Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1964

SovietRxiv

Fig. 1. General model of a water molecule perturbed by hydrogen bonds

Figure 1: Fig. 1. General model of a water molecule perturbed by hydrogen bonds

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 156, No. 3

PHYSICAL CHEMISTRY

G. V. YUKHNEVICH, A. V. KARYAKIN

RELATION BETWEEN THE FREQUENCIES OF THE VALENCE VIBRATIONS OF THE WATER MOLECULE AND THE ENERGY OF THE HYDROGEN BOND

(Presented by Academician A. P. Vinogradov, January 30, 1964)

The present work is devoted to finding a dependence by means of which, from the frequencies of the valence vibrations of the water molecule, it would be possible to determine the energy of its interaction with surrounding molecules. Analogous dependences have already been published earlier ([1,2]). However, they either contain an unknown coefficient, or have been constructed only for one definite class of compounds. In addition, these dependences completely fail to take into account the specific character of the vibrations of two coupled oscillators, which is of fundamental importance in the case of the water molecule. As a result of all this, none of the dependences previously found can be used for interpreting the vibrational spectra of water molecules in one system or another. In solving this question, we thereby also touch upon the more general problem of finding the dependence between the absorption spectrum of a substance and the nature of its interaction with the medium.

Fig. 1. General model of a water molecule perturbed by hydrogen bonds

The most suitable method for investigating the indicated systems is molecular spectroscopy. A detailed analysis of its capabilities ([3]) led the authors to the conclusion that, in general, the problem of the interaction of a substance with a medium is far from being completed. Interactions of different nature, which occur in every real system, have the same spectral manifestation—the shift of absorption bands and the change in their intensity. Consequently, the available experimental material cannot be explained even qualitatively from the point of view of the theoretical concepts currently existing.

The question we are considering, concerning the change in the frequencies of the valence OH vibrations of the water molecule under the influence of the surrounding medium, is narrower and therefore lends itself to a sufficiently rigorous mathematical analysis. Indeed, in the overwhelming majority of systems containing water molecules, the interaction of the latter with the medium always proves to be caused by hydrogen bonds and therefore must be attributed to a directed specific interaction. The universal dielectric interaction in these systems, on the contrary, plays the role of only a small correction, which will not be taken into account in the present treatment.

Let us now turn directly to the systems that interest us. It is obvious that in solutions, complexes, and crystalline hydrates—in the general case the position of any water molecule may be represented by the following model (Fig. 1). Here E^1 and $E^2 = E^1 + \Delta E$ are the energies of the hydrogen bonds formed by the water molecule, and K_H and $K_H + \Delta K_H$ are, respectively, their force constants. K_{11} and $K_{11} - \Delta K$ are the force constants of the OH bonds, depending on the perturbation of the latter by hydrogen bonds. It would be desirable to establish a dependence that would make it possible to determine, from the frequencies of the valence OH vibrations of the water molecule, the energies of the hydrogen bonds formed by it.

As was shown in solving the direct problem (4), a hydrogen bond causes a decrease in the force constant of the OH bond whose hydrogen atom forms this hydrogen bond. Therefore the desired dependence could

can be found from an analysis of the behavior of the natural vibration frequencies of two coupled (kinematically and due to electronic interaction) harmonic oscillators with arbitrary force constants.

Solving the secular equation of such a system,

$$\begin{vmatrix} D_{11} - \lambda & D_{12} \\ D_{21} & D_{22} - \lambda \end{vmatrix} = 0,$$

where

$$\begin{vmatrix} D_{11} D_{12} \\ D_{21} D_{22} \end{vmatrix} = \begin{vmatrix} A_{11} A_{12} \\ A_{21} A_{22} \end{vmatrix} \begin{vmatrix} K_{11} K_{12} \\ K_{21} K_{22} \end{vmatrix},$$

we find that

$$\Delta\lambda = \lambda^2_{\text{out-of-phase}} - \nu^2_{\text{in-phase}} =$$

$$= \sqrt{4(A_{11}K_{12} + A_{12}K_{11})^2 + A_{11}^2 \Delta K^2 - 4A_{12}\Delta K(A_{11}K_{12} + A_{12}K_{11})}, \quad (1)$$

and their derivative with respect to ΔK will be equal to

$$\frac{A_{11}^2\Delta K - 2A_{12}(A_{11}K_{12} + A_{12}K_{11})}{\sqrt{4(A_{11}K_{12} + A_{12}K_{11})^2 + A_{11}^2\Delta K^2 - 4A_{12}\Delta K(A_{11}K_{12} + A_{12}K_{11})}}. \tag{2}$$

In general form these expressions do not make it possible to establish how the difference of the squares of the vibration frequencies of the oscillators will change when K_{11} and ΔK change, since it will depend entirely on the ratio of the quantities $A_{11}, A_{12}, K_{11}, K_{12}$ and on their signs. As is seen from the expression for the derivative

$$\frac{\partial(\nu_n^2 - \nu_c^2)}{\partial\Delta K},$$

two cases are possible. If the quantity $A_{12}(A_{11}K_{12} + A_{12}K_{11})$ has a negative value, then the difference of the squares of the frequencies will also increase monotonically as ΔK increases. If, however, $A_{12}(A_{11}K_{12} + A_{12}K_{11})$ is a positive quantity, then as ΔK increases the difference of the squares of the frequencies will first decrease and then thereafter only increase. Finding from (2) the expression for ΔK at the extremum and substituting it into (1), we obtain:

$$\Delta\lambda_{\min} = 2|A_{11}K_{12} + A_{12}K_{11}|\sqrt{1 - \frac{A_{12}^2}{A_{11}^2}} = \Delta\lambda_0\sqrt{1 - \frac{A_{12}^2}{A_{11}^2}}\,, \tag{3}$$

where $\Delta\lambda_0$ is the difference of the squares of the frequencies at $\Delta K = 0$.

It is obvious that when the atom Y of the XYX group is considerably heavier than the atom X, the factor

$$\sqrt{1 - \frac{A_{12}^2}{A_{11}^2}}$$

is close to unity. In the case of the water molecule it has the form

$$\sqrt{1 - \frac{\varepsilon_0^2\cos^2\mathrm{HOH}}{(\varepsilon_H + \varepsilon_0)^2}}$$

and is approximately equal to 0.99987, which corresponds to a decrease in the initial frequency difference by 0.3 cm^{-1}. This quantity lies far beyond the limits of accuracy of frequency measurements in liquids and crystals and therefore practically cannot be taken into account. Moreover, the value of ΔK at the extremum is approximately $0.01\cdot10^{-6}$ cm^{-2} and, consequently, describes such weak interactions that at present they cannot be registered experimentally.

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

Thus, the appearance of asymmetry in the force field of the molecule XYX, on the one hand, as a consequence of a decrease in the resonance interaction of the X—Y bonds, causes convergence, and, on the other hand, owing to the increasing difference of the force constants, divergence of the frequencies of the valence OH vibrations. As is clear from the calculation carried out, the latter process predominates, and therefore, if atom Y is considerably heavier than atom X, or the angle XYX is close to a straight angle, then $\Delta\lambda$ can only increase.

Let us consider the case of a symmetric perturbation of the molecule XYX ($\Delta K = 0$). In this case $\Delta\lambda = 2|A_{11}K_{12} + A_{12}K_{11}|$, and consequently

$$\frac{\partial \Delta\lambda}{\partial K_{11}} = 2|A_{12}| = -2\varepsilon_Y \cos|\angle\text{XYX}.$$

If atom Y is sufficiently heavy or the angle XYX differs little from a straight angle, then this coefficient proves to be so small that the difference of the frequencies of the valence XY vibrations remains almost unchanged. Thus, in the case of the water molecule ($2|A_{12}| = 0.034$), with a decrease of K_{11} by 30%,

which causes a shift of the frequencies of the valence OH vibrations from 3700 to 3100-3000 cm^{-1}, the difference of these frequencies decreases by no more than 9 cm^{-1}. Hence it follows that, under symmetric perturbation of XYX molecules by weak or medium hydrogen bonds, the difference between the frequencies of their valence X—Y vibrations remains practically constant.

Both of the dependences obtained are completely general. Therefore they are valid both for the XYX system in general and for the HOH molecule in particular.

Fig. 2. *a*—dependence of the difference between the frequencies of the valence vibrations of the water molecule on the difference of the energies of the hydrogen bonds formed by it; *b*—plot of the lowering of the frequency of the antisymmetric vibration as a function of the asymmetric part of the load.

Fig. 3. Change in the frequency of the antisymmetric vibration of the water molecule when it is perturbed by symmetric hydrogen bonds.

HOH—in particular. Despite the universality of the formulas derived, they still do not make it possible to judge unambiguously the strength of the perturbing hydrogen bonds. For this, two further conditions must be fulfilled. First, it is necessary to make sure that the change in the force constants considered above (K_{11} and $K_{11} - \Delta K$) is the only, or at least the principal, manifestation of the hydrogen bond. Second, in order to make practical use of the available qualitative dependence, it must be transformed into a quantitative one.

Let us examine these conditions in more detail. When a hydrogen bridge is formed, a redistribution of electron density in the XY bond occurs. The latter manifests itself in a decrease of the force constant of the XY bond itself, and may also cause a change in the force constants of the interaction of this bond with the adjacent bond (K_{12}) and with the angle ($K_{1\gamma}$). There are no definite statements in the literature about the relationship between the changes of these force constants under the influence of a hydrogen bond. However, it may be assumed that the relative change in K_{11} will at least not be smaller than the relative changes in K_{12} and $K_{1\gamma}$. Calculation shows that, for an equal relative change in K_{11}, K_{12}, and $K_{1\gamma}$, the contribution of the latter two to the change in the frequencies of the valence OH vibrations is less than 5%. Therefore, in a first approximation, the shift of the frequencies of the valence OH vibrations may be regarded as due only to the change in the force constants of the OH bonds themselves.

To obtain quantitative characteristics, it is necessary to use a whole series of numerical data found from experiment. For the water molecules of interest to us, such an analysis has already been carried out earlier (^{4}). The dependences found correspond completely to the general regularities obtained and discussed above. In this connection, below we shall merely transform the results obtained earlier into a form more convenient for us, which may be recommended for determining the force constants and energies of the hydrogen bonds perturbing the water molecule under consideration.

The secular equation contains only kinematic coefficien-

ties and the force constants of the molecule; therefore the bond energies cannot be obtained directly from its solution. However, in the case considered here of weak and medium hydrogen bonds, their energy and force constant prove to be approximately proportional to one another (^4). This dependence is certainly approximate. Nevertheless, since the possibility of determining the hydrogen-bond energy with an accuracy of $±$0.3 kcal/bond is of practical interest, the corresponding energies are plotted on the ordinates of the graphs simultaneously with the force constants.

A symmetric load causes an equal decrease in both frequencies of the valence OH vibrations, whereas an asymmetric one mainly decreases only the frequency of the in-phase vibration, in which chiefly the length of the more strongly perturbed OH^(2) bond changes (^4). Using these regularities, from the difference in the frequencies of the valence OH vibrations and from their absolute magnitude one can find the force constants and energies of the symmetric (E) and asymmetric (ΔE) parts of the perturbation of the water molecule.

The difference in the force constants and in the energies of the hydrogen bonds formed by the atoms H^1 and H^2 can be found from the difference between the frequencies of the out-of-phase and in-phase vibrations (Fig. 2a). From the same frequency difference one can estimate the magnitude of the decrease in ν_{p}, which we shall denote $\delta\nu_{\mathrm{p}}$, owing to the presence of the asymmetric part of the load—ΔE (Fig. 2b). Then the quantity $\nu_\mathrm{p} + \delta\nu_\mathrm{p}$ will correspond to the frequency of the out-of-phase (antisymmetric) vibration of the water molecule which it would perform if the asymmetric part of the perturbation were removed from it. From the frequency thus found for the antisymmetric vibration of the symmetrically perturbed water molecule, one can determine the magnitude of this perturbation, which will be equal to the magnitude of the weaker perturbation (Fig. 3). The energy of the stronger perturbation of the given water molecule is equal to the energy of the weak perturbation plus the difference in interaction energies found above. Thus, from the two bands of the valence OH vibrations it is possible to establish the force constants and energies of the bonds perturbing the water molecule.

The graphical dependences presented are not very convenient for analyzing the behavior of the frequencies when one or another parameter of the system is varied. For this purpose analytical expressions for the dependences are more convenient. An exact expression of the experimental curves is very cumbersome. Moreover, the accuracy achieved in compiling these expressions may turn out to be superfluous if it exceeds the accuracy with which the curves themselves are obtained, or the accuracy of the experiment. Therefore simpler analytical expressions were compiled, which at the same time differ from the true ones by no more than $±$5 cm^{-1} or $±$0.1 kcal/bond.

Representing the first curve (Fig. 2a) as the difference between a straight line and a quadratic hyperbola, the second (Fig. 2b) also as a hyperbola, and the third (Fig. 3) as the difference between a straight line and an exponential, we obtain the following expressions for E^1 and E^2:

$$E^1 = \frac{3780 - (\nu_\mathrm{p} + \delta\nu_\mathrm{p})}{62} - e^{-\frac{3860-(\nu_\mathrm{p}+\delta\nu_\mathrm{p})}{120}}, \qquad E^2 = E^1 + 0.014\Delta\nu - \frac{1.8 \cdot 10^5}{\Delta\nu^2},$$

where $\delta\nu_\mathrm{p} = 45(1 - 10^4/\Delta\nu^2)$, ν_p, $\delta\nu_\mathrm{p}$, and $\Delta\nu$ are expressed in reciprocal centimeters, and E^1 and E^2 in kilocalories per bond.

Thus, from the frequencies of the valence OH vibrations of the water molecule, one can determine the force constants and energies of the hydrogen bonds perturbing it.

Institute of Geochemistry and Analytical Chemistry
named after V. I. Vernadsky
Academy of Sciences of the USSR

Received
19 I 1964

CITED LITERATURE

1. N. D. Sokolov, *UFN*, **57**, no. 2, 205 (1955).

2. S. S. Mirta, *J. Chem. Phys.*, **36**, no. 12, 3286 (1962).

3. O. P. Girin, N. G. Bakhshiev, *UFN*, **79**, no. 2, 235 (1963).

4. G. V. Yukhnevich, *Optics and Spectroscopy*, Collection of Articles, **2**, 223 (1963).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.