that two molecules of methanol, ethanol and *n*-propanol can be accommodated per cavity, and the infrared

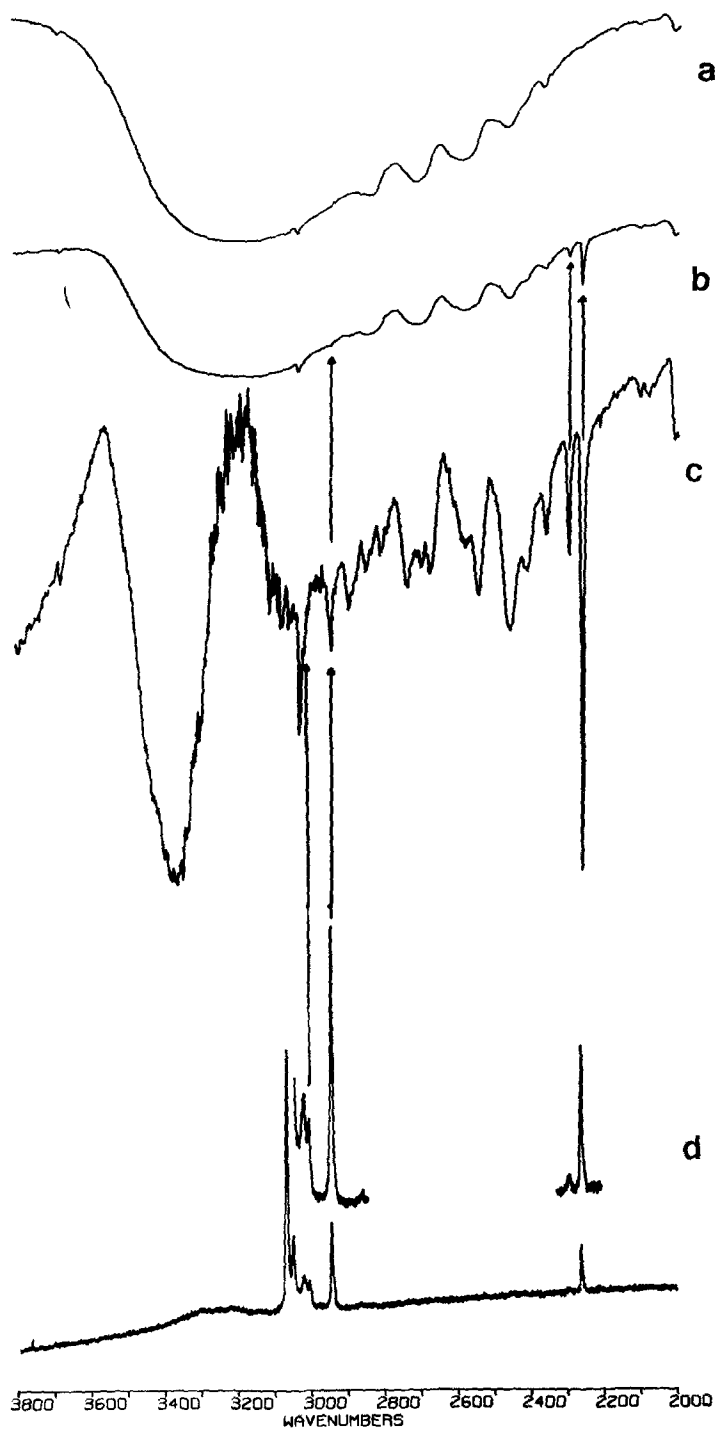


Fig. 4. The infrared spectra of (a) β -quinol and (b) the quinol/ CH_3CN clathrate. The difference spectrum (c) is compared with the Raman spectrum (d).

Table I. The vibrational frequencies (in cm^{-1}) of methanol, formic acid and acetonitrile in the vapour phase, and as guest molecules in β -quinol clathrates

Species	Mode	Vapour IR ^a	Quinol clathrate	
			IR ^b	Raman ^c
HCOOH	$\nu_1(a')$ OH stretch	3570	3481	3480(3.4)
	$\nu_2(a')$ CH stretch	2943	<u>2946</u>	2946(10.0)
	$\nu_3(a')$ C=O stretch	1770	1746	1747(6.0)
	$\nu_5(a')$ CH bend	1387		1385
	$\nu_6(a')$ OH bend	1229		±
	$\nu_4(a')$ C—O stretch	1105	1110	1111(2.3)
	$\nu_8(a'')$ CH bend	1033		
	$\nu_7(a')$ OCO bend	625	} 628vb	±
	$\nu_9(a'')$ OH bend	625		±
CH ₃ OH	OH stretch (a')	3682	3622	3628(4.2)
	CH ₃ asym. stretch ($a' + a''$)	2977	<u>2943</u>	2944(6.9)
	CH ₃ sym. stretch (a')	2844	<u>2835</u>	2839(10.0)
	CH ₃ asym. bend ($a' + a''$)	1477		} 1460vb
	CH ₃ sym. bend (a')	1455	<u>1450</u>	
	OH bend (a')	1340		
	CH ₃ rock (a'')	1150		±
	CH ₃ rock (a')	1100		
	CO stretch (a')	1034	1022	1028
	OH bend (a'')	232		
CH ₃ CN	$\nu_5(e)$ CH ₃ asym. stretch	3009	<u>3007</u>	3007(0.2)
	$\nu_1(a_1)$ CH ₃ sym. stretch	2954	<u>2942</u>	2944(10.0)
	$\nu_3(a_1) + \nu_4(a_1)$	2305	<u>2294</u>	2297(0.7)
	$\nu_3(a_1)$ CN stretch	2268	2260	2261(2.8)
	$\nu_6(e)$ CH ₃ asym. bend	1454	<u>1436</u>	1442
	$\nu_3(a_1)$ CH ₃ sym. bend	1389	<u>1390</u>	1385
	$\nu_7(e)$ CH ₃ rock	1041	<u>1034</u>	±
	$\nu_4(a_1)$ CC stretch	920	928	931 ±
$\nu_8(e)$ CCN bend	361		±	

^a Values taken from [8].

^b The underlined values are those of bands which have been observed for the first time during this study. The remaining values are those reported in [8].

^c Figures in parentheses after the Raman values indicate the relative peak heights of bands. No values are given for very weak and/or broad bands. The Raman values are taken from [8].

± Guest band obscured by a host lattice band.

spectra reported for the first time in Figure 6 confirm this deduction. The observation of two $\nu(\text{O—H})$ bands in the difference spectra is consistent with the presence of a hydrogen bonded noncyclic dimeric guest species [13].

Carboxylic Acid Guest Molecules

A previous infrared study of the clathrates of formic, acetic and hexanoic acids reported anomalous results for the acetic acid clathrate with the existence of two $\nu(\text{C=O})$ bands [14]. These were tentatively interpreted as arising from both monomeric and dimeric guest species,

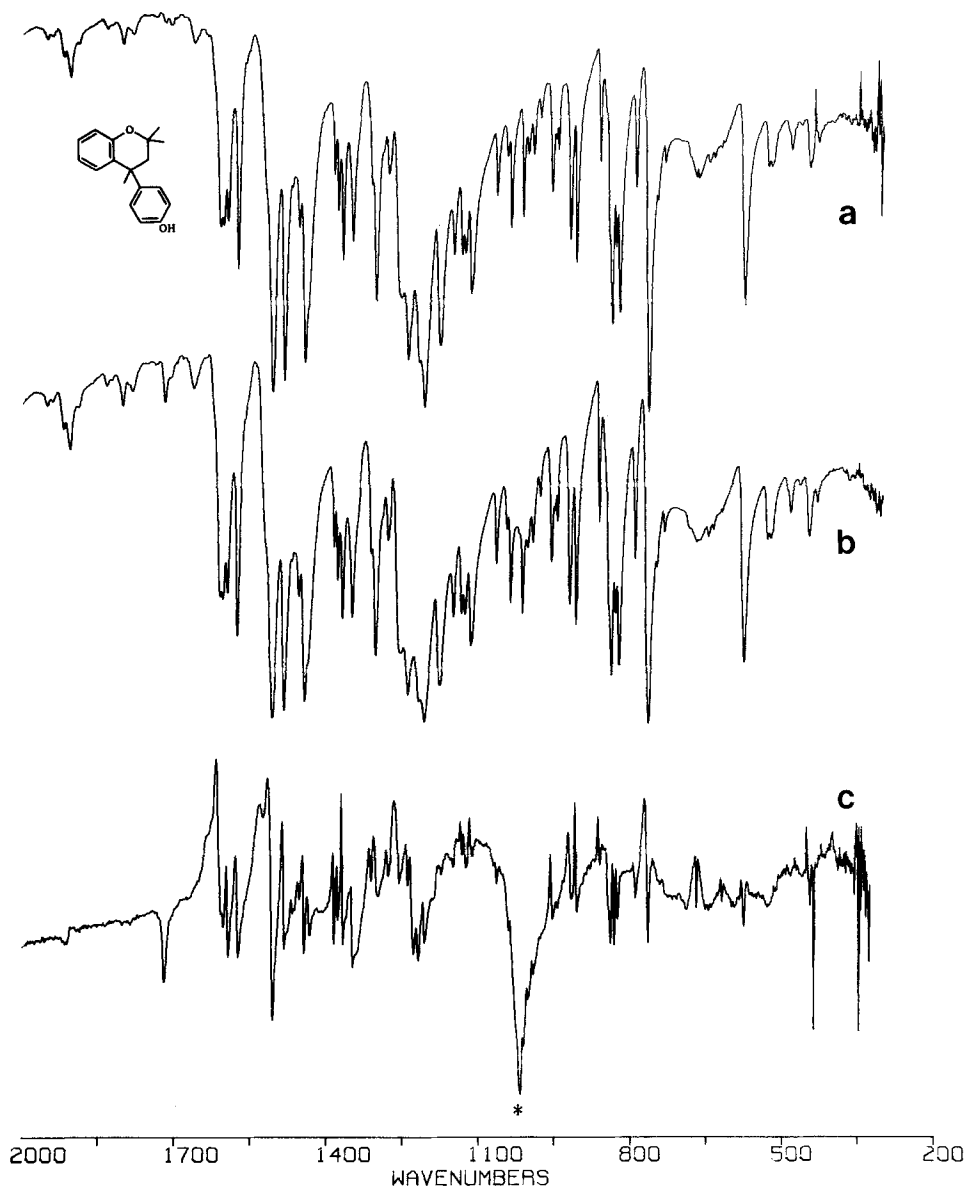


Fig. 5. The infrared spectra of (a) Dianin's compound and (b) its methanol clathrate, compared with the difference spectrum (c). Guest molecule band marked*.

although the bulk analysis of the sample used indicated the presence of two guest molecules per cavity. The spectrum of the formic acid clathrate was interpreted on the basis of a dimeric guest species and that of the hexanoic acid clathrate on the basis of a monomeric guest species.

The difference spectra obtained by us in the $\nu(\text{C}=\text{O})$ region for the six clathrates formed by the series of acids from formic to hexanoic are illustrated in Figure 7.

These spectra could be interpreted in terms of a gradual changeover from a dimeric species in the formic acid clathrate, to a mixture of dimeric and monomeric species in the acetic,

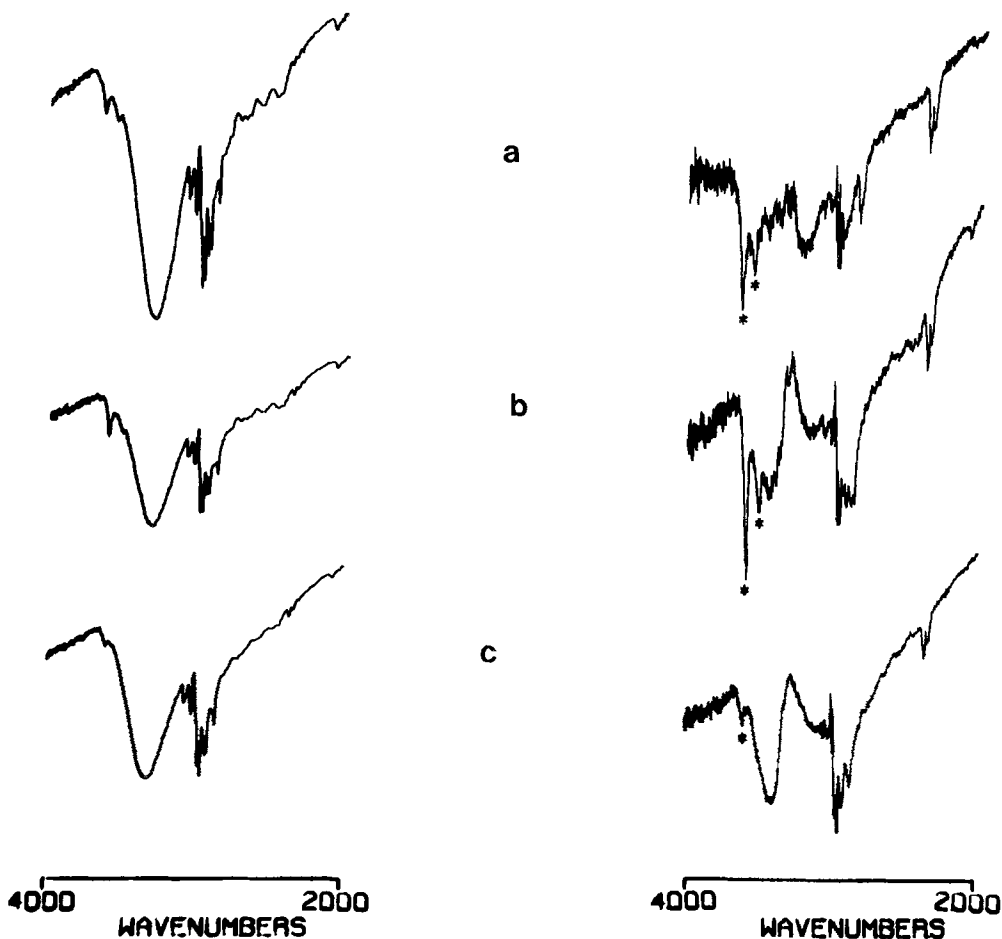


Fig. 6. The original (left) and difference (right) infrared spectra of the clathrates of Dianin's compound with (a) methanol, (b) ethanol and (c) *n*-propanol. Guest molecule bands marked*.

propionic, *n*-butyric and valeric acid clathrates, to a monomeric species in the hexanoic acid clathrate as the size of the guest molecule is increased. However, in view of Harrington's recent results [11] that the guest : cavity ratio is close to *three* for the acetic acid clathrate and greater than *two* for the propionic acid clathrate, a detailed interpretation of the spectra must be accompanied by reliable analyses of the samples, and such a study will be reported elsewhere.

4. Conclusions

The spectral subtraction technique has been shown to be useful in revealing the presence of guest molecule bands which are overlapped or obscured by host lattice bands. In the case of a host lattice which displays some flexibility depending on guest molecule size, the empty host lattice may not be the best choice of reference. In such cases another clathrate should be used as the reference with a good match of sample and reference unit cell dimensions. This

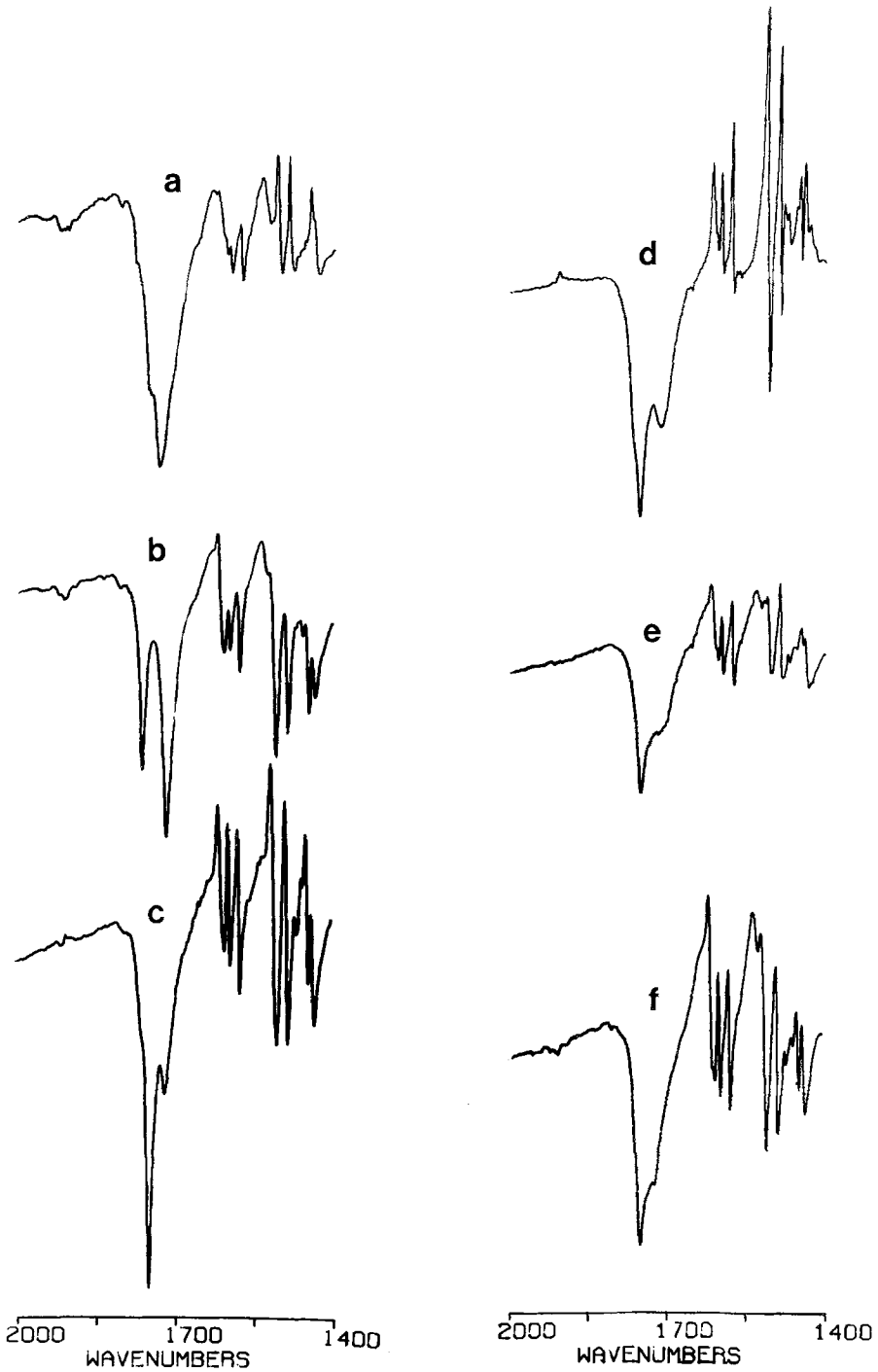


Fig. 7. The difference infrared spectra ($2000\text{--}1400\text{ cm}^{-1}$) of the clathrates of Dianin's compound with (a) formic acid, (b) acetic acid, (c) propionic acid, (d) *n*-butyric acid, (e) valeric acid and (f) *n*-hexanoic acid.

procedure would have to be used in cases where the empty host lattice forming polymorph is not available, e.g. urea and thiourea inclusion compounds.

References

1. Part 7: J. E. D. Davies, K. T. Holmes, and J. Waterhouse: *Pol. J. Chem.* **56**, 335 (1982).
2. J. E. D. Davies, in *Molecular Spectroscopy* (Eds. R. F. Barrow, D. A. Long, and J. Sheridan), The Chemical Society, London, Vol. 5, Chapter 2, pp. 60–105 (1978).
3. J. E. D. Davies in *Inclusion Compounds* (Eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol), Academic Press, London, Vol. 3, Chapter 2, pp. 37–68 (1984).
4. D. E. Palin and H. M. Powell: *J. Chem. Soc.* 815 (1948).
5. W. Baker, A. J. Floyd, J. F. W. McOmie, G. Pope, A. S. Weaving, and J. H. Wild: *J. Chem. Soc.* 2010 (1956).
6. D. F. Evans and R. E. Richards: *J. Chem. Soc.* 3295 (1952), *ibid.* 3932 (1952).
7. J. E. D. Davies, W. Kemula, H. M. Powell, and N. O. Smith: *J. Incl. Phenom.* **1**, 3 (1983/4).
8. J. E. D. Davies: *J. Chem. Soc., Dalton Trans.* 1182 (1972).
9. H. M. Powell and B. D. P. Wetters: *Chem. Ind. (London)* 256 (1955).
10. D. D. MacNicol in *Inclusion Compounds* (Eds. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol), Academic Press, London, Vol. 2, Chapter 1, pp. 1–45 (1984).
11. K. J. Harrington: *J. Therm. Anal.* **28**, 121 (1983).
12. J. L. Flippen, J. Karle, and I. L. Karle: *J. Am. Chem. Soc.* **92**, 3749 (1970).
13. L. Schriver, A. Burneau, and J. P. Perchard: *J. Chem. Phys.* **77**, 4926 (1982).
14. M. Davies and W. C. Child: *Spectrochim. Acta* **21**, 1195 (1965).