

# Mid- and near-infrared study of the hydrogen-bonded complexes between pentachlorophenol and proton acceptors

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**ABSTRACT:** The mid- and near-IR spectra of hydrogen-bonded complexes involving pentachlorophenol (PCP) and organic bases (acetonitrile and *O*-bases) were investigated in carbon tetrachloride solution. The complex between PCP and acetonitrile (ACN) was studied at different ACN: CCl<sub>4</sub> concentration ratios. The frequency of the simultaneous transition  $\nu(\text{OH}\cdots\text{N}) + \nu(\text{C}\equiv\text{N})$  depends on this concentration ratio. The anharmonicity of the  $\nu(\text{OH}\cdots\text{N})$  vibration is discussed as a function of the Onsager parameter of the medium. The anharmonicity of the  $\nu(\text{OH}\cdots\text{O})$  vibration of complexes involving PCP and *O*-bases increases with increasing enthalpy of complex formation. Other near-IR observations are discussed. Copyright © 2000 John Wiley & Sons, Ltd.

**KEYWORDS:** pentachlorophenol–proton acceptor complexes; hydrogen-bonded complexes; infrared spectroscopy

## INTRODUCTION

Anharmonicity is a fundamental quantity for the understanding of the nature of hydrogen bonding and, to gain insight into the nature of this bonding, it is essential to obtain information on the shape of the potential which is intimately related to the anharmonicity.<sup>1</sup> The anharmonicity can be calculated by *ab initio* methods for simple hydrogen-bonded systems such as the  $[\text{HOH}\cdots\text{OH}]^-$  (Ref. 2) and  $[\text{H}_2\text{NH}\cdots\text{NH}]^-$  (Ref. 3) systems or complexes involving hydrogen halides.<sup>4–6</sup> For more complicated systems, the anharmonicity can be obtained experimentally by measuring overtones in the infrared spectrum. However, as pointed out recently by Sandorfy,<sup>7</sup> the near-IR region where the overtones of the OH and NH stretching vibrations are observed is seldom used by researchers and in the last two decades very few near-IR data on hydrogen-bonded systems and on the effect of hydrogen bonding on the anharmonicity of the vibrations have been published. The reason is perhaps that overtones of hydrogen-bonded species have a very weak intensity and that the near-IR spectra of polyatomic molecules contain numerous bands originating not only from overtones, but also from combination or simultaneous transitions, which make the assignment of the

absorptions particularly difficult.<sup>8,9</sup> In this paper, we report results for pentachlorophenol complexed with organic bases. This molecule has been used as a model proton donor for the study of the thermodynamic and spectroscopic properties of hydrogen-bonded systems.<sup>10–13</sup> In PCP, the self-association is strongly reduced because the OH groups are involved in intramolecular hydrogen bonds. Some near-IR data on complexes between PCP and acetonitrile (ACN)<sup>14,15</sup> or *O*-bases<sup>16</sup> are available in the literature. Complexes between ACN and other proton donors such as phenol,<sup>17,18</sup> chloroform<sup>19</sup> and aliphatic alcohols<sup>20</sup> have also been investigated. These studies were carried out in binary or ternary solutions, at different concentrations of proton donor or proton acceptor molecules, so that no definitive conclusion on the variation of anharmonicity with the hydrogen bond strength could be drawn. Very recently, the vibrational spectrum of PCP has been analyzed and a combination of theoretical calculations and experimental data allowed us to assign the fundamental vibrations and their overtones or combinations in a very broad frequency domain (10000–400 cm<sup>-1</sup>).<sup>21</sup> This paper is arranged as follows: in the first part, the mid- and near-IR spectra of the PCP–ACN complex are considered in order to discuss the influence of the permittivity of the medium on the anharmonicity of the  $\nu(\text{OH}\cdots\text{N})$  vibration. In the second part, the spectra of complexes between PCP and *O*-bases are presented and the anharmonicity of the  $\nu(\text{OH}\cdots\text{O})$  vibration is

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discussed as a function of the strength of the hydrogen bond interaction.

## EXPERIMENTAL

IR spectra for the determination of the equilibrium constants were recorded on a Perkin-Elmer 883 instrument. The equilibrium constants are defined as

$$K = C_{ab}/C_a C_b = (F_a - C_a)/C_a(F_b - C_{ab})$$

where  $C_{ab}$ ,  $C_a$  and  $C_b$  are the molar concentrations of the complex, free pentachlorophenol and free base, respectively, and  $F_a$  and  $F_b$  are the formal concentrations of the proton donor and proton acceptor, respectively. The concentration  $C_a$  was determined from the absorbance of the  $\nu(\text{OH})$  stretching vibration of the free proton donor lying at  $3424 \text{ cm}^{-1}$ . The concentration  $F_a$  ranged between  $5 \times 10^{-3}$  and  $10 \times 10^{-3} \text{ mol dm}^{-3}$  and the base was always in excess. The measurements of the equilibrium constants were carried out in carbon tetrachloride. In order to have reliable intensities, the near-IR spectra were studied at a higher concentration of PCP ( $0.1 \text{ mol dm}^{-3}$ ) in binary mixtures (carbon tetrachloride–basic solvent) of various composition. At this concentration, no dimer band could be detected in the IR spectra.

The spectra in the mid- and near-IR region were recorded on a Bruker 66 Fourier transform IR spectrometer. The resolution was  $2 \text{ cm}^{-1}$  and the wavenumber accuracy  $0.01 \text{ cm}^{-1}$ . In the mid-IR region, the spectrometer was equipped with a Globar source, a KBr beamsplitter and a DTGS detector. The pathlength of the KBr cells used for the mid-IR region was  $0.3 \text{ cm}$ . In the near-IR region, a tungsten lamp was used as the source and a  $\text{CaF}_2$  beamsplitter and a cooled InSb detector were employed. The pathlength of the quartz cell was  $5 \text{ cm}$ .

The overtones of the  $\nu(\text{CH})$  vibrations often overlap with the broad absorption of the hydrogen-bonded complexes. For this reason, PCP was used as the proton donor and deuterated bases (diethyl- $d_{10}$  ether, dioxane- $d_8$  and tetrahydrofuran- $d_8$ ) were used as proton acceptors.

The spectra were analysed and subtracted using the Galactic GRAMS/386 program. To detect more accurately the position for very dilute solutions, second-derivative and curve-fitting methods were used. The errors in the maximum of the stretching bands of the complexes were  $\pm 5 \text{ cm}^{-1}$  for the dilute solutions,  $\pm 2 \text{ cm}^{-1}$  for the concentrated solution and  $\pm 0.5 \text{ cm}^{-1}$  for the other narrow absorptions.

PCP from Acros Chemica was crystallized from a petroleum–ether mixture. Carbon tetrachloride from Janssen Chimica was dried over molecular sieves. The bases and deuterated counterparts from Acros Chemica were used without further purification.

## RESULTS AND DISCUSSION

It is useful to remember that the second-order perturbation theory allows one to compute the mechanical anharmonicity  $X_{12}$  from the experimental frequencies of the fundamental ( $\nu^{01}$ ) and first overtone ( $\nu^{02}$ ).

$$X_{12} = \nu_{01} - \nu_{02}/2 \quad (1)$$

The second-order perturbation theory can be considered as valid for weakly hydrogen-bonded systems, but has been questioned for strongly interacting systems.<sup>22</sup>

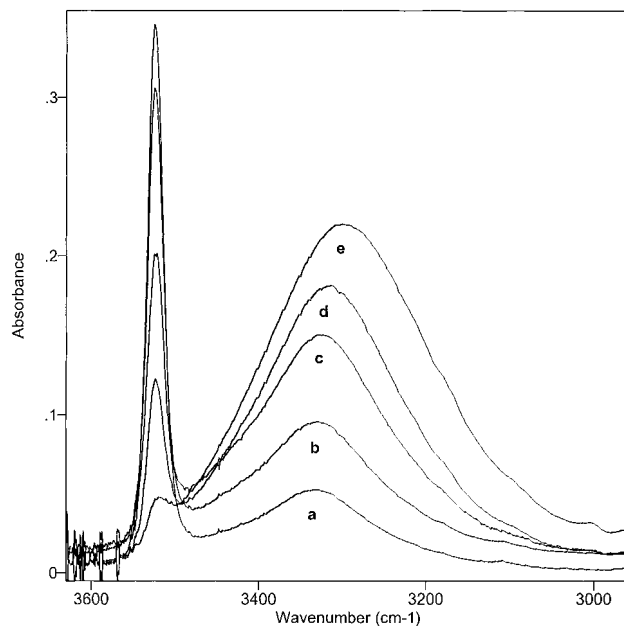
The coupling constants ( $X^{\text{coup}1}$ ) even in the polyatomic case are given by the equation

$$X^{\text{coup}1} = (\nu^{1_{01}} + \nu^{2_{01}}) - \nu^{\text{comb}} \quad (2)$$

where the superscripts 1, 2 and comb refer to two different normal modes and the combination between them, respectively.

### Mid- and near-IR spectra of PCP–ACN solutions in carbon tetrachloride

The existence of  $\text{OH}\cdots\pi$  complexes can be ruled out. Indeed, the molecular potential around the nitriles clearly indicates the N lone pair as the preferential site for H-bond formation;<sup>23</sup> further, no absorption to the high-frequency side of the main  $\nu_{01}(\text{OH}\cdots\text{N})$  complex band could be detected. The mid-IR spectra in the  $\nu(\text{OH})$  region are shown in Fig. 1 and the results are summarized



**Figure 1.** IR spectra of PCP–ACN solutions in the  $\nu_{01}(\text{OH}\cdots\text{N})$  region.  $C_{\text{PCP}} = 0.1 \text{ mol dm}^{-3}$ ;  $C_{\text{ACN}} =$  (a) 0.1, (b) 0.2, (c) 0.5, (d) 1 and (e)  $5 \text{ mol dm}^{-3}$

**Table 1.** Mid-IR data ( $\text{cm}^{-1}$ ) for solutions of PCP ( $c = 0.1 \text{ mol dm}^{-3}$ ) and ACN at different concentrations in carbon tetrachloride<sup>a</sup>

$c$ ( $\text{mol dm}^{-3}$ ) <sup>b</sup>	$\nu_{01}(\text{OH}\cdots\text{N})$	$\nu(\text{C}\equiv\text{N})^{\text{C}}$	$\nu(\text{C}\equiv\text{N})^{\text{F}}$	Combination
0.1 (0.01)	3332	2267	2256.5	2294
0.2 (0.02)	3328	2267	2256	2294
0.5 (0.04)	3325	2266	2255.5	2293
1 (0.09)	3315	2266	2255	2293
3 (0.26)	3304	2263	2254	2292.5
5 (0.39)	3298	2262	2254	2292
7 (0.51)	3296	—	2254	2292
19 (0.99)	3294	—	2254	2292
Pure				2292

<sup>a</sup>  $\nu(\text{C}\equiv\text{N})^{\text{C}}$  and  $\nu(\text{C}\equiv\text{N})^{\text{F}}$  refer to the frequencies in the complex and in free ACN, respectively.

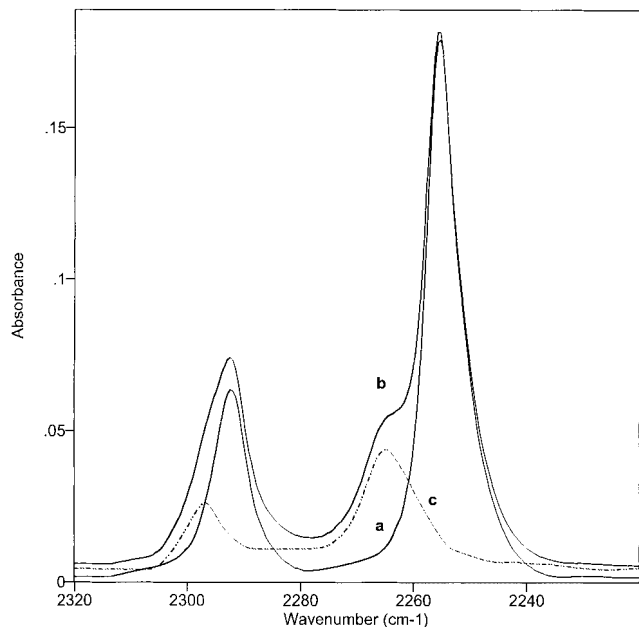
<sup>b</sup> The mole fraction of ACN is given in parentheses.

in Table 1. The maximum of the  $\nu_{01}(\text{OH}\cdots\text{N})$  absorption depends on the concentration of ACN, varying from 3332 to 3294  $\text{cm}^{-1}$  when the ACN concentration varies from 0.1 to 19  $\text{mol dm}^{-3}$  (or from 0.01 to 0.99 in mole fraction). This concentration dependence has also been observed for complexes involving phenol and other aliphatic nitriles.<sup>24</sup>

Examples of the spectra observed in the  $\nu(\text{C}\equiv\text{N})$  region are shown in Fig. 2. In pure ACN, the  $\nu(\text{C}\equiv\text{N})$  vibration is observed at 2253.5  $\text{cm}^{-1}$ ; this band is asymmetric and the secondary absorption observed at the low-frequency side of the main band has been assigned to the ACN dimer<sup>25</sup> or to a hot band.<sup>26</sup> A second band is observed at 2292  $\text{cm}^{-1}$  which originates from a combination of both  $\text{CH}_3$  bending and CC stretching modes in resonance with  $\nu_2$ .<sup>27</sup> Complex formation with

PCP results in a shift of the  $\nu(\text{C}\equiv\text{N})$  vibration to higher frequencies, in agreement with literature data on complexes between proton donors and nitriles.<sup>24,27–31</sup> The frequency of this absorption depends on the ACN concentration and is observed between 2267 and 2262  $\text{cm}^{-1}$ . The frequency of the free  $\nu(\text{C}\equiv\text{N})$  absorption also depends slightly on the ACN concentration, being observed at 2256.5  $\text{cm}^{-1}$  at very low concentration and at 2254  $\text{cm}^{-1}$  at a concentration of 3  $\text{mol dm}^{-3}$ . The same remark also holds for the combination band which is observed at 2294  $\text{cm}^{-1}$  in dilute carbon tetrachloride and at 2292  $\text{cm}^{-1}$  in pure ACN. In the presence of PCP, a broadening of this band is observed and after deconvolution of the spectrum, a band at 2297  $\text{cm}^{-1}$  is obtained. It is interesting to compare the present results with recent Raman data on binary mixtures of ACN and hydroxylic proton donors (water, methanol, ethanol, propanol) of various composition.<sup>32</sup> The frequency of the free  $\nu(\text{C}\equiv\text{N})$  band varies as a function of solvent by less than 0.5  $\text{cm}^{-1}$  and is almost the same as that observed in neat ACN (2253.2  $\text{cm}^{-1}$ ), in contrast with the results of the present work. For ACN–water mixtures, the  $\nu(\text{C}=\text{N}\cdots\text{HO})$  band moves progressively from 2259.7 to 2255.7  $\text{cm}^{-1}$  when the mole fraction of ACN increases from 0.001 to 0.9. This effect was explained by a steadily decreasing degree of solvation of ACN by the water molecules. This explanation cannot account for the observations of the present work, because our spectra were taken at a low concentration of PCP (0.1  $\text{mol dm}^{-3}$ ) where only 1:1 hydrogen bonds are formed. We attribute the red shift of the free and bonded  $\nu(\text{C}\equiv\text{N})$  absorptions to the increase in the polarity of the medium, which increases with increasing ACN concentration. This will be discussed later in connection with the anharmonicity of the  $\nu(\text{OH}\cdots\text{N})$  vibration.

The near-IR spectra (7400–5400  $\text{cm}^{-1}$ ) of solutions of PCP containing variable amounts of ACN are reproduced in Fig. 3. The broad absorption observed between 6538 and 6374  $\text{cm}^{-1}$  is assigned to the first overtone of the  $\nu(\text{OH}\cdots\text{N})$  vibration. Like the fundamental transition, its frequency also depends on the ACN concentration. In a binary solution of PCP (0.5  $\text{mol dm}^{-3}$ ) and ACN, the



**Figure 2.** IR spectrum of PCP–ACN– $\text{CCl}_4$  solution in the  $\nu_{01}(\text{C}\equiv\text{N})$  region. (a) Spectrum of ACN ( $c = 0.5 \text{ mol dm}^{-3}$ ) in  $\text{CCl}_4$ ; (b) spectrum of the same solution containing 0.1  $\text{mol dm}^{-3}$  of PCP; (c) difference spectrum [(b)–(a)]

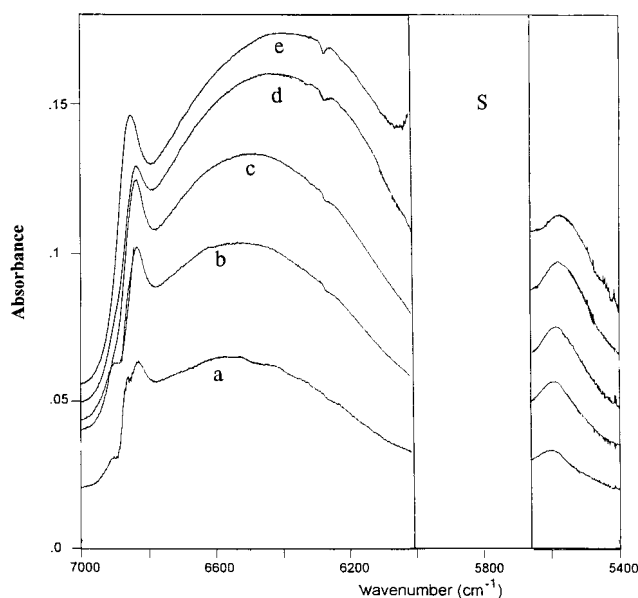
**Table 2.** Near-IR data ( $\text{cm}^{-1}$ ) for solutions of PCP ( $0.1 \text{ mol dm}^{-3}$ ) and ACN at different concentrations in carbon tetrachloride, anharmonicity ( $X_{12}$ ) of the  $\nu(\text{OH}\cdots\text{N})$  vibration and Onsager parameter of the medium

$c$ ( $\text{mol dm}^{-3}$ )	$\nu_{02}(\text{OH}\cdots\text{N})$	$\nu^{*\text{exp}}$	$\nu^{*\text{calc}}$	$X_{12}$	$(\epsilon-1)(\epsilon+2)$
0.1	6538	5601	5599	$63 \pm 5$	0.259
0.2	6530	5598	5594	$63 \pm 5$	0.351
0.5	6516	5592	5591	$67 \pm 5$	0.402
1	6480	5583	5581	$75 \pm 2$	0.503
3	6436	5570	5567	$86 \pm 2$	0.696
5	6414	5564	5560	$91 \pm 2$	0.774
7	6401	5560	—	$96 \pm 2$	0.823
19	6374	5560	—	$107 \pm 2$	0.923

$\nu_{02}(\text{OH}\cdots\text{N})$  vibration was observed at  $6446 \text{ cm}^{-1}$ ,<sup>14,15</sup> and a second absorption was observed at  $5563 \text{ cm}^{-1}$ . This absorption was assigned to a simultaneous transition ( $\nu^*$ ) involving the  $\nu_{01}(\text{OH}\cdots\text{N})$  and  $\nu(\text{C}\equiv\text{N})$  vibrations in the  $\text{OH}\cdots\text{N}\equiv\text{C}$  hydrogen bond. The simultaneous vibrational quantum jump in two groups coupled together by a hydrogen bond has been observed in self-associated  $\text{HCl}$ ,<sup>33</sup> self-associated alcohols<sup>34</sup> and water.<sup>35</sup> In  $\text{OH}\cdots\text{OH}\cdots$  hydrogen bonds, the simultaneous excitation involves the  $\nu_{01}(\text{OH})$  vibration in two neighbouring OH groups. The experimental  $\nu^*$  values ( $\nu^{*\text{exp}}$ ) are indicated in Table 2. This table also indicates the  $\nu^*$  value calculated by the expression

$$\nu^{*\text{calc}} = \nu_{01}(\text{OH}\cdots\text{N}) + \nu(\text{C}\equiv\text{N}) \quad (3)$$

The difference between the experimental and calculated values range between 4 and  $-3 \text{ cm}^{-1}$ . The concentration dependence confirms the assignment of Refs. 14 and 15.

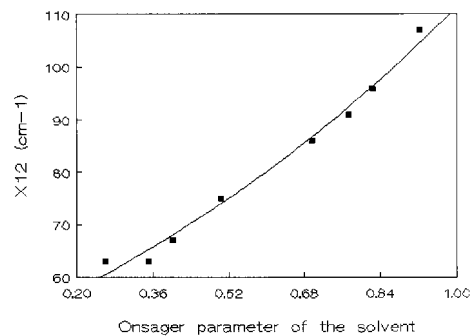
**Figure 3.** Near-IR spectra ( $7000\text{--}5400 \text{ cm}^{-1}$ ) of solutions of PCP-ACN- $\text{CCl}_4$ .  $C_{\text{PCP}} = 0.1 \text{ mol dm}^{-3}$ ;  $C_{\text{ACN}}$  = (a) 0.2, (b) 0.5, (c) 1, (d) 3 and (e) 7  $\text{mol dm}^{-3}$ . S indicates absorption of ACN

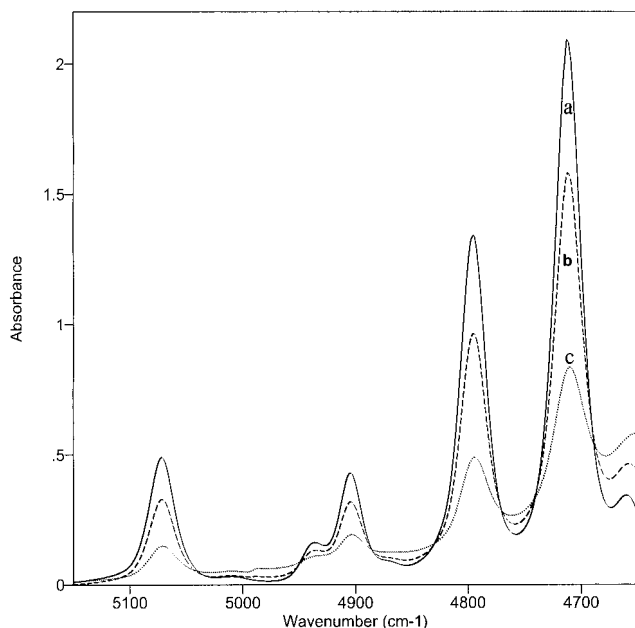
As indicated by the results of Table 2, the anharmonicity of the  $\nu(\text{OH}\cdots\text{N})$  vibration increases with increasing ACN content of the solution. The dielectric constant of the medium ( $\epsilon$ ) was calculated with the equation.<sup>36</sup>

$$\epsilon = \epsilon_1\varphi_1 + \epsilon_2\varphi_2 \quad (4)$$

where  $\epsilon_1$  and  $\epsilon_2$  refer to the dielectric constant of pure carbon tetrachloride (2.238) and pure ACN (37.50), respectively, and  $\varphi_1$  and  $\varphi_2$  to their volumetric fraction at a given concentration. Figure 4 clearly shows that the anharmonicity increases with increase in the Onsager parameter of the medium. These results clearly show that in order to have reliable results on the influence of the hydrogen bond strength on the anharmonicity of the vibrations, the spectroscopic measurements must be performed at constant proton donor-to-proton acceptor concentration ratio, if one of the species has a much higher dielectric constant than the other.

The increase in the anharmonicity with increase in the permittivity of the medium can be related to the shape of the potential curve, which becomes more asymmetric when the permittivity of the medium increases. Most theoretical calculations are related to the stabilization of the ion pairs; it has been shown, however, that an increase in the dielectric constant also stabilizes the neutral pairs.<sup>37</sup>

**Figure 4.** Anharmonicity of the  $\nu(\text{OH}\cdots\text{N})$  vibration of the PCP-ACN complex ( $\text{cm}^{-1}$ ) as a function of the Onsager parameter of the medium



**Figure 5.** Near-IR spectra ( $5150\text{--}4650\text{ cm}^{-1}$ ) of PCP-ACN- $\text{CCl}_4$  solution.  $C_{\text{PCP}} = 0.1\text{ mol dm}^{-3}$ ;  $C_{\text{ACN}} =$  (a) 0, (b) 0.2 and (c)  $1\text{ mol dm}^{-3}$

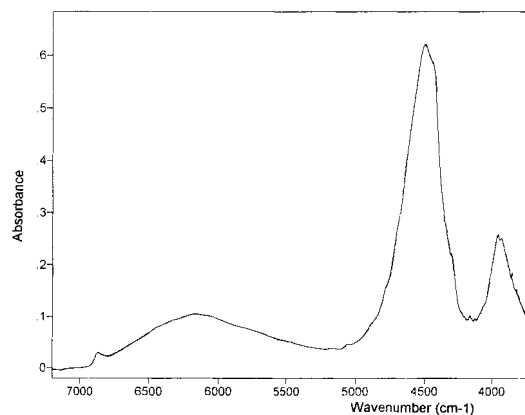
It is worth mentioning that the IR spectra of phenol-ACN have been investigated in carbon tetrachloride and chloroform solutions and that a downward shift of the  $\nu_{01}(\text{OH}\cdots\text{N})$  absorption from  $3424$  to  $3415\text{ cm}^{-1}$  has been observed on changing to a more polar solvent.<sup>38</sup> Two explanations have been adduced. The first is a specific interaction between the solvent molecules and

**Table 3.** Formation constants ( $K$ ) and enthalpy of complex formation ( $-\Delta H$ ) of complexes between PCP and bases in carbon tetrachloride

Base	$K^{298\text{ K}}$ ( $\text{dm}^3\text{ mol}^{-1}$ )	$K^{323\text{ K}}$ ( $\text{dm}^3\text{ mol}^{-1}$ )	$-\Delta H$ ( $\text{kJ mol}^{-1}$ )
Acetonitrile	2.9	2.2	8.8
Cyclohexanone	7.8	5.4	11.8
Dioxane	5.5	3.8	11.9
Dibutyl ether	2.6	1.7	13.6
Diethyl ether	3.5	2.3	13.4
Tetrahydropyran	7.0	4.5	14.1

**Table 4.** Spectroscopic data ( $\text{cm}^{-1}$ ) for complexes between PCP ( $c = 0.1\text{ mol dm}^{-3}$ ) and proton acceptors ( $c = 0.5\text{ mol dm}^{-3}$ ) in carbon tetrachloride and anharmonicity ( $X_{12}$ ) of the corresponding  $\nu(\text{OH}\cdots)$  vibration

Proton acceptor	$\nu^{01}(\text{OH}\cdots)$	$\nu^{02}(\text{OH}\cdots)$	$X_{12}$	1	2
None	3524	6868	90	4712	3938
Acetonitrile	3325	6516	67	4510	3937
Cyclohexanone	3230	6220	120	4511	3937
Dioxane	3220	6160	140	4496	3952
Dibutyl ether	3175	6010	169	4490	3965
Diethyl ether	3170	6000	170	4487	—
Tetrahydropyran	3150	5945	177	—	—
Tetrahydrofuran	3130	5880	190	4442	3944



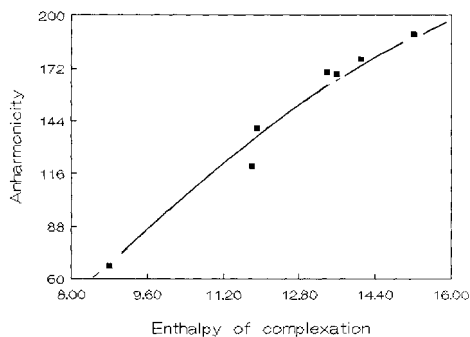
**Figure 6.** Near-IR spectrum ( $7000\text{--}3800\text{ cm}^{-1}$ ) of PCP-dioxane- $d_8\text{-CCl}_4$  solution.  $C_{\text{PCP}} = 0.1\text{ mol dm}^{-3}$ ;  $C_{\text{dioxane}} = 0.5\text{ mol dm}^{-3}$

the complex, which can be ruled out in the present case. The second is an increase in the reaction field resulting from the increased dielectric constant of the medium. As pointed out by Yarwood *et al.*,<sup>38</sup> a strengthening of the hydrogen bond may be expected to increase the anharmonic coupling constant, in full agreement with the present results.

The spectrum of PCP dissolved in carbon tetrachloride solution shows characteristic features at  $5072$ ,  $4938$ ,  $4904$ ,  $4796$  and  $4712\text{ cm}^{-1}$ , assigned to combinations between the  $\nu_{01}(\text{OH})$  vibrations and the ring modes, the in-plane deformation vibration [ $\delta(\text{OH})$ ] and the  $\nu(\text{C-O})$  mode. These values are not in agreement with the observations of absorptions at  $5950$ ,  $4750$  and  $4200\text{ cm}^{-1}$  by Burneau and Corset.<sup>14</sup> As shown in Fig. 5, these absorptions decrease in intensity when ACN is added to the solution, and this confirms our previous assignment. The same spectroscopic behaviour was observed for PCP complexed with other proton acceptors and will not be discussed further.

### Complexes between PCP and other proton acceptors

Table 3 indicates the complexation constants determined



**Figure 7.** Anharmonicity of the  $\nu(\text{OH}\cdots)$  vibration ( $\text{cm}^{-1}$ ) as a function of the enthalpy of complex formation ( $\text{kJ mol}^{-1}$ ) for complexes between PCP and bases

at 298 and 323 K and the enthalpy of complex formation for the interaction between PCP and ACN and *O*-bases. These thermodynamic parameters, determined at low PCP concentration and in excess of proton acceptor, are relative to complexes of 1:1 stoichiometry. We may note that the thermodynamic values are rather weak and this may result from the fact that the intramolecular  $\text{OH}\cdots\text{Cl}$  hydrogen bond must be broken before interacting with a proton acceptor.<sup>39</sup>

As discussed in the previous section, the frequencies of the fundamental  $\nu(\text{OH}\cdots)$  vibration and of its first overtone depends on the ACN: $\text{CCl}_4$  concentration ratio. The mid- and near-IR spectra were taken at a constant concentration of ACN of  $0.5 \text{ mol dm}^{-3}$ . Table 4 indicates the values of the  $\nu_{01}(\text{OH}\cdots)$  and the  $\nu_{02}(\text{OH}\cdots)$  frequencies along with the corresponding anharmonicity constants calculated from Eqn. (1).

Examples of spectra ( $7000\text{--}3800 \text{ cm}^{-1}$ ) of solutions of PCP and dioxane- $d_8$  are shown in Fig. 6. For PCP dissolved in dioxane and tetrahydrofuran, the experimental frequencies are about  $20 \text{ cm}^{-1}$ , lower,<sup>16</sup> and this agrees with the above discussion. These results indicate that for the weakest complex between PCP and ACN, the anharmonicity decreases from free PCP ( $90 \text{ cm}^{-1}$ ) but for the stronger complexes between PCP and *O*-bases, an increase in the anharmonicity is observed. The correlation between the anharmonicity and the enthalpy of complex formation is illustrated in Fig. 7. Similar results have been obtained for phenol dissolved in organic solvents; the anharmonicity of the  $\nu(\text{OH})$  vibration decreases in weak proton acceptor solvents and increases in dioxane, diethyl ether and dibutyl ether.<sup>17</sup>

Finally, we must mention that two bands labelled 1 and 2 in Table 4 were observed between  $4500$  and  $3900 \text{ cm}^{-1}$ . In free PCP, two intense absorptions were observed at  $4712$  and  $3938 \text{ cm}^{-1}$ , assigned to combinations between the  $\nu_{01}(\text{OH})$  and the in-plane  $\delta(\text{OH})$  and out-of-plane  $\gamma(\text{OH})$  modes.<sup>21</sup> We have shown that the combinations with the highest intensities and highest coupling constants are those involving the  $\nu(\text{OH})$ ,  $\delta(\text{OH})$  and  $\gamma(\text{OH})$  vibrations. In free PCP, these vibrations were

observed at  $3524$ ,  $1215$  and  $412 \text{ cm}^{-1}$ . In the ACN complex, the  $\delta(\text{OH})$  and  $\gamma(\text{OH})$  vibrations were observed at  $1185$  and around  $610 \text{ cm}^{-1}$ , respectively. The fact that band 2 is almost independent of the strength of the complex can be explained by the decrease in the  $\nu_{01}(\text{OH}\cdots)$  frequency, which is nearly cancelled by the increase in the  $\gamma(\text{OH}\cdots)$  frequency. For the other complexes, Eqn. (2) allows us to predict the  $\delta(\text{OH})$  and  $\gamma(\text{OH})$  vibrations near  $1280\text{--}1315$  and  $705\text{--}815 \text{ cm}^{-1}$  respectively. We were not able to observe these modes owing to the overlapping with the intense absorptions of free PCP at  $1282$ ,  $1129$ ,  $759$  and  $713 \text{ cm}^{-1}$ .

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