

CLATHRATE AND INCLUSION COMPOUNDS. PART 9 [1].
THE USE OF THE SPECTRAL SUBTRACTION AND ADDITION
TECHNIQUES IN ANALYSING THE VIBRATIONAL SPECTRA OF
INCLUSION COMPOUNDS

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ABSTRACT The usefulness of the spectral subtraction and addition techniques in analysing the infrared and Raman spectra of clathrates and intercalates has been explored. With both types of compounds the techniques have revealed guest molecule bands which were previously obscured by host lattice bands.

1. INTRODUCTION

The study of the infrared and Raman 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]

The main limitation to the usefulness of these spectroscopic techniques 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.

A previous paper [1] reported on the usefulness of the spectral subtraction technique in analysing the infrared spectra of clathrates formed by quinol and by Dianin's compound. Here we report on the use of the technique in analysing the infrared spectra of some intercalates of zirconium phosphate, and the Raman spectra of some clathrates of quinol.

2. EXPERIMENTAL

The clathrates of quinol were prepared by recrystallisation from the liquid guest or by bubbling the gas through a saturated ethanol solution [3]. Samples of the α -zirconium phosphate intercalates were kindly donated by Prof. U. Costantino, University of Perugia, Italy.

Infrared spectra were recorded from KBr discs over the range 4000-225 cm^{-1} using a Nicolet MX-1 interferometer, and Fourier transformed at 2 cm^{-1} resolution.

The Raman spectra were excited using the 514.5 nm line of a CRL argon ion laser, and recorded on a Cary 81 spectrometer, which had been modified to 90° viewing by Anaspec. The spectrometer was coupled to an Apple 11e microcomputer through an Adalab interface card. The spectra were plotted on a Hewlett Packard 7470A plotter.

3. RESULTS AND DISCUSSION

3.1 Infrared Spectra

A previous paper [1] has reported a detailed study of the usefulness of the technique in analysing the infrared spectra of clathrates formed by quinol and Dianin's compound. Figure 1 illustrates its application to the infrared spectrum of the imidazole intercalate of $\text{Zr}(\text{HPO}_4)_2$. The broad band at around 1000 cm^{-1} in Fig. 1a, arising from the P-O stretching modes, shows evidence in Fig. 1b of being overlapped by several imidazole bands. The difference spectrum (Fig. 1c) clearly illustrates the numerous bands which are obscured in Fig. 1b.

3.2 Raman Spectra

The Raman spectra of quinol clathrates, unlike the infrared spectra [4], are not dominated in the 2700-3700 cm^{-1} region by the OH band of the host lattice. It is consequently quite easy to observe the methanol guest molecule bands in the Raman spectrum of the clathrate (Fig. 2a), and the difference spectrum (Fig. 2c) merely highlights the intensity of the guest molecule bands.

One of the problems encountered in the previous infrared study [1] concerned the choice of reference. It was found that a large difference between the unit cell dimensions of the sample and reference led to poor difference spectra, and this effect can be clearly seen in Fig. 3c, the difference spectrum obtained when subtracting the spectrum of β -quinol from that of the acetonitrile clathrate. When the CD_3CN clathrate is used as the reference, there is a better compensation of the host lattice bands (Fig. 4c). Note also that the $\nu_5(\text{e})$ band of guest CH_3CN , marked with an asterisk in Fig. 4a, and which overlaps with a host lattice band is completely revealed in Fig. 4c.

It is also possible to simulate spectra of clathrates simply by adding two spectra. Figure 5c is the synthesised spectrum of the acetonitrile clathrate obtained by adding the spectra of β -quinol (Fig. 5a) and liquid CH_3CN (Fig. 5b). Note that the resulting spectrum (Fig. 5c) is not identical to that of the clathrate (Fig. 4a), since the acetonitrile guest molecule has lost some of the rotational freedom possessed by the molecule in the liquid phase. This loss of rotational freedom leads to many characteristic features in the Raman spectra of the β -quinol clathrates of CH_3CN and CD_3CN [4].

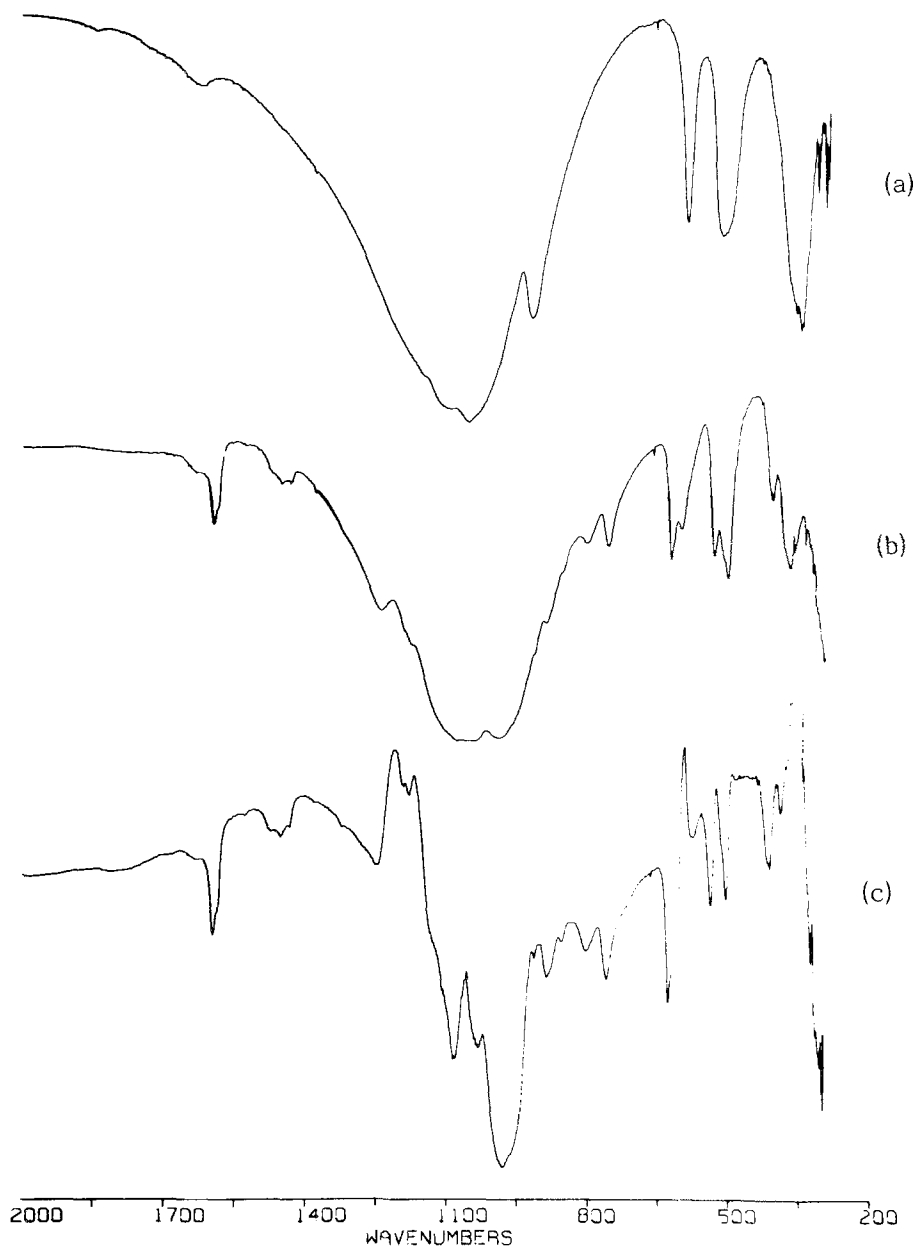


Figure 1. The infrared spectra of (a) α -Zr(HPO₄)₂, (b) its imidazole intercalate and (c) the difference spectrum obtained by subtracting (a) from (b).

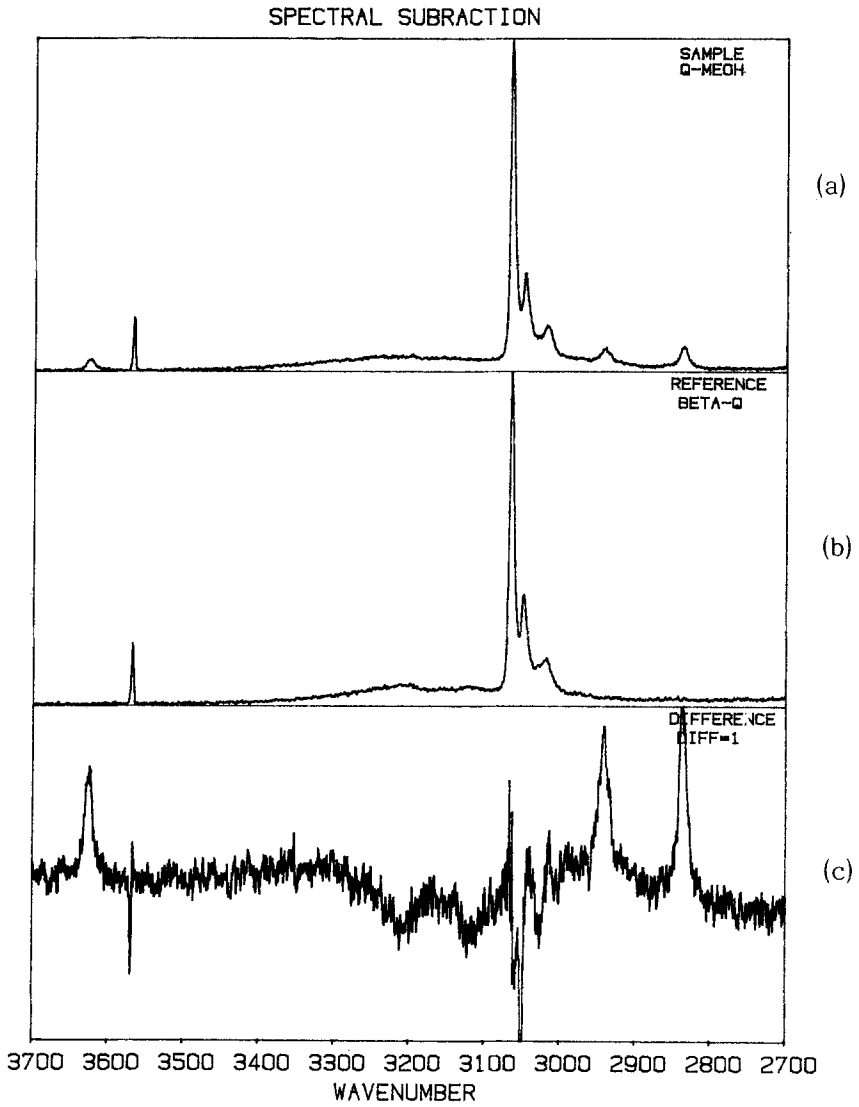


Figure 2. The Raman spectra of (a) the quinol methanol clathrate (b) β -quinol and (c) the difference spectrum.

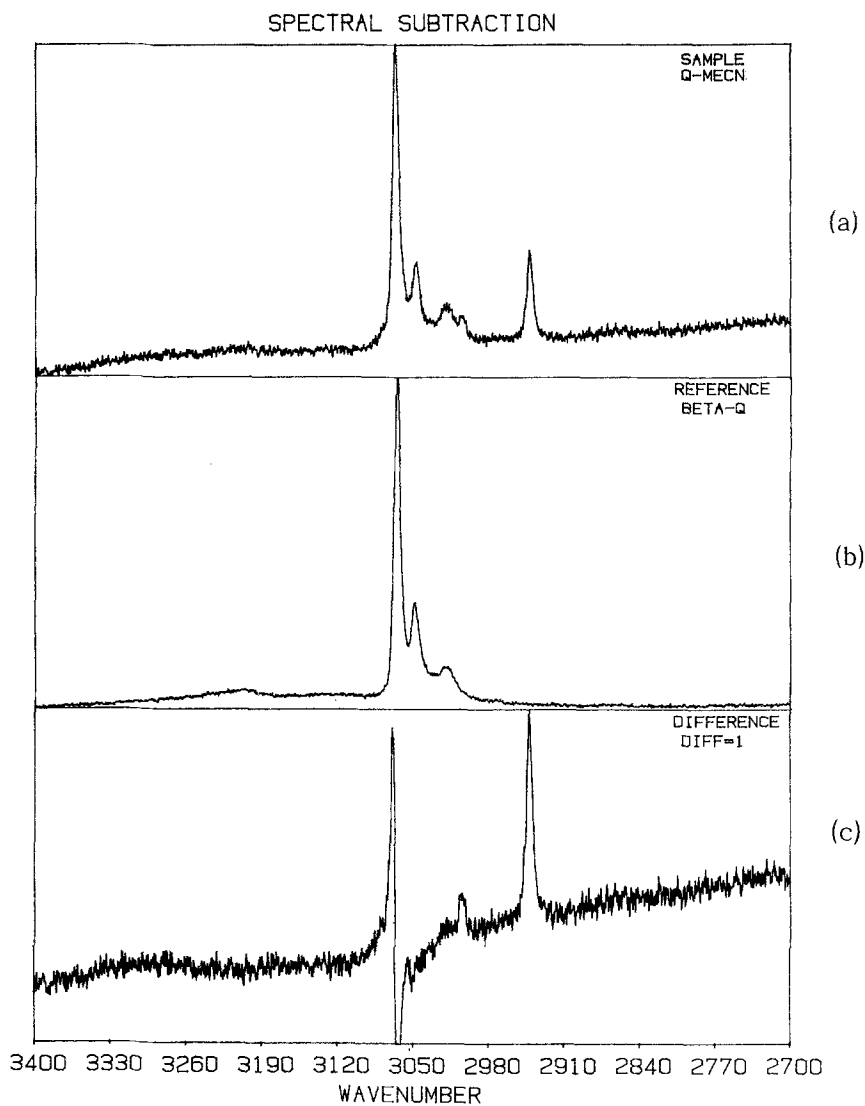


Figure 3. The Raman difference spectrum obtained (c) when the spectrum of β -quinol (b) is used as the reference.

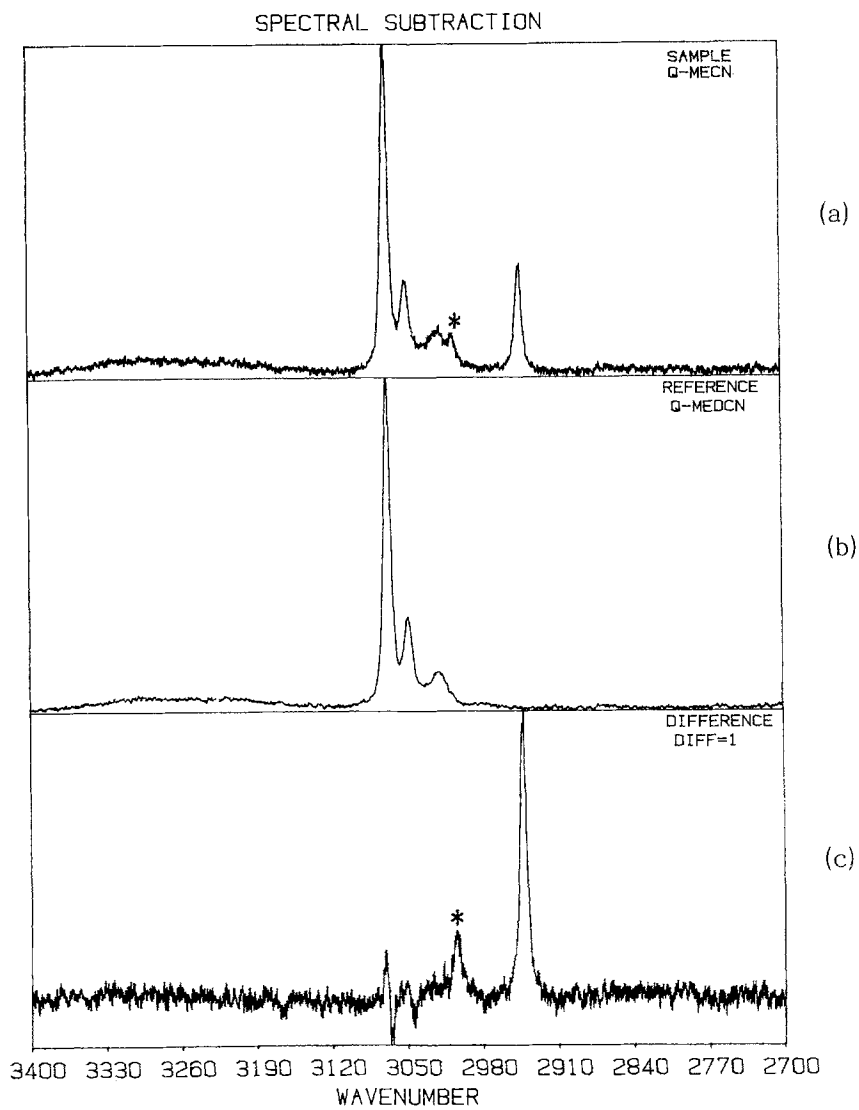


Figure 4. The Raman difference spectrum obtained (c) when the spectrum of quinol/ CD_3CN (b) is used as the reference.

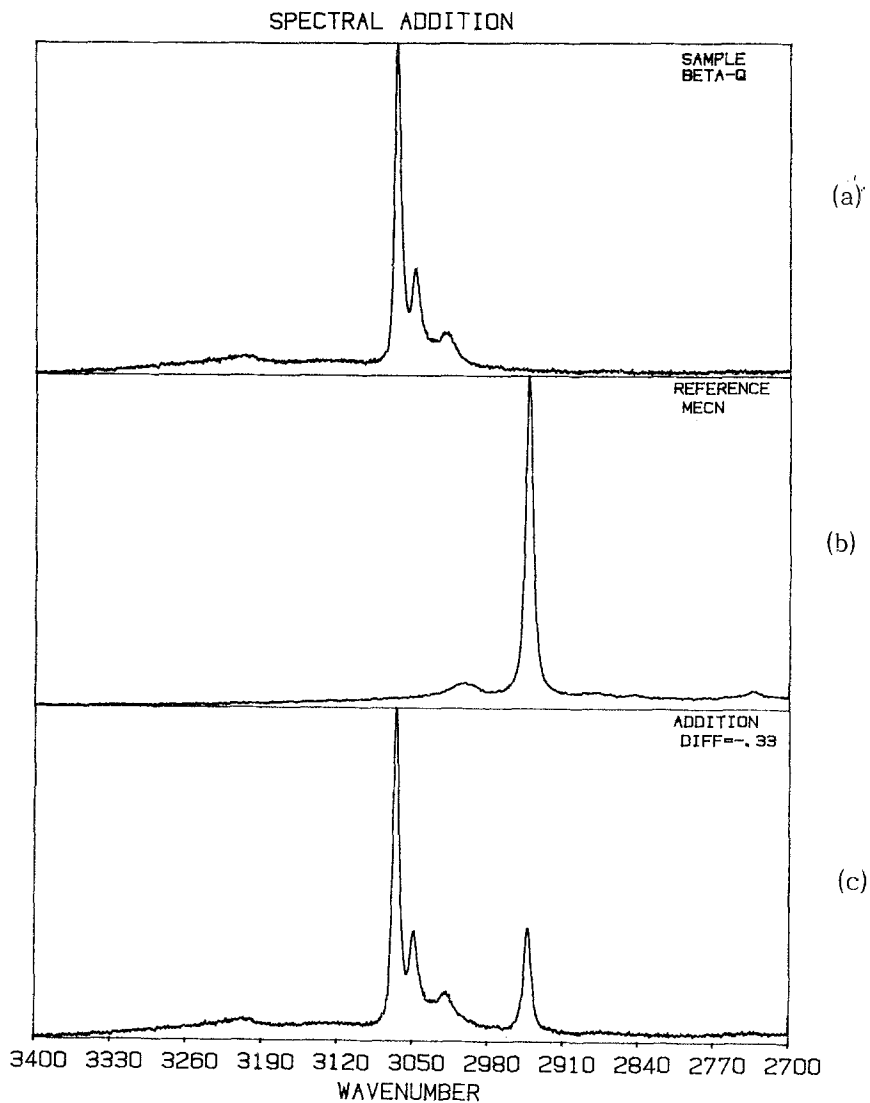


Figure 5. An illustration of the use of the spectral addition technique to simulate the Raman spectrum of the quinol/ CH_3CN clathrate (c) by adding the spectra of β -quinol (a) and liquid CH_3CN (b).³

4. CONCLUSIONS

The spectral subtraction technique can be applied equally successfully in the analysis of both the infrared and Raman spectra of inclusion compounds, revealing guest molecule bands which would otherwise be obscured by the more intense host lattice bands. The spectral addition technique is also shown to be useful in simulating clathrate spectra.

5. REFERENCES

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