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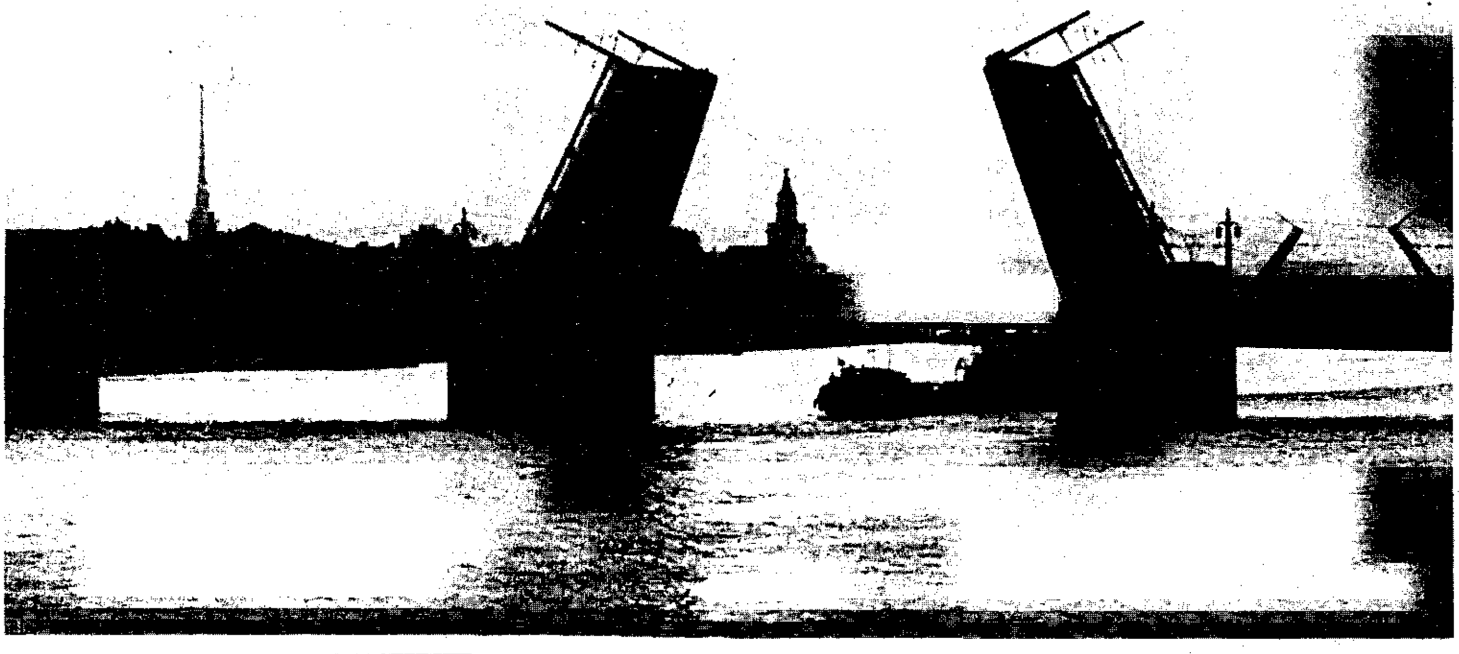

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ESTIMATION OF MEAN INTERNUCLEAR DISTANCES IN HYDROGEN BRIDGES IN LIQUID SOLUTIONS BY MEANS OF NUCLEAR MAGNETIC RELAXATION TECHNIQUE

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ABSTRACT. A method of evaluating the mean internuclear distances in hydrogen bonds in liquid solutions is suggested involving the measurement of the T_1 longitudinal magnetic relaxation times for different magnetic nuclei (S=1/2) of a complex and its deuterio substitute. This technique is applied to studying the structure of the extensively examined $HC^{15}N...HF$ complex in liquid solutions at low temperature. It is found that polar solvents cause a shortening of the N...H hydrogen bond and a lengthening of the covalent F-H bond. For theoretical treatment of the effect, a two-dimensional anharmonic model in combination with the Onsager-Butcher potential has been used which, with the required parameters taken from IR spectra, has provided a satisfactory quantitative agreement with the experiment. A qualitative explanation of the effect is based on a specific feature of the dipole moment function common for nearly all molecular hydrogen bonded complexes, XH...Y, namely, its derivative with respect to hydrogen bond length at the equilibrium point is negative whereas that with respect to the X-H covalent bond length is positive. For hydrogen bonded ionic pairs, $X^-...HY^+$, inversion of the sign of the effect is predicted.

1. INTRODUCTION

Mean internuclear distances, R_{X-Y} and r_{X-H}, are the main characteristics of a hydrogen bonded complex, XH...Y, while being in close connection to its physical (formation enthalpy, dipole moment, polarizability, IR and NMR spectroscopic features) as well as to many chemical properties **[1]**. At present, these geometric parameters can be measured within a high accuracy in a crystalline state, using X-ray and neutron diffraction technique **[2-5]**. Proton location in solid complexes can also be studied using the nuclear magnetic dipolar coupling and nuclear quadrupolar coupling in NMR spectra **[6]**. In the gaseous phase, the $R_{X\text{-}Y}$ distance is easily measured using high-resolution rotational and rovibrational spectra **[7]**. For estimating the $r_{X\text{-}H}$ value, a method was recently suggested by Legon and Millen involving hyperfine nuclear (magnetic dipolar and quadrupolar) splitting in high resolution rotational spectra **[8,9]**.

When comparing structural parameters of H-bonds in the gaseous and crystalline states, the conclusion may be drawn that the same crystalline complexes are often more compact. In some cases the lengthening of an X-H bond upon the gas-solid state transfer was detected. Well-known examples of this effect are the HalH-amine complexes, which, while giving typical ionic crystals, $r_{NH} \approx 1A$, are of obviously molecular structure ($r_{NH} = 1.4 \div 1.5A$) when in the gaseous phase **[9-11]**. (Very few gaseous complexes having a structure close to an ionic pair, like $(CH_3)_3N$...HBr, are known **[10, 11]**.) The origin of this transformation may be the influence of crystalline field as well as the co-operativity effect. At any rate, the influence of environment on the structure of easily polarisable hydrogen bonds can be very strong. Thus, use of the values obtained by diffractional techniques, which are valid for the solid state only, for interpretation of spectroscopic or chemical effects in liquid solutions is incorrect. Any data referred to liquid solutions are of special interest from the point of view of chemistry and, especially, biochemistry. So far, no general technique suitable for direct determination of internuclear distances in hydrogen bridges valid for dissolved complexes is known.

In this paper an attempt is made to apply the magnetic relaxation technique to solving this problem. The idea of the proposed method is as follows: the longitudinal magnetic relaxation time, T_1, of nuclei, S=1/2, in dissolved organic molecules is determined mainly by magnetic dipolar coupling with the neighbouring protons modulated by rotational diffusion. Supposing that covalent C-H bond lengths of molecules involved are only very slightly affected by formation of a comparatively weak hydrogen bond, it is possible to determine geometric parameters of the hydrogen bond and the rotational correlation time, τ_c, using T_1 values for several nuclei of the complex. The proposed method was recently applied **[12]** to the determination of the $r_{N...H}$ value for a number of complexes of ^{15}N-labeled pyridine with different OH-acids (the second distance, $R_{O...H}$, was impossible to measure due to the absence of magnetic oxygen isotopic nuclei with S=1/2)). It was found that this distance decreases regularly from 1.5 A down to the value characteristic of the typical N-H covalent bond, 0.98 A, with the OH acidity rising. A similar transformation was observed also for the case of one particular complex, i.e., pyridine-dichloroacetic acid, by increasing the solvent polarity.

In the present paper, the $^{19}FH...^{15}N{\equiv}^{13}CH$ complex is investigated, as a hydrogen bonded system most intensively studied before both experimentally and by model and ab initio calculations **[13-27]**. Presence of five magnetic nuclei, S=1/2, in this complex makes it possible to obtain maximum structural information from magnetic relaxation measurements. As it will be seen from our results, the hydrogen bond length, $R_{X\text{-}Y}$, measured by this technique for liquid solution, proved to be somewhat less than cited in the literature for the same complex in the gas. We believe that this difference is reasonable and has some physical sense as a result of the influence of medium.

The question, how the solvent polarity influences H-bond length and the proton location in intermolecular hydrogen bonds, has been discussed in the literature for a long time. In Ref.**[29-33]** it was found that the low frequency shift of the stretching ν_{XH} vibration for a range of polar XH...Y complexes rises by 10-50 % upon transfer from the gaseous phase to an apolar solvent. The rising proceeds with increasing the solvent dielectric constant, ε. This effect is largest for compact highly polar complexes, like FH...N≡CH. Since the frequency shift (as compared to the ν_{XH} vibration in "free" XH molecules) can be correlated with the H-bond enthalpy **[34]**, these data may indicate some "strengthening" of intermolecular H-bonds upon their transfer into a polar medium. A theoretical model developed in Ref. **[26, 27]** allowed the correlation of the ν_{XH} frequency displacement with the X-H bond lengthening as a result of hydrogen (or van der Waals) bond formation. For the FH...N≡CH complex trapped in an argon matrix, the 90.6 cm^{-1} low frequency shift points to some lengthening (by 0.004 A) of the F-H bond as compared to that when in the gaseous phase. This effect seems, however, to be too small for any direct measurement.

In Ref.**[35, 36]** an attempt of quantitative evaluation of the frequency shifts was made for two vibrations, ν_{XH} and ν_{XY}, using a two-dimensional anharmonic model of H-bond, the medium influence being taken into account using the Onsager-Butcher potential. This approach accounted for the medium effects observed in IR spectra of weakly H-bonded complexes. Besides, more direct manifestations of H-bond strengthening were predicted, i.e., some decrease of the $R_{X...Y}$ bond length and increase of the r_{X-H} covalent bond length due to the polarization of a complex by the reactive field of a medium. Our data may give some experimental evidence for the predicted medium effect on hydrogen bond geometry.

2.METHOD OF EVALUATION OF THE R_{X-Y}, r_{X-H} DISTANCES IN LIQUIDS

Let us consider a linear ($C_{\infty v}$) complex with a hydrogen bridge formed by several magnetic nuclei, S=1/2, like $^{19}F-H...^{15}N{\equiv}^{13}C-H$. In the "extreme narrowing limit", which holds for not very viscous liquids, longitudinal magnetic relaxation times, T_1, for ^{19}F, ^{15}N and ^{13}C nuclei can be described by the following expressions **[37]**:

$$\mathrm{T}_1^{-1}(\mathrm{F}) = h^2\gamma_H^2\gamma_F^2(r_{F-H})^{-6}\tau_c$$
$$\mathrm{T}_1^{-1}(\mathrm{C}) = h^2\gamma_H^2\gamma_C^2(r_{C-H})^{-6}\tau_c \qquad (1)$$
$$\mathrm{T}_1^{-1}(\mathrm{N}) = h^2\gamma_H^2\gamma_N^2(r_{N...H})^{-6}\tau_c + T_1^{-1}$$

where γ_i are gyromagnetic ratios; τ_c is the correlation time for rotational diffusion; T_1 describes additional mechanisms of the ^{15}N nucleus magnetic relaxation (magnetic coupling with nuclei other than the neighboring proton, spin-rotational relaxation etc.). For the relaxation of fluorine and carbon nuclei, with covalently bound protons, these additional mechanisms can be neglected. Analogous expressions can be written for the F-D...N≡C-H.

To eliminate the unknown values, τ_c and T_1, the following suppositions were made.

1. It seems reasonable to assume that, under the identical conditions (solvent and temperature), the additional relaxation rate of the ^{15}N nucleus is the same (T_1 = const) for both XH...Y and XD...Y complexes.

2) For a linear complex, the only correlation time is valid for all the nuclei;

3) The relaxation of the ^{13}C nucleus is determined by magnetic coupling with the only covalently bound proton; the r_{CH} distance is independent of H-bond formation and can be taken from literature;

4) Geometric parameters and rotational correlation times of the XH...Y and XD...Y complexes are identical. The last supposition is not quite correct, since the H/D isotope effect on the bond lengths in various hydrogen bonded systems is well known **[2-5, 38]**. However, our evaluations showed that neglecting this effect cannot lead to the error in measuring r_{NH} more than 0.1%. (Our attempt to measure the distances in the deuterated complex, FD...NCH, has failed, as only a small part of the ^{15}N relaxation rate is due to the ^{15}N-^{2}H dipolar coupling.)

Upon writing and solving the **(1)** equations for the H- and D- complexes, we obtain:

$$(r_{N...H})^6 = (\gamma_N/\gamma_C)^2\left[1-(\gamma_D/\gamma_H)^2\right]\frac{T_1^{-1}(C)}{T_1^{-1}(NH)-T_1^{-1}(ND)}(r_{C-H})^6 \quad (2)$$

$$(r_{F-H})^6 = (\gamma_F/\gamma_C)^2\frac{T_1^{-1}(F)}{T_1^{-1}(C)}(r_{C-H})^6 \quad (3)$$

$$R_{FH...N} \approx r_{F-H} + r_{N...H}$$

The accuracy in estimating the geometric parameters depends on standard deviation, $\Delta T_1/T_1$, and reproducibility in measuring the relaxation times. At present, due to high sensitivity and stability of modern FT NMR instruments, long acquisition can provide the T_1 accuracy as high as 0.5 %. For the standard deviation in the r values, the **(2, 3)** equations give $\Delta r/r \leq 0.003$; $\Delta r \leq 0.003$A. This can be compared with that characteristic of the Dipolar Solid State NMR technique **[6]**. Indeed, although the accuracy in measuring the Pake doublet splitting is better than in measuring T_1, the $T_1^{-1} = f(r_{XH})$ dependence is much stronger ($\sim r^{-6}$ as compared to $\sim r^{-3}$ for the dipolar splitting). Actually, the reproducibility of thus measured distances proved to be not worse than 0.003 A.

The proposed procedure can be applied to investigation of a limited but important number of linear hydrogen bonded complexes which involves several magnetic nuclei, like FH...^{15}N≡C-R. For the largest group of hydrogen bonds of the OH...X (O^-...HX^+) type, only one of the internuclear distances, r_{X-H}, can be measured using the T_1 technique. In addition to linear complexes, those with the hydrogen bond formed along the symmetry axis, like XH...$^{15}NC_5H_5$, could be investigated. For other complexes, existence of several τ_c values for different nuclei is to be taken into account.

Consider the question of possible effect of different exchange processes on the measured T_1 values. There exist two types of fast chemical processes in solutions containing hydrogen bonded molecules, i.e., the intermolecular proton exchange (PE) and the hydrogen bond exchange involving dissociation and reforming of hydrogen bonds (HBE). The latter is able to modulate the dipole-dipole magnetic coupling between two nuclei connected with a hydrogen bridge, in addition to the rotational diffusion process. However, the typical lifetimes of hydrogen bonds at the temperature as low as 150-170 K are usually higher than 10^{-6} s **[39]**. Such a "slow" process cannot contribute to the energetic relaxation, since, in the case of several dynamic processes modulating the dipolar coupling, the effective correlation time is determined as $\tau_c^{eff} = (\sum_i \tau_{ci}^{-1})^{-1}$ **[37]**, and, for not very viscous liquids, the rotational correlation time does not exceed 10^{-10}s.

The intermolecular proton exchange can provide the "1-st kind scalar relaxation" **[37]**. This mechanism, most essential for T_2 and $T_{1\rho}$ relaxation times, contributes to the T_1 value as follows:

$$T_{1sc}^{-1} = 2\pi^2 J_{XH}^2 \tau_{ex}\left[1+(\omega_H-\omega_X)^2\tau_{ex}^2\right]^{-1} \tag{4}$$

where J is the scalar spin coupling constant and τ_{ex} is the correlation time of an exchange process. Typical are the following orders of magnitude for the values involved: $J_{XH} \leq 600$ Hz; $\tau_{ex} \geq 10^{-6}$ s **[39, 40]**. Thus, the maximum contribution of the scalar relaxation under experimental condition must be less than $(T_{1sc})^{-1}=10^{-4}$ s^{-1}, which is hard to measure.

Although these exchange processes cannot contribute directly to the measured T_1 values, the experiment should be performed under conditions of no exchange between different molecular forms in equilibrium in solution, to avoid averaging the signals and, therefore, the values obtained. This can be achieved by lowering the temperature down to 100-150 K, where different hydrogen bonded species give usually separate NMR signals **[41-43]**. The only exception is the case of "tautomeric" complexes with the reversible proton transfer, $XH...Y \rightleftharpoons X^-...HY^+$

This process usually goes fast (in the NMR time scale) down to 100 K **[41, 44].** It is supposed that the frequency of the reversible intracomplex proton transfer can approach the characteristic X-H vibration frequency, 10^{13} - 10^{14} Hz. In this case, the measured using the T_1 technique effective internuclear distances would be averaged according to the following expression:

$$r^6_{N-H_{eff}} = (1+K)\left(\frac{r^6_{N-H} r^6_{N...H}}{r^6_{N-H} + K r^6_{N...H}}\right) \qquad \textbf{(5)}$$

where K is the equilibrium constant.

3. EXPERIMENTAL

T_1 measurements were made on Bruker AC-200 (200.1 MHz for ^1H, 20.3 MHz for ^{15}N) and AMX 500 (50 MHz for ^{15}N, 470 MHz for ^{19}F nuclei) instruments. To shift the equilibrium between the "free" molecules and the complex, as well as to slow down intermolecular proton exchange processes, lowering the temperature down to 150-170 K was required. Absence of "free" molecules, or HF self-associates, in solutions was verified by the only bridging proton signal to be observed in ^1H NMR spectra down to 120 K as well as by IR absorption spectra (an IFS 25 Bruker instrument). The dissolved oxygen which might give an electronic paramagnetic contribution to nuclear spin relaxation was removed by repeated evacuation of samples, frozen with liquid nitrogen at 10^{-7} mbar, followed by thawing and refreezing. Special quartz 5 mm NMR sample tubes, sealed under evacuation at 77K, were used. Preliminary experiments have shown that, with water-free substances, the dissolved HF does not react with the quartz surface. To diminish the contribution of intermolecular dipolar magnetic relaxation to T_1, proton-free solvents were used.

The temperature was maintained and measured within the accuracy ±1 K using a BVT-1000 Bruker system and a low temperature probehead. The T_1 measurement was performed using the conventional 180-τ-90 (INVREC) pulse sequence. The acquisition of the spectra was continued until the standard deviation upon computer processing the data became as low as $\Delta T_1/T_1=0.01$. The viscosity of solvents could be varied by changing the temperature so that the T_1 values were found in a convenient region, 0.01 ÷15 s.

The ^{15}N labeled HCN was prepared from $KC^{15}N$ (Aldrich, 95 atom % ^{15}N), dried with Al_2O_3 and purified by repeated distillation *in vacuo*. HF and DF (98 % ^2H) were purchased from Aldrich and dried over P_2O_5.

The solvents (methyl cyclohexane-D_{14} and $(CF_2Br)_2$) from "Sigma" were used without purification. The synthesis of the deuterated freon, $CDFCl_2$, was described in Ref.**[43]**.

4. EXPERIMENTAL DATA

In **Table 1** the internuclear distances, $r_{F\text{-}H}$ and $r_{N...H}$, $R_{N\text{-}F} \approx r_{F\text{-}H} + r_{N...H}$ calculated using equation **(3)** for the complex dissolved in several solvents at 150-170 K are given. As it is seen, the standard deviation, calculated from five independent measurements for different samples, is not worse than $\Delta r<0.003$ A; $\Delta R<0.005$ A.

Table 1. Geometric parameters (A) of the $HC^{15}N...HF$ complex in the gaseous phase **[7]** and dissolved in various solvents at 160 K.

Solvent	**F**	$r_{F\text{-}H}$	$r_{N\text{-}H}$	$R_{N\text{-}F}$
	0.00	0.935	1.819	2.754
$CD_3\text{-}C_6D_{11}$	0.19	0.941±0.0022	1.754±0.0033	2.695±0.005
$(CBrF_2)_2$ (+5% $Si(CD_3)_4$)	0.30	0.948	1.716	2.663
$CDFCl_2$	0.45	0.956	1.666	2.624

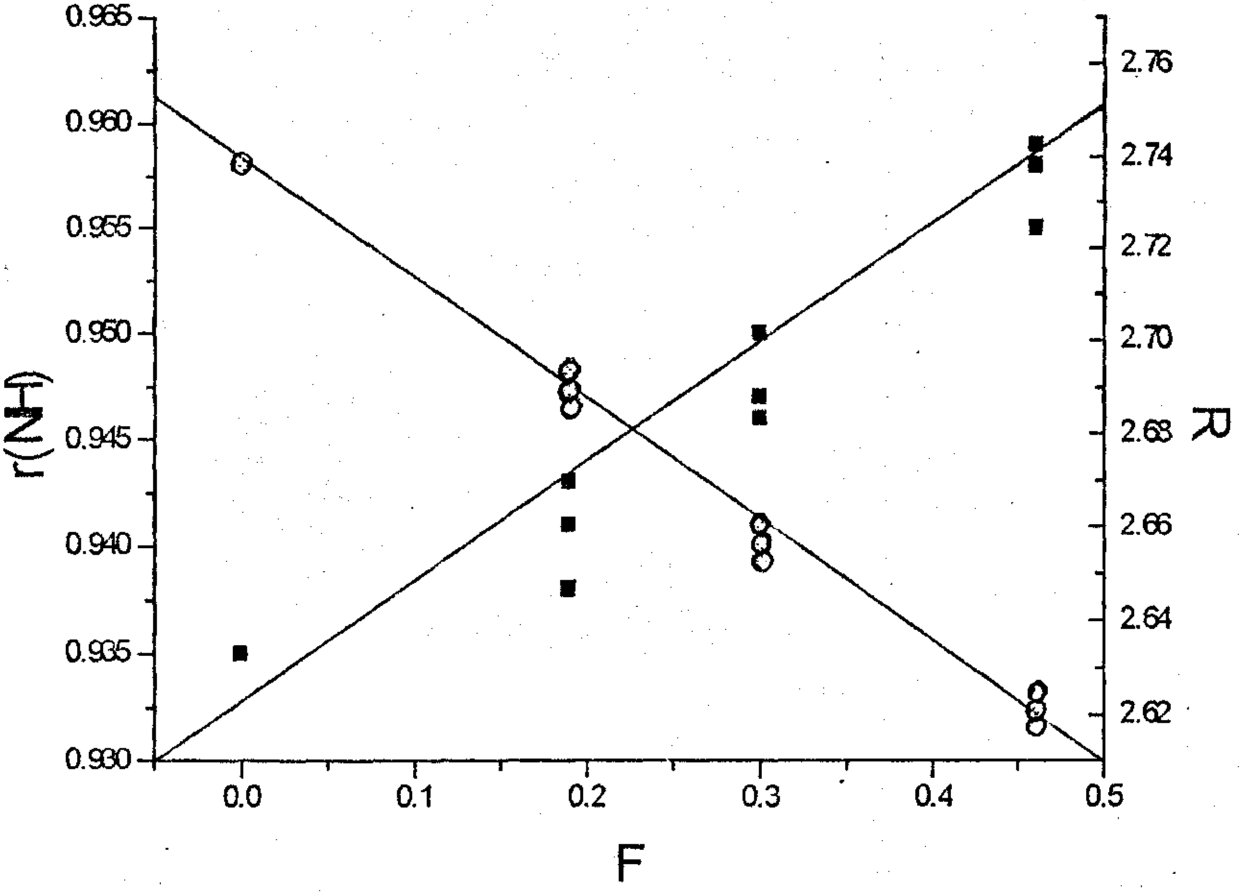

Fig.1. The $r_{F\text{-}H}$, $R_{N\text{-}F}$ values plotted against the reactive field factor, $F_1=(\varepsilon-1)/(2\varepsilon+1)$, of a solvent at 160 K.

In **Figure 1** the $r_{F\text{-}H}$, $R_{N\text{-}F}$ values are plotted against the reactive field factor, **$F=(\varepsilon-1)/(2\varepsilon+1)$**, for three solvents, from an apolar, methylcyclohexane ($\varepsilon_{160K} = 2.2$), to a rather polar at low temperature $CDFCl_2$ ($\varepsilon_{160K} = 25$). Here the analogous data are also given for this complex in the gaseous phase, $\varepsilon=1$, obtained in Ref.[7] from microwave spectra. (The latter values are corrected taking into account thermal population of low frequency vibrations at 160 K). When going from the gas to the polar solvent, a regular decrease of the hydrogen bond length and increase of the covalent one is observed, with the value of the effect exceeding considerably the possible experimental error. Unfortunately, our attempts to estimate the distances in the gas by the T_1 technique have failed due to, probably, a high contribution of spin-rotational relaxation. Thus, no direct comparison with data obtained by any different technique could be made and, therefore, the systematic error of the method is difficult to estimate. However, the straight lines, r=f(F), being drawn through our experimental points, give at F=0 the values which are rather close to internuclear distances in the isolated HCN...HF complex referred in the literature.

6. INTERPRETATION OF THE EFFECT

Description of the model

Our interpretation is based on a linear three-mass model developed in Ref. **[12, 17, 19, 35, 36]** characterized by three normal vibrations, namely, two completely symmetric stretching vibrations, $\nu_1 \approx \nu_{XH}$, $\nu_3 \approx \nu_{XY}$ and one twice degenerated bending vibration, $\nu_2 \approx \delta_{X\text{-}H}$, . The potential energy (measured in wavenumber units, cm^{-1}) can be written as:

$$V = V_0 + V_1 + \qquad (6)$$

where $V_0 = 1/2\omega_1 q_1^2 + 1/2\omega_3 q_3^2 + 1/2\omega_2\rho$ is the harmonic part of the potential;

$$V_1 = \alpha_{111} q_1^3 + \beta_{1111} q_1^4 + \alpha_{333} q_3^3 + \alpha_{113} q_1^2 q_3 + \alpha_{133} q_1 q_3^2 +$$
$$+\beta_{1113} q_1^3 q_3 + \beta_{1133} q_1^2 q_3^2 + \alpha_{122} q_1 \rho^2 + \alpha_{223} \rho^2 q_3 + \dots$$

is its anharmonic part up to quartic terms;

$U = U_0 + U'_1 q_1 + U'_3 q_3 + 1/2 U''_{11} q_1^2 + U''_{13} q_1 q_3 + 1/2 U''_{33} q_3^2 + 1/2 U''_{22} \rho$ is an expansion of the energy of interaction with a solvent with respect to the intramolecular dimensionless normal coordinates. In the first approximation,

$$q_1 = (\gamma_1)^{1/2} \Delta r_{XH};\ q_3 = (\gamma_3)^{1/2} \Delta R_{XY};\ \gamma_i = 4\pi^2 h^{-1} \omega_i\, cm_i$$

$$\rho^2 = q_{2x}^2 + q_{2y}^2, \text{where } q_{2x} = (\gamma_2)^{1/2} \varphi_x$$

where ω_i and m_i are the harmonic frequency and reduced mass for the i-th vibration.

In order to obtain expressions for the changes of the equilibrium bond lengths, Δr_{XH} and ΔR_{XY}, wave functions in the 1st and 2nd orders of the perturbation theory were used with $\mathbf{V_I + U}$ as a perturbation **[12]**. The relation, $\omega_1 >> \omega_3$, was accounted (the adiabatic approximation), a part of small members being neglected. Due to this approximation, the obtained expressions are not fully symmetric with respect to the permutation of the 1,3 subscripts:

$$\Delta q_1 = -\frac{U'_1}{\omega_1} + \frac{U'_1 U''_{11}}{\omega_1^2} + \frac{U'_3 U''_{13}}{\omega_1 \omega_3} + (v_1 + 1/2)(\frac{9U''_{11}\alpha_{111}}{2\omega_1^2} + \frac{12U'_1\beta_{1111}}{\omega_1^2} + \frac{U''_{13}\alpha_{113}}{\omega_1\omega_3} + \frac{3U'_3\beta_{1113}}{\omega_1\omega_3} +) + (v_3 + 1/2)(\frac{U''_{11}\alpha_{133}}{\omega_1^2} + \frac{3U''_{13}\alpha_{333}}{\omega_1\omega_3} + \frac{U''_{33}\alpha_{133}}{2\omega_1\omega_3} + \frac{2U'_1\beta_{1133}}{\omega_1^2} + \frac{3U'_1\beta_{1333}}{\omega_1\omega_3}) + \quad (7)$$

$$+(v_2+1)\left(\frac{U''_{11}\alpha_{122}}{\omega_1^2}+\frac{U''_{13}\alpha_{223}}{\omega_1\omega_3}+\frac{U''_{22}\alpha_{122}}{2\omega_1\omega_2}+\frac{U'_3\beta_{1223}}{\omega_1\omega_3}+\right.$$

$$\left.+\frac{2U'_1\beta_{1122}}{\omega_1^2}\right)$$

$$\Delta q_3=-\frac{U'_3}{\omega_3}+\frac{U_3U''_{33}}{\omega_3^2}+\frac{U'_1U''_{13}}{\omega_1\omega_3}+(v_1+1/2)\left(\frac{U''_{33}\alpha_{113}}{\omega_3^2}+\right.$$

$$\left.\frac{3U''_{13}\alpha_{111}}{\omega_1\omega_3}+\frac{U''_{11}\alpha_{113}}{2\omega_1\omega_3}+\frac{2U'_3\beta_{1133}}{\omega_3^2}+\frac{3U'_1\beta_{1113}}{\omega_1\omega_3}\right)+\tag{8}$$

$$+(v_3+1/2)\left(\frac{9U''_{33}\alpha_{333}}{2\omega_3^2}+\frac{12U'_3\beta_{3333}}{\omega_3^2}+\frac{3U''_{13}\alpha_{133}}{\omega_1\omega_3}+\frac{3U'_3\beta_{1333}}{\omega_1\omega_3}\right)+$$

$$+(v_2+1)\left(\frac{U''_{33}\alpha_{223}}{\omega_3^2}+\frac{U''_{13}\alpha_{122}}{\omega_1\omega_3}+\frac{U''_{22}\alpha_{223}}{2\omega_2\omega_3}+\frac{2U'_3\beta_{2233}}{\omega_3^2}\right)$$

The second order members in **(5,6)** depend on the quantum numbers, $\mathbf{v_i}$. For T>0, the thermal population of excited vibrational levels must be accounted:

$$\overline{\langle (V_i+\frac{g_i}{2})\rangle}=\frac{g_i\exp(-hc\omega_i/kT)}{1-\exp(-hc\omega_i/kT)}+\frac{g_i}{2}\tag{9}$$

where g_i is the degeneracy.

For the high frequency vibration, $\boldsymbol{\omega_1 \gg kT/hc}$, and $\boldsymbol{\langle v_1+1/2\rangle \approx 1/2}$. As to the $\boldsymbol{\omega_2}$ and $\boldsymbol{\omega_3}$ vibrations, their frequencies are comparable to **kT/hc**, and the account of their thermal population can contribute noticeably to the result.

Potential of interaction with solvent

For highly polar H-bonded complexes (μ=5÷10 D), the main contribution to the interaction energy can be written as **[45, 46]:**

$$U = -\mu[\mu \frac{1}{a^3}\frac{\varepsilon_\upsilon - 1}{2\varepsilon_\upsilon + 1} - \mu_e \frac{2}{a^3}(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\varepsilon_\upsilon - 1}{2\varepsilon_\upsilon + 1})] / hc = \tag{11}$$

$$= -\frac{\mu}{a^3}[\mu F_2 + 2\mu_e(F_1 - F_2)] / hc$$

where μ is the dipole moment depending on vibrational coordinates; μ_e - the static dipole moment of a complex; **a** - the radius of Onsager's cavity; ε - the static dielectric constant of a medium; ε_v - the dielectric constant for vibrational frequencies. Upon differentiation, at the equilibrium point ($\mu=\mu_e$) we obtain:

$$\mu = \mu_0 + \mu'_1\Delta q_1 + \mu'_3\Delta q_3 + 1/2\mu''_{11}(\Delta q_1)^2 + \tag{12}$$

$$+ 1/2\mu''_3(\Delta q_3)^2 + \mu''_{13}\Delta q_1\Delta q_3 + \ldots$$

$$U'_{1(3)} = -2\mu_e\mu'_{1(3)}F_1 \;/ hca^3$$

$$U''_{11(33)} = -2[(\mu'_1)^2F_2 + \mu_e\mu''_{11}F_1] / hca \tag{13}$$

$$U''_{13} = -2[\mu'_1\mu'_3F_2 + \mu_e\mu''_{13}F_1] / hca$$

$$U''_{22} = -2F_1\mu_e(\partial^2\mu / \partial\varphi_2) / hca \tag{14}$$

The above formulae allow to calculate alterations of the average bond length in hydrogen bridges as a result of its transfer from vacuum into a solvent, if the needed anharmonic force field and electrooptical parameters are known. The FH...N≡CH complex is a rare example of hydrogen bonded systems where many of the required values can be taken from the literature on high resolution vibrational spectra in the gaseous phase (see Ref.[35, 36]), although the full set of anharmonic constants is unknown. Therefore, the corresponding terms in (7, 8) were neglected.

Let us consider the effect of transferring the complex from the gas ($F_1 = F_2 = 0$) to a strongly polar solvent ($F_1 \approx 0.5$; $F_2 \approx 0.2$). The value of Onzager's cavity radius, **a**, can be approximately estimated by the formula,
$a^3 = 3(M_{XH}/\rho_{XH} + M_Y/\rho_Y)/4\pi N \approx 30\ A^3$, where **M** are masses of the molecules involved, ρ are the densities of the corresponding liquid substances, and N is Avogadro's constant.

With the values taken from Ref. **[35, 36]**, the calculated effect is as follows:
$\Delta q_1 = +0.140 - 0.006(v_1+1/2) - 0.003(v_3+1/2) - 0.011(v_2+1)$;
$\Delta q_3 = -1.316 - 0.151(v_1+1/2) + 0.282(v_3+1/2) - 0.057(v_2+1)$.
On calculating the average values of v_i at 160 K and returning to the natural vibrational coordinates, the following result is obtained:
$\Delta r_{FH} = +0.012$ A, $\Delta R_{N...F} = -0.158$ A.
The experimental values (see **Fig.1**) are as follows:
$\Delta r_{FH} = 0.023 \pm 0.003$ A, $\Delta R_{N...F} = -0.129 \pm 0.005$ A).
Thus, the calculation gives the correct sign and order of magnitude of the effect on both the bond lengths. It underestimates, however, the lengthening of the covalent bond, whereas the result for shortening the hydrogen bond is overestimated. It should be noted that, in our model, the dispersive and repulsive parts of the potential were neglected. Although such approximation seems reasonable for complexes with high dipole moment, an account of repulsion must result in some additional lengthening of the covalent X-H bond and in some decrease of the effect on the hydrogen bond length. The quantitative result depends strongly on the Onsager

radius, **a**, which is difficult to estimate independently and is better to be considered as a parameter of the model.

The main part (90%) of the effect on hydrogen bond length is due to the first order terms in **(7, 8)**. The account of thermal population of the low frequency vibration (ω_3= 168 cm^{-1}) at 160 K decreases the value of the effect by several percent. The bending vibration gives a considerable (-10%) contribution to the effect on the covalent bond length.

7. DISCUSSION

The quantitative estimations show that, in order to discuss the effect of transfer of a hydrogen bonded complex from one liquid solvent to another it is sufficient to consider only the first order terms in **(7, 8)** and the part of the interaction potential depending on the static dielectric constant:

$$\Delta q_i = -\frac{\Delta U_i'}{\omega_i} = \frac{2\mu_e \mu_i' \Delta F_1}{hc\omega_i a^3} \qquad \Delta F_1 \approx \Delta \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} \tag{15}$$

or, in natural vibrational coordinates,

$$\Delta R_{XY} = \frac{\mu_e (\partial\mu / \partial R_{XY})_e}{2\pi^2 c^2 \omega_3^2 m_3 a^3} \Delta F_1 \qquad \Delta r_{XH} = \frac{\mu_e (\partial\mu / \partial r_{XH})_e}{2\pi^2 c^2 \omega_1^2 m_1 a^3} \Delta F_1 \tag{16}$$

It is seen that the effect must be zero for non-polar complexes (μ_e=0). Indeed, in **[33, 34]** it was mentioned that IR spectra of non-polar cyclic dimers (trimers) are practically insensitive to alteration of medium. The sign of medium influence on different bond lengths is determined by the relative sign of dipole moment of a complex and its derivative with respect to the corresponding vibrational coordinate, μ'_i. For uncharged molecular complexes, the total dipole moment can be approximately represented as a sum, $\mu=\mu_{\infty}+\mu_{ind}$, where $\mu_{\infty}= \mu_{XH}+\mu_y$ refers to non-perturbed molecules and μ_{ind} is the moment induced by the interaction. For most molecular complexes, as a rule, the dipole moment induced by hydrogen bonding, which rises with shortening the bond, increases the "intrinsic" moment, $\mu_{ind} >0$. Since, $\mathbf{\mu'_1 >0; \mu'_3 <0; \Delta r_{XH} >0; \Delta R_{XY} <0}$. Thus, polar solvent must cause hydrogen bond to shorten (strengthen) and the covalent, X-H, bond to lengthen.

A special case are hydrogen bonded ionic pairs, $X^-...HY^+$, formed as a result of intracomplex proton transfer, like $Hal^-...HNR_3^+$. The main part of the total dipole moment is determined in this case by a large value arising from charge separation, $\mu_{\infty} \approx \mathbf{e}R + \mu_X + \mu_{YH}$, where **e** is the charge of electron. The total dipole moment increases up to infinity with lengthening the hydrogen bond. The induced dipole moment near the equilibrium point decreases this value due to some charge transfer from anion to cation, $\mu_{ind} < 0$. Therefore, $\mathbf{\mu'_1 < 0; \mu'_3 > 0; \Delta r_{YH} < 0; \Delta R_{XY} > 0}$. Thus, in this case a polar medium makes hydrogen bond longer (weaker), with the bridging proton shifting to the Y^+ atom. Such a picture was recently described for some ionic complexes of pyridine **[12]**. As a result of the transfer of these complexes into a polar solvent, some lengthening of the hydrogen bond was observed. This fact is also in accordance with the studies of solvent polarity influence on IR spectroscopic parameters of hydrogen bonded ionic pairs referred in Ref. **[33, 34]**.

Thus, it can be concluded that our model describes qualitatively the main features the medium polarity effect on hydrogen bond geometry.

This effect can be treated also in terms of the vibrational, or atomic, polarizability hydrogen bonds. The reaction field induced by any polar molecule on itself, vi medium, tends to increase its dipole moment. For usual, "rigid" molecules, this se polarization is mainly electronic, with the effect of changing the atomic geometry dipole moment being not more than several percents **[45]**. However, in a series papers by Zundel **[47-48]** and Bogris **[49]** it was shown that the "protoni polarizability of hydrogen bonds strong enough can even exceed its electro polarizability so that the dipole moment can increase mainly by a proton shift insi a hydrogen bridge.

When considering the expansion of the dipole moment of a complex with respect the q_1, q_3 normal coordinates, **(12)**, and replacing the Δq_i by their approxima expressions **(15)**, the dipole moment can be represented as a function of the reacti field, $E = a^{-3}\mu F_1$, which is directed always along the static dipole moment :

$$\mu = \mu_0 + [\frac{(\mu_1')^2}{hc\omega_1} + \frac{(\mu_3')^2}{hc\omega_3}]\ E \qquad (17)$$

Using the electrooptical parameters from Ref.**[36]**, for the FH...NCH complex, t vibrational polarizability value, $\alpha_v = [\Delta\mu(q_1) + \Delta\mu(q_3)]/E = 0.22 + 0.66 = 0.88\ A^3$, obtained, as compared to the electronic one, $\alpha_{el} = 3.5\ A^3$ **[46]**. For a strong hydrogen bonded complex, the increase of the dipole moment due to some alterati of its geometry must be much higher. It should be noted that the atom polarizability caused by contraction of the hydrogen bond is thrice higher than t "protonic" polarizability. Since the derivatives of the induced dipole moment wi respect to both the coordinates are connected to one another **[34, 19]**, one shoul expect that a similar relation is also characteristic of strongly hydrogen bonded complexes.

For ionic pairs with the transferred proton, $X^-...HY^+$, the dipole moment is the higher the longer is the interionic hydrogen bond and the closer is the bridging proton to Y atom, which inverts the effect on the bond lengths. Of most interest seems to be the question, how the inversion of the sign of the medium effect proceeds in the case of "quasi-symmetric", or "low-barrier", hydrogen bonds, with the proton located in between the heavy atoms: $X^{\delta-}...H...Y^{\delta+}$. The model used in the present paper does not, however, hold for this intermediate case.

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