Fourier transform infrared study of gas phase H-bonding: Absorptivities and formation equilibrium constants of fluoroalcohol complexes

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Fourier transform infrared study of gas phase H-bonding: absorptivities and formation equilibrium constants of fluoroalcohol complexes

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Abstract

We have recorded gas-phase Fourier transform infrared spectra (4000–400 cm^{-1}) of CF_3CH_2OH, $(CF_3)_2CHOH$ and $(CF_3)_3COH$ and of the complexes that these alcohols form with bases such as diethyl ether, acetone, tetrahydrofuran, ammonia and trimethyl- and triethylamine. The spectrum of each complex has been "isolated" from the spectra of mixtures of the corresponding alcohol (AH) and base (B) through spectral subtraction techniques. All efforts were made to obtain good estimates of the absorptivity of the complex leading to the determination of an accurate set of equilibrium constants for the corresponding formation reactions $AH + B \rightleftharpoons AH \cdots B$. A statistical procedure using a series of mixtures is proposed to calculate this absorptivity from their spectra, their total pressure and the sum of partial pressures $p_{AH} + p_B$. The evaluated equilibrium constants quantitatively fit the Abboud–Bellon–Taft–Abraham bilinear model. We found: $\log K_c = (-0.48 \pm 0.15) + (7.90 \pm 0.39) \alpha_2^H \beta_2^H$ with $n = 13$, $r = 0.987$, S.D. $= 0.12$ log units.

The spectra of the complexes show, in addition to the typical $\Delta\nu(OH)$, $\Delta\delta(OH)$ and $\Delta\gamma(OH)$ shifts, well defined features related to other molecular group vibrations [mainly $\nu(CF_3)$, $\nu(CO)$, $\nu(CC)$ and $\gamma(CF_3)$], clearly different from those seen in the spectra of the pure alcohols. These features are understood in terms of conformational isomerism: the formation of *intermolecular* H-bonds implies the breaking of the *intramolecular* $OH \cdots F$ bonds which stabilize the pure alcohols in definite conformations.

Keywords: Infrared spectrometry; Acid–base complexes; Fluoroalcohols; Hydrogen bonding

The study of the vibrational infrared (IR) spectra of H-bonded (HB) complexes has been a topic of recurrent interest in the scientific literature ever since commercial IR spectrometers became available in the early fifties [1–5]. Most of the papers published over the following thirty years deal with H-bonded systems in solution in CCl_4 and other inert solvents. The vibrational spectral characteristics of gas-phase HB complexes have been reviewed in refs. 5–8.

The introduction in the last ten years of a range of new high-resolution and high-sensitivity spectroscopic techniques has provided a wealth of detailed information on the structure and dynamics of a number of simple gas-phase systems, among which $HCN \cdots HF$ has been thoroughly discussed as an spectroscopic prototype [9]. Generalizations for selected series of complexes derived mainly from very sensitive rotational spectroscopy methods, have recently been reviewed [10–13].

The work we present here deals with low-resolution (2 cm^{-1}) vibrational spectroscopy of systems formed by donors like fluoroalcohols [namely

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2,2,2-trifluoroethanol, (TFE), 1,1,1,3,3,3-hexafluoroisopropanol (HFP) and perfluoro-*tert*-butanol (PFtB)] with acceptors such as ethers, ketones, amines, pyridine and ammonia. For complexes of this kind, previous infrared studies, both in gas phase and in solution, were usually limited to the consideration of the frequency and intensity spectral changes of the characteristic hydrogen stretching, and sometimes also deformation, bands of the hydrogen-bonding (HB) donor.

The wide dynamic range and photometric accuracy of FT-IR allows to obtain full range spectra (4000–400 cm^{-1} routinely) of complexes present in relative concentrations of $1:10^3$ or higher, which may be "isolated" from the equilibrium mixture of the reagents through spectral subtraction procedures. Together with the spectral features of the characteristic HB vibrations, finer details on the perturbation of the molecular vibrations of the partners due to the formation of the H-bond may then be detected.

Complete vibrational spectra may also be obtained with the technique of matrix isolation spectroscopy. Work on H-bonded systems has been reviewed by Andrews and by Barnes [14]. It must be realized, however, that matrix-isolated species are not free from interactions with the matrix environment.

The present work intends also to verify with gas phase data the relation found in solutions in inert solvents (C_6H_{12}, CCl_4) first by Abboud and Bellon and Abraham et al. [15], between the equilibrium constant of the reaction of formation of the H-bond complex, $AH + B \rightleftharpoons AH \cdots B$, and the hydrogen-bonding acidity and basicity parameters characteristic of AH and B. This relation takes the form $\log K_c = c + m\alpha_m\beta_m$ and has been checked for hundreds of systems, with K_c values ranging over six orders of magnitude. We wished to find out whether the α_m and β_m parameters refer to intrinsic properties of AH and B or are solvent mediated properties. This question may be experimentally answered through the determination of a number of equilibrium constants.

A different approach has been used by Legon and Millen [16]. Measuring the bonding strength in a hydrogen-bonded dimer $AH \cdots B$ by the H-bond stretching force constant, K_σ, a scale of

nucleophilicities of B and electrophilicities of AH may be deduced from the experimental K_σ values, which may be used in turn to predict the strength of binding for a large number of dimers. Justification of this procedure is based on an electrostatic model of the hydrogen-bond.

EXPERIMENTAL

General background

Some well known characteristics of the infrared spectra of hydrogen-bonded complexes are illustrated in Fig. 1a. This figure shows the high-frequency part of the gas phase IR spectrum of 2,2,2-trifluoroethanol (TFE, AH) compared with two other spectra run in succession with the same cell after two corresponding additions of tetrahydrofuran (THF, B). The mixing of AH and B causes a decrease in the intensity of the alcohol band centered at 3657 cm^{-1}, the characteristic *free* OH stretching vibration, and the appearance of a new broader band around 3440 cm^{-1} due to a *bonded* OH stretching vibration, characteristic
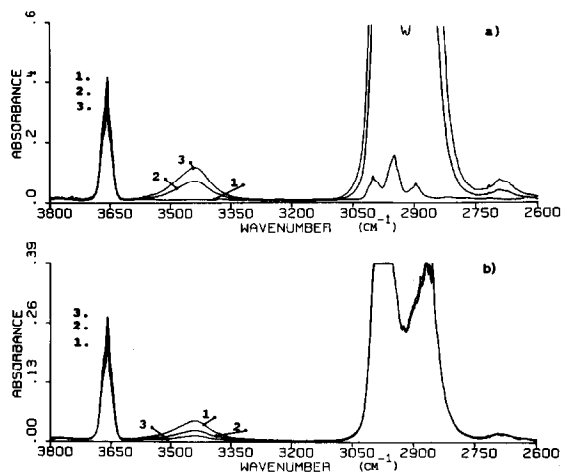
Fig. 1. IR spectral features of the HB equilibrium between trifluoroethanol (TFE) and tetrahydrofuran (THF), in gas phase. (a) Spectra of TFE (16 mbar, 10 cm) and two mixtures with THF (addition of 26 and 52 mbar into the same cell). (b) Spectral changes in a 1:1 mixture of TFE and THF under different total pressure (approximately 11, 21 and 47 mbar with corresponding pathlengths of 16, 8 and 4 cm).

of the complex (AH $\cdots$ B). Adding more B causes a further decrease in the free OH band and the rising of the bonded OH band, according to the reversible reaction

$$AH + B \rightleftharpoons AH \cdots B$$
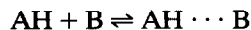
The corresponding equilibrium is expressed by the equilibrium constant $K_p = p_{AB}/(p_A p_B)$ [a]. Assuming that the Lambert–Beer law holds, so that the spectral absorbance due to each component at any convenient wavenumber ν is proportional to the corresponding partial pressure $a_A(\nu)/l = \epsilon_A(\nu)p_A$, etc., [$l$ being the absorption path-length and $\epsilon_A(\nu)$ the band absorptivity], the equilibrium condition may be directly verified through the spectral absorbances. For that we take K_p factorized in the form $K_p = \eta l K_a$, where $K_a = a_{AB}(\nu_{AB})/[a_A(\nu_A)a_B(\nu_B)]$ and η is a corresponding reciprocal relation of absorptivities. The ν_i are convenient wavenumbers at which only i absorbs or, else, where corrections are feasible for the absorbance of other components. In writing $a_i(\nu_i)$ we assume that all necessary corrections have been made. Turning to our TFE–THF system, we have plotted 17 values of $a_{AB}(3437$ cm$^{-1})$, ranging from 0.028 to 0.104 absorbance units versus the corresponding products $a_A(3657)$ $\times a_B(2924)$ obtaining a straight line with a slope $K_a = 0.2937 \pm 0.0077$ and intercept -0.002 ± 0.002. [Statistics: $r^2 = 0.99970$; standard deviation (S.D.) = 0.0011.]

The existence of an equilibrium can also be proved through the study of pressure and temperature effects. Figure 1b shows the case of a 1:1 mixture at three different total pressures. With decreasing total pressure, the free $\nu(OH)$ band at 3657 cm^{-1} increases while simultaneously the bonded $\nu(OH)$ band at 3437 cm^{-1} decreases. The $\nu(CH)$ bands at 2900–3050 cm^{-1} remain apparently unchanged. We used for this experiment a cell with three compartments which can be filled successively, so that a given mixture can be expanded twice, thus maintaining the ratio path length : volume approximately constant.

The spectrum of any mixture of AH and B, and a fortiori AH $\cdots$ B, can be expressed as a linear combination of three "unitary spectra", $\epsilon_A(\nu)$, $\epsilon_B(\nu)$, $\epsilon_{AB}(\nu)$ with coefficients equal to the corresponding partial pressures:

$$a(\nu)/l = p_A\epsilon_A(\nu) + p_B\epsilon_B(\nu) + p_{AB}\epsilon_{AB}(\nu)$$

The absorptivities $\epsilon_i(\nu)$ represent the absorbance per unit pressure and unit path-length for each of the three pure substances i. If $\epsilon_A(\nu)$ and $\epsilon_B(\nu)$ are known (through calibration of pure AH and B), a "scaled absorbance subtraction" [17] method (also called spectral subtraction procedure) allows the determination of p_A and p_B, and therefore the estimation of the absorbance due to the complex at any wavenumber, $a_{AB}(\nu) = lp_{AB}\epsilon_{AB}(\nu)$. Since other factors may contribute to the total pressure of the sample, as will be discussed below, the calculation of $\epsilon_{AB}(\nu)$ needs additional data from which the pressure or the concentration of complex present in the mixture could be deduced. It should be noted that the determination of the equilibrium constant K_p through spectroscopic data is tantamount to the determination of the absorptivity of the complex, $\epsilon_{AB}(\nu)$.

Figure 2 illustrates the application of the spectral subtraction operations to a spectrum similar to those of Fig. 1. High- and low-frequency parts are shown in the upper and lower sections of the figure, respectively. While the subtraction of AH (trifluoroethanol) may be fairly accurate, due to the presence of highly sensitive characteristic OH bands, that of B (tetrahydrofuran) requires a careful handling. We will deal later with some of the precautions to be taken for a successful spectral subtraction.

The spectrum of the complex, AH $\cdots$ B, has been expanded in Fig. 3, where the sum of the spectra of 1 mbar of each AH and B is also shown for comparison. The absorbance scale refers to the spectral addition of AH and B; the absorbance of the complex has been scaled so that the 1292 and 665 cm^{-1} bands, proposed below as reference bands, present similar heights in both spectra.

From a quantitative point of view, the accurate determination of p_{AB} (or equivalently the concentration of complex, n_{AB}) in the equilibrium mix-

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[a] Throughout this paper we use the subscript A to refer to the alcohol (AH), B to the base (B) and AB to the complex (AH $\cdots$ B).
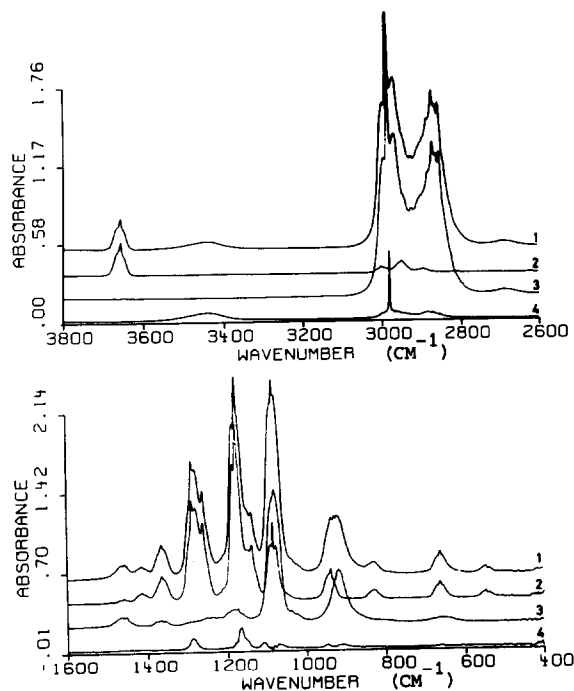
Fig. 2. Spectral subtraction to isolate the dimer spectrum from the equilibrium mixture. (1) TFE–THF equilibrium mixture (42.6 mbar, 10 cm); (2) pure TFE, 9.6 mbar; (3) pure THF, 32.0 mbar; (4) TFE $\cdots$ THF dimer, ca. 1.1 mbar.

However, this may be done only in a limited range, due to condensation under low temperatures or excessive dissociation at higher temperatures. This method has been discussed, for example, by Maréchal [8] who, however, needed to resort to some kind of internal reference in some of the cases he studied. The difficulty is due not only to the complications inherent to the existence of the equilibrium with the monomers, but also to the interference of impurities and, more important, to adsorption and condensation phenomena. In most of previous works in solution it could be assumed that the free OH disappearing on H-bonding were quantitatively converted to bonded OH (possibly with two or more coexisting equilibria). Tokhadze et al. [20b] found this "conservation property" useful to study the gas phase TFE–trimethylamine complex using a fused silica cell (including the windows) in which, they claimed, the reactants were not adsorbed; they shifted the equilibrium by varying the temperature. Our experience is that adsorption interferences cannot be overlooked when working with fluoroalcohols and with the usual IR window materials, like KBr.

Apparatus and experimental details

Infrared spectra were recorded on a Nicolet 60SX FT-IR spectrometer. Cells with KBr windows and path-lengths of 2, 10 and 12.5 cm, as well as a multipass cell with path-length variable

ture is the most difficult step when working in gas phase. In principle, to determine the concentration of the dimer one should measure both temperature and pressure and vary these quantities.
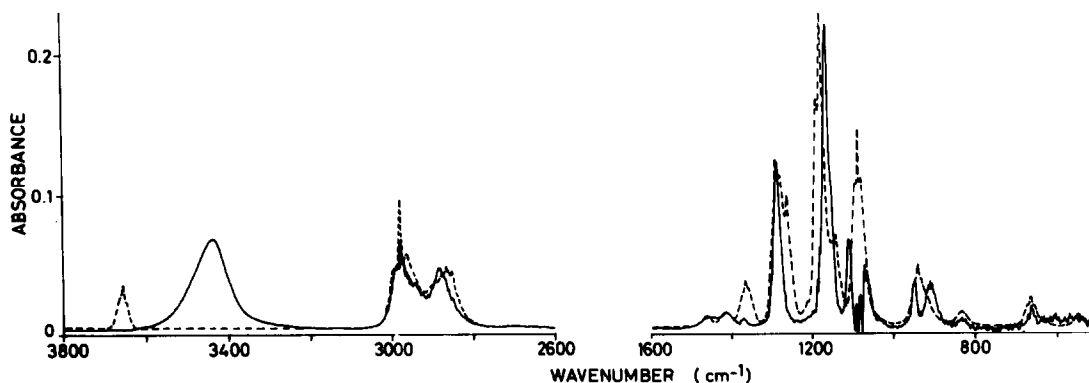

Fig. 3. Comparison of the sum of the spectra of TFE and THF and that of the complex TFE $\cdots$ THF. Solid line, AH $\cdots$ B; broken line, AH + B.

from 0.75 to 20 m, were used. In general, 32 interferograms were coadded to obtain each spectra, with 2 cm^{-1} resolution. All spectra were taken at room temperature, which was recorded in every case.

We simplified the apparatus and methods as much as possible. We found it most convenient to use a microsyringe to inject the liquid components, as pure compounds or as previously prepared (weighted) mixtures, into the cell through a septum. As an example, for qualitative studies with the more frequently used 10-cm cell, (volume ≈ 120 cc) we injected 3–4 μl of AH (TFE) to which two to four successive additions of ca. 5 μl of B were made. Whenever one of the reagents was a gas, we introduced it first into the cell using a vacuum line. For the stronger complexes, which have very small vapor pressure at room temperature (including the ammonia and triethylamine complexes of perfluoro-*tert*-butanol which appear as solids under normal conditions), we prepared the mixtures not in the cell but in a small glass bulb directly attached to the cell. This prevented condensation onto the cell walls.

For quantitative work we designed a new cell made of fused silica (12.5 cm length), with KBr windows and with embodied pressure and temperature sensors. The pressure sensor is a piezo-electric silicon transducer, Model Druck PDCR-920, 0–350 mbar, accurate to 0.1 mbar; for temperature measurements a Keithley K thermocouple, Model 874C, resolution 0.1°C was used.

Chemicals. Methanol, diethyl ether and THF, all from Aldrich, were of spectrograde quality. Acetone (Merck), pyrrole (Fluka) and propanal (Fluka) were distilled under dry nitrogen in a Perkin-Elmer auto-annular still. Pyridine and triethylamine, both from Merck, were refluxed over and carefully distilled from CaH$_2$. Ammonia and trimethylamine, both from Aldrich, were degassed through several pump-thaw cycles in a vacuum line and stored in carefully dried bulbs. 2,2,2-Trifluoroethanol, 1,1,1,3,3,3-hexafluoroisopropanol, both from Merck, and perfluoro-*tert*-butanol, from PCR, were used as received.

In all cases, the absence of significant amounts of water was systematically checked by IR spectroscopy.

Notes on the spectral subtraction procedure

Figures 2 and 3, showing the isolation of the TFE–THF dimer spectrum from that of an equilibrium mixture, through a scaled subtraction of the spectra of the monomers, are useful to illustrate some of the difficulties found when applying these spectral subtraction procedures.

As indicated above, the subtraction of the free alcohol may conveniently be achieved by cancelling the free ν(OH) band (ca. 3657 cm^{-1}) until a flat line remains in the resultant difference spectrum. However, flatness around this position does not necessarily imply a proper subtraction of other alcohol bands in the low-frequency region below 1600 cm^{-1}. The stronger bands in this region, that in some mixtures may present absorbances greater than 2, may give large errors under various circumstances. Sharp features, like Q branches, even when moderately prominent, are almost impossible to nullify, yielding positive or negative residual peaks. Positive (negative) deviations are found whenever the absorbance of the component being subtracted is smaller (larger) in the mixture than in the spectrum taken as reference for the subtraction. As a general rule the spectrum of the component being subtracted should correspond to a pressure as close as possible to that of the component in the mixture for the same path-length; otherwise large errors and some ghosts may appear in the difference spectrum. A different source of problems arises in cases of overlapping of two strong (or one strong and other medium intensity) bands, one of each partner. Again negative deviations may appear, which will be the larger the higher is the total absorbance of the mixture. In the TFE–THF system sharp Q branches as well as a close overlap of medium intensity bands occur notably around 1085 cm^{-1}. As seen in Figs. 2 and 3, noise-like deviations attributable to the Q branches are prevalent in the spectrum of the complex. Deviations due to the overlapping are not apparent in these spectra; they are seen however as a negative absorbance band in the TFE–THF spectrum shown in Fig. 6. Non-linearity deviations like these were experimentally observed with the three-compartment cell mentioned above. The absorbances of AH and B were

measured both individually and also simultaneously in adjoining separate compartments; for absorbances greater than 1 in the overlapping region the absorbance of the latter experiment was seen to be smaller than the sum of the individual absorbances $a_A(\nu) + a_B(\nu)$; the difference grows with absorbance.

From the last observations it follows that the intensities of some of the strongest bands of the complex, which are near coincident with AH or B bands, may be affected by those non-linearity deviations; therefore they are not suitable for quantitative analytical purposes. Instead, the most suitable band in that respect is the bonded $\nu(OH)$ band of the complex which is hardly affected by the subtraction of any of both AH or B spectra.

Another difficulty in the application of the spectral subtraction procedure is to determine precisely how much B should be subtracted when the spectra of the complex and that of B are only slightly different in their common bands. Figures 2 and 3 again illustrate that point, particularly in

the CH stretching region, 3100–2600 cm^{-1}. Carrying out this procedure on a number of spectra, with different initial conditions, helps to identify band shifts and other features. An important final comparison is given by the ratio of the absorbance in the CH stretching region to that of the characteristic bonded $\nu(OH)$ band. Values of this ratio differing as much as 15% for different initial mixtures are not uncommon in independent initial trials; after more careful subtractions the integrated intensity of the CH stretching region in the case of the TFE–THF complex may be considered accurate within 5%, with respect to that of the $\nu(OH)$ band.

Condensation and adsorption problems in the determination of the absorptivity of the complex

Figure 4a is a plot of the absorbance at 3437 cm^{-1}, the characteristic bonded OH band of the complex, as a function of the decrease in the free OH band of TFE, for a series of experiments made according to the liquid injection procedure
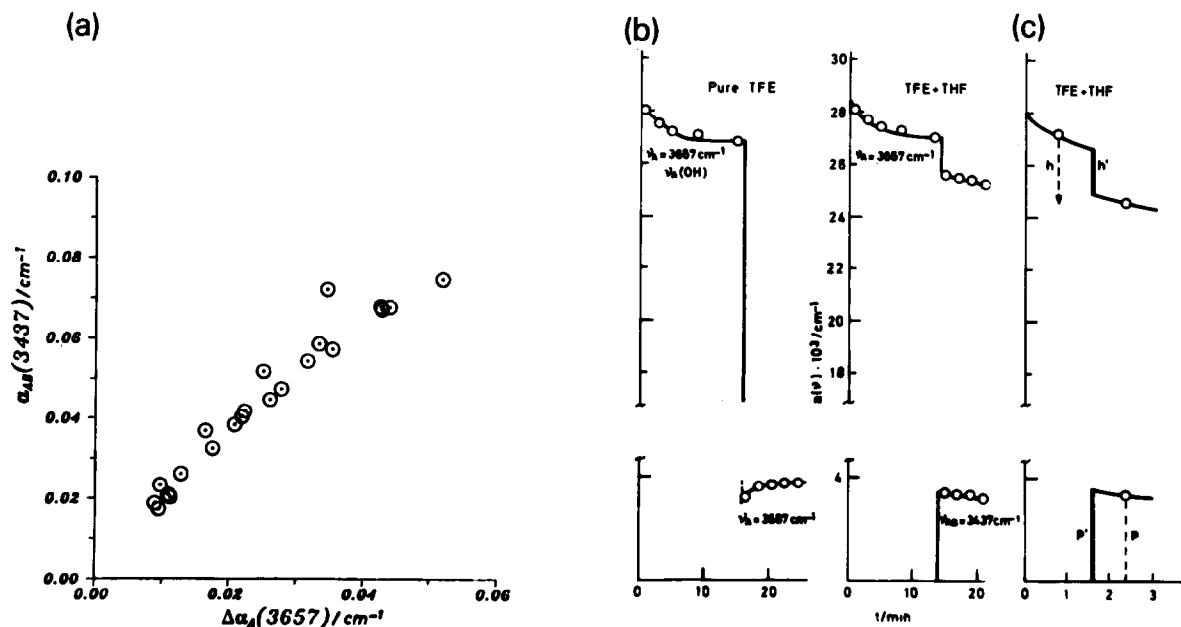

Fig. 4. (a) Absorbance of the 3437 cm^{-1} band of AH $\cdots$ B vs. the decrease in the absorbance of the 3657 cm^{-1} of free AH. (b) Adsorption effects monitored through the absorbance of characteristic bands of AH and AH $\cdots$ B. Shown are plots of absorbance vs. time. Discontinuities correspond to additions of B. (c) In a blown-up time scale, it is shown that ignoring adsorption the values of the ratio $\epsilon_{AB}(3437)/\epsilon_A(3657)$ are 15% lower than taking it into account (see text for details).

previously described. There is a tendency of a_{AB} to reach a saturation value, which would correspond to condensation of the complex, so the relation of the absorptivity of the bonded TFE to that of the free TFE, ϵ_{AB} (3437 cm^{-1})/ϵ_A (3657 cm^{-1}) may be taken as reliable for small conversions only.

To assess the influence of adsorption on these measurements, we tried also to establish the change with time of the absorbances of TFE and the TFE $\cdots$ B complexes. The case of pure TFE is illustrated in Fig. 4b, left. At $t = 0$, 3 μl of liquid TFE were injected into the cell and the IR spectrum was taken at various times within ca. 16 min. The cell was then partially evacuated and again several spectra were run to follow the time evolution of TFE pressure. The presence of adsorption–desorption phenomena is clearly shown by the changes in the spectral absorbance of the TFE.

The right part of Fig. 4b refers to the case of complex formation reaction. Now 5 μl of THF were injected into the cell about 14 min after the TFE introduction; the concentrations of the alcohol and the complex were monitored by the characteristic OH stretching free (3657 cm^{-1}) and bonded (3437 cm^{-1}) bands, respectively. The plot shows that after complex formation both AH and AH $\cdots$ B slowly but continuously disappear from the gas phase, which may be interpreted as due to adsorption of the complex, and the consequent depletion of AH to maintain the equilibrium.

The diagram in Fig. 4c, which is drawn in a blow-up scale, shows that the values of the ratio ϵ_{AB} (3437)/ϵ_A (3657) estimated from the variation of the corresponding absorbances (as made in Fig. 4a) will necessarily be distorted because of adsorption. THF was injected immediately (within ca. 1 min) after recording the spectrum of the pure TFE sample. The spectrum of the mixture was taken also immediately (ca. 1 min) afterwards. The experimental measurements as used in the plot of Fig. 4a correspond to the ratio of the broken segments (p/h) for each ν_{AB} and ν_A. However, if adsorption were properly taken into account, this ratio should be calculated using the vertical solid lines (p'/h') at the time of mixing. For the conditions illustrated in Fig. 4b, the latter

ratio should be around 15% higher than the former.

Direct pressure measurements and reference spectra

The only way out of these difficulties is to rely on the total pressure measurements carried out during the scanning of the spectrum of each mixture, and its apportioning in terms of p_A, p_B and p_{AB}.

As previously discussed, we may secure a reasonable IR spectrum for each of the complexes studied by "isolating" it from the corresponding equilibrium mixture. From series of spectra of different mixtures of a given system, we can establish a single reference spectrum of the complex, for example, by choosing the one with better signal-to-noise ratio, or, preferably, by taking a weighted average of all of them. All we need now in order to determine the absorptivity of the complex is a procedure to find the partial pressure, p_{AB}^*, corresponding to this reference spectrum $a_{AB}^*(\nu)$. To this end, we resort to the "quantitative" measurements done with the 12.5 cm length cell. Recording the spectra of several mixtures and at the same time the total pressure (P) and the temperature inside the cell, we can try to reproduce the spectrum of each mixture (in area and in contour) as a sum of contributions from AH and B and from AB, taken as f_{AB}^* times its reference spectrum. A plot of f_{AB}^* versus $p_{AB} = P - (p_A + p_B)$ should give a straight line through the origin with a slope $m^* = 1/p_{AB}^*$; the absorptivity of the complex follows as $\epsilon_{AB}(\nu) = a_{AB}^*(\nu)/p_{AB}^* l$.

As an example of the determination of ϵ_{AB}, Fig. 5 shows one such plot for the TFE–THF complex; its assigned reference spectrum, which was the result of averaging over six different spectra, is found to correspond to a complex partial pressure of 0.85 ± 0.06 mbar in the 12.5 cm path-length cell. Since the reference spectra are necessarily arbitrary, we can normalize them to 1 mbar pressure of the complex. We show in Figs. 6–8 the normalized spectra for several complexes in the 12.5-cm cell grouped together according to their common alcohol partner.
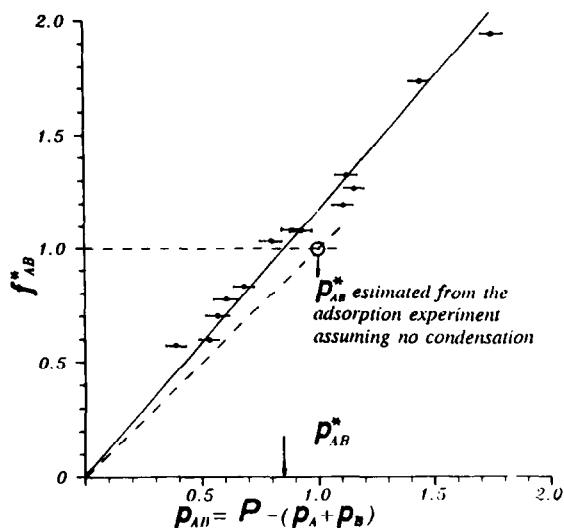
Fig. 5. f_{AB}^* vs. $p_{AB} = P - (p_A + p_B)$. Plot used for the determination of the absorptivity of the complex.

In Fig. 5 we have also shown the partial pressure that would be assigned to the TFE–THF reference spectrum according to the absorbance relations $\epsilon_{AB}(3437)/\epsilon_A(3657)$ derived from the adsorption experiment, assuming no condensation (Fig. 4b right). We confirm that AH $\cdots$ B condensation may easily occur when the reactants are mixed by injecting one of them (here B) into the cell. (More free OH's disappear than bonded OH's appear.)

Although p_{AB}^* is still given essentially as a difference between two larger numbers, the averaging operation implicit in our procedure turns it into a statistical magnitude, thus improving its reliability. In favorable cases (complexes of medium strength and some other stronger ones with high enough vapor pressures) accuracies of 5% or better may be obtained. In other cases, one should give estimated accuracies not higher than 10%.

Some additional details may be illustrated with the complexes of perfluoro-tert-butanol with ammonia, trimethyl- and triethylamine. All of them condensate as solids when mixing the alcohol and the base in the small glass bulb close to the IR cell. There was an additional problem with the alcohol: the commercial sample, as received, had

some impurities. The main impurity, however, lacked acid character and did not react with the base, remaining in the vapor phase when the alcohol was almost quantitatively removed with an excess of the base [a]. We got rid of this impurity by fractional removal of the vapor until the spectrum showed no trace of the impurity. The remaining solid is mainly a solution of AH $\cdots$ B in B, as was verified from the spectra of successive fractions. We used these spectra to plot f_{AB}^* for the trimethylamine complex where the partial pressure p_{AB} ranged from 0 to 3 mbar. It was not possible to use a similar procedure for the triethylamine complex because the complex vapor pressure at 22°C was not higher than 0.3 mbar. (The triethylamine spectra were run using our long-path cell.) For the ammonia complex, the f_{AB}^* plot could not be applied either because pressure broadening effects on the NH_3 spectra made a precise determination of p_{NH_3} impossible.

HB insensitive bands as internal standards

An interesting question concerns the possible existence of bands which appear in the spectra of series of complexes derived from the same alcohol, and which are not sensitive to the strength of the H-bonding. Such bands could be used as internal references to calibrate absorptivities of complexes in unfavorable situations, e.g. the above-mentioned cases of low vapour pressure, or very small equilibrium constants.

This question may be experimentally answered by comparing the spectra within each group of complexes, looking for coincidences (or near-coincidences) in both frequency and intensity. As previously noted, the stronger bands of the complex, being closer to the most intense bands of the monomers, are prone to suffer from important non-linearity deviations, and therefore they are not the most suitable for that comparison. As the weaker bands are not good candidates either because of signal-to-noise considerations, only a few bands remain which could be used for calibration purposes.

[a] The IR spectrum of that impurity points to a perfluorinated hydrocarbon which we could not identify.
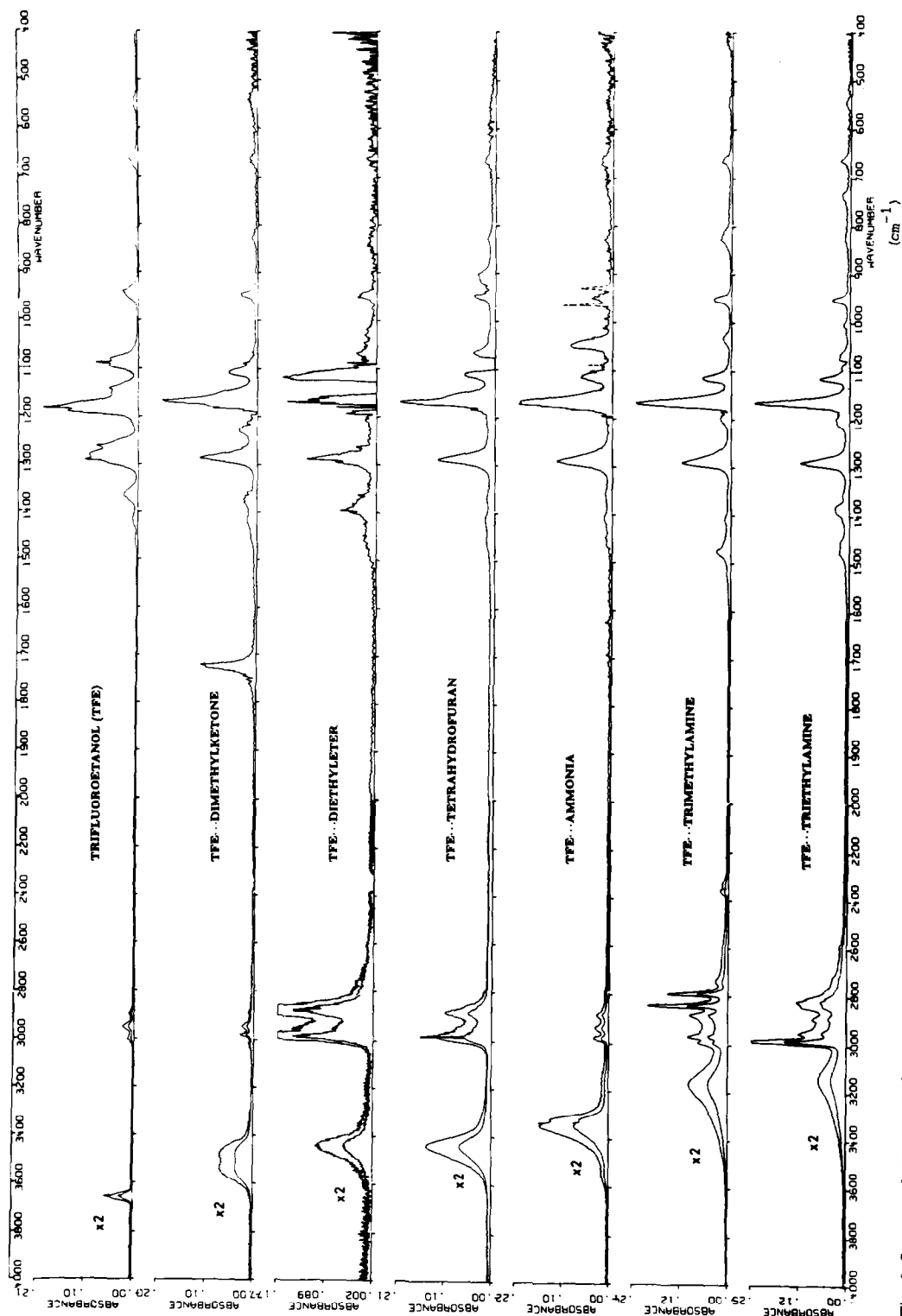
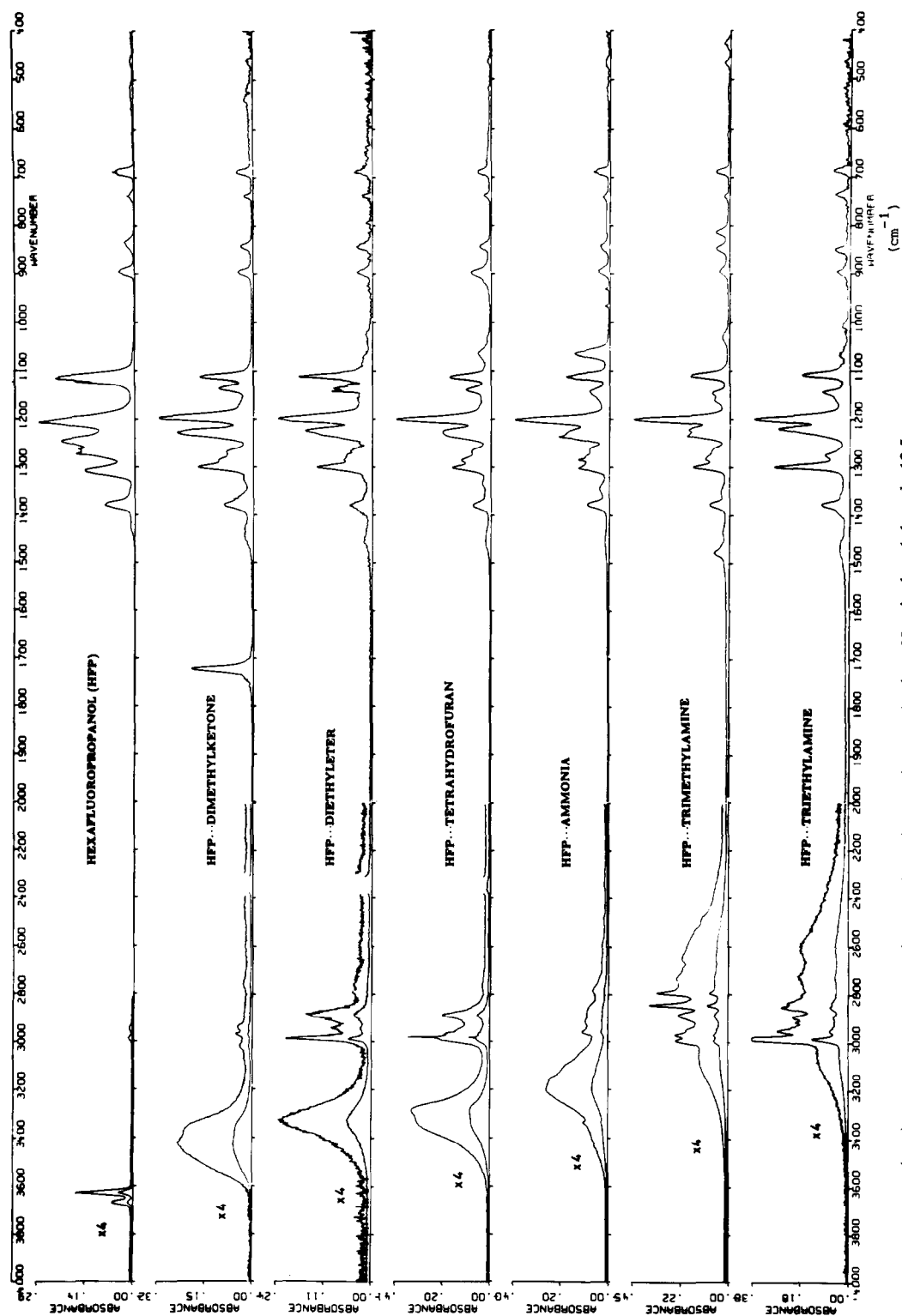Fig. 6. Spectra of CF_3CH_2OH and some of its complexes in gas phase at 1 mbar. Nominal path length, 12.5 cm.

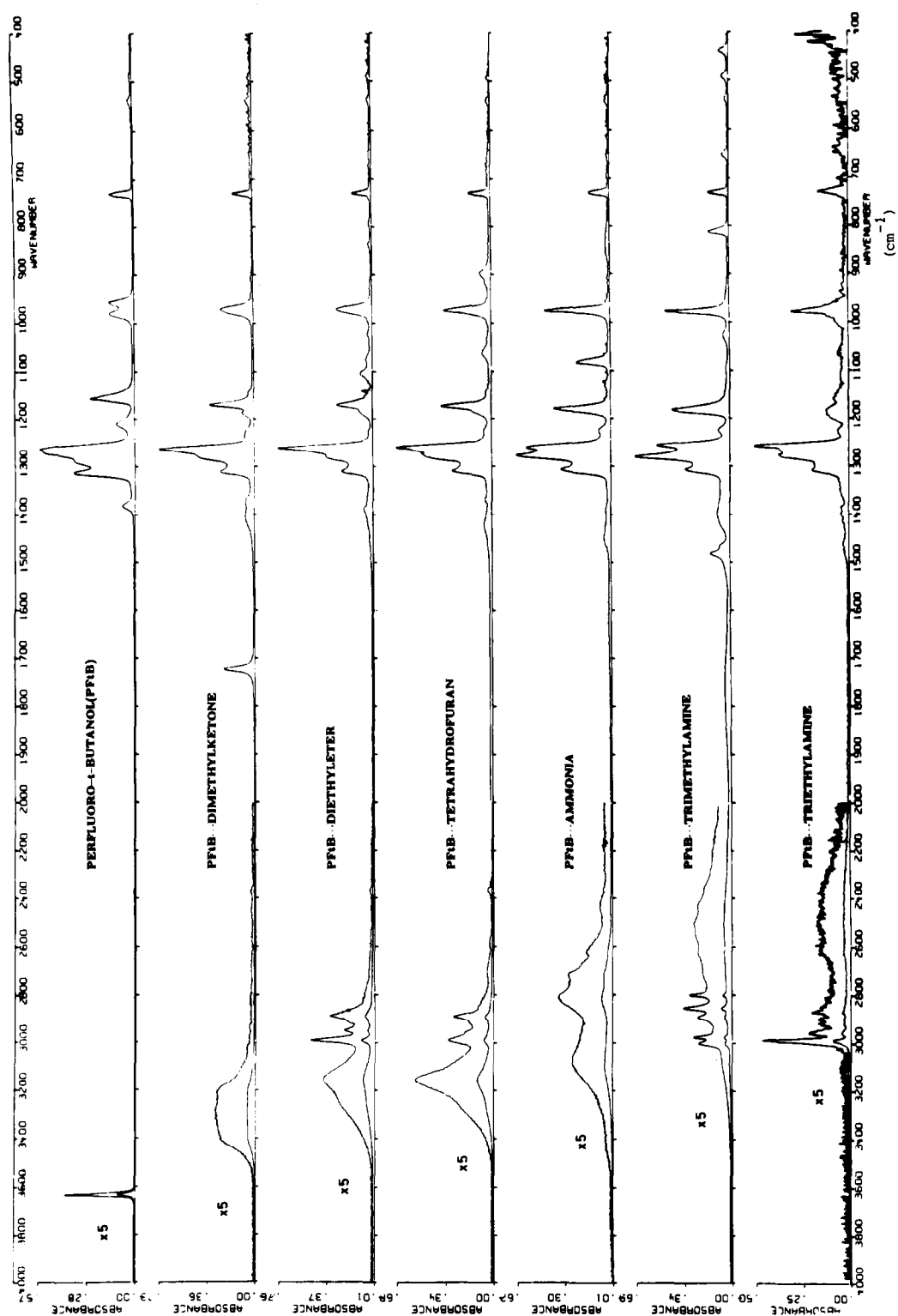Fig. 7. Spectra of (CF$_3$)$_2$CHOH and some of its complexes in gas phase at 1 mbar. Nominal path length, 12.5 cm.

Fig. 8. Spectra of $(CF_3)_3COH$ and some of its complexes in gas phase at 1 mbar. Nominal path length, 12.5 cm.

When looking closely enough, no truly insensitive band exits; frequency shifts of up to 5 or 6 wavenumbers are found, as well as changes in band contours, the bands of the complexes being generally narrower than those of the components. We thought of a way of relating the absorptivity of these insensitive bands in the complex to that of the corresponding band in the alcohol, by writing $\epsilon_{AB}(\nu_i') = R\epsilon_A(\nu_i)$ where ν_i and ν_i' are the wavenumber of the maxima of the bands in the alcohol and in the complex, respectively, and R is expected to be a number close to 1 and probably the same for all complexes in a series. If this is accomplished for those favourable cases where the absorptivity has been measured, the resulting R can ben used for the unfavourable cases mentioned above. For the TFE complexes, the insensitive bands are found to be those at 1292, 830 and 665 cm^{-1}; they show in fact the same absorbance, within $\pm 10\%$, in the maximum of the band in the complexes and in the free alcohol. For the PFtB case only the 729 cm^{-1} band seems to be adequate for the complexes as well as for the free alcohol. For the HFP series, however, no bands seem to have a constant intensity ($\pm 10\%$) in the free alcohol and in the complexes. A band of the alcohol at 1116 cm^{-1} splits in the complexes into two components, one of them staying near 1116 cm^{-1}; this component is a possible standard for the series of complexes.

A more direct approach to estimate the complex absorptivity is based on the localization of isobestic points. Such points were found for the ν(CO) stretching bands of the complexes of the various fluoroalcohols with dimethylketone and for the ν(CN) band of tetramethylguanidine. Figure 9 shows spectra of a number of mixtures of HFP and dimethylketone in this region, where the isobestic point is found at 1734.8 ± 0.2 cm^{-1}. The equal absorptivity value at this point for acetone and the complex can be used as a calibration reference for the whole spectrum of the complex.

Summarizing all the precedent discussions on the determination of complex absorptivities we have considered essentially the following procedures: (a) determination of the partial pressure of a reference spectrum through total pressure mea-
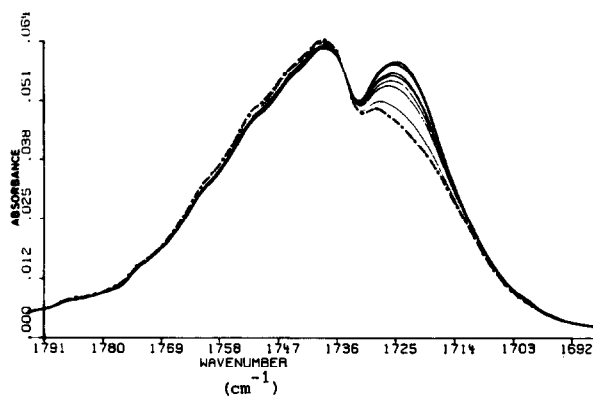

Fig. 9. HB effects on the CO stretching band of acetone; broken line pure ketone, solid lines mixtures with $(CF_3)_2CHOH$. The spectra were normalized to a constant initial pressure of ketone.

surement and spectroscopic analysis of a number of mixtures; (b) ratios of variation of free and bonded ν(OH) bands, $a_{AB}(OH')/a_A(OH)$, corrected for adsorption and extrapolated to low conversions or, better, normalized by reference bands; (c) direct comparison of intensities of selected reference bands (assumed to present the same intensity in the various complexes with a common partner); (d) localization of isobestic points. The first three methods were applied for comparison purposes to the systems formed by the three fluoroalcohols and the bases tetrahydrofuran, acetone and trimethylamine (with HFP and PFtB) or triethylamine (with TFE). Isobestic points were localized and the resulting ϵ values compared with those derived using procedure (a) for all the acetone complexes. Deviations are not higher than 10% in any case. In all these cases the value taken to calculate the equilibrium constant is that resulting from method (a). In the remaining cases this value was that obtained from method (c).

RESULTS AND DISCUSSION

Equilibrium constants

Table 1 gathers the experimental values found for the spectral shifts of the ν(OH) stretching vibration and the equilibrium constant of the complex formation reaction for a number of HB

complexes derived from three fluoroalcohols and several organic bases. Besides the systems shown in the table we have also obtained the spectra and equilibrium constants of the 1:1 complexes formed by methanol and pyrrole with trimethylamine, finding K_p values of 0.66×10^{-3} and 1.0×10^{-3} mbar^{-1}, respectively, at 25°C (temperatures are indicated in the table as bracketed small type numbers).

These results allow us to treat the general problem of modeling HB interactions. In particular, it is known that in carbontetrachloride or cyclohexane solutions, equilibrium constants, K_c, for the reaction AH + B $\rightleftharpoons$ AH $\cdots$ B follow Eqn. 1 to a satisfactory level of precision:

$$\log K_c = 7.354\alpha_2^H\beta_2^H - 1.094 \qquad (1)$$

wherein α_2^H and β_2^H are descriptors of the HB acidity and basicity of AH and B, respectively. (The form of this equation was predicted in 1970 [15a] and its existence demonstrated in 1988 [15b].) Using our data for the K_p constants and tabulated values of α_2^H and β_2^H [15c], we find the following regression equation for the gas-phase data:

$$\log K_c(\mathrm{g}) = (7.90 \pm 0.39)\alpha_2^H\beta_2^H - (0.48 \pm 0.15) \qquad (2)$$

The quality of the fit to Eqn. 2 is quite satisfactory: $r = 0.987$, S.D. $= 0.12$ and $n = 13$. The slope

of Eqn. 2 is very close to that of Eqn. 1 (they agree within the respective limits of uncertainty). The intercepts differ by some 0.5 log units, perhaps indicating a small difference between the onsets of gas-phase and solution HB interactions.

Possibly the most important conclusion from Eqn. 2 is that the ranking of HB acidity and basicity found in solution is still quite valid in the gas-phase. Taken together with the above, it suggests that (at least for the molecules considered in this work), differential solution activity effects on AH, B and AH $\cdots$ B cancel to a very large extent. Furthermore, cyclo-C$_6$H$_{12}$ [21] and CCl$_4$ would turn out to be much more "inert" than generally believed. Last, Eqn. 2 allows to determination of β_2^H values for two gaseous bases, NH$_3$ and N(CH$_3$)$_3$ for which no values had been previously reported; they are 0.54 and 0.71, respectively.

Characteristic HB vibrations

We want here to comment briefly on some general regularities observed in the spectra of the fluoroalcohol complexes shown in Figs. 6–8 and advance some hints on their interpretation in terms of association and conformational isomerism effects. An assignment of most of the observed bands to characteristic group frequencies of the fluoroalcohol will also be proposed.

TABLE 1

Gas phase $\Delta\nu$(OH) spectral shifts and equilibrium constants of some HB fluoroalcohol complexes (temperature is 22°C unless otherwise indicated inferior between parentheses)

	Trifluoroethanol			Hexafluoro-2-propanol		Perfluoro-*tert*-butanol	
	$\Delta\nu$(OH) (cm^{-1})	$K_p \times 10^3$ (mbar^{-1})		$\Delta\nu$(OH) (cm^{-1})	$K_p \times 10^3$ (mbar^{-1})	$\Delta\nu$(OH) (cm^{-1})	$K_p \times 10^2$ (mbar^{-1})
		This work	Literature				
Propanal	108	0.76$_{(25)}$					
Diethylether	216	1.2$_{(28)}$		297	6.3$_{(25)}$	478	2.8
Dimethylketone	119, 179	2.2	1.9$^a_{(25)}$	204	10.4	230, 432	4.5
Tetrahydrofurane	218	3.4	2.84$^b_{(28)}$; 2.22$^c_{(25)}$	294, 339	23	477	15.6
Ammonia	311	2.3		427	24	570	21
Pyridine	370	7.8					
Trimethylamine	489	15.7$_{(23)}$	8.1^d; 11.2$^e_{(23)}$	876	333		667
Triethylamine	517	11.8		896	156	~1110	142
Tetramethylguanidine	468	158					

References: a [18]; b [19a]; c [19b]; d [20a]; e [20b].

We first consider the stretching, $\nu(OH)$, and in-plane and out-of-plane bending, $\delta(OH)$ and $\gamma(OH)$, vibrational modes. To emphasize the effect of H-bonding on the $\nu(OH)$ bands we have included in Figs. 6–8, in the region 2000–4000 cm^{-1}, magnified absorbance runs for the collection of complex spectra. All the usually considered conspicuous symptoms of H-bonding in the vibrational spectra are present here: $\nu(OH)$ band shifts, intensity enhancement and broadening. All of them are connected with the strength of the H-bond and accompanied, for the strongest bonds, by the appearing of several submaxima. As it is well known [3,4], the current theoretical interpretations of these effects are made in terms of strong coupling of the high-frequency $\nu(OH)$ mode with low-frequency modes, together with Fermi resonances with overtone and combination modes.

The bending (OH) bands are much weaker and difficult to localize. In a previous paper [22] we have related the $\delta(OH)$ vibrational mode of TFE with two bands of the pure alcohol which disappear in the HB complexes and are also affected by OH/OD deuterium substitution. The doubling, at 1367 and 1263 cm^{-1}, was attributed to a Fermi resonance. In the TFE complexes the bonded $\delta(OH)$ mode appears as a broad and weak band, 150–200 cm^{-1} wide, shifting from ca. 1400 cm^{-1} (propanal) to ca. 1500 cm^{-1} (trimethylamine). Similarly weak and broad bands were found for the bonded $\gamma(OH)$ mode, shifting from 500–600 cm^{-1} (propanal complex) to 725–800 (trimethylamine complex).

Bending (OH) modes are also difficult to localize in the spectra of HFP and PFtB complexes. Based on the analogy of the TFE case, we propose to assign the $\delta(OH)$ mode of pure HFP to one of the two bands, at 1273 and 1263 cm^{-1}, which seems to be lacking in the H-bonded complexes. If pure gaseous HFP is in fact a mixture of two isomeric forms, as proposed for example in [23], these two bands could be assigned to their respective $\delta(OH)$ modes. The spectra of all HFP complexes show a weak IR absorption in the 1450–1480 cm^{-1} region, which may be considered to come from the $\delta(OH)$ mode. Similarly, a band of pure PFtB at 1271 cm^{-1} (strongly over-lapped by near bands at 1292 and 1263 cm^{-1}), which seems to be absent in the PFtB complexes, looks as the best candidate to be assigned to the $\delta(OH)$ mode; it would be shifted to ca. 1450 cm^{-1} in all the H-bonded complexes.

Absorption assignable to the $\gamma(OH)$ mode in the HFP and PFtB complexes is observed only in some of them in the form of a broad background wave, which shifts from ca. 500 to ca. 800 cm^{-1} in the HFP adducts and from ca. 600 to ca. 900 in those of PFtB when passing from weak to stronger H-bonds.

Spectra–structure correlations for the HB fluoroalcohols

A remarkable feature common to all spectra of the various HB complexes in the mid-infrared region below 1600 cm^{-1} is the close similarity shown by all those derived from the same alcohol. It is evident that all the spectra are dominated by bands characteristic of the fluoroalcohol moiety and a same definite pattern is found in all the complexes, which is different from that of the pure alcohol. The molecules of the three fluoroalcohols considered here are supposed to have structures stabilized by intramolecular OH $\cdots$ F bonds. The formation of intermolecular H-bonds in the complexes implies the breaking of the intramolecular ones and consequent changes in conformational structure and spectra.

Noting that the stronger IR bands in the spectra of TFE and its derivatives come from the $\nu(CF)$ vibrations, more or less coupled with other internal coordinates, we advanced in our previous paper on the TFE complexes [22] a simple qualitative argument which aids in understanding the spectral differences shown by pure gas TFE and its HB complexes. This argument is based on the symmetry of the environment about the CF$_3$ group, which approaches a C_{3v} site in the complexes and a C_s site, at most, in the OH $\cdots$ F bonded isolated molecules. The stretching $\nu(CF_3)$ vibrations may thus appear as only two bands ($A_1 + E$) in the complexes and as three bands (with different couplings with other group vibrations) in the spectrum of gaseous TFE. A practical way of discarding the effects of the internal OH $\cdots$ F bonds on the spectra of the TFE com-

plexes is to compare them with the spectra of other simple CF_3 compounds, as similar as possible but without the OH group. Edgell et al. [24] studied thirty years ago the series CF_3CH_2X, with X representing halogen atoms, condensing their results in a correlation diagram including all the compounds and almost all their fundamental frequencies. Our spectra of TFE complexes nicely fit into the Edgell diagram and the assignment thus derivable agrees very well with our previous assignments.

The same reasoning and procedures were applied to the IR spectra of HFP and PFtB complexes compared to the spectra of $(CF_3)_2CX_2$ and $(CF_3)_3CX$ (X = H, D, F, Cl, Br, I) studied by Bürger and coworkers [25–27] as part of a large series on the vibrational spectra of CF_3 compounds. The resulting correlations and the derived vibrational assignments for the three fluoroalcohols are shown in Table 2. All the wavenumbers quoted in this table correspond to the ammonia complexes of the three alcohols; the $\Delta\nu$ given are the shifts of the "free" alcohol

bands on HB complexation (positive: upward; negative: downward shifts).

It is worth remarking the very good correlation found between the PFtB complexes and the perfluorinated hydrocarbons studied in [27] under the assumption of C_{3v} molecular symmetry. While PFtB complexes conform well to this assumption, the pure PFtB shows some deviations. Notice especially the single band shown in all the complexes around 975 cm^{-1}, assignable as the ν_{21} doubly degenerated $\nu(CC_3)(e)$, which in pure PFtB appears split into two bands. This may be easily understood as being due to the symmetry lowering following the formation of an internal OH $\cdots$ F bond in the free PFtB molecule. The vibrational assignments for pure PFtB resulting from Table 2 differ in a few instances from those of Murto et al. [28].

In the HFP case the spectrum of pure HFP is apparently simpler than that of the bonded one, but on a closer look a number of bands of HFP seem to have a double structure. Because of the clear doubling of the $\nu(OH)$ and $\nu(CH)$ bands, it

TABLE 2

Characteristic group vibrations in the IR spectra of fluoroalcohol–ammonia complexes (1500–400 cm^{-1}) ($\Delta\nu = \nu_{dimer} - \nu_{monomer}$, in gas phase)

Group vibrations	$CF_3CH_2OH \cdots NH_3$			$(CF_3)_2CHOH \cdots NH_3$			$(CF_3)_3COH \cdots NH_3$		
	ν (cm^{-1})	type	$\Delta\nu$	ν (cm^{-1})	type	$\Delta\nu$	ν (cm^{-1})	type	$\Delta\nu$
δ(OH)	~ 1450		150	~ 1450		~ 176	~ 1450		~ 180
						186			
	1460	$\delta(CH_2)$	2						
CH deformations	1415	$\omega(CH_2)$	0	1373	δ(CH)	−2			
	~ 1150	t(CH$_2$)	10	897	γ(CH)	1			
	940	r(CH$_2$)	0						
	1288	$\nu_s(a_1)$	−4	1302	$\nu_s(a')$	−5	1308	$\nu_s(a_1)$	−4
				1289	$\nu_s(a'')$		1278	$\nu_s(e)$	−8
$\nu(CF_3)$	1162	$\nu_a(e)$	−20	1236	$\nu_{as}(a')$	−9	1261	$\nu_{as}(a_1, e)$	−2
	−			1228	$\nu_{as}(a'')$		1225	$\nu_{as}(e)$	−15
				1201	$\nu_{as}(a')$	−5	1127	$\nu_{as}(a_2)$	
				1111	$\nu_{as}(a'')$	−5			
ν(CO)	1106		18	1143		26	1179		23
NH$_3(\nu_2)$	1041		91	1064		114	1084		134
ν(CC)	830		0	841		7	976		
				741		3			
γ(OH)	~ 660			~ 780			~ 830		
	~ 668	$\delta_s(CF_3)$	~ 0	688	$\delta_s(a')$		730	$\delta_s(e)$	
$\delta(CF_3)$	548	$\delta_{as}(CF_3)$	~ 0	550	$\delta_{as}(a'')$	−5	537	$\delta_{as}(e)$	
	−			520	$\delta_{as}(a'')$	3	~ 490	$\delta_{as}(a_1)$	

is generally agreed that HFP consists of two conformers, with symmetries C_s and C_1 [29,30]. Our spectra of HB complexes, which may be interpreted in terms of only one conformer, are compatible with two conformers for the pure alcohol.

In our previous paper on TFE [22] we concluded that our evidence from the IR spectra of TFE and some deuterated derivatives pointed to the presence of only one conformer (*gauche*, internally hydrogen-bonded) in pure gaseous TFE. In a recent study on torsional vibrations and barriers to internal rotation in ethanol and TFE, Durig and Larsen [30] assign their new data on far-infrared and Raman spectra of gaseous TFE and deuterated analogues to both *gauche* and *trans* conformers. However, difficulties are found for totally fitting the *trans* conformer data and the authors point out the interest of carrying out an ab initio study to determine the molecular motions for the low-frequency modes of this molecule.

A previous ab initio calculation on the geometry of TFE (STO-3G) was published by Curtiss et al. [31], who found that the two lowest energy structures are the *gauche*-staggered and the *trans*-staggered, the former being apparently stabilized by an internal OH $\cdots$ F hydrogen bond. We note that the ν(OH) wavenumbers shown by the three alcohols (TFE: 3657 cm^{-1}; HFP: 3666 and 3626 cm^{-1}; PFtB: 3630 cm^{-1}) point to internal H-bonding in all three cases, increasing in strength with the number of CF$_3$ substituents. The two bands shown by HFP could be due to a doubling because of proton tunnelling between two equivalent OH $\cdots$ F hydrogen-bonded structures.

Additional important information on these points, widening the experimental data base in which to found vibrational assignments and spectra–structure correlations, could come from the study of HB effects in the far-IR region, 50–500 cm^{-1}. We intend to extend our work in this direction in the near future.

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