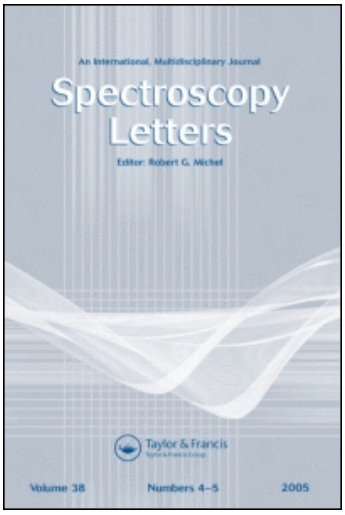

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ANOMALOUS ISOTOPIC FREQUENCY RATIO OF THE STRETCHING $\nu(N^+H)$ VIBRATIONS IN ION PAIRS

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Earlier, when investigating H-complexes of the $RO-H...BR_1$ type in solutions [1-3] and crystalline state [4], the isotopic shift for frequencies of the stretching vibrations $\nu(OH)$ at substitution of H for D was shown to systematically decrease with increased strength of the H-bond. In strong H-complexes, the $\nu(OH)$ and $\nu(OD)$ bands in the i.r. spectra have a complex structure: depending on the strength of the H-complex in a wide range of frequencies (3000-1000 cm^{-1}), several submaxima caused by a Fermi-resonance interaction of the fundamental tone of $\nu(OH)$ with combinations and overtones of the bending vibrations of R-O-H were observed [1-5]. Hence, the frequencies and intensities of the $\nu(OH)$ and $\nu(OD)$ bands in strong H-complexes should be considered as corresponding to the gravity centre (ν_0) and overall intensity (A_0) of all the components of the complex absorption contour of $\nu(OH)$, not to the frequency and intensity of the principal maximum. Actually the A_0 and ν_0 of the $\nu(OH)$ band in complexes with hydrogen bonds between neutral molecules (HB NM), not the frequencies

and intensities of individual maxima, represent the strength of the hydrogen bond [6-8] and undergo the following characteristic changes with increase of the said bond: A_0 naturally grows, while ν_0 shifts to low frequencies. In this case, the isotopic ratio $\nu_0(OH)/\nu_0(OD)$ changes its usual value (1.35) for free OH groups for ~1.10 in H-complexes with $-\Delta H \sim 10$-12 kcal/mole [1-3] and $R(O...O) \sim 2.5$-2.6 Å [4].

As was shown in our recent investigation [9] of hydrogen bonds in ion pairs (HB IP) that form at interaction of carbonic acids with aromatic and aliphatic amines in $CHCl_3$ and CH_2Cl_2 (R_1R^+-H...$^-$OOCR), the stretching vibration band $\nu(N^+H)$ has a complex nature similar to the $\nu(OH)$ bands in complexes HB NM. Similarly, a complex structure of the $\nu(N^+H)$ band was observed in a study of HB IP in the crystalline salts of pyridine, pyrimidine and aliphatic amines [4,10,11].

Hence, it would appear interesting to examine A_0 and ν_0 in the $\nu(N^+H)$ bands of HB IP with respect to the strength of the H-complex in the solutions and to compare their isotopic shifts with the above-noted changes in the isotopic shift of $\nu(OH)$ for HB NM.

In the present work, we have measured the frequencies and intensities of the bands of stretching $\nu(N^+H)$ and $\nu(N^+D)$ vibrations in NH and ND groups linked by a HB IP, which form at interaction of organic acids (carboxylic acids and nitrophenols) and inorganic acids ($HClO_4$ and hydrogen halides) with pyridine (Pyr), 2,4,6-trimethylpyridine (Me_3Pyr) and Et_3N in CH_2Cl_2, $CHCl_3$ and CH_3CN solutions. The spectra were recorded in the range of 400-3600 cm^{-1} on a UR-20 spectrophotometer

with a logarithmic self-recorder. Numerical integration of the spectrogram data was performed to estimate the frequency of the gravity centre (ν_0); areal computation was done to determine the integral intensity (A_0) of the entire complex contour of the absorption of the $\nu(N^+H)$ and $\nu(N^+D)$ bands. To exclude interaction of the solutions examined with the material of window when recording the i.r. spectra, we used cells with windows made of KRs-5 and CaF_2. Acids and solvents were purified of admixtures and water. Solutions of the samples studied were prepared in a dry box by weighting in calibrated pycnometers. Deuteration was performed by the method of Iogansen and Rosenberg [12]. The deuterium content was higher than 96%.

Examples of the i.r. spectra for certain HB IP are shown in Fig.1. Data for ν_0 and A_0 of the $\nu(N^+H)$ and $\nu(N^+D)$ bands of the H-complexes studied are given in Table 1. As is apparent from Fig.1 and Table 1, with increase of cation ($Et_3N^+H <$ $< Me_3Pyr^+H < Pyr^+H$) and anion ($ClO_4^- < Br^- < Cl^- <$ $< 2,4,6\text{-}(NO_2)_3PhO^- < CF_3COO^- < 2,4\text{-}(NO_2)_2PhO^- < CHCl_2COO^- <$ $< CH_2ClCOO^-$) strength, the $\nu(N^+H)$ bands undergo characteristic alterations. Thus, several additional maxima (see Fig.1) appear, whose frequencies are little dependent on the anion and cation. On the other hand, ν_0 naturally lowers its frequency with increased anion and cation strengths (Table 1). Contrariwise, the intensities of bands "A,B,C,D and E" (Fig.1) essentially depend on the anion and cation. With stronger H-complexes, the intensities are "transferred" from the high-frequency to the low-frequency components of the $\nu(N^+H)$

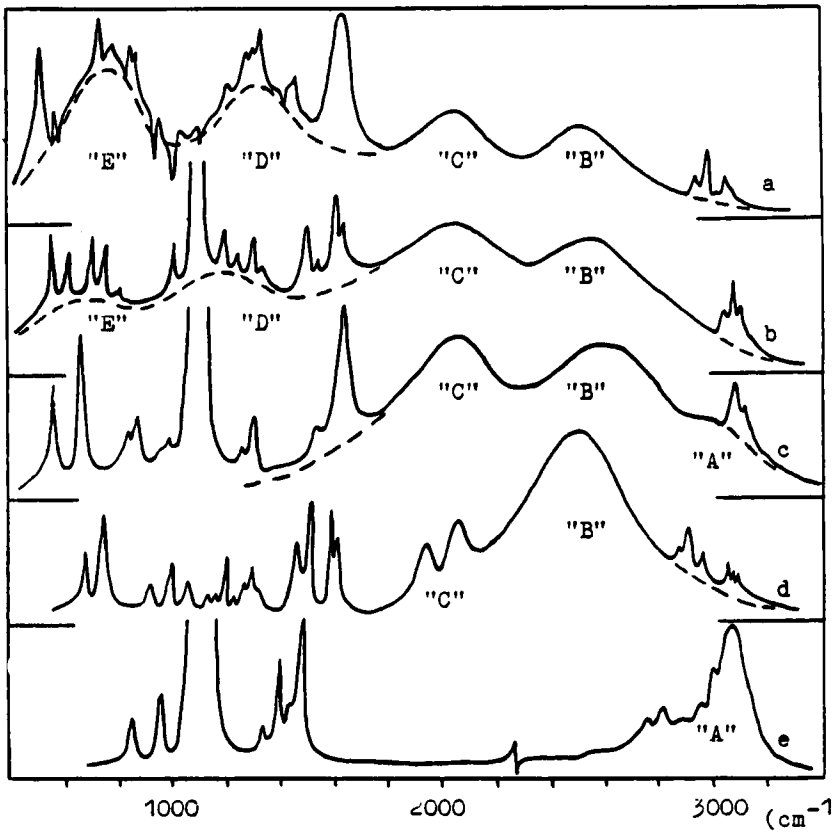

Fig.1. I.r. spectra of complexes HB IP: $Me_3Pyr^+H...^-OOCCHCl_2$ in CH_2Cl_2 (a); $(Pyr...H...Pyr)^+ClO_4^-$ in Pyr (b); $(Me_3Pyr^+H...Pyr)ClO_4^-$ in Pyr (c); $Pyr^+H...Br^-$ in CH_3CN (d); $Et_3N^+H...ClO_4^-$ in $CDCl_3$.

band; at the same time, the overall intensity of A_0 increases. The above-cited specificities in the behavior of the $\nu(N^+H)$ band may also be fully assigned to $\nu(N^+D)$ (see Table 1).

The study of the i.r. spectra of the above H-complexes IP shows the absence of any basic differences in the nature

Table 1. Characteristics of $\nu(N^+H)$ and $\nu(N^+D)$ i.r. bands and isotopic ratio of frequencies.

Complex*)	Solv.	$\nu_o(H)$	$\nu_o(D)$	$A_o(H)$	$A_o(D)$	$\nu_o(H)/\nu_o(D)$	$-\Delta H_{ip}$
		cm^{-1}		$l \cdot mole^{-1} cm^{-2}$			kcal/m
Et_3N^+H							
ClO_4^-	$CDCl_3$	2975	2230	6.0	-	1.334	4.2
$(NO_2)_3PhO^-$	CH_2Cl_2	2700	2105	15.4	7.0	1.283	8.5
CF_3COO^-	CH_2Cl_2	2400	1885	12.0	6.5	1.273	7.2
$(NO_2)_2PhO^-$	CH_2Cl_2	2480	1970	17.6	8.0	1.259	9.3
CH_2ClCOO^-	CH_2Cl_2	1830	1560	24.0	11.5	1.173	11.3
Me_3Pyr^+H							
ClO_4^-	CH_3CN	3080	2315	8.1	3.8	1.330	5.4
$Pyr(ClO_4^-)$	Pyr	2290	1900	25.0	12.3	1.205	11.6
CCl_3COO^-	CH_2Cl_2	2150	1800	21.0	10.0	1.190	10.4
$CHCl_2COO^-$	CH_2Cl_2	1570	1450	32.0	16.7	1.083	13.6
Pyr^+H							
ClO_4^-	CH_3CN	3055	2330	9.0	4.0	1.311	5.8
Br^-	CH_3CN	2500	1980	21.4	10.4	1.263	10.6
Cl^-	CH_3CN	2240	1880	24.0	9.7	1.191	11.3
$Pyr(ClO_4^-)$	Pyr	1770	1580	30.0	16.0	1.120	13.0
CF_3COO^-	CH_2Cl_2	1600	1440	32.0	16.6	1.111	13.6

*) $(NO_2)_3PhO^-$, $(NO_2)_2PhO^-$ - 2,4,6-$(NO_2)_3PhO^-$ and 2,4-$(NO_2)_2PhO^-$, respectively.

of the changes taking place in the $\nu(N^+H)$ bands and the $\nu(OH)$ absorption bands with HB NM. Hence, the gravity centre frequencies and overall intensities of all the components observed in the structure of $\nu(N^+H)$ are essentially indicators of the strength of HB IP. Using the known relationship [6-8]

$$-\Delta H = 2.91\,\Delta A^{1/2}$$

(where $\Delta A^{1/2} = A^{1/2}_{compl.} - A^{1/2}_{free(CCl_4)}$) between the intensity changes in $\nu(OH)$ and the formation energy of the complex HB NM, we calculated the energies ($-\Delta H_{ip}$) of the N^+-H...$^-$B H-bonds for the HB IP examined. In calculating $\Delta A^{1/2}$, the value of A_{free} for $\nu(N^+H)$ was taken to equal $1.0\cdot10^4$ $l\cdot mole^{-1}cm^{-2}$ like pyrrole in CCl_4 [13]. The $-\Delta H_{ip}$ values cited in Table 1 are essentially the formation energies of HB IP from free ions in CCl_4 ($R\text{-}N^+H + B^- \longleftrightarrow R\text{-}N^+H...B^-$).

A comparison of the change in the isotopic ratio of $\nu_0(N^+H)/\nu_0(N^+D)$ with the calculated values of $-\Delta H_{ip}$ is shown in Fig.2, from which it is apparent that $\nu_0(N^+H)/\nu_0(N^+D)$ systematically decreases with strengthening of HB IP. For maximum values of $-\Delta H_{ip} \sim 13$ kcal/mole, $\nu_0(N^+H)/\nu_0(N^+D)$ is close to 1. In this case, the H-complex structure is close to symmetric ($[Pyr...H...Pyr]^+ClO_4^-$ and $Me_3Pyr^+...H...^-OOCCHCl_2$). These data are in good agreement with those obtained previously for the H-complexes O-H...O [2-4]. It should be noted that the value $\nu_0(N^+H)/\nu_0(N^+D) \sim 1.20$ cited for the H-complex $(Pyr...H...Pyr)^+ClO_4^-$ [14] differs from our value 1.12 (see Table 1). This difference is due to the fact that Clements *et al.* [14] did not account the low-frequency components $\nu(N^+H)$

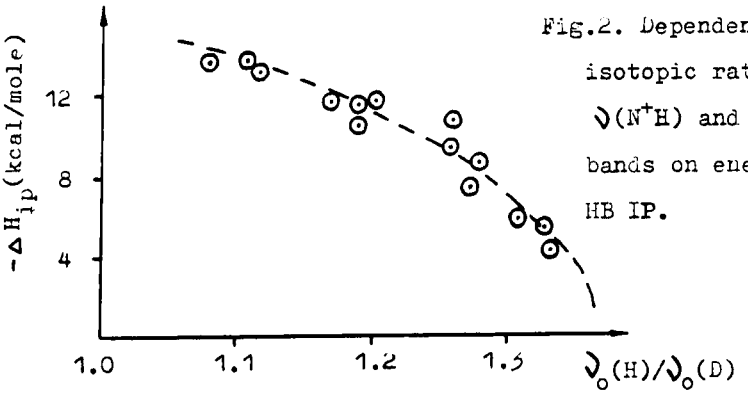

Fig.2. Dependence of isotopic ratio for $\nu(N^+H)$ and $\nu(N^+D)$ bands on energies of HB IP.

(bands "D and E"), which are very characteristic for H-complexes with very strong H-bonds [3,9].

The results of the present work show that there are no discrepancies in the spectral behavior of stretching vibrations $\nu(N^+H)$ and $\nu(OH)$ (A_o, ν_o, $\nu_o(N^+H)/\nu_o(N^+D)$) for complexes HB IP and HB NM. Similar results were reported recently [15] for alterations in the NMR chemical shifts of the N^+H protons and OH groups of some H-complexes. This gives grounds to assume that HB IP and HB NM have the same donor-acceptor nature.

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