Spectroscopic Investigations of Intermolecular Interactions between Different Parts of Molecules *

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Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

With the low temperature matrix techique we have observed different isolated IR OH vibration bands caused by van der Waals forces of single atom groups of the matrix molecules. With a series of different perhalogenated matrix molecules these different OH band frequency shifts $\Delta\nu_{OH}$ can be correlated to OH interactions with C–F, C–Cl, C–Br resp. C–I groups. At higher temperatures T (solution spectra) the band positions of the different interactions become more similar because $d\nu/dT$ increases with increasing interaction. This result clarifies why at room temperature band shoulders are observed and correlates these clearly to the different matrix bands and therefore to different interactions. These experiments demonstrate that intermolecular van der Waals potentials of asymmetric molecules cannot be approximated by one spheric potential but are angle dependent. This indicates the complexity of describe condensed media.

1. Introduction

In the last years we have demonstrated with sensitive IR spectroscopy [1–5] that the OH-stretching vibrations of alcohols and water change significantly in frequency and intensity when these molecules are hydrogen-bonded to H-bond-acceptor molecules [6, 7]. In such systems the frequency shifts of the OH stretching band-maximum $\Delta\nu_{OH}$ ($\Delta\nu_{OH}=\Delta\nu_{OH,\,gas}-\Delta\nu_{OH}$) are proportional to the interaction strength ΔH_H of the H-bond ($\Delta\nu_{OH}=a_H\,\Delta H_H$) [6–10]. A similar relation

$$\Delta\nu_W = a_W \cdot \Delta H_W \quad \text{with} \quad a_W \approx a_H/30 \qquad (1)$$

holds for van der Waals interactions of strength ΔH_W between OH-groups and neighbouring molecules [2, 5, 8]. Fluorinated alcohols are very sensitive to intermolecular interactions, as evidenced by their IR-absorption spectrum, because of the high acidity of the OH-group [10–15]. Perfluorinated 2-methylpropan-2-ol (perfluoro-tert.-butanol, PFTB) is especially suitable to study weak van der Waals interactions [12–17] as well as H-bond interactions by means of $\Delta\nu_{OH}$.

Solvent effects on $\Delta\nu_{OH}$ depend on $(U_{11}\,U_{22})^{1/2}$ (U_{11}: maximum pair potential of the oscillator, U_{22}: maximum pair potential of the solvent) [3, 5, 18]. Figure 1 demonstrates the $\Delta\nu$-dependence on U_{22} and the dependence on U_{11}. The comparison of $\Delta\nu$ with the values of trifluoroethanol (TFE) [17] gives

$$\Delta\nu((CF_3)_3COH) = 2.1 \cdot \Delta\nu((CH_3)_3COH) \quad [2, 17]$$

for weak interacting solvents corresponding to the larger acidity and larger interaction energies of PFTB compared with $(CH_3)_3COH$.

Recently it was demonstrated that in van der Waals systems the pressure dependence of ν_{OH} can be used to calculate potential parameters of OH···solvent potentials [14, 15, 17–20]. It was also shown that in perhalogenated solvents containing fluorine- and chlorine-groups the ν_{OH} absorption band has an asymmetric shape. This asymmetry was explained as an overlapping of ν_{OH}-bands which arise from "specific interactions" of OH with different parts (halogen-substituents) in the solvent molecules [4, 14, 15].

This asymmetry could be described by two OH bands, one induced by the C–F environment and the second one by the C–Cl environment of the OH group of PFTB. It was found that the asymmetry increases with increasing pressure p. A band analysis had the result that the Cl induced OH band is shifted more by a pressure increase than the F-induced one. This is in agreement with the observations that

$$d\nu/dp \sim \Delta\nu_{1\,bar}. \qquad (2)$$

At a pressure of 1 bar it is found that $\Delta\nu(OH\cdots Cl) > \Delta\nu(OH\cdots F)$. Asymmetric ν_{OH} bandshapes have al-

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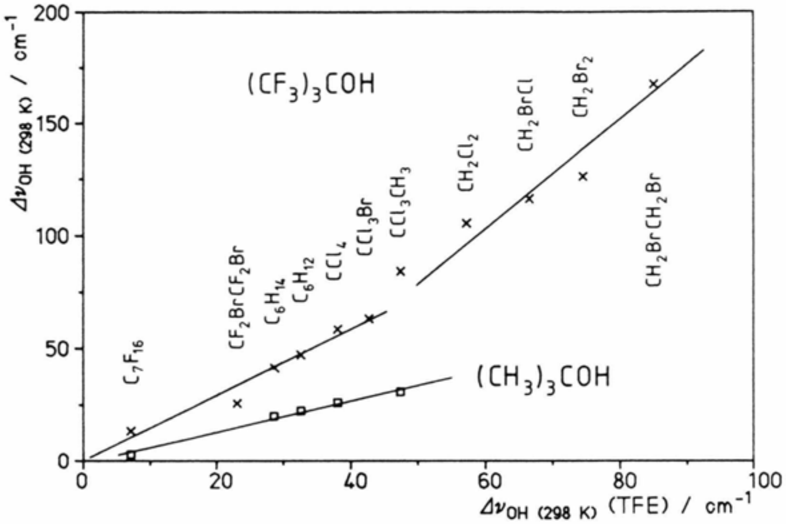

Fig. 1. Shifts $\Delta\nu_{OH}$ of the OH stretching band (main maximum) of PFTB $(CF_3)_3COH$ and tert.-butanol $(CH_3)_3COH$ induced by different solvents in comparison to $\Delta\nu_{OH}$ of trifluoroethanol (TFE).

ready been observed in solutions of alcohols and substituted phenols [21–24]. The asymmetry was assumed as an overlapping of two absorption bands induced by interactions with specific solvent groups. Such asymmetric absorption bands have not been found with methanol in solvent mixtures [2] probably because the ratio

$$(\nu_A - \nu_B) : \Delta\nu_{1/2} \qquad (3)$$

of the expected two absorption bands ν_A and ν_B is too small to yield an observable asymmetry [25]. Specific interactions have already been supposed in the literature with PFTB as probe [12, 13], finding asymmetric bandshapes of PFTB in frigen-mixtures as well as in a heterogen-substituted perhalogenated solvent. In an Ar-matrix doped with $CFCl_3$, spectra of PFTB showed different band-parts which have been assigned to OH ··· Ar-, OH ··· F- and OH ··· Cl-interactions of PFTB [12, 13].

In this work we extend the study of specific interactions of PFTB on systems with solvents containing Br- and I-substituents between room temperature and matrix temperatures (6 K) to indentify directly the bands which have been concluded till now more indirectly from the asymmetric bands in solutions.

2. Experimental

The infrared absorption spectra have been recorded with a Perkin-Elmer 325 grating spectrometer which is connected to a personal computer for digitizing and working up the spectra.

Spectra at room temperature were recorded using quartz-infrasil (QI) cuvettes (Fa. Hellma, Mühlheim, FRG) with a pathlength of 0.5 mm; the absorption of the solvents was carefully compensated by placing equivalent QI-cells filled with the corresponding solvent in the reference-beam of the spectrometer. The matrix equipment for preparing the matrices consisted of a vacuum-system with components made of glass and of stainless steel and a Pfeiffer-Balzer turbo molecular pump (Type TPH 200 S) with which we obtained pressures below 10^{-6} Torr. As cryostat we used the model LT-3-110 B from Fa. Air-Products, which works with a continuous flow of liquid helium. The gaseous mixtures were prepared and sprayed onto a CsI matrix window by standard manometric procedures. Deposition rates of the matrix samples were about 0.1 mmol/h. The temperature of the matrix window was controlled with an Fe-Au (0.07% Fe)/chromel thermocouple.

With an infrared cell for low temperature studies of our own design, which is placed after filling into the cryostat instead of the matrix window we have recorded spectra of solutions from room-temperature down to 10 K.

Perfluorinated 2-methylpropan-2-ol (PFTB) was obtained from SCM Chemicals, Gainesville (Florida). Liquid solvents, which were kept over 3 Å molecular sieves for removing traces of water, were obtained from E. Merck, Darmstadt, the matrix gases from Messer-Griesheim, Düsseldorf.

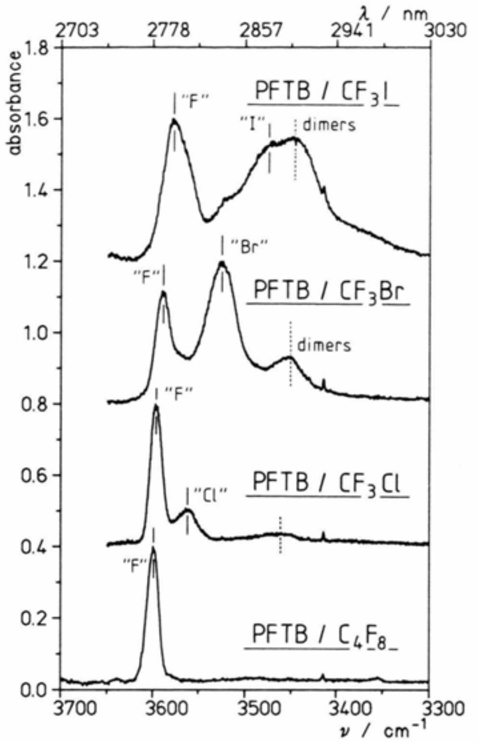

Fig. 2. IR spectra of PFTB in different solvents at 6 K (ratios PFTB : solvent are about 1:150) show different OH stretching bands induced by the C–F, C–Cl, C–Br and C–I solvent groups. The ν_{OH}-shifts are proportional to the van der Waals interaction energies and demonstrate different interactions of the F-, Cl-, Br- and I-substituents of the four solvents.

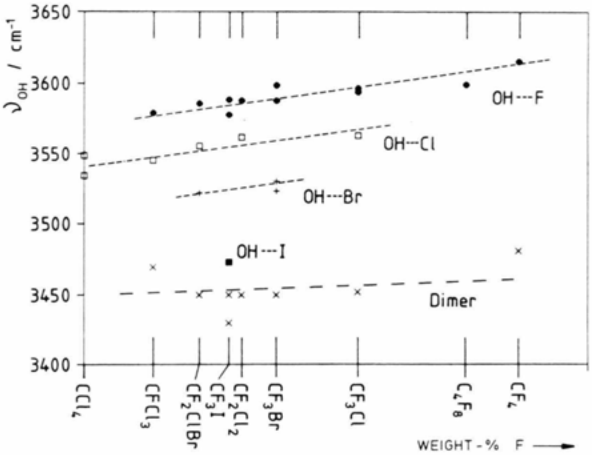

Fig. 3. Frequencies of the OH spectra of PFTB at 6 K in different solid perhalogenated solvents as matrices.

3. Results and Discussion

a) Spectra of PFTB in Solid Matrices

We call them matrix spectra for brevity. As matrices we have chosen a variety of perhalogenated hydrocarbons with different halogen-substituents. Figure 2 shows matrix spectra with perhalogenated molecules of one fluorine-atom substituted by a Cl-, Br-, resp. I-atom as matrix [16].

The spectra reveal the following: With the C_4F_8-matrix one obtains only one absorption band at 3609 cm^{-1} which is to be assigned to OH ··· F-interactions. The CF_3Cl-matrix induces a second band at 3562 cm^{-1} and a faint band at ≈3452 cm^{-1} due to PFTB dimers. The two main bands can be assigned to OH ··· F (3596 cm^{-1}) and OH ··· Cl (3562 cm^{-1}) interactions.

The CF_3Br-matrix gives an intense band at 3523 cm^{-1} due to OH ··· Br interactions. The OH ··· F interactions yield the band at 3588 cm^{-1} and dimers that at 3450 cm^{-1}.

In the CF_3I matrix the situation is more complex since the PFTB dimer band is very near to the expected band due to OH ··· I interactions appearing as a shoulder at 3470 cm^{-1} on the high-frequency side of the dimer band (3450 cm^{-1}).

Annealing experiments did not give more information on the specific interactions because the spectra become more complex due to the absorption of open-end groups of the originating linear dimers [17].

In Fig. 3 the frequencies of the OH-band-maxima of PFTB in a variety of perhalogenated matrix molecules are plotted versus the content by weight of fluorine in these molecules.

Figure 3 shows that on substitution of fluorine in a molecule by higher halogen atoms the OH ··· F interaction band is shifted to lower wave numbers, probably due to a higher polarizability of the fluorine as consequence of the higher electron density in the molecule. On the other hand, the fluorine atoms may diminish the polarizabilities of the higher halogen atoms in the molecule which can be seen by a shift of the OH ··· X (X = Cl, Br) interaction bands to higher wave numbers. In the order of the matrix molecules given in Fig. 3 on the abscissa the critical temperatures of the matrix molecules decrease from the left to the right. The found increase of the OH-frequencies is in accordance with the "Berthelot-rule" as has already been discussed by us in case of other examples [17, 18]. The coordination of the band-maxima with OH ··· F,

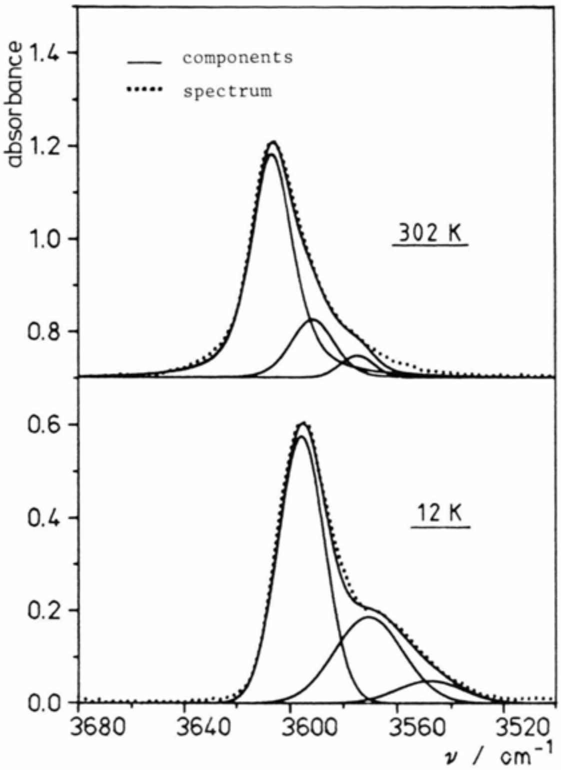

Fig. 4. The OH stretching bands of PFTB in poly-(CF_2CFCl) (PCFE) caused by the F-groups (band-maximum) and Cl-groups (shoulder at lower wavenumbers).

OH···Cl, OH···Br and OH···I interactions agrees with the polarizabilities of the halogen atoms, which increase in this order, and the experience $\Delta\nu \sim \Delta H$.

The position of the dimer band maximum seems not to depend much on the used matrix, as has already been observed in the earlier paper on PFTB in rare-gas matrices [17]. This has been explained by the sterical hindrance of the matrix molecules to affect the OH-groups in the PFTB dimer, which is very voluminous due to the $-CF_3$ groups. The matrix molecules act mainly on PFTB dimers by the intermolecular "inner pressure" [5, 17] changing the H-bond distances.

b) Spectra of PFTB in Liquid Solvents

We call them solution spectra for brevity. In contrast to the separated band components of the matrix spectra (Fig. 2), at room temperature the different atom groups of the solvents induce only band shoulders (Fig. 4, compare Fig. 4 in [15]). This difference is caused by the different T-dependencies of the bands. We have found [5, 16, 17] that $d\nu/dT \sim \Delta\nu$. The T-dependence of the two main-band components of monomeric PFTB in $(CF_2CFCl)_N$ (=PCFE) as solvent is given by:

F-component:

$$\Delta\nu = \Delta\nu_0 - 0.045\,(\mathrm{cm}^{-1}\,\mathrm{K}^{-1}) \cdot T, \quad \Delta\nu_0 = 40.2\ \mathrm{cm}^{-1};$$

Cl-main component:

$$\Delta\nu = \Delta\nu_0 - 0.070\,(\mathrm{cm}^{-1}\,\mathrm{K}^{-1}) \cdot T, \quad \Delta\nu_0 = 62.3\ \mathrm{cm}^{-1}.$$

$\Delta\nu_0$: extrapolated shift at 0 K.

The larger $d\nu/dT$ of the OH···Cl band-component reduces at higher temperatures the separation of the two band-components (Figure 5).

In Fig. 4, the OH band with its shoulder is analysed in terms of two components, each one assumed as superposition of a Gaussian and a Lorentzian part. The main maximum, belonging to the F-induced interaction, has a smaller half width $\Delta\nu_{1/2}$ according to the rule $\Delta\nu_{1/2} \sim \Delta\nu_0$ [17, 26] and induces therefore the maximum. The Cl-induced band can be observed more distinctly at 12 K (Figure 4).

The asymmetric OH bandshape of PFTB is emphasized when using a solvent with a higher chlorine content, $CFCl_3$ (Fig. 6, above). With fluorinated solvents containing bromine in addition the asymmetric shape is even more pronounced (Fig. 6, bottom). This Br-induced asymmetry increases with the relative Br-content.

The main maximum is given by the F-induced component. The band half width $\Delta\nu_{1/2}$ is proportional to $\Delta\nu_0$ as well by H-bond interactions as by van der Waals ones. This experience contributes to the observation that generally the F-induced band induces the main band maximum. The bands induced by different atom groups obey the Badger-Bauer rule: $\Delta\nu$ induced by different groups is proportional to the local intermolecular potential (see Figure 1). The experience for $\Delta\nu_0$ and $d\nu/dT$: $F < Cl < Br < I$, is observed as well with solution spectra as with matrix ones.

The influence of a halogen solvent group on the matrix spectra depends (Fig. 3) on its neighbour groups. Figure 7 compares the F-component of the solvent spectra at 283 K with the results of matrix spectra at 6 K. The plots of Fig. 7 demonstrate that the rule $d\nu/dT \sim \Delta\nu_0$ is valid too for the different F-induced bands if their $\Delta\nu_0$ is changed by different neighbour groups. This established the common validity of this rule and the similar behaviour of matrix bands

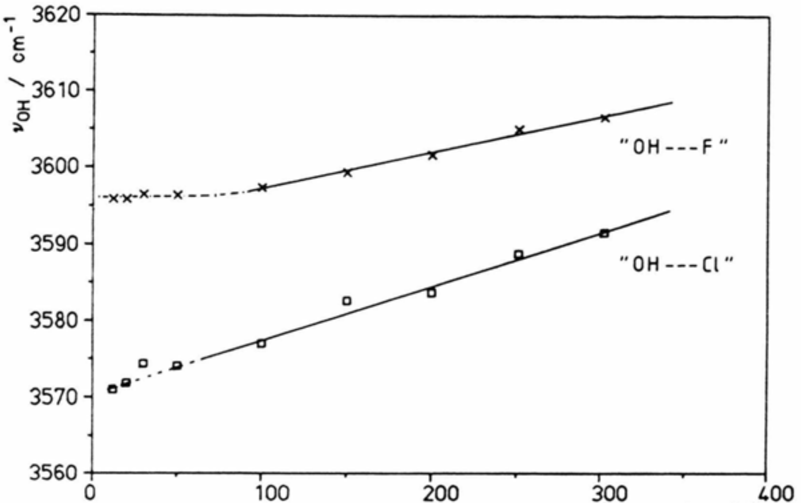

Fig. 5. The temperature-dependences of the C–F and C–Cl induced OH band-components of PFTB in PCFE.

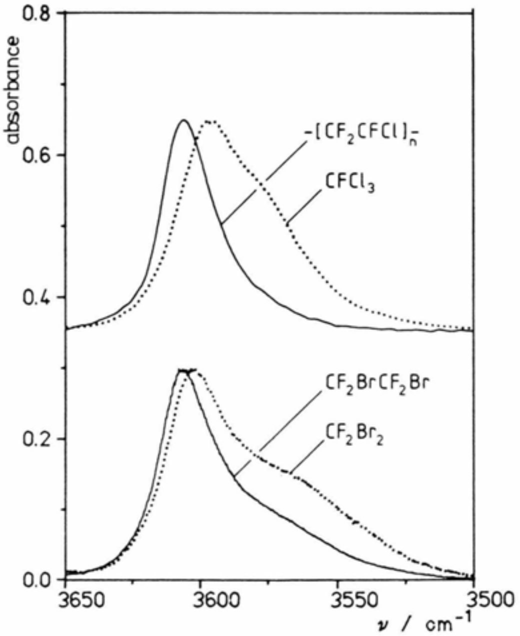

Fig. 6. The OH stretching bands of PFTB in different solvents at room temperature in F-/Cl-perhalogenated (top) and F-/Br-perhalogenated (bottom) solvents.

and solution band shoulders. Overlapping of the band components or of the intermolecular force-fields may contribute to the results of Figure 7.

The experience $d\nu/dT \sim \Delta\nu_0$ corresponds to the rule $d\nu/dp \sim \Delta\nu$ (1 atm) [14, 15]. $d\nu/dT$ and $d\nu/dp$ are both based on changes of the intermolecular distances. Therefore Fig. 4 is very similar to Figs. 7 and 8 in [4] on the p-dependence of the band component resolution.

In Fig. 5 the frequency of the F-induced component seems to become constant for $T < 80$ K. This can be explained with the T-dependent population of the intermolecular vibration levels [5, 25]. The distances between the lowest level and the higher ones ($V_{0\rightarrow 1} \approx 120\ \text{cm}^{-1}$) seems to be too large in the case of the weaker OH···F interactions to be occupied significantly at low T [17]. The lack of this effect for the OH···Cl component* could indicate smaller distances between the intermolecular vibration levels in this case. Details will be discussed in another paper. Correspondingly it is observed [14, 15] that the OH···F component is red shifted by increased p and shows a maximum of $\Delta\nu$ at about 2 GPa, but the OH···Cl component shows only a continuous red shift in the same p-region till 9 GPa.

4. Conclusions

IR vibrational spectroscopy of the OH stretching band indicates different intermolecular interactions induced by different atom groups of molecules. This can be recognized better at low T or high p because $d\nu/dT$ and $d\nu/dp$ (at not too high p) are proportional

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* The OH···Cl (CCl_4) band of PFTB in PCFE/CCl_4 (4:1) mixture is T-linear till about 65 K and non T-dependent at lower T [16].

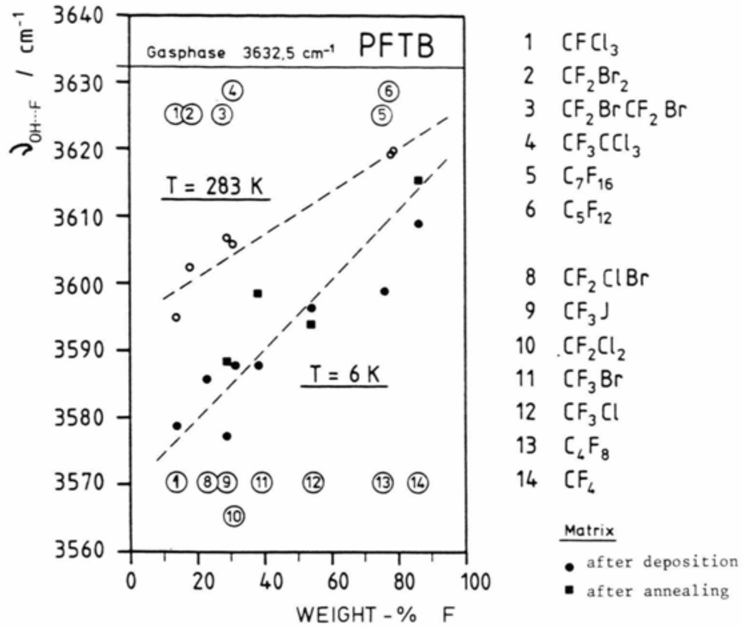

Fig. 7. Frequencies of the OH stretching band induced by OH ··· F interaction in different perhalogenated solvents. The frequency shift decreases with increasing number of F-atoms (weaker interaction); the differences increase with decreasing temperature.

to $\Delta\nu$. This way we could observe at low T isolated OH bands induced by different atom groups of a solvent containing different halogen atoms. Our observations in a large T-interval demonstrate why at room temperature such effects are only inducing band shoulders.

These experiments are part of the development of a "van der Waals spectroscopy" [5], which uses similar rules as the extended H-bond IR spectroscopy. Van der Waals forces induce similar IR effects, but they are smaller than those induced by H-bonds [28].

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