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ON THE H/D SUBSTITUTION IN SYSTEMS WITH NON-EQUIVALENT HYDROGEN BONDS*

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The IR intensities of the bands due to OD stretching vibrations of HDO molecules increase, as a rule, with the increasing strength of the hydrogen bonds. One is apt to explain this behaviour in terms of non-statistical substitution of hydrogen with deuterium, the deuterium thus preferring the *stronger* bonds. It has been shown [1] that this notion fails to explain the intensity differences in the OH stretching region. In the present paper an Einstein model of a crystal containing two types of hydrogen bond is considered, at a temperature low enough to prohibit creation/existence of phonons in the crystal. The most probable H/D distribution is the one leading to minimisation of the Gibbs energy of the crystal. The results of the model show that deuterium atoms, as a rule, prefer *weaker* hydrogen bonds but in certain cases (two very strong bonds or one extremely weak hydrogen bond) might prefer stronger hydrogen bonds as well.

Key words: hydrogen bonds; non-statistical H/D substitution; one-dimensional crystal; Einstein model; Gibbs energy; minimisation of

INTRODUCTION

In more than 30 years, our distinguished Professor Šoptrajanov has given quite a remarkable contribution in the study of hydrogen bonded systems and the aspects of the hydrogen bonding itself [2–7]. The problem of the non-equal intensities of the various OD stretchings in the IR spectra of crystallohydrates, which was briefly mentioned in his Ph.D. Thesis [2] still deserves attention. Very often, namely, the studied IR spectra of deuterated crystallohydrates, follow the same general pattern: the band intensity of the OD stretching vibrations increases with increasing the hydrogen bond strength [8, 9]. One might be inclined to conclude that these findings clearly show that deuterium atoms, for some reason, prefer the *stronger* hydrogen bonds.

The results of Lutz [1], suggest that this notion is probably incorrect, in the sense that it is not capable of explaining the spectral picture in the OH stretching region of the HDO molecules. One may assume, at first, that deuterium indeed prefers stronger H-bonds. In that case, however, protium should be forced to occupy the weaker ones, and the OH stretching bands at highest frequencies should be the most intense. This not being the case [1], one is left with alternative explanations. Lutz *et al.* [10] and Corn and Strauss [11] proposed an explanation, based on the (empirical) fact of the correlation between the intensity of ν(X-H) mode and the hydrogen bond strength. According to this explanation, one would *a priori* expect the lower frequency stretchings to give more intense bands in the IR spectra. Even this explanation is not justified in all experiments. The explanation of Lutz [1] (in the case of asymmetrically bonded water molecules) which seems to be in agreement with all experimental results, was based on the existence of non-equal normal coordinates for the stretching OH/OD vibrations of the H_1OD_2 and D_1OH_2 species present in the crystal.

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* Dedicated to prof. Bojan Šoptrajanov, on the occasion of his 60th birthday.

It seems that in certain cases non-statistical H/D ordering really takes place. Nelander [12] reports that the above occurs in the partly deuterated water-formaldehyde complex, studied in solid argon and nitrogen matrices. According to Nelander, such findings might be a result of zero-point energy differences of the $HOD\cdots O(CH_3)_2$ and $DOH\cdots O(CH_3)_2$ species, the first one being preferred. Another example is given by Ayers and Pullin [13] who studied the water dimer in argon matrices at low temperatures and concluded that the HOD molecules show strong preference to form a D-bond, in this case too (in both cases, only one proton from the water molecules is involved in hydrogen bonding). These results were "*...understood as once more showing that the OD···O bond is more favourable than the OH···O bond, as predicted by Scheraga...*" [13]. However, when the cited paper of Shipman, Owicki and Scheraga [14] was carefully reviewed, no such prediction/statement could be found within it. Anyway, these results might suggest that deuterium prefers forming *stronger* hydrogen bonds.

On the other hand, crystallographic results seem to show clearly that deuterium atoms prefer forming *slightly weaker* (the ammonium ions in $(NH_4)_2C_2O_4{\cdot}H_2O$ [15]) and *much weaker* (the water molecules in $H_2C_2O_4{\cdot}2H_2O$ [16]) hydrogen bonds. The conclusions were derived on the basis of the measured values of the separation factor S, which was originally introduced [15] in the following way:

$$S = \frac{(\mathrm{H/D})_{\text{water}}}{(\mathrm{H/D})_{\text{ammonium ion}}}$$

i.e.

$$S = \frac{(\mathrm{H/D})_{\text{oxalic acid}}}{(\mathrm{H/D})_{\text{water}}}$$

where (H/D) denotes the distribution ratio of protium and deuterium in particular entity. The values of S were 1.07 ± 0.02 and 1.42 ± 0.03, respectively, and both were found to be statistically significant. Again, the zero-point energy differences were mentioned as a possible cause. Other groups have studied systems containing several types of hydrogen bonds, one of which is very strong [17, 18] and concluded that deuterium prefers *weaker* hydrogen bonds. In addition Brunton and Johnson [17] studied the crystal structure of protiated, deuterated and partly deuterated $YH(C_2O_4)_2{\cdot}3H_2O$ at various temperatures. The results show that at low temperatures the deuterium content in the *weaker* hydrogen bonds *increases*, and that in the *very strong* hydrogen bond *decreases*.

Kakiuchi and Matsuo [19] studied the H/D fractionation in the aquaous urea solution. Their conclusion is that "*...deuterium is enriched in the weaker hydrogen-bonding site (the urea-water cluster) and depleted in the stronger hyrogen bonding site (free water).*"

In conclusion to this brief introduction, it should be mentioned that Petruševski and Sherman [20] pointed to a somewhat similar phenomenon: the preferred substitution of K^+ with NH_4^+ ions in the potassium sulfate – ammonium sulfate system. Namely, there are two crystallographically distinct sites (I and II) occupied by ammonium (potassium) ions in these crystals. In the mixed crystal ammonium prefers site II, whilst potassium prefers site I. The (qualitative) explanation which they offered was based on the minimum value of the Gibbs energy of the mixed crystal.

One might say from the above that the results seem to be somewhat confusing, hence the problem deserves attention. To the best of our knowledge, no detailed quantitative study of the isotopic effects on the possible non-statistical distribution of protium and deuterium has been done so far. In the present paper a model is developed, which accounts for preferred H/D distribution, on a basis of some elementary thermodynamic considerations. This model resembles the one introduced by Newton and Friedman [21]. The purpose is to, possibly, answer the question: do deuterium atoms prefer stronger or weaker hydrogen bonds?

THE THEORETICAL MODEL

Let us consider one-dimensional crystal (*i.e.* one-dimensional linear chain) built of two chemically identical, but crystallographically non-equivalent X-H molecules, connected via hydrogen bonds of unequal strength, as shown below :

$$\cdots X_A{-}H_A\cdots X_B{-}H_B\cdots\cdots X_A{-}H_A\cdots X_B{-}H_B\cdots$$

Several different situations will be discussed. The following approximations are assumed to be valid in all cases:

1) X is a heavy atom : $m(X) >> m(H)$.

2) Hindered translations are considered unimportant and are omitted from the model.

3) The Einstein model [22] is suitable in the description of the lattice dynamics (as a consequence, there is neither correlation field splitting, nor phonon dispersion).

4) The temperature is low compared with Einstein's temperature θ_E.

It should be mentioned that none of the approximations seems to be critical or unrealistic, as to affect appreciably the results derived form it. The above approximations serve only as a tool used to simplify the otherwise rather involved treatment of the crystal dynamics.

Case 1: HA1D50 (harmonic vibrations; one degree of freedom; $x_D = 50\%$)

The starting configuration is one in which 2N hydrogen atoms are placed at 2N sites (N of A-type and N of B-type). Then half of the total number of hydrogens (N) are substituted by deuterium. The final state is characterised by K deuterium atoms and N – K hydrogen atoms at type A sites, while N – K deuteriums and K hydrogens occupy sites of type B (K ≤ N). The basic idea is to calculate the characteristic thermodynamic functions (more precisely, their changes) as functions of K and to reduce the question of finding the most stable configuration (H/D distribution) to the question of finding the minima of those functions with respect to K. The thermodynamically preferable configuration is the one leading to minimisation of the Gibbs energy change as a consequence of the change of system's state[1]. Therefore, it is necessary to derive an expression for ΔG as a function of K and to find the value of K for which this function reaches its minimum.

One may start with the Gibbs-Helmholtz equation. Since $\Delta U \approx \Delta H$ for condensed systems ($\Delta H = \Delta U + P\Delta V$, the $P\Delta V$ part being vanishingly small) one gets:

$$\Delta G = \Delta U - T\Delta S \tag{1}$$

where U is the internal energy of the system, S is its entropy and T is the thermodynamic temperature.

The change of the internal energy upon deuteration may be easily calculated. In the initial state (when no deuterium is present), as a consequence of approximations 3 and 4, the main contribution to the internal energy of the system is the zero-point energy. In that case the internal energy function U_1 takes the form:

$$U_1 = E_1 + C \tag{2}$$

where C is some constant, and E_1 is the zero-point energy of the crystal:

$$E_1 = \frac{\mathrm{N}}{2}\hbar\omega_\mathrm{H}^\mathrm{A} + \frac{\mathrm{N}}{2}\hbar\omega_\mathrm{H}^\mathrm{B} \tag{3}$$

with $\omega_\mathrm{H}^\mathrm{A}$ and $\omega_\mathrm{H}^\mathrm{B}$ being the eigenfrequencies of XH oscillators of the type A and B, correspondingly and $\hbar = h/2\pi$ is the Dirac constant.

The final state is characterised by K deuterium atoms at sites of type A and the internal energy function characterising this state will be of the form:

$$U_2 = E_2 + C \tag{4}$$

E_2 is given by:

$$\begin{aligned} E_2 = {} & \frac{\mathrm{K}}{2}\hbar\omega_\mathrm{D}^\mathrm{A} + \frac{(\mathrm{N}-\mathrm{K})}{2}\hbar\omega_\mathrm{D}^\mathrm{B} + \\ & + \frac{(\mathrm{N}-\mathrm{K})}{2}\hbar\omega_\mathrm{H}^\mathrm{A} + \frac{\mathrm{K}}{2}\hbar\omega_\mathrm{H}^\mathrm{B} \end{aligned} \tag{5}$$

where $\omega_\mathrm{D}^\mathrm{A}$ and $\omega_\mathrm{D}^\mathrm{B}$ are the eigenfrequencies of the XD oscillators of the types A and B correspondingly. Assuming that there are no changes in the potential energy of the oscillators as a result of deuteration (that is, C is a true constant), the internal energy change $\Delta U = U_2 - U_1$ may be calculated as :

$$\begin{aligned} \Delta U = {} & \frac{\mathrm{K}}{2}\hbar\left(\omega_\mathrm{D}^\mathrm{A} - \omega_\mathrm{D}^\mathrm{B}\right) + \frac{\mathrm{K}}{2}\hbar\left(\omega_\mathrm{H}^\mathrm{B} - \omega_\mathrm{H}^\mathrm{A}\right) + \\ & + \frac{\mathrm{N}}{2}\hbar\left(\omega_\mathrm{D}^\mathrm{B} - \omega_\mathrm{D}^\mathrm{A}\right) \end{aligned} \tag{6}$$

Now it may be seen that approximation 2 is fully justified, since for heavy nuclei X there will be virtually no frequency shifts upon deuteration and the corresponding terms that describe the hindered translations, even if taken into account in equations (3) and (5) would simply cancel in equation (6).

The second term in the equation (1), (the entropy term), may be calculated in the following way: the entropy change of the system ΔS, is equal to the difference of the entropies of the final (S_2) and initial states (S_1). Both S_2 and S_1 may be calculated employing Boltzmann equation:

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[1] The Gibbs energy of the initial configuration does not depend on K. Therefore, both the Gibbs energy of the final state and the difference of the Gibbs energies of the final and initial states (ΔG) regarded as functions of K will be characterised by the same stationary points.

$$S = k\ln W \tag{7}$$

where W is the thermodynamic probability of the state (the number of microstates that define particular macrostate), and k is Boltzmann constant. The thermodynamic probability of the initial state is 1 (it is a perfectly ordered state), so $\Delta S = S_2$. S_2 may be calculated assuming simply that there are N "holes" of type A and N "holes" of type B in the linear alternate chain, which are filled with protium/deuterium according to the above scheme :

$$\Delta S = k\ln\left(C_N^K C_N^K C_N^{N-K}\right) \tag{8}$$

In equation (8), C_N^K and C_N^{N-K} denote combinations of N elements, of K-th and (N-K)-th class, respectively (see appendix 1). Making use of the properties of binomial coefficients, equation (8) may be transformed into:

$$\begin{aligned}\Delta S &= k\ln\left[\frac{N!}{K!(N-K)!}\right]^3 = \\ &= 3k\ln\left[\frac{N!}{K!(N-K)!}\right]\end{aligned} \tag{9}$$

or, using Stirling approximation (appendix 2):

$$\begin{aligned}\Delta S = 3k(N\ln N - N) + 3kN - 3kK\ln K -\\ - 3kN\ln(N-K) + 3kK\ln(N-K)\end{aligned} \tag{10}$$

Combining equations (9), (6) and (1), one obtains expression for ΔG as a function of K:

$$\begin{aligned}\Delta G = \frac{K}{2}\hbar\left(\omega_D^A - \omega_D^B\right) + \frac{K}{2}\hbar\left(\omega_H^B - \omega_H^A\right) +\\ + \frac{N}{2}\hbar\left(\omega_D^B - \omega_D^A\right) - 3kT\ln\left[\frac{N!}{K!(N-K)!}\right]\end{aligned} \tag{11}$$

This function has its minimum (see appendix 3) when

$$\frac{\partial(\Delta G)}{\partial K} = 0 \tag{12}$$

Differentiation of equation (1) with respect to K gives:

$$\frac{\partial(\Delta G)}{\partial K} = \frac{\partial(\Delta H)}{\partial K} - T\frac{\partial(\Delta S)}{\partial K} \tag{13}$$

and after some algebra manipulations, one finally obtains:

$$\begin{aligned}\frac{\partial(\Delta G)}{\partial K} = \frac{\hbar}{2}\left(\omega_D^A - \omega_D^B\right) + \frac{\hbar}{2}\left(\omega_H^B - \omega_H^A\right) -\\ - 3kT\ln\left(\frac{N}{K} - 1\right)\end{aligned} \tag{14}$$

It is more convenient to express the stationary point in terms of the quantity K/N, that is, the fraction of deuterium atoms placed at type A sites. Combining equations (12) and (14), solving for K/N (recalling that $\omega = c\cdot\tilde{\nu}$) and rearranging, an expression for the stationary point is obtained:

$$\frac{K}{N} = \frac{1}{1 + \exp\left[\frac{hc}{6kT}\left(\tilde{\nu}_D^A - \tilde{\nu}_D^B + \tilde{\nu}_H^B - \tilde{\nu}_H^A\right)\right]} \tag{15}$$

Finally, as a consequence of approximation 1 and assuming harmonic vibrations, the ratio of the frequencies $\rho = \omega_H/\omega_D$ is very close to $\sqrt{2}$ and one may write for simplicity :

$$Z = \frac{1}{1 + \exp\left[\frac{hc}{6kT}\left(1 - \frac{1}{\sqrt{2}}\right)\left(\tilde{\nu}_H^B - \tilde{\nu}_H^A\right)\right]} \tag{16}$$

where Z denotes the ratio K/N.

Case 2: HA3D50 (harmonic vibrations; three degrees of freedom; x_D = 50%)

The model presented above was somewhat oversimplified. Firstly, it was based on the assumption that only longitudinal vibrations (the stretching OH/OD modes) are allowed. Allowing for perpendicular vibrations (the two doubly-degenerate hindered rotations [Note that the two bending modes are not necessarily degenerate in a three-dimensional crystal (even in one containing linear chains).] or bending modes), leads to differences only in the enthalpy (*i.e.* internal energy) term of the expression for ΔG, while the entropy term remains unchanged. Accounting for the bending modes, one arrives to the following expression for the oscillator energies:

$$\begin{aligned}E_1 = \frac{N}{2}\hbar\omega_{H(s)}^A + \frac{N}{2}\hbar\omega_{H(b1)}^A + \frac{N}{2}\hbar\omega_{H(b2)}^A +\\ + \frac{N}{2}\hbar\omega_{H(s)}^B + \frac{N}{2}\hbar\omega_{H(b1)}^B + \frac{N}{2}\hbar\omega_{H(b2)}^B\end{aligned} \tag{17}$$

where $\omega_{H(s)}^A$ is the eigenfrequency of the stretching OH mode for the type A oscillators (the subscript "s" stands for stretching), while $\omega_{H(b1)}^A$ and $\omega_{H(b2)}^A$ are the eigenfrequencies of the correspondent bending (subscripts "b1" and "b2") modes for these oscillators. The same reasoning may be applied to the oscillators of type B. As a consequence of degeneracy, it follows that $\omega_{H(b1)}^A = \omega_{H(b2)}^A = \omega_{H(b)}^A$, so:

$$E_1 = \frac{\mathrm{N}}{2}\hbar\omega_{\mathrm{H(s)}}^{\mathrm{A}} + \mathrm{N}\hbar\omega_{\mathrm{H(b)}}^{\mathrm{A}} + \frac{\mathrm{N}}{2}\hbar\omega_{\mathrm{H(s)}}^{\mathrm{B}} + \mathrm{N}\hbar\omega_{\mathrm{H(b)}}^{\mathrm{B}} \tag{18}$$

For the final state 2, the corresponding E_2 value is:

$$E_2 = \frac{\mathrm{K}}{2}\hbar\omega_{\mathrm{D(s)}}^{\mathrm{A}} + \frac{(\mathrm{N-K})}{2}\hbar\omega_{\mathrm{D(s)}}^{\mathrm{B}} + \frac{(\mathrm{N-K})}{2}\hbar\omega_{\mathrm{H(s)}}^{\mathrm{A}} + \frac{\mathrm{K}}{2}\hbar\omega_{\mathrm{H(s)}}^{\mathrm{B}} + \mathrm{K}\hbar\omega_{\mathrm{D(b)}}^{\mathrm{B}} + \mathrm{N-K})\hbar\omega_{\mathrm{D(b)}}^{\mathrm{B}} + (\mathrm{N-K})\hbar\omega_{\mathrm{H(b)}}^{\mathrm{A}} + \mathrm{K}\hbar\omega_{\mathrm{H(b)}}^{\mathrm{B}} \tag{19}$$

The first partial derivative of ΔG with respect to K takes the form:

$$\frac{\partial(\Delta G)}{\partial \mathrm{K}} = \frac{\hbar}{2}\left[\left(\omega_{\mathrm{D(s)}}^{\mathrm{A}} - \omega_{\mathrm{D(s)}}^{\mathrm{B}}\right) + \left(\omega_{\mathrm{H(s)}}^{\mathrm{B}} - \omega_{\mathrm{H(s)}}^{\mathrm{A}}\right)\right] + \hbar\left[\left(\omega_{\mathrm{D(b)}}^{\mathrm{A}} - \omega_{\mathrm{D(b)}}^{\mathrm{B}}\right) + \left(\omega_{\mathrm{H(b)}}^{\mathrm{B}} - \omega_{\mathrm{H(b)}}^{\mathrm{A}}\right)\right] - 3kT\ln\left(\frac{\mathrm{N}}{\mathrm{K}} - 1\right) \tag{20}$$

Equating the right-hand side to zero and solving for Z gives :

$$\mathrm{Z} = \frac{1}{1 + \exp\left[\dfrac{hc}{3kT} F\left(\tilde{\nu}_{\mathrm{D(s)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{D(s)}}^{\mathrm{B}}, \tilde{\nu}_{\mathrm{D(b)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{D(b)}}^{\mathrm{B}}, \tilde{\nu}_{\mathrm{H(s)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{H(s)}}^{\mathrm{B}}, \tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{B}}\right)\right]} \tag{21}$$

where $F\left(\tilde{\nu}_{\mathrm{D(s)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{D(s)}}^{\mathrm{B}}, \tilde{\nu}_{\mathrm{D(b)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{D(b)}}^{\mathrm{B}}, \tilde{\nu}_{\mathrm{H(s)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{H(s)}}^{\mathrm{B}}, \tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{B}}\right)$ is a function of the wavenumbers of all included vibrational modes, that has the form:

$$F(\tilde{\nu}_{\mathrm{D(s)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{D(s)}}^{\mathrm{B}}, \tilde{\nu}_{\mathrm{D(b)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{D(b)}}^{\mathrm{B}}, \tilde{\nu}_{\mathrm{H(s)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{H(s)}}^{\mathrm{B}}, \tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{A}}, \tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{B}}) = \frac{1}{2}\left(\tilde{\nu}_{\mathrm{D(s)}}^{\mathrm{A}} - \tilde{\nu}_{\mathrm{D(s)}}^{\mathrm{B}} + \nu_{\mathrm{H(s)}}^{\mathrm{B}} - \tilde{\nu}_{\mathrm{H(s)}}^{\mathrm{A}}\right) + \left(\tilde{\nu}_{\mathrm{D(b)}}^{\mathrm{A}} - \tilde{\nu}_{\mathrm{D(b)}}^{\mathrm{B}} + \tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{B}} - \tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{A}}\right) \tag{22}$$

<u>Case 3</u> : AN3D50 (anharmonic vibrations; three degrees of freedom; x_{D} = 50%)

Further extension of this model accounts for anharmonicity effects. These effects are reflected through the changes of the ρ factors of the vibrational modes :

$$\tilde{\nu}_{\mathrm{D(i)}}^{\mathrm{j}} = \frac{1}{\rho_{\mathrm{i}}^{\mathrm{j}}}\tilde{\nu}_{\mathrm{H(i)}}^{\mathrm{j}} \tag{23}$$

which are now allowed to deviate from the harmonic oscillator values (the subscripts in ρ factors refer to particular vibrational modes, and the superscripts to particular sites *i.e.*: $\mathrm{i} \in \{\mathrm{s, b}\}$ and $\mathrm{j} \in \{\mathrm{A,B}\}$).

The expression (21) is transformed into :

$$\mathrm{Z} = \frac{1}{1 + \exp\left\{\dfrac{hc}{3kT}\left[\dfrac{1}{2}\tilde{\nu}_{\mathrm{D(s)}}^{\mathrm{A}}\left(\dfrac{1}{\rho_{\mathrm{s}}^{\mathrm{A}}} - 1\right) + \dfrac{1}{2}\tilde{\nu}_{\mathrm{D(s)}}^{\mathrm{B}}\left(1 - \dfrac{1}{\rho_{\mathrm{s}}^{\mathrm{B}}}\right) + \tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{A}}\left(\dfrac{1}{\rho_{\mathrm{b}}^{\mathrm{A}}} - 1\right) + \tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{B}}\left(1 - \dfrac{1}{\rho_{\mathrm{b}}^{\mathrm{B}}}\right)\right]\right\}} \tag{24}$$

<u>Case 4</u> : AN3DA (anharmonic vibrations; three degrees of freedom; x_{D} = arbitrary)

All previous expressions are valid for half-deuterated compounds. However, in quite a general case, the deuterium content may be arbitrary. The treatment of this problem is given below.

Let N_1 be the number of deuterium, and N_2 the number of hydrogen atoms present in the linear chain. Obviously, $\mathrm{N}_1 + \mathrm{N}_2 = 2\mathrm{N}$. As earlier, $\Delta U \approx \Delta H$ is valid. The energy due to the zero-point oscillations of the initial state, is the same as in the previous simple model (because no deuterium atoms are present in the chain), so it is given by equation (18). The energy of the final state (the one characterised by K deuterium atoms present at sites of type A), is now given by the following expression:

$$E_2 = \frac{\mathrm{K}}{2}\hbar\omega_{\mathrm{D(s)}}^{\mathrm{A}} + \frac{\left(\mathrm{N}_1 - \mathrm{K}\right)}{2}\hbar\omega_{\mathrm{D(s)}}^{\mathrm{B}} + \frac{(\mathrm{N-K})}{2}\hbar\omega_{\mathrm{H(s)}}^{\mathrm{A}} + \frac{\left(\mathrm{N} - \mathrm{N}_1 + \mathrm{K}\right)}{2}\hbar\omega_{\mathrm{H(s)}}^{\mathrm{B}} + \mathrm{K}\hbar\omega_{\mathrm{D(b)}}^{\mathrm{A}} + (\mathrm{N-K})\hbar\omega_{\mathrm{H(b)}}^{\mathrm{A}} + \\ + \left(\mathrm{N}_1 - \mathrm{K}\right)\hbar\omega_{\mathrm{D(b)}}^{\mathrm{B}} + \left(\mathrm{N} - \mathrm{N}_1 + \mathrm{K}\right)\hbar\omega_{\mathrm{H(b)}}^{\mathrm{B}} \tag{25}$$

According to this, the change in the internal energy due to the change of the state of the system, is given by:

$$\Delta U=\frac{\mathrm{K}}{2}\hbar\left(\omega_{\mathrm{D(s)}}^{\mathrm{A}}-\omega_{\mathrm{D(s)}}^{\mathrm{B}}\right)+\frac{\mathrm{N}_1}{2}\hbar\left(\omega_{\mathrm{D(s)}}^{\mathrm{B}}-\omega_{\mathrm{H(s)}}^{\mathrm{B}}\right)+\frac{\mathrm{K}}{2}\hbar\left(\omega_{\mathrm{H(s)}}^{\mathrm{B}}-\omega_{\mathrm{H(s)}}^{\mathrm{A}}\right)+\mathrm{K}\hbar\left(\omega_{\mathrm{H(b)}}^{\mathrm{B}}-\omega_{\mathrm{H(b)}}^{\mathrm{A}}\right)+\mathrm{K}\hbar\left(\omega_{\mathrm{D(b)}}^{\mathrm{A}}-\omega_{\mathrm{D(b)}}^{\mathrm{B}}\right)+\mathrm{N}_1\hbar\left(\omega_{\mathrm{D(b)}}^{\mathrm{B}}-\omega_{\mathrm{H(b)}}^{\mathrm{B}}\right) \tag{26}$$

the same expression being valid for ΔH, too.

The change of the entropy of the system, assuming again that the thermodynamic probability of the initial state (this is the same as in the previous model: a perfectly proton ordered state) is equal to 1, may be calculated using the expression:

$$\Delta S=k\ln\left(C_{\mathrm{N}}^{\mathrm{K}}C_{\mathrm{N}}^{\mathrm{K}}C_{\mathrm{N}}^{\mathrm{N}_1-\mathrm{K}}\right) \tag{27}$$

where $C_{\mathrm{N}_1}^{\mathrm{K}}C_{\mathrm{N}}^{\mathrm{K}}C_{\mathrm{N}}^{\mathrm{N}_1-\mathrm{K}}$ is the thermodynamic probability of the state 2 (see appendix 5). Therefore :

$$\Delta S=k\ln\left[\left(\frac{\mathrm{N}!}{\mathrm{K}!(\mathrm{N}_1-\mathrm{K})!}\right)^2\frac{\mathrm{N}_1!}{(\mathrm{N}-\mathrm{K})!(\mathrm{N}-\mathrm{N}_1+\mathrm{K})!}\right] \tag{28}$$

The first partial derivative of ΔG with respect to K is given by:

$$\frac{\partial(\Delta G)}{\partial\mathrm{K}}=\frac{\hbar}{2}\left[\left(\omega_{\mathrm{D(s)}}^{\mathrm{A}}-\omega_{\mathrm{D(s)}}^{\mathrm{B}}\right)+\left(\omega_{\mathrm{H(s)}}^{\mathrm{B}}-\omega_{\mathrm{H(s)}}^{\mathrm{A}}\right)\right]+\hbar\left[\left(\omega_{\mathrm{H(b)}}^{\mathrm{B}}-\omega_{\mathrm{H(b)}}^{\mathrm{A}}\right)+\left(\omega_{\mathrm{D(b)}}^{\mathrm{A}}-\omega_{\mathrm{D(b)}}^{\mathrm{B}}\right)\right]-3kT\ln\left(\frac{(\mathrm{N}_1-\mathrm{K})^2}{\mathrm{K}^2}\frac{\mathrm{N}-\mathrm{K}}{\mathrm{N}-\mathrm{N}_1+\mathrm{K}}\right) \tag{29}$$

Equating the previous expression to zero, one obtains:

$$\frac{\mathrm{N}_1^2\mathrm{N}-\left(\mathrm{N}_1^2+2\mathrm{N}_1\mathrm{N}\right)\mathrm{K}+\left(2\mathrm{N}_1+\mathrm{N}\right)\mathrm{K}^2-\mathrm{K}^3}{(\mathrm{N}-\mathrm{N}_1)\mathrm{K}^2+\mathrm{K}^3}=\mathcal{A} \tag{30}$$

where $\mathcal{A}$ is defined by the following expression:

$$\mathcal{A}=\exp\left\{\frac{\hbar}{kT}\left[\frac{1}{2}\left(\omega_{\mathrm{H(s)}}^{\mathrm{B}}-\omega_{\mathrm{H(s)}}^{\mathrm{A}}\right)+\frac{1}{2}\left(\omega_{\mathrm{D(s)}}^{\mathrm{A}}-\omega_{\mathrm{D(s)}}^{\mathrm{B}}\right)+\left(\omega_{\mathrm{H(b)}}^{\mathrm{B}}-\omega_{\mathrm{H(b)}}^{\mathrm{A}}\right)+\left(\omega_{\mathrm{D(b)}}^{\mathrm{A}}-\omega_{\mathrm{D(b)}}^{\mathrm{B}}\right)\right]\right\} \tag{31}$$

or, including the ρ factors for particular sites:

$$\mathcal{A}=\exp\left\{\frac{hc}{kT}\left[\frac{1}{2}\left(\frac{1}{\rho_{\mathrm{s}}^{\mathrm{A}}}-1\right)\tilde{\nu}_{\mathrm{H(s)}}^{\mathrm{A}}+\frac{1}{2}\left(1-\frac{1}{\rho_{\mathrm{s}}^{\mathrm{B}}}\right)\tilde{\nu}_{\mathrm{H(s)}}^{\mathrm{B}}+\left(\frac{1}{\rho_{\mathrm{b}}^{\mathrm{A}}}-1\right)\tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{A}}+\left(1-\frac{1}{\rho_{\mathrm{b}}^{\mathrm{B}}}\right)\tilde{\nu}_{\mathrm{H(b)}}^{\mathrm{B}}\right]\right\} \tag{32}$$

Some algebra manipulations lead to the following cubic equation with respect to K:

$$(\mathcal{A}+1)\mathrm{K}^3+\left[\mathcal{A}(\mathrm{N}-\mathrm{N}_1)-(2\mathrm{N}_1+\mathrm{N})\right]\mathrm{K}^2+\left(\mathrm{N}_1^2+2\mathrm{N}_1\mathrm{N}\right)\mathrm{K}-\mathrm{N}_1^2\mathrm{N}=0 \tag{33}$$

Dividing by N^3 and substituting the molar fraction of deuterium atoms x_{D} instead of the number of deuterium atoms, one finally arrives to:

$$(\mathcal{A}+1)Z^3+\left[\mathcal{A}(1-2x_{\mathrm{D}})-(4x_{\mathrm{D}}+1)\right]Z^2+4x_{\mathrm{D}}(x_{\mathrm{D}}+1)Z-4x_{\mathrm{D}}^2=0 \tag{34}$$

It is obvious that the equation (34), in the case of $x_{\mathrm{D}}=0.5$ takes the form :

$$Z=\frac{1}{1+\mathcal{A}^{\frac{1}{3}}} \tag{35}$$

which is, of course, equivalent to equation (24).

A BASIC-coded computer program was developed for the calculation of the value of Z which characterises the equilibrium H/D distribution (the program is available from the authors, upon request).

RESULTS AND DISCUSSION

The second derivative of the function $\Delta G = f(K)$ (see appendix 3) for the simplest case (HA1D50), shows that the stationary point (Eq. 16) indeed corresponds to a minimum of this function. The same (or slightly modified) reasoning for the character of the stationary points is also applicable in cases 2, 3 and 4 (HA3D50, AN3D50 and AN3DA).

In the HA1D50 case, the behaviour of the described system is governed by Eq. 16. If the condition $\tilde{\nu}_H^B > \tilde{\nu}_H^A$ is satisfied (in other words, if sites B correspond to weaker hydrogen bonds), than the second term in the denominator is greater than one and the most stable configuration will be characterised with some excess of the deuterium atoms present on sites B. It is also obvious that a temperature increase leads to diminishing of the isotope effects. In a case of hydrogen bonds of equal strengths, the most stable configuration would be determined by the entropy factor solely, that is, it would be the configuration with equal number of deuterium atoms placed on both site types. As the temperature approaches the absolute zero, the isotope effect becomes more pronounced (in agreement with the results of Brunton and Johnson [17]). However, this does not mean that the temperature lowering will always be accompanied by immediate changes in the actual H/D distribution. The previous theoretical model is based on purely thermodynamic arguments. Consequently, the conclusions regarding the stability of a particular state are purely thermodynamic. In case of the change in the distribution (which is a dynamic process) with temperature, one should account for kinetic factors and be aware of the significance of potential barriers in particular cases.

The important thing to summarise is that in the simplest HA1D50 case the deuterium *always* exhibits preference for the *weaker* hydrogen bond, for this is the condition ensuring minimisation of the Gibbs energy function.

Now, let us consider somewhat more realistic picture of a crystal containing one weaker and one stronger hydrogen bond, employing the AN3D50 model. The variations of the separation factor will be presented as a function of temperature and the isotopic shift ratios. One may start with $\tilde{\nu}_H^A = 3400\ \text{cm}^{-1}$; $\tilde{\nu}_H^B = 3000\ \text{cm}^{-1}$; $\delta_H^A = 1200\ \text{cm}^{-1}$; $\delta_H^B = 1250\ \text{cm}^{-1}$ (the bending vibrations are known to be less sensitive to the hydrogen bond strength). Knowing from experience [23] that when $\rho_s^A > \rho_s^B$, then also $\rho_b^A < \rho_b^B$, a series of calculations, covering a variety of possibilities, were done and the results are presented in Table I.

Table I

Values for the separation factor (S_f) as a function of temperature and isotopic shift ratios
($\tilde{\nu}_H^A = 3400\ \text{cm}^{-1}$; $\tilde{\nu}_H^B = 3000\ \text{cm}^{-1}$; $\delta_H^A = 1200\ \text{cm}^{-1}$; $\delta_H^B = 1250\ \text{cm}^{-1}$ as well as $\rho_s^A = \rho_b^A = 1.34$ were the default values)

T/K	$\rho_s^B = 1.340$	$\rho_s^B = 1.330$	$\rho_s^B = 1.320$	$\rho_s^B = 1.300$
	$\rho_b^B = 1.340$	$\rho_b^B = 1.345$	$\rho_b^B = 1.350$	$\rho_b^B = 1.360$
300	$S_f = 0.885$	$S_f = 0.872$	$S_f = 0.857$	$S_f = 0.829$
250	$S_f = 0.864$	$S_f = 0.848$	$S_f = 0.831$	$S_f = 0.798$
200	$S_f = 0.833$	$S_f = 0.814$	$S_f = 0.794$	$S_f = 0.754$
150	$S_f = 0.784$	$S_f = 0.760$	$S_f = 0.735$	$S_f = 0.687$
100	$S_f = 0.694$	$S_f = 0.662$	$S_f = 0.630$	$S_f = 0.569$
50	$S_f = 0.482$	$S_f = 0.438$	$S_f = 0.397$	$S_f = 0.324$

It might be seen that, again, deuterium prefers the weaker hydrogen bond. One may vary the input parameters within certain limits, but unless systems with two very strong hydrogen bonds are taken into account or highly unrealistic estimates for the isotopic shift ratios are made, the results will *invariably show that deuterium prefers weaker hydrogen bonds*.

Let us now briefly discuss the behaviour of systems containing very strong hydrogen bonds. It might be instructive to analyse a system containing two very strong and symmetric hydrogen bonds, one characterised with ss-type potential, and the other with sd-type. In this case, the values $\tilde{\nu}_H^A = 1000\ \text{cm}^{-1}$; $\tilde{\nu}_H^B = 800\ \text{cm}^{-1}$; $\delta_H^A = 1500\ \text{cm}^{-1}$; $\delta_H^B = 1550\ \text{cm}^{-1}$; $\rho_s^A = 0.95$; $\rho_s^B = 1.40$; $\rho_b^A = 1.45$; $\rho_b^B = 1.32$ may be considered as being feasible. (By the way the cross-over of the stretching and bending frequencies is a well established phenomenon [23, 24]. In the case of systems with ss-type potential of the proton in the hydrogen bond, the X-H stretching vibrations may show large H/D isotopic ratios (close to √2) [24], while the corresponding ratios for sd-type potentials have abnormally low values (~1 or even lower) [25]). The separation factor $S_f = (H/D)_A/(H/D)_B$ equals 1.117 (for $x_D = 0.5$, at 300 K), showing that deuterium might prefer stronger hydrogen bonds, as well.

How should the results of Nelander [12] and Ayers and Pullin [13] be explained in terms of the present model? First of all, it should be mentioned that in both cases, the studied systems contain water molecules forming *a single hydrogen bond*. This is in a way equivalent to the study of a system forming two hydrogen bonds, one of which is extremely weak. Second, both groups have worked at very low temperatures (Nelander at 11 K [12] and Ayers and Pullin at 7 K [13]). In such cases, in the light of the proposed model, $\Delta U \approx \Delta G$ (at low temperatures, the $T\Delta S$ term may be disregarded) and the isotope effect is expected to be very pronounced.

The situation may be pictured by the scheme:

$$\cdots X_A{-}H_A \cdots X_B{-}H_B \cdots\cdots\cdots X_A{-}H_A \cdots X_B{-}H_B$$
$$\cdots\cdots\cdots X_A{-}H_A \cdots X_B{-}H_B \cdots\cdots\cdots$$

in which $H_A \cdots X_B$ corresponds to a weak hydrogen bond and $H_B \cdots\cdots\cdots X_A$ to an absence of hydrogen bonding. One may assume $\tilde{\nu}_H^{\ A} = 3600\ \text{cm}^{-1}$; $\tilde{\nu}_H^{\ B} = 3700\ \text{cm}^{-1}$; $\delta_H^{\ A} = 400\ \text{cm}^{-1}$; $\delta_H^{\ B} = 150\ \text{cm}^{-1}$; $\rho_s^{\ A} = \rho_s^{\ B} = \rho_b^{\ A} = \rho_b^{\ B} = 1.35$; $T = 11$ K; $x_D = 0.5$ (the values for the bending vibrations are selected in such a way, that the first one be in the range of typical librational frequencies of weakly hydrogen bonded water molecules and the second one in the range typical for the *hydrogen bond deformation mode*, that is the $H_A \cdots X_B{-}H_B$ bending). The value of the separation factor is $S_f = 0.011$, thus showing that about 90.6 % deuterium atoms enter the A-type sites which correspond to stronger hydrogen bonds. Although the proposed model is a simple one, the results of the calculations are in good agreement with the observations of Nelander [12] and Ayers and Pullin [13].

CONCLUSION

From the results presented above, it might be seen that, as a rule, deuterium atoms prefer *weaker* hydrogen bonds. This finding indicates, once again, that the mentioned variations in the intensity of the OD stretching bands (in partly deuterated crystallohydrates) *could not be interpreted* in terms of H/D distribution isotopic effects. Under certain circumstances (when both hydrogen bonds are very strong, or when one is extremely weak) the deuterium might prefer stronger hydrogen bonds as well. It is thus not possible to answer *a priori* the question given in the introduction. For both weaker and stronger hydrogen bonds the preferred distribution is the one that leads to minimum Gibbs energy of the final state. The deuterium preference over weaker or stronger hydrogen bond, will depend on the details of the potential energy hypersurface of the studied system.

The future goal is to make the model more realistic and to account for the vibrations of polyatomic molecules (H_2O, NH_3, H_3O^+, NH_4^+, $H_5O_2^+$ *etc.*), in order to make an attempt to give a quantitative explanation for the H/D distribution in deuterated $(NH_4)_2C_2O_4{\cdot}H_2O$ [15] and $H_2C_2O_4{\cdot}2H_2O$ [16].

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APPENDIX 1

The expression for the thermodynamic probability of state 2 can be obtained considering the number of all possible "microstates" that would lead to a macrostate characterised by K deuterium atoms placed on type A sites. Treating the linear alternate chain as consisting of "holes" of type A and B, the process of deuteration could be regarded as a process of distributing the N deuterium atoms on the linear chain. The question is how to count the microstates. There are C_N^K ways to choose K deuterium atoms of a total number N. For each such choice, there are C_N^K ways for the distribution of K deuterium atoms at N "holes" of the type A. Further, for each particular distribution described, there are C_N^{N-K} ways for the distribution of the rest N-K deuterium atoms at N type B sites. Finally, the following expression for the thermodynamic probability of the state B is obtained:

$$W = C_N^K C_N^K C_N^{N-K} \tag{A1.1}$$

APPENDIX 2

The Stirling approximation is often used in calculations involving logarithms of factorials of large numbers. On the basis of the geometrical meaning of Riemann's integral, for large values of N, the following approximate equality is valid:

$$\ln N! \approx N \ln N - N \tag{A2.1}$$

APPENDIX 3

As is well known from a viewpoint of mathematical analysis, in a stationary point a function may reach maximum, minimum or an inflection, depending on the value of the second derivative in this point. The second derivative of ΔG as a function of K can be calculated as follows. Starting from the expression for the first derivative of ΔG with respect to K for the simplest case (HA1D50), given by the equation (14):

$$\frac{\partial(\Delta G)}{\partial K} = \frac{\hbar}{2}\left(\omega_D^A - \omega_D^B\right) + \frac{\hbar}{2}\left(\omega_H^B - \omega_H^A\right) - 3kT\ln\left(\frac{N}{K} - 1\right) \tag{A3.1}$$

it follows that:

$$\frac{\partial^2(\Delta G)}{\partial K^2} = \frac{\partial}{\partial K}\left(\frac{\partial(\Delta G)}{\partial K}\right) = -3kT\frac{\partial}{\partial K}\left[\ln\left(\frac{N-K}{K}\right)\right] \tag{A3.2}$$

Partially differentiating the logarithmic term in parentheses, one finally arrives at:

$$\frac{\partial^2(\Delta G)}{\partial K^2} = \frac{3kTN}{K(N-K)} \tag{A3.3}$$

Since this expression is always non-negative, it follows that the stationary point corresponds to a minimum of the function $\Delta G(K)$. The same reasoning is also valid for cases 2 and 3, because the first term in the expression for the corresponding first derivative, given by (20) is not a function of K, and the second term in (20) coincides with the second term in (14). So, the expressions for the second derivatives will coincide.

In the case of an arbitrary content of deuterium, the expression for the second derivative of ΔG with respect to K (note that the first derivative is given by Eq. 29) takes the form

$$\frac{\partial^2(\Delta G)}{\partial K^2} = -3kT\frac{K^2}{(N_1-K)^2}\frac{N-N_1+K}{N-K}\frac{\left[-2(N_1-K)(N-K)-(N_1-K)^2\right]K^2(N-N_1+K)-(N_1-K)^2(N-K)\left[2K(N-N_1+K)+K^2\right]}{K^4(N-N_1+K)^2} \qquad \text{(A3.4)}$$

Since $N_1 \le N+K$, the second derivative is also positive, and the stationary point also corresponds to a minimum of the function $\Delta G(K)$.

APPENDIX 4

In the case of arbitrary deuterium content, the thermodynamic probability of the final state (K deuterium atoms at sites of type A) can be calculated in an analogous way as in the particular case of 50% deuterium content. Let the number of deuterium atoms present in the one-dimensional chain after deuteration be denoted as N_1, and the number of hydrogen atoms as N_2. Obviously

$$N_1 + N_2 = 2N \qquad \text{(A4.1)}$$

where 2N is the total number of sites. There are $C_{N_1}^{K}$ independent ways of choosing K deuterium atoms out of N_1, and C_N^K independent ways of choosing K of N sites (of type A). The number of correspondent possible choices of the remaining $N_1 - K$ sites (of N of type B) for the rest of the deuterium atoms is $C_N^{N_1-K}$, so the total number of microstates corresponding to the macrostate characterised by K (of a total number N_1) deuterium atoms present at sites of type A is given by:

$$W_2 = C_{N_1}^{K} C_N^{K} C_N^{N_1-K} \qquad \text{(A4.2)}$$

Резиме

ЗА СУПСТИТУЦИЈАТА НА ВОДОРОД СО ДЕУТЕРИУМ ВО СИСТЕМИ СО НЕЕКВИВАЛЕНТНИ ВОДОРОДНИ ВРСКИ

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Клучни зборови: водородна врска; несиметрична H/D замена; замена на еднодимензионален кристал; Ајнштајнов модел; Гибсова енергија, мимимизација

Инфрацрвените ленти од валентните OD вибрации на HDO молекулите се, по правило, поинтензивни при посилни водородни врски. Привлечна е идејата ваквиот наод да се објасни како резултат на нестатистичка замена на водородот со деутериум, при што деутериумот би ги преферирал посилните водородни врски. Покажано било [1] дека ваква претпоставка не е во состојба да ги објасни разликите во интензитетите на лентите од валентните OH вибрации. Во статијава е дискутиран модел на ајнштајновски кристал што содржи два типа водородни врски, на доволно ниска температура за да биде оневозможено постоење на фонони. Најверојатна H/D распределба е онаа што води до минимална вредност на Гибсовата енергија на кристалот. Резултатите покажуваат дека деутериумот може да преферира послаби, но и посилни водородни врски.