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FT-IR (7500−1800 cm^{-1}) Study of Hydrogen-Bond Complexes between Phenols−OH(OD) and Pyridine. Evidence of Proton Transfer in the Second Vibrational Excited State

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The FT-IR spectra (7500−1800 cm^{-1}) of phenol−OH(OD)·pyridine complexes are investigated at 25 °C in carbon tetrachloride. The pK_a of the phenols range from 10.2 to 6, and no proton transfer occurs in the fundamental and first excited vibrational state. The anharmonicities of the ν(OH···N) and ν(OD···N) vibrations are determined from the experimental frequencies of the fundamental transitions and of the first overtones. The anharmonicities of the ν(OH···N) vibration are rather high (between 180 and 235 cm^{-1}) and are lower for the ν(OD···N) vibration (between 115 and 125 cm^{-1}). The first overtone of the ν(OH···N) vibration shows for the stronger phenol−OH·pyridine complexes a splitting assigned to proton transfer in the second vibrational excited state. The principal values of the potential shape (barrier height and values of the two minima) are calculated by the Lippincott−Schroeder potential function. The computed parameters indicate that for the weakest complexes the second minimum potential is higher than the $v = 2$ vibrational level, in contrast with the strongest complexes, where the second minimum occurs at lower values than the $v = 2$ level. The isotopic ratio varies between 1.346 and 1.255. The lowest values are observed for the complexes where the barrier top is in the vicinity of the first excited vibrational level. The correlation between the enthalpies of complex formation and the experimental and harmonic frequency shifts is discussed. The overtones and combination bands of pyridine are more perturbed in the stronger complexes.

Introduction

To gain insight into the nature of hydrogen bonding, it is essential to obtain information on the shape of the potential surface in these systems; of particular interest are its anharmonicity and possible double-minimum character. One might try to answer this experimentally by measuring overtones in the IR spectrum, comparing free and associated species. However, as pointed out recently by Sandorfy,[1] the near-infrared region, where the overtones of the OH, NH stretching vibrations are observed, is seldom used by researchers and in these last two decades, very few experimental near-IR data have been published. The reason is perhaps that the overtones of hydrogen-bonded species have a very weak intensity and that the near-IR spectra of polyatomic molecules are generally characterized by numerous bands originating not only from overtones but also from combinations or simultaneous transitions, which make the assignment of the absorptions particularly difficult.[2−4]

Studies performed on hydrogen bonds of medium strength (self-associated alcohols or phenols,[5−9] pyrrole,[10] aliphatic amides[11]) have shown that the anharmonicity of the OH or NH stretching vibration generally increases by hydrogen bond formation. However for weakly hydrogen-bonded systems such as in aliphatic amines,[12] the experimental anharmonicity of the NH stretching vibration is nearly the same in free and self-associated species. These data are relative to different proton donors and proton acceptors, solvents, and temperatures. The present investigation represents an attempt to observe and to discuss the near-IR spectra of closely related complexes, namely, the phenol·pyridine complexes where the choice of phenols characterized by different acidities (pK_a ranging from 10.2 to 6) allows the modulation of the hydrogen bond strength. These complexes were also chosen because, as suggested by their thermodynamic parameters,[13−19] they are relatively strong, their complexation enthalpies ranging from 25 to 36 k J mol^{-1}.

It is useful to remember here that the potential energy ruling the vibrational motions can be written, to second order,

$$V = {}^{1}\!/_{2}k_2q^2 + k_3q^3 + k_4q^3 + ... \qquad (1)$$

where k_2, k_3, and k_4 are the harmonic, cubic, and quartic potential constants and q is a normal coordinate.

The second-order perturbation treatment considers the cubic and quartic terms as perturbating potential, and this yields the following expression for the vibrational energy,

$$E_v = h\nu_e[(v + {}^{1}\!/_{2}) - x_e(v + {}^{1}\!/_{2})^2] \qquad (2)$$

where ν_e is the harmonic frequency, v the vibrational quantum number, and x_e the anharmonicity constant. In particular, the experimental wavenumbers of the fundamental (ν_{01}) and the first overtone (ν_{02}) are related to the anharmonicity (X_{12}) and to the harmonic frequency by the expression

$$X_{12} = \nu_{01} - \nu_{02}/2 = \nu_e x_e \quad \text{or} \quad \nu_e = \nu_{01} + 2X_{12} \qquad (3)$$

This perturbation theory can be considered as valid for weakly hydrogen bonded systems but has been questioned for strongly interacting systems.[20]

The same theory also predicts that the anharmonicity constants should be inversely proportional to the square root of the ratio of the corresponding reduced masses (ρ). When considering OH and OD vibrations, the ratio of the experimental frequencies and anharmonicities can be expressed by

$$\nu^D/\nu^H = \rho \qquad (\nu_e x_e)^H/(\nu_e x_e)^D = \rho^2 \qquad (4)$$

In the case of a free OH(OD) group considered as a diatomic oscillator, $\rho = 0.7278$ and $\rho^2 = 0.53$. Correlation (3) is in

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TABLE 1: Mid-IR Data (cm^{-1}) for Phenol−OH and Phenol−OD Complexed with Pyridine and Experimental Enthalpies of Complex Formation ($kJ\ mol^{-1}$). $T^0 = 298$ K. Solvent = Carbon Tetrachloride

phenol	$\nu_{01}(OH\cdots N)$	$\Delta\nu_{01}{}^{H}$ [a]	$\nu_{01}(OD\cdots N)$	$\Delta\nu_{01}{}^{D}$ [b]	ISR_{01} [c]	$-\Delta H$ [d]
4-CH_3 phenol	3130	483	2325	343	1.346	24.7
phenol	3115	496	2320	346	1.343	25.9
4-Cl phenol	3070	540	2290	376	1.341	28.9
4-Br phenol	3060	547	2285	380	1.339	28.8
3-Br phenol	3020	585	2280	382	1.324	29.6
3,4-diCl phenol	2910	690	2240	422	1.299	31
3,5-diCl phenol	2860	740	2210	449	1.294	32.1
3-CF_3,4−NO_2 phenol	2700	890	2150	500	1.255	39

[a] The $\nu_{01}(OH)$ values for the free phenols range from 3613 to 3588 cm^{-1}. The values for the phenol and 4-CH_3 phenol complexes are within 10 cm^{-1} in agreement with those reported in ref 23. [b] The $\nu_{01}(OD)$ values for the free phenols−OD range between 2668 and 2651 cm^{-1} (ref 24). [c] The experimental error on the $\nu(OH\cdots N)$ frequencies is ± 20 cm^{-1} and on the ISR_{01} values ± 0.020. [d] From refs 15, 16, 19.

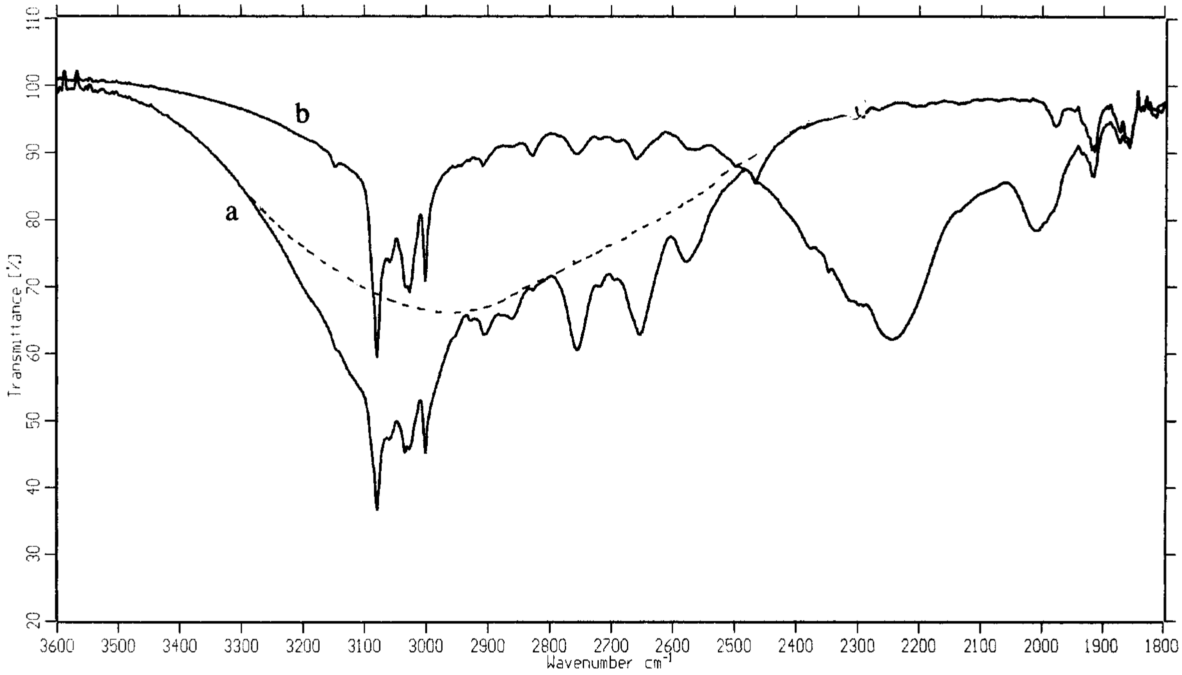

Figure 1. IR spectrum (3600−1800 cm^{-1}) of (a) a solution of 3,4-diCl phenol−OH ($c = 0.1$ mol dm^{-3}) and pyridine ($c = 0.3$ mol dm^{-3}), (b) a solution of 3,4-diCl phenol−OD ($c = 0.1$ mol dm^{-3}) and pyridine ($c = 0.3$ mol dm^{-3}). Solvent = carbon tetrachloride. Path length of the cell = 0.02 cm.

general not satisfied when the OH groups are involved in hydrogen bonds.[21,22]

Experimental Section

The IR spectra were recorded on the Bruker 66 spectrometer at a resolution of 2 cm^{-1}. For the near-IR spectra a Tungsten source, a CaF_2 beam splitter, and a cooled InSb detector were used. Cells in quartz infrasil of 5 cm path length were used. For the mid-IR spectra, the spectrometer was equipped with a Globar source, a KBr beam splitter, and a DTGS detector. Cells equipped with KBr windows of 0.02 cm path length were used.

Phenols from Across Chemica or Fluka were crystallized from a petroleum ether mixture. Pyridine from Fluka was dried on sodium sulfate. Phenol−OD were prepared by several exchanges with methanol−OD, and about 90% deuteration was achieved.

All the spectra were recorded at 25 °C in carbon tetrachloride.

Experimental Results and Discussion

1. Mid-IR Spectra. Table 1 reports the $\nu_{01}(OH\cdots N)$ and $\nu_{01}(OD\cdots N)$ values and the frequency shifts $\Delta\nu^{H}{}_{01}$ and $\Delta\nu^{D}{}_{01}$ computed from the free $\nu(OH)$ or $\nu(OD)$ vibration in the same solvent. Table 1 also lists the values of the isotopic ratios (ISR_{01}) of the stretching frequencies along with the enthalpies of complex formation ($-\Delta H$).[16,21] Figure 1 reproduces the IR spectrum of the 3,4-diCl phenol·pyridine complex in the fundamental region. This figure shows that the $\nu(OH)$ absorption is characterized by several submaxima, which have been assigned to Fermi resonance between the broad $\nu(OH\cdots N)$ level and internal vibrational modes of the proton donor moiety.[23] In all the phenol−(OD)·pyridine complexes, two main bands are observed. In the 3,4-diCl phenol−OD complex for example, the first absorption is observed at 2256 cm^{-1} and the second one at 2010 cm^{-1}. The intensity of the second band increases when the difference between the frequencies of the two bands decreases. This behavior is typical of a Fermi resonance, in the present case between the $\nu(OD\cdots N)$ and the first overtone of the $\delta(OD\cdots N)$ levels. A similar pattern was observed for the v(OD) vibrations of Shiff bases complexed with phenols.[25] The frequencies of the bands were calculated by the equation

$$\nu = \frac{\sum A_i \nu_i}{\sum A_i} \qquad (5)$$

where A_i are the intensities of the absorptions and ν_i their frequencies.

The isotopic ratio of the fundamental frequencies remains within experimental error practically constant when the com-

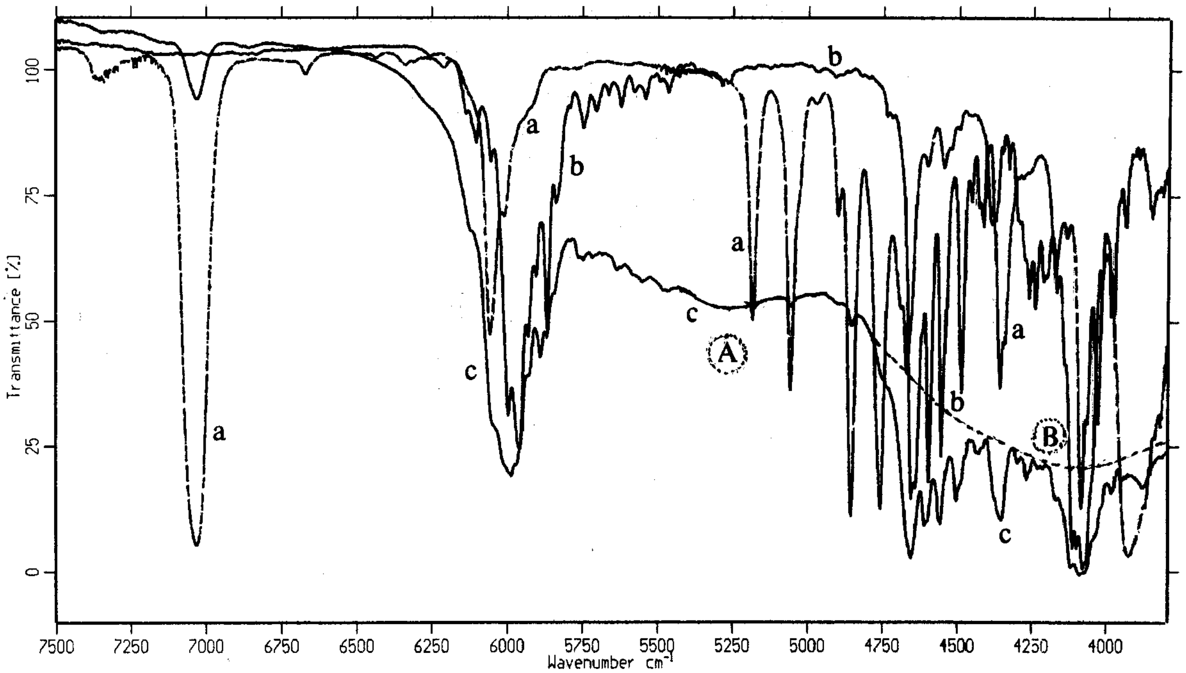

Figure 2. IR spectrum (7500−3800 cm^{-1}) of (a) 3,5-diCl phenol−OH (c = 0.1 mol dm^{-3}), (b) pyridine (c = 0.15 mol dm^{-3}), (c) a solution of 3,5-diCl phenol−OH and pyridine at the same concentrations as in a and b. Solvent = carbon tetrachloride. Path length of the cell = 5 cm.

plexation enthalpy varies between 24.7 and 29 kJ mol^{-1} and the $\Delta\nu$(OH) values between 340 and 380 cm^{-1}. For higher $-\Delta H$ or $\Delta\nu$ values a marked decrease can be observed. As discussed for OH···O hydrogen bonds, the curves ISR vs R(O···O) show that the ISR slowly decreases for weak and medium hydrogen bonds (those longer than 2.7 Å); the potential barrier separating the two wells remains relatively high, the proton staying preferentially in one well.[26−35] In most of the calculations, the potential energy of the proton was expressed as a polynomial function of the proton coordinate. In the present work, the height of the barrier was evaluated by using the Lippincott−Schroeder function, and this will be discussed in section 4.

It is worth mentioning here that the complexes investigated in this work are of the normal OH···N type and that no proton transfer in the first excited vibrational state occurs. This can be deduced from the decrease of the ν(OH···N) or ν(OD···N) wavenumbers with the acidity increase of the proton donor and from the fact that the typical vibrations of the pyridinium ion generally observed between 1650 and 400 cm^{-1} are not observed even for the strongest complexes.[36] The proton-transfer constant (K_{PT}) can be evaluated by the equation[37−39]

$$\log K_{\mathrm{PT}} = \xi \Delta \mathrm{p}K_{\mathrm{a}} + C$$

where ΔpK_a is the difference between the pK_a of the proton acceptor and the proton donor and C a constant depending on the solvent, the temperature, and the system. For amine−phenols systems, $\xi = 0.33$ and $C = -1.50$. For the stongest complex investigated in this work, the 4-NO$_2$,3-CF$_3$ phenol·pyridine complex, ΔpK_a is about −1 and the K_{PT} value takes a value of about 0.015.

2. Near-IR Spectra. The near-IR spectra of solutions of 3,5-dichlorophenol−OH·pyridine and 3,5-dichlorophenol−OD·pyridine are reproduced in Figures 2 and 3. For the weakest complexes (phenol and 4-CH$_3$ phenol), only one broad absorption culminating beween 5850 and 5680 cm^{-1} is observed (band A); for the more acidic phenols, two broad absorptions labeled A and B are observed. It is also noteworthy that all the absorptions previously assigned to binary combinations involving the ν(OH) and ring, δOH, or ν(C−O) stretching vibrations [24] show a strong intensity decrease. This is illustrated in Figure 2 for the 3,5-diCl phenol−OH·pyridine complex, where not only the ν_{02}(OH) absorption at 7033 cm^{-1} but also the absorptions at 5185, 5060 , 4901, and 4856 strongly decrease in intensity.

For the phenol−OD complexes, only one ν_{02}(OD···N) absorption is observed in the near-IR region. The intensity of the ν_{02}(OD) vibration decreases, and this is also the case for the combinations observed at 4239 and 3926 cm^{-1}.

Table 2 indicates the wavenumbers of the ν_{02}(OH···N) and ν_{02}(OD···N) absorptions, the frequency shifts from the free ν_{02}(OH) or ν_{02}(OD) vibrations, and the isotopic ratios observed for the first overtone (ISR$_{02}$). The corresponding anharmonicities X_{12}^{H} and X_{12}^{D} computed from eq 3, the harmonic frequencies ν^{e}(OH···N) and ν^{e}(OD···N), and the harmonic frequency shifts ($\Delta\nu_{01}^{\mathrm{H}}$ and $\Delta\nu_{01}^{\mathrm{D}}$) are listed in Table 3.

These data show that the anharmonicities of the ν(OH) vibrations are rather high , between 180 and 235 cm^{-1}, and are of the same magnitude as those observed for the ν(OH···N) vibration of aliphatic alcohols complexed with ammonia or trimethylamine in the gas phase (174−210 cm^{-1}).[40] For methanol and ethanol dissolved in pyridine, the experimental anharmonicities of the ν(OH···N) vibration are equal to 114 and 116 cm^{-1}, respectively,[41] and as suggested by the $\Delta\nu_{01}$(OH···N) frequency shifts of 325 and 315 cm^{-1}, the hydrogen bond is weaker in this case. For methanol−OD dissolved in pyridine, the anharmonicity of the ν(OD···N) vibration, 57 cm^{-1}, is also weaker than for the present phenol−OD complexes.

For the first five phenol−OH complexes investigated in this work, the anharmonicities seem to increase sligthly (from 205 to 235 cm^{-1}) with the hydrogen bond strength and decrease up to 180 cm^{-1} for the strongest complexes. Owing to the experimental error, which is on the order of magnitude of 20 cm^{-1}, these results must be taken with caution. The difference between 180 and 235 cm^{-1} is probably meaningful. For the phenol−OD complexes, the anharmonicities remain almost constant.

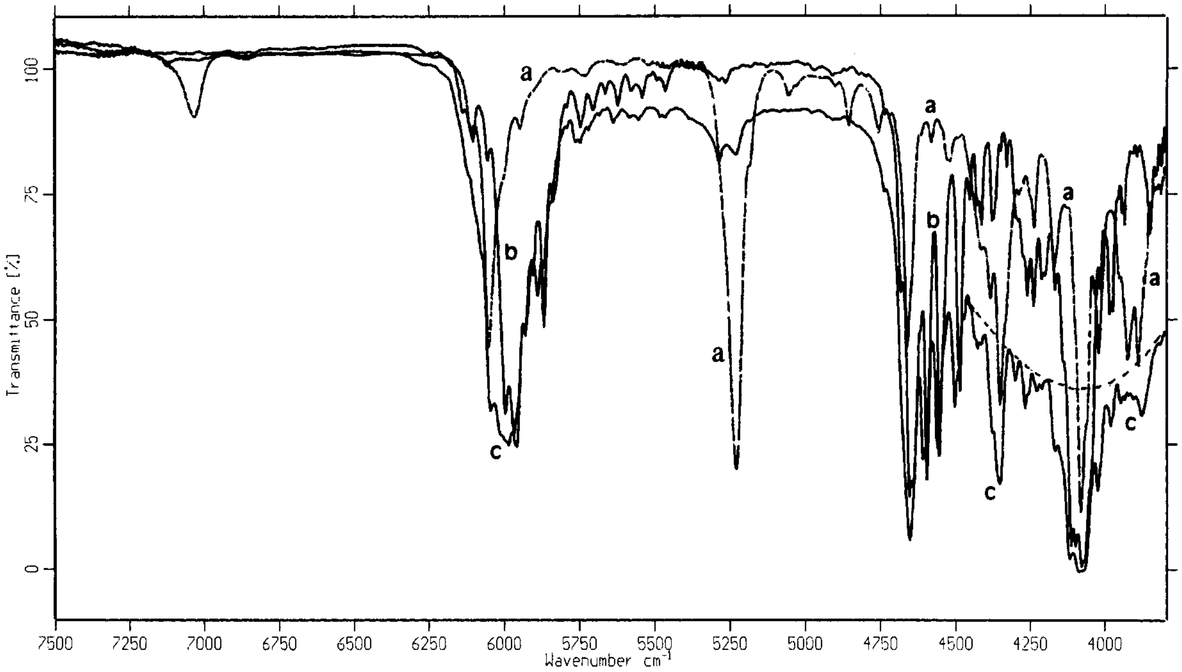

Figure 3. IR spectrum (7500−3800 cm^{-1}) of (a) 3,5-diCl phenol−OD, (b) pyridine, (c) their mixtures. Same experimental conditions in Figure 2.

TABLE 2: Near-IR Data (cm^{-1}) for Phenol−OH and Phenol−OD Complexed with Pyridine. T^0 = 298 K. Solvent = Carbon Tetrachloride

	ν_{02}(OH···N)					
phenol	A	B	$\Delta\nu_{02}^{H}$ [a]	ν_{02}(OD···N)	$\Delta\nu_{02}^{D}$ [b]	ISR$_{02}$ [c]
4-CH$_3$ phenol	5850		1207	4420	860	1.323
phenol	5800		1252	4410	865	1.315
4-Cl phenol	5700		1348	4340	900	1.313
4-Br phenol	5680	4100	1367	4330	900	1.312
3-Br phenol	5570	4100	1491	4310	930	1.292
3,4-diCl phenol	5350	4075	1690	4230	1005	1.264
3,5-diCl phenol	5280	4100	1773	4170	1060	1.266
3-CF$_3$,4-NO$_2$ phenol	2700	4200	1973	4030	1150	1.253

[a] The experimental ν(OH) values in free phenols range from 7057 to 7013 cm^{-1}. [b] The experimental ν(OD) values in free phenols−OD range from 5247 to 5220 cm^{-1} (ref 24). [c] The experimental errors on ν_{02}(OH···N) and on ν_{02}(OD···N) are 20 and 50 cm^{-1}, respectively, and the error on the isotopic ratio is ±0.02.

TABLE 3: Anharmonicities and Harmonic Frequency Shifts of the ν(OH···N) or ν(OD···N) Vibrations of Phenol−OH(OD)·Pyridine Complexes (All Data in cm^{-1})

phenol	X$_{12}^{H}$	ν_e(OH···N)	$\Delta\nu^{eH}$ [a]	X_{12}^{D}	ν^e(OD···N)	$\Delta\nu_e^{D}$ [b]
4-CH$_3$ phenol	205	3540	243	115	2555	203
phenol	215	3545	246	115	2550	204
4-Cl phenol	220	3510	270	120	2530	225
4-Br phenol	220	3500	277	120	2525	230
3-Br phenol	235	3500	283	125	2530	219
3,4-diCl phenol	220	3350	424	125	2490	260
3,5 diCl phenol	220	3300	466	125	2460	286
3-CF$_3$,4-NO$_2$ phenol	180	3060	692	125	2400	343

[a] The anharmonicities for the ν(OH) vibration of the free phenols−OH range between 85 and 82 cm^{-1} and the harmonic frequencies between 3782 and 3752 cm^{-1} (ref 24). [b] The anharmonicities of the ν(OD) vibration in free phenols−OD range between 45 and 41 cm^{-1} and the harmonic frequencies between 2758 and 2735 cm^{-1} (ref 24).

We did not find in the literature correlations between experimental anharmonicities and frequency shifts or complexation enthalpies. Such correlations have been however theoretically predicted for OH···O bonds from the maximum positions of the ν_{01}(OH) and ν_{02}(OH) transitions calculated with the aid of the asymmetrical distribution function.[42] For these bonds a slow increase of the anharmonicity was predicted for $\Delta\nu$(OH) frequency shifts ranging from 200 to 600 cm^{-1}. Recent MO-LCAO calculations performed at the 6-31G** level have demonstrated that for weak and medium OH···O hydrogen bonds the anharmonicity increases and reaches a maximum for a $R_{O\cdots O}$ distance of about 2.7 Å. For lower values of the distances, the anharmonicity decreases and becomes negative. The vibrations become superharmonic, and this should correspond to transitions in one single minimum.[43] For the NH···N bonds, the curves are shifted by about 0.1 Å to higher R distances. These results are in line with recent computations on the $O_2H_5^+$ cation, where the anharmonicity correction has been estimated to increase the computed harmonic frequency.[44] In this case, the potential energy surface is extremely flat and more similar to a quartic than to an anharmonic potential. In the present complexes, the decrease of the anharmonicity represents probably a real effect connected with a broadening and a flattening of the potential surface in the stronger complexes. Further it is known from second-order perturbation theory that the anharmonicity is related to the cubic and quartic potential constants by the expression

$$X = 15k_3^2/4\nu_e - (3/2)k_4 \qquad (6)$$

where k_3 is negative and k_4 positive. A decrease of X is probably connected with higher values of the quartic potential constant, the cubic one remaining approximately constant.[41] This must be however taken with caution because the validity of the second-order perturbation theory can be questioned for strong hydrogen bonds.[20]

3. Correlation between the Enthalpies and the Frequency Shifts. As discussed by C. Sandorfy,[2] it might appear astonishing that good linear relationships have been often obtained between ΔH and $\Delta\nu$. The explanation is probably that the change in anharmonicity is roughly proportional to the change in ΔH. In the present case, the anharmonicities are high and contribute to the frequency shifts by amounts between 200 and

250 cm^{-1}. The correlation between the experimental enthalpies and the experimental and harmonic frequency shifts can be written as

$$-\Delta H\ (\text{kJ mol}^{-1}) = (11.4 + 0.030)\Delta\nu^{\text{exp}}\ (\text{cm}^{-1})\ (r = 0.966) \quad (7)$$

$$-\Delta H\ (\text{kJ mol}^{-1}) = (8.4 + 0.087)\Delta\nu^{\text{e}}\ (\text{cm}^{-1})\ (r = 0.965) \quad (8)$$

The intercepts of eqs 7 and 8 do not greatly differ, but the slopes are about 3 times higher when the frequency shifts are corrected for the anharmonicities. A smaller difference between the slopes can however be expected for weaker hydrogen bonds.

4. Splitting of the Bands in the Second Vibrational Excited State. For the most acidic phenols (3-Br, 3,4-diCl, 3,5-diCl, and 4-CF$_3$,4-NO$_2$ phenol), a second absorption (labeled B) is observed between 4075 and 4200 cm^{-1}. Owing to the broadness of the absorption and the overlapping with phenols and pyridine absorptions, no difference between the absorption maxima of the different systems could be observed. This second absorption can be interpreted in terms of a proton transfer in the second vibrational excited state resulting from a double-minimum potential for the proton. For the phenol−OD complexes, only one broad band is observed. Because of the lower ν(OD) frequencies, we expect the second vibrational excited state below the barrier top.

To verify this mechanism, the proton-transfer barrier has been calculated by the Lippincott−Schroeder function.[46,47] It has been shown that this model supplies the general features for proton tunneling, proton delocalization beyond the barrier, and other types of processes in OH···O hydrogen bonds.[48] The OH···N bond is assumed to be linear.[49] Under the equilibrium conditions ($R_{\text{OH}\cdots\text{N}} = R_{0\text{OH}\cdots\text{N}}$), the Lippincott−Schroeder function can be written as

$$V = D_0\,[1 - \text{e}^{-\alpha}] - D_0{}^*[\text{e}^{-\beta}] + \frac{D^*{}_0 n^*[1 - (r_0{}^*/r_0)^2]\text{e}^{-\beta}}{[b - 1/(2R_0)]}$$

where D_0 and D_0* are the dissociation energies of the OH and NH$^+$ bonds, *b* is the repulsion parameter between the O and N atoms, r_0 and r_0* are the equilibrium distances of the free OH and NH$^+$ bonds, and *a* and *b* are functions of the elongations of the OH and NH$^+$ bonds.

The following standard set of potential parameters have been used:[46,47]

$$D_0 = 493\ \text{kJ mol}^{-1}$$

$$D_0{}^* = 290\ \text{kJ mol}^{-1}$$

$$n = 9.07 \times 10^8\ \text{cm}$$

$$n^* = 13.49 \times 10^8\ \text{cm}$$

$$r_0 = 0.97\ \text{Å}$$

$$r_0{}^* = 1.014\ \text{Å}$$

$$b = 4.8 \times 10^8\ \text{cm}$$

The potential parameters of the Lippincott−Schroeder function can be adjusted to allow for a stabilization of the ionic complexes in more polar solvents[50] or to reproduce the shape of the potential function in the gas phase.[51] For all the present complexes a double-minimum potential is obtained. For strong OH···N complexes in the gas phase, the potential trough (37 kJ mol^{-1}) is centered at $R = 2.6$ Å, but only one single minimum corresponding to the reactant configuration exists.[52] The gas-phase potential along the OH and O···N stretch coordinates is also quite anharmonic and becomes very shallow for large O···N separations.

TABLE 4: Principal Values of the Potential Shape for the Phenol·Pyridine Complexes Computed from the Lippincott−Schroeder Potential (Distances in Å, potentials in cm^{-1})

phenol	$R_{\text{O}\cdots\text{N}}$	r_{OH}	barrier height	V_{min}	V'_{min}
4-CH$_3$ phenol	2.751	0.990	11560	−1410	7900
phenol	2.748	0.991	11445	−1425	7850
4-Cl phenol	2.730	0.992	10760	−1565	7380
4-Br phenol	2.725	0.993	10565	−1610	7245
3-Br phenol	2.713	0.994	10110	−1715	6910
3,4-diCl phenol	2.667	1.001	8385	−2175	5485
3,5-diCl phenol	2.655	1.005	7945	−2320	5070
3-CF$_3$,4-NO$_2$ phenol	2.6	1.015	6025	−3080	2930

TABLE 5: Vibrational Energy Levels (v = 0, v = 1, and v = 2) for Complexes between Phenols−OH and Phenols−OD and Pyridine

phenol	$E^{\text{H}}_{v=0}$	$E^{\text{H}}_{v=1}$	$E^{\text{H}}_{v=2}$	$E^{\text{D}}_{v=0}$	$E^{\text{D}}_{v=1}$	$E^{\text{D}}_{v=2}$
4-CH$_3$ phenol	1718	4848	7568	1249	3573	5669
phenol	1716	4834	7520	1246	3567	5657
4-Cl phenol	1700	4770	7400	1235	3525	5575
4-Br phenol	1695	4755	7376	1232	3535	5575
3-Br phenol	1691	4721	7281	1233	3515	5543
3,4-diCl phenol	1620	4530	7000	1214	3454	5444
3,5-diCl phenol	1595	4455	6875	1198	3408	5368
3-CF$_3$,4-NO$_2$ phenol	1485	4185	6525	1169	3319	5218

The principal values of the potential shape (barrier heights and values of the first (V) and second (V') minima) are indicated in Table 4. The barrier heights are about 200 cm^{-1} higher than those computed by the same approach for OH···O hydrogen bonds.[48] As expected, the separation between the two minima decreases when the strength of the hydrogen bond increases.

The vibrational energy levels corresponding to $v = 0$, $v = 1$, and $v = 2$ are calculated by eq 1 taking into account the anharmonicities indicated in Table 3. The results are reported in Table 5 for the phenol−OH and phenol−OD complexes. The results are very similar to those computed by the semiclassical Planck−Sommerfeld phase integral

$$\int 2\sqrt{2m(E_{\text{v}} - V_{\text{r}})}\text{d}r = (\nu + {}^1\!/_2)\ \text{h}$$

from the smallest to the largest r_{OH} distances.

For a value of ν(OH···) equal to 3060 cm^{-1}, values of the zero-point energy of 1640 cm^{-1} and of the energy of the first vibrational level of 4700 cm^{-1} were indeed obtained by this method.[53] These values are very similar to the values of the present work, where the energies of the three first vibrational levels have been computed independently of the Lippincott−Schroeder function.

Inspection of the results of Tables 4 and 5 indicates that for the 4-CH$_3$ and phenol−OH·pyridine complexes the second minimum potential is higher than the $v = 2$ vibrational level, and this is illustated in Figure 4a. For the 4-Cl phenol complex, the two potential minima have about the same height. For the stronger complexes, the second minimum occurs at lower values than the $v = 2$ level (Figure 4b). These findings parallel the observation of a second absorption near 4100 cm^{-1}.

Since the $v = 2$ level for OD is much lower than the corresponding OH level, one would not expect the first OD overtone to be split at least for complexes of medium strength. The results of Tables 4 and 5 show however that for the two strongest complexes the V' level lies below the $v = 2$ level.

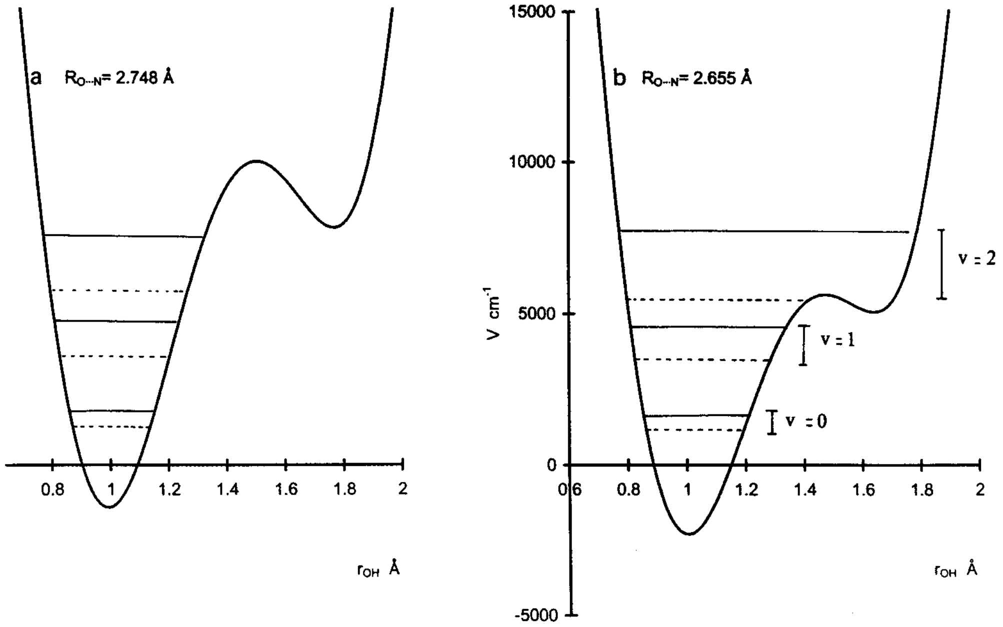

Figure 4. Shape of the potential profile of the OH(D)···N fragment at two different $R_{O\cdots N}$ values: (a) $R_{O\cdots N}$ = 2.748 Å, (b) 2.655 Å. The vibrational levels of the OH···N and OD···N fragments are indicated by — and - - -, respectively.

The second absorption should most probably occur in the mid-IR region and could not be observed under the experimental conditions (concentrations and path lengths) used in this range.

The energy level splitting occurring when the second minimum lies in the vicinity of the second vibrational level has been theoretically anticipated by Bell and Barrow in 1959.[54] This splitting was observed for ethanol or phenol dissolved in basic solvents such as ethyl acetate, acetone, or diethyl ether. The first absorption was observed between 7000 and 6700 cm^{-1} and the second one between 6600 and 6200 cm^{-1}. For these complexes, the barrier height calculated from the Lippincott–Schroeder function must be at least 13000 cm^{-1},[48] and the splitting is more likely due to the existence of two kinds of complexes in solution.[55]

5. Isotopic Ratio. For free phenol dissolved in carbon tetrachloride, the experimental isotopic ratio ISR_{01} is slightly lower (1.354) than the theoretical value predicted by eq (1.374), and the ratio of the experimental anharmonicities (1.900) is near the predicted one. In the complexes, the isotopic ratios of the frequencies are lower and the ratios of the anharmonicities—which are expected to be more sensitive to a change of masses—are also significantly lower. For the 3-CF_3,4-NO_2·pyridine complex, the ISR_{01} value is 1.255 and the ratio of the anharmonicities 1.440.

As illustated in Figure 5, the ISR_{01} values decrease with a lowering of the barrier height. For the weaker complexes, the ISR_{01} values vary between 1.346 and 1.339, and this variation does not exceed the possible experimental errors. This is not the case for the stronger complexes characterized by ISR_{01} values between 1.324 and 1.255. For the 3,5-diCl- and 3-CF_3,4-NO_2–phenol·pyridine complexes, the barrier top is in the vicinity of the first excited vibrational level (Figure 4), and in this case, a strong decrease of the isotopic ratio is usually observed. Note here that for OH···O hydrogen bonds an isotopic ratio of 1.25 should correspond to a barrier of 6000 cm^{-1},[56] suggesting that the principal values of the potential shape do not strongly differ in OH···N and OH···O hydrogen bonds. This fully agrees with the variation of the barrier height as a function of the R distance in both systems.

6. Pyridine Vibrations. Last, it must be mentioned that the overtones or combination bands of the pyridine moeity are more perturbed in the stronger complexes than in the weaker ones. In free pyridine dissolved in carbon tetrachloride absorptions are observed at 5960 [2ν(CH)], 4589 [ν(CH) + ν8b], 4487 [ν(CH) + ν19b], and 4080 [ν(CH) + ν12] cm^{-1}. These absorptions are shifted to 5967, 4599, 4487, and 4081 cm^{-1} in the phenol·pyridine complex and to 5988, 4612, 4505, and 4091 cm^{-1} in the 3,5-diCl phenol·pyridine complex. The bands become somewhat broader, but no splitting arising from the existence of both normal hydrogen bonds and proton-transfer species could be observed.

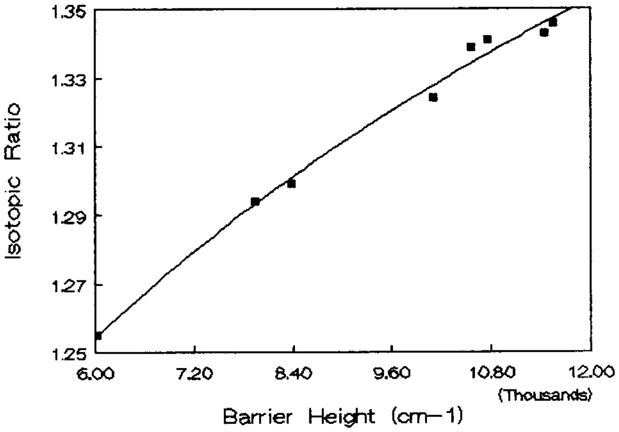

Figure 5. ISR_{01} as a function of the barrier height (cm^{-1}).

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