Brief Communications

Correlations between bond lengths and stretching frequencies in the O—D...O hydrogen bridge and their consequences

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Based on modern neutron diffraction data and the known empirical correlations between the geometric and spectroscopic parameters of hydrogen bonds, the analytical expression describing the relation between the O—D covalent and D...O hydrogen bond lengths in the O—D...O hydrogen bridge was obtained. The distribution functions of the interatomic and nearest intermolecular distances in heavy water were calculated from the Raman band shapes in the 10 to 90 °C temperature interval in the framework of the fluctuation theory of hydrogen bonding.

Key words: hydrogen bond, liquid water, geometric parameters, vibrational spectra, distribution functions.

The problem on correlations between the lengths of the hydrogen bridge (O...H...O), chemical (covalent, O—H) and hydrogen bonds (HB, H...O), and the stretching frequency of the OH group at different HB strengths has a long history.[1] These correlations are being periodically refined as the experimental technique and theoretical concepts developed.[2—4] The selections of the most exact neutron diffraction data on the equilibrium r_{O-H}, $r_{H...O}$, and $R_{O...O}$ distances in bridging bonds of various organic molecules and water in crystals at temperatures below 130 K have recently[5,6] been published. Researchers have studied 136 HB formed by carboxylic acids and their salts, oxalates, phthalates, quinones, peroxides, and other compounds and their deuterated analogs. We are interested in the part of these data concerning standard HB (in systems without bifurcations, *i.e.*, when a proton binds only two O atoms), which are presented in Ref. 6 and in Fig. 1, *a* (squares and triangles) under the assumption of the equivalent geometry of the O—H...O and O—D...O bonds. Below these structural data are compared to the already known correlations between the bond lengths and stretching vibrations. This comparison allowed their relation to be analytically described. Then thus found formulas were applied to the calculation of the pairwise correlation functions of the interatomic (r_{O-D}) and intermolecular ($r_{D...O}$ and $R_{O...O}$) distances in heavy water (D_2O) on the basis of interpretation of the band shape in the Raman spectra of vibrations of the O—D bond in the framework of the fluctuation theory of hydrogen bonding.[7,8]
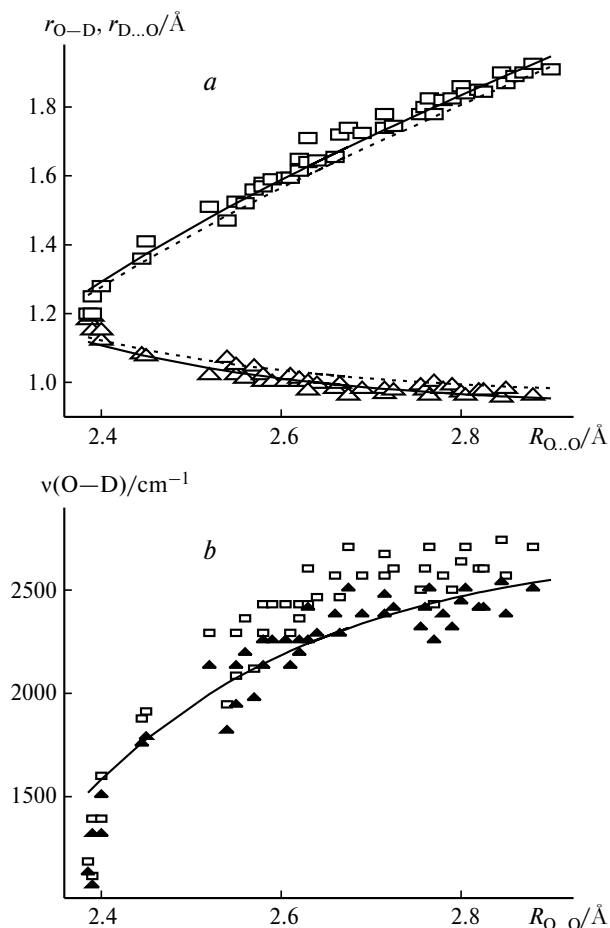
Fig. 1. *a*. Plots of the O—D (r_{O-D}) and D...O ($r_{D...O}$) bond lengths *vs*. length of the O—D...O hydrogen bridge ($R_{O...O}$) ($r_{D...O}$ and r_{O-D} are designated[6] by squares and triangles, respectively); dotted lines are calculated by Eq. (3) at $r_{O-D}^u = 0.9575$ Å corresponding to the water monomer in the gas phase, solid lines are calculated at $r_{O-D}^u = 0.925$ Å found by us for the condensed phase. *b*. Stretching frequency of the O—D ($v(O-D)$) bond as a function of $R_{O...O}$ for the points presented in Fig. 1, *a*: calculation by Eqs. (1) and (3) through r_{O-D} at $r_{O-D}^u = 0.9575$ Å and $k_{O-D} = -6925$ cm^{-1} Å^{-1} [10] (squares), at the refined values of these parameters (triangles) and directly (through $R_{O...O}$) by experimental formula (2) (solid line).

Relation of OH group and hydrogen bridge lengths. A few data on the relation between r_{O-H} and $R_{O...O}$ for HB of the O—H...O type have been presented.[1] They agree with the later neutron diffraction measurements, which confirm the theoretical concepts[9] on the formation of the symmetrical HB (the H atom is equally bonded to the both O atoms, and the difference between the covalent and hydrogen bonds is eliminated) at $R_{O...O} = 2.4$ Å (see Fig. 1, *a*). The analytical form of the desired relation can be obtained by the application of the already known empirical regularities including the vibrational spectroscopic data rather than formal fitting of the curve to the structural data[6]). Since the particularly used spectral band

shapes are referred to the OD oscillator (dilute solution of D_2O in H_2O), hereafter HB implies a bond through heavy hydrogen.

Analysis of the geometry and spectra of water molecules in deuterated crystal hydrates[10] allowed an almost linear correlation between the low-frequency shift of the $v(O-D)$ band and elongation of the O—D bond to be established

$$\Delta v(O-D) = k_{O-D}\Delta r_{O-D}, \tag{1}$$

where $\Delta v(O-D)/cm^{-1} = v(O-D) - v(O-D)^u$, $\Delta r_{O-D}/Å = r_{O-D} - r_{O-D}^u$ ("u" symbol designates belonging to the unbound water molecule), and $k_{O-D} = -6925$ cm^{-1} Å^{-1}.

Taking into account the known[4] correlation between $v(O-D)$ and $R_{O...O}$

$$\Delta v(O-D) = -8.810 \cdot 10^6 exp(-3.7295 R_{O...O}) \tag{2}$$

we can express r_{O-D} through $R_{O...O}$ in Eq. (1)

$$r_{O-D} = r_{O-D}^u + 8810/6.925 exp(-3.7295 R_{O...O}). \tag{3}$$

Accepting $r_{O-D}^u = 0.9575$ Å (water molecule in the gas phase) in expression (3), we get dotted lines in Fig. 1, *a*. It was considered in the calculation of the upper branch that $r_{D...O} = R_{O...O} - r_{O-D}$, *i.e.*, the hydrogen bridge is linear (it has been shown previously[5] that the inflection of the hydrogen bridge to at least 30° does not distort the correlation between $R_{O...O}$ and r_{O-D}). Figure 1, *b* was plotted by points of the bottom branch in Fig. 1, *a* using formula (2) following from experiment (solid line) and our formula (1) and taking into account Eq. (3) (squares) at $v(O-D)^u = 2727$ cm^{-1} (mean value of frequencies of the symmetrical and antisymmetrical vibrations of the unbound D_2O molecule).

It is seen in Fig. 1, *a* that Eq. (3) somewhat overestimates the r_{O-D} values compared to the experimental values, including the asymptotic r_{O-D}^u value. This results in the different behavior of the $v(O-D) = f(R_{O...O})$ correlations calculated from formulas (1) + (3) and (2), respectively (see Fig. 1, *b*). This means that the r_{O-D}^u limit (to which r_{O-D} asymptotically tends in the condensed phase when HB weakens) differs from the value in the gas phase (0.9575 Å).

Equating expressions (1) and (2) allows r_{O-D}^u and k_{O-D}, which must be constants by definition, to be determined in the explicit form

$$k_{O-D} = -8.810 \cdot 10^6 exp(-3.7295 R_{O...O})/\Delta r_{O-D}. \tag{4}$$

Inserting the experimental $R_{O...O}$ and r_{O-D} values presented in Fig. 1, *a* into formula (4) shows that the linear approximation of the k_{O-D} values calculated using the least-squares method is parallel to the abscissa (*i.e.*, independent of $R_{O...O}$) at $r_{O-D}^u = 0.925$ Å and gives

$k_{O-D} = -6250$ cm^{-1} Å^{-1}, which differs from the published value (-6925 cm^{-1} Å^{-1})[10] within the experimental error. The plots corresponding to these values are presented in Fig. 1, *a* by solid lines and in Fig. 1, *b* by triangles. The agreement between the experiment and plots of r_{O-D} and $r_{D...O}$ *vs.* $R_{O...O}$ and the $v(O-D)$ correlations obtained directly with $R_{O...O}$ and through r_{O-D} $(v(O-D)[r_{O-D}(R_{O...O})])$ has evidently improved.

Calculation of distribution functions of interatomic distances. After the correlations between the geometric characteristics of the hydrogen bridge were matched with each other and the stretching frequency of the OH group, one can state the problem of calculation of the radial distribution functions (P) of the intramolecular covalent (r_{O-D}) and intermolecular hydrogen bond lengths in liquid water. According to the fluctuation theory of HB,[7] anomalously broad bands in the spectrum ($v(O-H)$ and $v(OD)$) reflect the statistical distribution of equilibrium geometric configurations of the hydrogen bridge, which is inherent in liquids (unlike crystals). The stronger the HB, the greater the low-frequency shift of the maximum $v'(O-H)$ of the intrinsic (sufficiently narrow) absorption band $\varphi(v - v'(O-H))$ of the involved oscillator relatively to the frequency of the unbound OH group and the shorter the $R_{O...O}$ distance. This is quantitatively described by formula (2). Thus, the frequency distribution $P(v)$ in the spectrum of the isotropic component of the Raman spectrum of the HOD molecules in H$_2$O (or D$_2$O) reflects the energy distribution $P(E)$ and geometric configurations of HB.[11,12] The IR spectra are less appropriate for this purpose because require to exclude preliminarily the influence of the H bond strength on the intensity of absorption by a specific OH oscillator, which changes along the band by a factor of tens.[11] Of course, the accuracy of such a calculation is not greater than that of the used empirical correlations constructed for HB of water and many other molecules, which average, in essence, the influence of other factors (difference in the properties of the donor and acceptor groups, inflection of the H bond, possible coordination of the O atom by the metal atom in crystal hydrates, *etc.*). These influences are considered to be the main reason for scatter of experimental points around correlation curves. In addition, the calculation ignores polyfurcate HB, which are possible, in principle, in liquid water, because it compares each $v(O-D)$ frequency to the single $r_{D...O}$ distance, which thus plays the role of effective mean.

The problem of calculation of the statistical distribution of frequencies, *i.e.*, exclusion of the contribution of homogeneous broadening $\varphi(v - v'(O-H))$ from experimental spectra, has been solved.[8] To obtain $P(v(O-D))$, we processed the experimental spectra of vibrations of the O—D bond in liquid HOD (in the absence of the dynamic bonding of the OD oscillators, which distorts the initial statistical frequency distribution in D$_2$O) at 10, 50,

and 90 °C in the isotropic Raman component[13] according to the described[8] algorithm.

The distribution function of the chemical bond lengths $P(r_{O-D})$ is determined as

$$P(r_{O-D}) = P(v(O-D)) \left| \partial v(O-D)/\partial r_{O-D} \right|, \qquad (5)$$

and the distribution function of the hydrogen bond lengths $P(r_{D...O})$ is determined by an analogous formula with the substitution of the $\partial v(O-D)/\partial r_{O-D}$ Jacobian by $\partial v(O-D)/\partial r_{D...O}$.

The results of calculations show that the lengths of the OH group in liquid water range from 0.925 to 1.0 Å and those of hydrogen bonds are distributed from 1.6 to 2.5 Å (Fig. 2). The calculation of the distribution function of the nearest O atoms

$$P(R_{O...O}) = P(v(O-D)) \left| \partial v(O-D)/\partial R_{O...O} \right|$$

almost completely reproduces Fig. 2, *b* if the abscissa is scaled by the substitution of $r_{D...O} = 1.6$ Å by $R_{O...O} = 2.6$ Å and $r_{D...O} = 2.4$ Å by $R_{O...O} = 3.3$ Å.

A comparison of the structural and spectroscopic characteristics of the O—D...O hydrogen bridge allowed one to find the analytical formula for the correlation between r_{O-D} and $R_{O...O}$, depending on the strength of HB. It turned out that the best agreement with experiment is achieved if the length of the unbound OH group in the
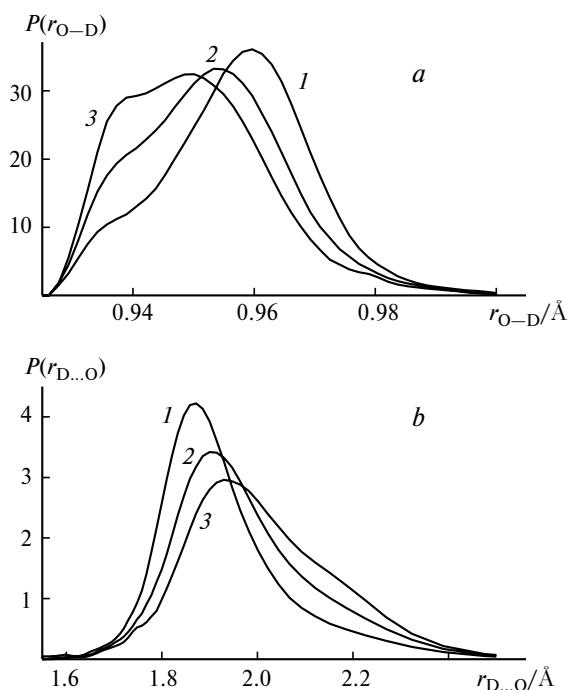

Fig. 2. Distributions (P) of the covalent (O—D, *a*) and hydrogen (D...O, *b*) bonds at 10 (*1*), 50 (*2*) and 90 °C (*3*) (calculation by Eq. (5) and its analog for $r_{D...O}$ from the statistical distributions of stretching vibrations of the O—D bond found using the algorithm[8] from the Raman spectral band shapes of semideuterated water[13]).

condensed phase is somewhat shorter than that in the gas phase. This can be a manifestation of the known internal field effect.[14,15] The calculation of the distribution functions of the covalent (O—D) and hydrogen (D...O) bond lengths showed that the equilibrium length of the OD group in different liquid water molecules changed from 0.925 to 1.00 Å and that of HB changed from 1.6 to 2.5 Å due to fluctuations of the local environment.

The distribution functions obtained in this work cannot yet be compared with neutron diffraction data. The position and temperature function of the distribution maxima in calculation and experiment are the same. However, the first peak $g(r) \approx 1$ Å in experimental works either is not presented at all[16] or off-scaled.[17] The second peak (at 1.9 Å) is strongly overlapped by the $g(r_{H,H})$ distribution,[16] which impedes analysis of its shape. A shoulder[17] similar to that at 2.15 Å (see Fig. 2, *b*) is formed on this distribution with temperature increase. These data indicate a qualitative agreement of the calculated and experimental results.

It is somewhat unexpected that two groups of substantially heterogeneous data (hydrogen bonds of different pairs of organic molecules in crystals and water molecules in crystal hydrates) result in mutually matched correlations. This was explained in part in Ref. 5, where special attention was given to correlations of bond lengths for HB with the same donor and different acceptors and *vice versa*. It turned out that the experimental points lie in different regions of the figure plane but form, on the whole, the single smooth curve without breaks and inflections. Thus, HB has a parallel effect on the intra- and intermolecular distances, although its energy for different donor—acceptor pairs varies in very wide limits. It can be assumed by analogy that the coordination (possible in crystal hydrates) of water molecules by metal atoms modifies (enhances or weakens) but does not substantially change the ratio between its characteristics (bond lengths, stretching frequency).

It is important that the obtained results are based on the supplementing structural and spectroscopic information. The temperature evolution of the distribution functions was established in detail and, when direct data (neutron diffraction) are deficient, it can be helpful both for theoretical analysis of the liquid water structure and as a test for interaction potentials used in molecular dynamic and Monte Carlo calculations.

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