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The theory of the equilibrium isotope effects of hydrogen

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ABSTRACT. The present state of the theory of the equilibrium isotope effects of hydrogen has been examined using a new approach developed by the present authors, namely the coordinate analysis of isotope effects. The mathematics of the theory have been described briefly. The conditions under which the isotopic effect is localised have been formulated. The relationship of the isotope effects in protium–deuterium and protium–tritium replacements has been refined. Particular attention has been made to clear methods for interpreting the parameter $\ln\beta$, making it possible to reveal the relationship between the isotope effect and intramolecular properties, and to systematise isotope effects on the basis of concepts having a clear physical significance. The isotope effects for the principal classes of hydrogen compound have been analysed and systematised. The factors determining the magnitude and nature of the variation in the equilibrium isotope effect have been established.

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I. Introduction

The use of deuterium and tritium as isotopic tracers makes it possible to solve research problems in the most varied branches of physics, chemistry, and biology. These studies must take account of chemical isotope effects,[1] which may be anomalously large for the isotope pairs protium/deuterium and more particularly protium/tritium. The differences in the chemical behaviour of protium, deuterium, and tritium are themselves used as an effective means of studying the molecular and dynamic aspects of chemical and cellular mechanisms.[1] This approach is based on the fact that the equilibrium isotope effects are determined by the specific features of the chemical bonds and the structural characteristics of molecules. The prediction of the separation coefficients of the hydrogen isotopes in chemical exchange systems remains an important problem.

The statistical thermodynamics of isotope effects must solve three main problems: 1, the establishment of the quantitative relationship between isotope effects and the geometric parameters and force field of a molecule; 2, the interpretation of available experimental material on this basis in terms of molecular structure; and 3, the prediction of the magnitude of isotope effects in systems which have not been studied experimentally. From the viewpoint of statistical thermodynamics, the isotopic replacement of hydrogen is the most interesting general case, since hydrogen effects are large and can be measured accurately. Moreover, the theoretical results obtained for hydrogen replacement are applicable to the replacement of the atoms of all other elements. In addition, the extremely large amount of data that has been accumulated on hydrogen effects can be used to analyse the thermodynamics of isotopic exchange.

II. Basic postulates of the theory of equilibrium isotope effects of hydrogen

The theory of equilibrium isotope effects is based on statistical thermodynamics and the theory of molecular vibrations. In the present work, we shall restrict ourselves to an examination of the isotope effects of hydrogen in the harmonic oscillator–rigid rotator approximation. This is related to the fundamental fact that the decisive contribution to the isotope effect at room temperature is made by the harmonic vibrational component of the isotopic differences in the thermodynamic functions, so that all the basic regularities in the isotope effects can be explained in the above approximation. Allowance is made for anharmonicity only by introducing a correction, which may alter the numerical values slightly but which cannot lead to the appearance of qualitatively new phenomena.

1. Chemical isotopic exchange. Calculation of the separation coefficient

The term equilibrium chemical isotope effect denotes the deviation of the distributions of isotopes between chemical forms (components of the system) in the state of thermodynamic equilibrium from those corresponding to equal probabilities. The isotopic exchange of hydrogen atoms between the components AH_n and BH_m (A and B are arbitrary molecular residues, and m and n the numbers of equivalent hydrogen atoms of a given type) involves molecular exchange reactions of the type[2]

$$AH_{n-i+1}D_{i-1}+BH_{m-j}D_j \rightleftharpoons AH_{n-i}D_i+BH_{m-j+1}D_{j-1}, \qquad (1)$$

and also homomolecular isotopic exchange reactions. Each of these reactions is characterised by its own individual equilibrium constant. The isotope effect is revealed in the equilibrium constants of reactions (1) deviating from the equal-probability isotope distribution.

The quantity used as a measure of the thermodynamic isotope effect is the separation coefficient α, defined for the replacement of protium by deuterium as

$$\alpha_{D/H} = \frac{([D]/[H])_A}{([D]/[H])_B} \quad (2)$$

To calculate the separation coefficient α by statistical thermodynamics it is necessary to establish its relationship to the equilibrium constants of reactions (1). The separation coefficient α is given by the equation:[2,3]

$$\alpha = \beta_{A^*/A}/\beta_{B^*/B}, \quad (3)$$

where A* and B* are the heavy isotopic forms of the molecules A and B.

The quantity $\beta_{A^*/A}$ (the "β-factor") [the term "ratio of the reduced partition functions" and the notation $(s/s')/f$ are also used] characterises the thermodynamic non-equilibrium distribution of the isotopes only in the molecule of the given substance A. The physical significance of the $\beta_{A^*/A}$-factor is that it is the equilibrium constant of the hypothetical isotopic exchange reaction between the substance AH_n and the ideal monatomic gas D.

The β-factor is a basic concept in the theory of isotope effects. The advantage of using the β-factors is that the calculated values of the β-factors of molecules and Eqn. (3) can be used to calculate the separation coefficients of the systems which they form. The concept of the β-factor is also convenient for analysing isotope effects in terms of molecular structure, since it makes it possible to restrict the examination to one molecule.

In a number of cases a molecule contains hydrogen in different non-equivalent groups. Thus the molecule of propionic acid CH_3CH_2COOH contains three groups of hydrogen atoms: the three hydrogen atoms of the methyl group, the two hydrogen atoms of the methylene group, and the hydrogen atom of the carboxyl group. The hydrogen atoms of these groups differ from the viewpoint of their chemical behaviour, and each group must be characterised by its own individual value of the β-factor. It is possible in principle to have intramolecular (intrastructural) isotope effects, that is the isotopic enrichment of individual groups by intramolecular exchange. Intrastructural effects are valuable as a means of study in those cases where it is possible to be confident that true equilibrium has been established (for example in geochemical systems). When true equilibrium has been established with respect to several non-equivalent groups, the separation coefficient can be estimated using the concept of the overall β-factor of the molecule (β_Σ), proposed by Galimov; the method for calculating β_Σ from the β-factors of individual groups has been described.[4]

2. Isotope effects and the theory of molecular vibrations

From the viewpoint of mechanics, an n-atom molecule is a system of n material points of mass m_i connected by elastic forces. This system has $N = 3n$ degrees of freedom, of which $3n-6$ correspond to vibrations ($3n-5$ for a linear molecule). In the harmonic approximation, the frequencies of these vibrations are given by the matrix equation

$$\hat{G}\hat{F}\hat{L} = \hat{L}\hat{\Lambda}, \quad (4)$$

where $\hat{G}$ is the kinetic energy matrix, expressed in terms of the generalised momenta, and $\hat{F}$ the potential energy matrix in generalised coordinates. The elements of the matrix $\hat{G}$ (the so-called kinematic coefficients) can be calculated if the geometric parameters of the molecule and the masses of the atoms are known. The elements of the matrix $\hat{F}$ (the force constants) are the values of the second derivatives of the potential energy with respect to the generalised coordinates at the point corresponding to the equilibrium geometric configuration of the molecule. The matrix Λ is the diagonal matrix of the eigenvalues of the matrix $\hat{G}\hat{F}$, which with an accuracy corresponding to a constant coefficient are equal to the squares of the frequencies of the vibrations ($\lambda_i = C\nu_i^2$, where C is a constant which depends on the chosen dimensions). The matrix $\hat{L}$ (the so-called matrix of the modes of the vibrations) is the matrix of the eigenvectors of the matrix $\hat{G}\hat{F}$, and is the matrix for changing from generalised to normal coordinates. The generalised coordinates usually employed to solve Eqn. (4) are the so-called natural vibrational coordinates, that is the deviations of the geometric parameters of the molecule (bond lengths and valence and dihedral angles) from their equilibrium values.

To take better account of the symmetry and specific features of the molecule, it is usual to introduce as coordinates the deviations from the equilibrium values of all the bonds and valence angles in the molecule (complete system of natural coordinates). The number of coordinates is then greater than the number of vibrational degrees of freedom. In this case, zero frequencies appear in the solution of the vibrational problem.

The natural vibrational coordinates make it possible to relate the vibrational-spectroscopic properties of a molecule to the concepts of the classical theory of chemical structure, such as the chemical bond, molecular fragments, their properties, etc. In particular, the force constants expressed in natural coordinates have the property of transferability, that is they change little in series of similar molecules.

In isotopic replacement, the potential energy of a molecule and hence the force constant matrix remain unchanged (to a high approximation), and changes take place only in the kinematic coefficients, which depend on the masses of the atoms. For replacement by a heavier isotope, the vibrational frequencies can only decrease. The sums and products of the frequencies of the vibrations of the isotopic forms of a molecule are related by various rules.[5]

3. Calculation of ln β in the harmonic approximation

In practice, it is more convenient to deal not with the β-factor itself but with its logarithm. The value of ln β in the harmonic oscillator–rigid rotator approximation is calculated using the equation:[3]

$$\ln\beta = \sum_{i=1}^{N}\ln\beta_i = \frac{1}{l}\sum_{i=1}^{N}\ln\left[\left(\operatorname{sh}\left(\frac{u_i}{2}\right)\Big/u_i\right)\Big/\left(\operatorname{sh}\left(\frac{u_i^*}{2}\right)\Big/u_i^*\right)\right] = \frac{1}{l}\left\{\sum_{i=1}^{N}\ln\frac{u_i^*}{u_i} - \frac{1}{2}\sum_{i=1}^{N}(u_i^*-u_i) + \sum_{i=1}^{N}\ln\frac{1-\exp(-u_i)}{1-\exp(-u_i^*)}\right\}.$$

Here and subsequently, $u_i = hc\nu_i/kT$ represents the dimensionless so-called reduced frequencies, h is Planck's constant, c the velocity of light, ν_i the vibrational wavenumbers, cm^{-1}, N the number of vibrational degrees of freedom of the molecule, and l the number of atoms replaced; the superscript "*" indicates that the corresponding

quantity is associated with the heavy isotopic form. The last two terms on the right-hand side of Eqn. (5) reflect the contribution made to $\ln\beta$ by the vibrational degrees of freedom of the molecule; the second term, with an accuracy corresponding to a certain factor, is the difference in the energies of the zero-point vibrations, and the third term reflects the contribution of vibrational excitation. The first term on the right-hand side of Eqn. (5) reflects the contribution of translational and rotational motion, and is expressed in terms of the vibrational frequencies using the Teller–Redlich theorem.[6]

4. Analysis of the accuracy of the basic assumptions

The accuracy of Eqns. (3) and (5) is determined by the accuracy of the assumptions forming the basis of the theoretical premises from which they are derived, primarily the Born–Oppenheimer approximation and the harmonic oscillator–rigid rotator approximation. Deviations from the Born–Oppenheimer approximation lead to the appearance of the so-called "electronic isotope effect", which has been studied in detail.[7–10] It is revealed to the greatest extent for ions, and also for the simplest molecules. Thus for the gas-phase reaction

$$D^+ + H_2 \rightarrow H^+ + HD\,,$$

the electronic isotope effect is 15% of the value of the equilibrium constant at 300 K.[7] For the gas-phase reaction

$$D_2 + 2HCl \rightleftarrows H_2 + 2DCl\,,$$

this error in K_{equil} is 3.3%.[11] In other systems in which the deviations can be related unambiguously to the electronic isotope effect, such high values have not been observed. For most molecules at temperatures around 300 K, the separation of the electronic component of the isotope effect in the Born–Oppenheimer approximation does not introduce a significant error.

When considering the separation of, and separate allowance for, the contributions of the vibrational and rotational motion, it should be noted that the influence of this assumption on the accuracy has been studied in detail. All possible corrections related to this assumption have been calculated for molecular hydrogen and a number of simple hydrogen-containing molecules,[12] and it has been shown that the influence of this factor does not exceed 1% of $\ln\beta$. The correction for the effect of quantisation of the rotation, and the correction for the contribution of the nuclear–spin component,[13] are significant only for molecular hydrogen and only at low temperatures ($T < 100$ K).

The anharmonicity of the vibrations must be considered, since vibrations involving the hydrogen atom have the greatest anharmonicity. A special study[14] of this question showed that the anharmonicity does not in fact make such significant differences to the value of $\ln\beta$ as usually assumed. In particular, if $\ln\beta_{D/H}$ is calculated using the so-called frequencies "corrected for anharmonicity", then the result differs by not more than 6.5% from the value obtained using the experimentally observed frequencies. The difference between the wavenumbers "corrected for anharmonicity" and the observed values may reach 200 cm^{-1} (for the O–H and N–H stretches). The small difference in the values of $\ln\beta$ for such a large difference in the wavenumber is related to the fact that, in accordance with Eqn. (5), there is partial compensation of the systematic shift of the wavenumbers for the two isotopic forms.

A similar result is obtained by comparing $\ln\beta$ calculated using Eqn. (5) with the value obtained by direct summation with respect to the vibrational–rotational energy levels.[15] It is necessary to avoid calculating the separation coefficient using $\ln\beta$ values obtained in different approximations, since in this case compensation will not take place, and the error in the value of α may be considerable.

Particular mention must be made of the error introduced by the ideal gas approximation (that is when no account is taken of the phase state of the substance). For hydrogen compounds, this question is related, apart from anything else, to the tendency of many of them to associate by hydrogen bond formation, accompanied by changes in the geometry and force field of the molecule. The values of α calculated theoretically for an ideal gas may differ from the values measured experimentally in the liquid or solid phases. It is of interest to estimate the magnitude and sign of this error for different chemical exchange systems involving hydrogen-containing molecules.

The change in the logarithm of the β-factor of a substance with change in the phase state is equal to the logarithm of the separation coefficient for the phase transformation. Neglecting the correction for non-ideal character and other small corrections, for the chemical isotopic exchange reaction

$$AH + BD \rightleftarrows BH + AD$$

we have

$$\ln\alpha_l - \ln\alpha_g = \ln\beta^l_{AH/AD} - \ln\beta^l_{BH/BD} - \ln\beta^g_{AH/AD} + \ln\beta^g_{BH/BD} = \ln(p_{AH}/p_{AD}) - \ln(p_{BH}/p_{BD})\,. \quad (6)$$

Equations taking account of the small corrections have been published.[16]

Sufficient data on the equilibrium vapour pressure above isotopic forms are now available to make possible their evaluation.[17] Eqn. (6) shows that the maximum error from neglect of the phase effect arises when for the exchanging forms A and B the distillation effects have different signs, for example when for form A the vapour pressure $p_{AH} > p_{AD}$ and for B, $p_{BH} < p_{BD}$. In this case the two contributions in the right-hand side of Eqn. (6) have the same sign.

The group of compounds for which $p_D > p_H$ consists mainly of substances which are not associated in the liquid phase, but also substances which are associated both in the vapour and in the liquid (organic acids and hydrogen fluoride). Thus for $CHCl_3$ at 283 K, the ratio p_D/p_H is 1.016, and for other similar substances the value calculated for one atom being replaced at room temperature is even smaller. For compounds which form hydrogen bonds only in the liquid, usually, $p_H > p_D$; the greatest isotopic vapour-pressure difference is shown by alcohols and hydroperoxides. For t-butyl hydroperoxide, $\ln(p_H/p_D) = 0.08$ at 300 K (highest known value). Combined with the above value for chloroform, this gives $\ln\alpha_l - \ln\alpha_g = 0.10$. Since for the chloroform–t-butyl hydroperoxide system the logarithm of the separation coefficient is small (~ 0.1), we find that the relative error in the determination of $\ln\alpha$ for this case is more than 100%. At the same time it must be borne in mind that, usually, the separation coefficients for systems of practical importance are large, and for them the error is smaller than that given above. Since for each specific class of substance the sign of the error is known and its approximate value can be estimated, it is obvious that the calculation of the β-factors for the gas phase combined with data on the vapour pressure of the isotopic forms of

model classes of compound can be used to estimate the separation coefficient in condensed phases with an accuracy sufficient for practical purposes.

Another important assumption made in the derivation of Eqns. (3) and (5) is the so-called rule of the geometric mean, analysed below. Here it may be noted that for all compounds except molecular hydrogen, the error introduced by departure from this rule does not exceed 1% (at 300 K).

When considering reactions involving the isotopic forms of molecular hydrogen when homomolecular exchange takes place, however, the departures from this rule are large, and Eqns. (3) and (5) cannot be used. In this case it is necessary to take separate account of all reactions of type (1) and reactions of homomolecular exchange with corresponding constants. The required equations have been published.[18,19]

Before analysing numerical data on $\ln\beta_{D/H}$, the following summary is appropriate. It was noted above that the accuracy of the harmonic oscillator–rigid rotator approximation and the rule of the geometric mean is ~2%. The absolute values of the vibrational frequencies are determined experimentally for the gas phase with an accuracy of ~1 cm^{-1}. At the same time, published data give estimates of the accuracy of the frequencies of 1–35 cm^{-1}. This is related to the fact that many spectra have been obtained for condensed phases; moreover, various wavenumbers are not observed experimentally, and are estimated using approximate isotope rules.

The values of the error in $\ln\beta_{D/H}$ given subsequently in the Tables include only the error in the initial vibrational frequencies, and were obtained from the equation:

$$\delta\ln\beta=\sum_{i}^{N}\left(\frac{\partial\ln\beta}{\partial\nu_i}\delta\nu_i+\frac{\partial\ln\beta}{\partial\nu_i^*}\delta\nu_i^*\right).$$

The values given for ν_i and $\delta\nu_i$ are the most reliable recommended published values.[20,21]

In most cases the errors in the $\ln\beta$ data are smaller than those given below. Cases where the vibrational frequencies are determined with large errors are encountered, however. Thus the calculation of $\ln\beta_{D/H}$ from published[20] frequencies for $HDCO/H_2CO$ gives the value 1.99, and for D_2CO/H_2CO the value 2.13, whereas according to the rule of the geometric mean the difference between them should not exceed 1%. According to data from other sources,[22] the value of 2.13 is close to the true value, so that the published[20] frequencies for HDCO are incorrect.

Thus to guarantee reliability of the error in $\ln\beta$, we have taken for $\delta\nu_i$ the largest values of the estimate of the error in the frequencies given in the works cited.[20,21] The influence of errors in the original data on the error in the β-factor has been studied by other workers.[23,24] Calculation of the error in $\ln\beta_{D/H}$ on the basis of an estimate of the inaccuracy of the vibrational frequencies gives an error of about 2%, which corresponds to the error of the harmonic approximation. From this it is apparently meaningless to speak of a value of $\ln\beta_{D/H}$ with an accuracy of better than 1%. The values of $\ln\beta$ obtained from experimental spectroscopic data are therefore given below to two decimal places. We are interested, however, not only in the actual numerical values of α for specific systems but also in the correlations between $\ln\beta$ and the parameters of the force field and the structure of the molecule. In the theoretical analysis, therefore, the values of $\ln\beta$ are given with an extra significant figure.

5. Relationship between the equilibrium isotope effects for proton–deuterium and protium–tritium replacement

In recent years, tritium has been used increasingly as an isotopic tracer in research work. The trend, observed in the eighties, towards the preferential use of stable isotopes compared with radioactive tracers has not affected the use of tritium, which continues to increase rapidly. It is therefore often necessary to have data on the β-factors of the tritiated forms of compounds. In most cases these data are not available, since spectroscopic studies are carried out mainly using the deuteriated forms.

This gives considerable interest to the problem of the relationship between the values of the equilibrium isotope effects with respect to different atoms, that is the problem of calculating the magnitude of the tritium effect from the known deuterium effect, and *vice versa*.

For different molecules, the ratio

$$\gamma=\ln\beta_{T/H}/\ln\beta_{D/H}\ , \qquad (7)$$

is almost constant.[25–27] A detailed analysis of Eqn. (7) has been carried out.[28,29] It has been shown that γ depends on the factors on which $\ln\beta$ depends, that is the geometry of the molecule, the masses of its atoms, and the force field (that is on its nature), and on temperature. By varying the parameters of a molecular model it is always possible in principle to obtain the maximum and minimum theoretical limits of γ (lower limit 1.33, upper 1.44). It should be emphasised that the published observation[25,28,29] that the value of γ for real molecules is constant and is related not to the properties of Eqn. (7) but to the fact that the values of the masses of the atoms and the force constants in real molecules lie in fairly narrow ranges.

The analysis[28,29] of the behaviour of the ratio γ for a representative large number of molecules has established that γ is highly characteristic with respect to the type of bond (that is to the nature of the atom directly joined to the hydrogen being replaced).

Table 1. Recommended values of γ for molecules of different types at different temperatures.

Molecule	*T*, K			
	100	200	300	400
H*F	1.435	1.429	1.423	1.416
H*Cl	1.436	1.427	1.417	1.407
H*Br	1.436	1.426	1.414	1.402
H*I	1.436	1.424	1.410	1.396
HOH*	–	1.412	1.407	1.400
CH_3OH*	1.418	1.410	1.402	1.396
CH_3SH*	1.419	1.407	1.396	1.386
H_2*O	1.434	1.426	1.418	1.418
H_2*S	1.419	1.407	1.396	1.385
H_2*Se	1.442	1.428	1.415	1.402
H*CN	1.417	1.409	1.403	1.396
C_2H_4*	1.418	1.407	1.397	1.389
NH_3*	1.432	1.422	1.413	1.404
PH_3*	1.433	1.418	1.405	1.394
AsH_3*	1.432	1.415	1.401	1.388
SbH_3*	1.428	1.409	1.394	1.381
CH_4*	1.421	1.409	1.398	1.388
SiH_4*	1.419	1.402	1.388	1.377
GeH_4*	1.420	1.402	1.388	1.376
SnH_4*	1.420	1.401	1.386	1.373

Note. The asterisk indicates the atom being replaced.

In addition, γ also depends on the number of equivalent atoms being replaced (it increases with increase in this number). The influence of other factors is insignificant.

Since γ is characteristic, the most correct method of finding $\ln\beta_{T/H}$ is by direct calculation from $\ln\beta_{D/H}$ using the relationship $\ln\beta_{T/H} = \gamma\ln\beta_{D/H}$. The recommended values of γ for molecules of different types are given in Table 1, compiled using published data.[29] The contributions to $\ln\beta$ from individual frequencies do not necessarily satisfy Eqn. (7). Moreover, Eqn. (7) can be used as a criterion of the correctness of regarding molecular fragments as individual molecules, and also for verifying the reliability of data on the vibrational frequencies of D- and T-forms.

Thus the use of Eqn. (7) makes it possible, for isolated molecules, to restrict the study to only the deuterium or only the tritium equilibrium isotope effect.

III. Theoretical methods for interpreting isotope effects

1. Approximate representations of the β-factor

Although Eqn. (5) is fairly convenient for calculations, it is not suitable for interpreting the data obtained in the study of isotope effects. This is related primarily to the fact that the vibrational frequencies depend on all the characteristics of a molecule, and not only on the characteristics of the atom being replaced and its immediate environment. The association of a frequency with a given vibrational coordinate, reflected in its assignment, is in general provisional. Each vibration involves a change in not one but all of the natural coordinates (bonds and angles), and each coordinate makes its own contribution to the form of a given vibration. An assignment is usually made with respect to the natural coordinates making the greatest contribution to the given vibration. The distribution of the contributions depends on the masses of the atoms, and the assignment of the frequencies often changes on deuteriation. For this reason it cannot be expected that the contributions of the ith pair of vibrational frequencies to $\ln\beta$, denoted $\ln\beta_i$ in Eqn. (5), will effectively describe the dependence of $\ln\beta$ on the nature of the molecule. It is more correct to interpret the quantity $\ln\beta$ in terms of the structural elements of molecules, that is the bonds between the atoms and the valence and dihedral angles, and this requires appropriate representations.

There are now more than 30 published papers dealing with the development of methods for interpreting isotope effects on the basis of the approximate representation of $\ln\beta$ as an analytical function of the force field and the geometry of the molecule. Historically, the first such representation was the expansion of $\ln\beta$ with respect to the force constants, carried out by Bigeleisen and co-workers.[3,30] This approximation is too crude for the study of most characteristics of isotope effects, so that it was necessary to develop more complex methods of interpretation, primarily the approximation of $\ln\beta$ by polynomials, proposed by Bigeleisen and Ishida,[31–33] and its improved versions.[34–38]

The most general form of the Ishida–Bigeleisen representation is the equation:

$$\ln\beta = \sum_{j=1}^{M} W_j A_j \sum_{i=1}^{N} (u_i^{2j} - u_i^{*2j}), \qquad (8)$$

where u_i represents the reduced frequencies. The sum with respect to i in this equation, with an accuracy corresponding to a temperature-dependent coefficient, is equal to $\Delta\,\mathrm{tr}(\hat{G}\hat{F})^i$, so that $\ln\beta$ is clearly expressed in terms of the geometric parameters and force constants. The numbers A_j are the Bernoulli coefficients, and W_j represents the so-called "modulating factors". The appearance of the coefficients W_j in the expansion (8) is related to the need to increase the rate of convergence of this series; for this purpose, the authors cited resort to scaling of the reduced frequencies by dividing them by the highest frequency in the spectrum of the molecule being considered.

An unsatisfactory feature of the polynomial approximation is its indeterminacy, which is revealed, in particular, by the fact that the relative values of the contributions to $\ln\beta$ from different molecular parameters depend on the value taken as u_{max} in the analysis of $\ln\beta$ for a large number of molecules, and more particularly on the chosen number of terms in the expansion of M.

Bigeleisen and co-workers[33,39] used another method of interpretation, which they called the method of "total effects". The method can be described as follows. The value of $\ln\beta$ for the molecule is calculated using data on its geometry and force field. One of the force constants is then put equal to zero, and a new value of $\ln\beta$ is calculated. In practice, this cannot be done directly, because of the appearance of imaginary frequencies, and the value of $\ln\beta$ with a zero force constant is estimated by extrapolation. The difference between the total value of $\ln\beta$ and the value obtained with a force constant equal to zero is taken as the contribution made to $\ln\beta$ by this constant. This contribution is then associated with the corresponding coordinate (bond, angle, coordinate interaction). Thus the value of $\ln\beta$ in the method of "total effects" is represented as the sum of the products of the crude estimates of the partial derivatives of $\ln\beta$ with respect to the force constant and the finite increase in the argument (in the present case the actual force constant). The proposed method is clearly one of the forms of the crude approximation of $\ln\beta$ as a function of the molecular parameters, so that it does not differ fundamentally from the method of orthogonal polynomials. From our viewpoint, it is less satisfactory than the method of orthogonal polynomials primarily because it has been less developed theoretically. The accuracy of the method of "total effects" for the replacement of protium by deuterium is not very high, and for molecules of medium complexity having out-of-plane vibrations it is equal to 4–6% at 300 K.

Another approach is that of Wolfsberg and co-workers.[40,41] This approach represents the application of perturbation theory to the calculation of $\ln\beta$, where the quantity taken as the zeroth approximation $\ln\beta_0$ is obtained by neglecting all the non-diagonal terms in the matrices $\hat{G}$ and $\hat{F}$. The basic principle of the method is that $\ln\beta_0$ is represented as the sum of contributions with respect to the "zeroth" frequencies ν_{0i} and ν^*_{0i}, each of which (since the matrix of the zeroth approximation $\hat{G}_0\hat{F}_0$ is diagonal) can be associated with a corresponding vibrational coordinate (bond, angle, etc.). For this, naturally, the values of the zeroth approximation $\ln\beta_0$ must be close to the exact value of $\ln\beta$ (that is the matrix $\hat{G}\hat{F}$ should not contain significant non-diagonal elements).

The concept of "zeroth frequencies" ν_{0i} leads to serious methodological difficulties. Thus for the methane molecule, the use of the complete system of natural coordinates gives ten "zeroth frequencies" ν_{0i}, whereas this molecule has only nine vibrational degrees of freedom. This difficulty arises as a result of the methodological inconsistency of the Wolfsberg method. In fact, since $\ln\beta$ is represented in terms of the geometry and force field, this

method still uses the concept of the contributions of the vibrational frequencies.

The methods considered, for all their differences, reduce to the representation of $\ln\beta$ as a simple algebraic function, which after transformation is reduced to the form of a power series with respect to the molecular parameters, for example the force constants. The series is terminated after account has been taken of the first few terms.

It has been shown[42] that all expansions of this type are "non-physical", that is from the coefficients of this series and from the calculated contribution made by a molecular parameter, nothing can be said about the contribution which this parameter in fact makes to $\ln\beta$. This is related to the fact that the value of the derivative of $\ln\beta$ with respect to the parameter, obtained from the expansion, depends decisively on the number of terms of the expansion taken into account.

This conclusion follows from Eqn. (5) itself, in which the molecular parameters appear via the frequencies ν_i. The latter are described by the branches of a multiple-value function $\nu_i = [\lambda_i(\zeta_1,...,\zeta_N)]^{1/2}$, where ζ represents the molecular parameters, the dependence on which is being considered. In this case, however, in accordance with the theory of power series, the radius of convergence of the power expansion of $\ln\beta$ cannot be greater than the distance from the point at which the derivative is calculated to the nearest branch point of the function $[\lambda_i(\zeta_1,...,\zeta_N)]^{1/2}$. The positions of these unique points have been studied for a number of molecules,[42] and it has been shown that the change in the assignment of frequencies with change in a parameter takes place close to them. Thus attempts to expand $\ln\beta$ in a Taylor series are not promising; if however approximate power expansions are used, then with increase in the accuracy and hence in the number of terms taken into account, this expansion approaches a Taylor series; since this series is diverging, the terms of higher powers make increasing contributions to $\ln\beta$, distorting the structure of the contributions of the molecular parameters and concealing the real reason for the variability of $\ln\beta$. This was previously noted[43] for the expansion in series of orthogonal polynomials.

Since it is impossible to construct a universal analytical expansion of the β-factor, there remain two possibilities: either to construct transcendental universal expansions suitable for the analysis of particular cases, or to represent $\ln\beta$ directly as the sum of the contributions of structural elements using numerical methods.

2. Representation of $\ln\beta$ as an infinite transcendental series

An accurate representation of $\ln\beta$ in the harmonic approximation as the sum of the terms of an infinite series of functions which are clearly and simply determined by the force constants, the geometry, and the masses of the atoms of the isotopic forms of the molecule has been proposed.[44,45] The representation has the form

$$\ln\beta = \sum_{p=1}^{\infty} \ln\beta_p = \sum_{p=1}^{\infty} \frac{1}{l} \ln \cdot$$

$$\cdot \left[1 + \frac{(\varkappa/p)^2\Delta\sigma_1 + (\varkappa/p)^4\Delta\sigma_2 + \ldots + (\varkappa/p)^{2N}\Delta\sigma_N}{1 + (\varkappa/p)^2\sigma_1^* + (\varkappa/p)^4\sigma_2^* + \ldots + (\varkappa/p)^{2N}\sigma_N^*}\right]. \qquad (9)$$

The quantities σ_p are equal to the sums of all the principal minors of pth order of the matrix $\hat{G}\hat{F}$, $\sigma_i = \sigma_i^* + \Delta\sigma_i$, $\varkappa = h/4\pi^2kT$.

The expansion (9) converges for all positive u_i. The existence of a simple equation for estimating the error for a restricted number of terms taken into account, the fact that the signs of the logarithmic terms are constant, and the rapid decrease in the contributions of these terms with increase in p distinguishes the expansion (9) from familiar approximate expansions. Eqn. (9) has been used successfully[44-46] to analyse the regularities of the behaviour of $\ln\beta$.

3. The representation of the vibrational component of $\ln\beta$ as the sum of the contributions of structural elements of the molecule

As noted above, it is most correct to interpret the quantity $\ln\beta$ in terms of the contributions of the structural elements, that is the bonds between atoms and the valence and dihedral angles.

A clear and accurate representation of the differences in the heat capacities and internal energies of isotopic forms as the sums of the contributions with respect to the vibrational coordinates corresponding to the above structural elements has been proposed.[47] A similar representation of the isotopic difference in the vibrational components of the entropies and the vibrational component of $\ln\beta$ has also been proposed.

To construct this representation we note that the logarithm of the β-factor, with an accuracy corresponding to an additive constant, is the difference, divided by kT, between the free energies for the two isotopic forms of the molecule AX_l and AX_l^*, calculated for one atom being replaced:

$$\ln\beta_{AX_l/AX_l^*} = \frac{1}{l}\left[\frac{F_{AX_l} - F_{AX_l^*} + F_X - F_{X^*}}{kT}\right]. \qquad (10)$$

Here, $(F_X - F_{X^*})kT$ is the difference between the free energies of the isotopes of the hypothetical monatomic gas X (which is constant for a given type of isotopic replacement).

For the difference between the internal energies of the isotopic forms we can write:

$$\Delta U = U^* - U = kT^2\left(\frac{\partial \ln(Q^*/Q)}{\partial T}\right), \qquad (11)$$

where Q is the partition function. Adopting the Born–Oppenheimer approximation and the harmonic oscillator–rigid rotator approximation, we have $Q = Q_tQ_rQ_v$ (subscripts; t = translational, r = rotational, v = vibrational motion). The translational and rotational motions do not contribute to the isotopic difference in the energies. Thus their zero-point energy (the energy at the absolute zero) is equal to zero, and the ratios Q^*/Q for the translational and rotational partition functions are independent of temperature, and the derivatives of these ratios with respect to T are equal to zero. Thus the difference in the internal energies of the isotopic forms is equal to the difference in the vibrational energies.

Substituting in Eqn. (11) the expression for Q_v taking account of the energy of the zero-point vibrations gives[47]

$$\Delta U = \sum_{i=1}^{N}\left[\frac{hc\nu_i^*}{2}\operatorname{cth}\frac{hc\nu_i^*}{2kT} - \frac{hc\nu_i}{2}\operatorname{cth}\frac{hc\nu_i}{2kT}\right] = E^* - E, \qquad (12)$$

where E is the vibrational energy of the molecule in the harmonic approximation. We now introduce the system of natural vibrational coordinates corresponding to the above structural elements of the molecule.

The vibrational energy of the molecule can be represented as[48]

$$U_v = \mathrm{tr}\,\hat{\Sigma}\hat{F} \tag{13}$$

where $\hat{F}$ is the force constant matrix, and $\hat{\Sigma}$ the matrix of the mean-square amplitudes of the vibrations.

According to the Binet–Cauchy theorem,[49] the trace of the product of two matrices A and B is equal to the sum of the paired products of the corresponding elements

$$\sum_{i,j} a_{ij}b_{ij} \ .$$

Thus

$$U_v = \mathrm{tr}\,\hat{\Sigma}\hat{F} = \sum_{i,j}\sigma_{ij}F_{ij}, \tag{14}$$

where σ_{ij} represents the elements of the matrix of the mean-square amplitudes in natural coordinates, and F_{ij} the force constants.

The relationship (14) can be represented in the following clear form.[47] We write the matrix $\hat{A}_{U_v}$, whose elements are the products of the corresponding elements of the matrices $\hat{\Sigma}$ and $\hat{F}$:

$$\hat{A}_{U_v} = \begin{pmatrix} \sigma_{11}F_{11} & \sigma_{12}F_{12} & \ldots\ldots & \sigma_{1N}F_{1N} \\ \sigma_{12}F_{12} & \sigma_{22}F_{22} & \ldots\ldots & \sigma_{2N}F_{2N} \\ \ldots\ldots & \ldots\ldots & \ldots\ldots & \ldots\ldots \\ \sigma_{1N}F_{1N} & \sigma_{2N}F_{2N} & \ldots\ldots & \sigma_{NN}F_{NN} \end{pmatrix} \tag{15}$$

This matrix is obviously symmetrical. According to Eqns. (14), the sum of all the elements of the matrix (15) is equal to the vibrational energy U_v of the molecule. The term at the intersection of the ith column and the jth row of matrix (15) represents the contribution made to the vibrational energy by the interaction of the ith and jth vibrational coordinates. In particular, the terms on the diagonal of matrix (15) represent the contributions due to the interaction of each vibrational coordinate with itself.

The matrix (15) readily gives the representation of the isotopic difference in the energies as the sum of the contributions with respect to the coordinates. Thus

$$\Delta U = \Delta\,\mathrm{tr}\,\hat{\Sigma}\hat{F} = \mathrm{tr}\,(\Delta\hat{\Sigma})\,\hat{F},$$

since the matrix $\hat{F}$ remains unchanged on isotopic replacement (here, $\Delta\hat{\Sigma}$ is the matrix $\hat{\Sigma}^* - \hat{\Sigma}$).

Thus we can write the matrix

$$\hat{A}_{\Delta U} = \hat{A}^*_{U_v} - \hat{A}_{U_v}, \tag{16}$$

made up of the elements $\Delta\sigma_{ij}F_{ij}$, where the term at the intersection of the ith column and the jth row represents the contribution made to the isotopic difference in the energies by the interaction of the ith and jth vibrational coordinates. The sum of all the elements of matrix (16) is equal to ΔU.

To obtain the corresponding expansion with respect to vibrational coordinates for the difference in the heat capcities ΔC_V, we have to differentiate the matrix (16) with respect to temperature. This can easily be done by representing the matrix $\hat{\Sigma}$ as $\hat{\Sigma} = \hat{L}\hat{\Delta}\hat{\tilde{L}}$, where $\hat{L}$ is the matrix of the modes of the vibrations, the tilde above the letter denotes transposition of the matrix, and $\hat{\Delta}$ is the diagonal matrix with the elements[48]

$$\delta_{ii} = [h/8\pi^2 c\nu_i]\,\mathrm{cth}\,[hc\nu_i/2kT] \ .$$

From this we have[47]

$$\Delta C_v = C_v^* - C_v = \left(\frac{\partial\,\Delta U}{\partial T}\right)_v = \mathrm{tr}\left(\frac{\partial\hat{\Sigma}^*}{\partial T} - \frac{\partial\hat{\Sigma}}{\partial T}\right)\hat{F}. \tag{17}$$

Here,

$$\partial\hat{\Sigma}^*/\partial T = \hat{L}^*(\partial\hat{\Delta}^*/\partial T)\hat{\tilde{L}}^*;\ \partial\hat{\Sigma}/\partial T = \hat{L}\,(\partial\hat{\Delta}/\partial T)\,\hat{\tilde{L}},$$

where $\partial\hat{\Delta}/\partial T$ is the diagonal matrix with the elements

$$\frac{\partial\delta_{ii}}{\partial T} = h^2/\{16\pi^2T^2k\,\mathrm{sh}^2[hc\nu_i/2kT]\} \ .$$

Using the Binet–Cauchy theorem, we can represent the trace of the product of the two matrices in Eqns. (17) as the matrix

$$\hat{A}_{\Delta C_V} = \hat{A}^*_{C_{V_v}} - \hat{A}_{C_{V_v}},$$

whose (i,j)th element is the product of the (i,j)th element of the matrix $(\partial\hat{\Sigma}^*/\partial T - \partial\hat{\Sigma}/\partial T)$ and the (i,j)th element of the matrix $\hat{F}$. The matrices

$$\hat{A}_{C_{V_v}} \text{ and } \hat{A}^{\Delta}_{C_V}$$

are respectively the representations of the vibrational heat capacity and the isotopic difference in the total heat capacities as contributions with respect to the coordinates.

For the isotopic difference in the entropies we have

$$\Delta S = (S_0^* - S_0) + \int_0^T \frac{(C_V^* - C_V)}{T}\,dT = (S_0^* - S_0) + \\ + \mathrm{tr}\left[\int_0^T\left(\frac{\partial\hat{\Sigma}^*}{\partial T}\right)\frac{dT}{T} - \int_0^T\left(\frac{\partial\hat{\Sigma}}{\partial T}\right)\frac{dT}{T}\right]\hat{F} \\ \int_0^T\left(\frac{\partial\hat{\Sigma}}{\partial T}\right)\frac{dT}{T} = \hat{L}\left\{\int_0^T\left(\frac{\partial\hat{\Delta}}{\partial T}\right)\frac{dT}{T}\right]\hat{\tilde{L}} \ . \tag{18}$$

Here,

$$\int_0^T\left(\frac{\partial\hat{\Delta}}{\partial T}\right)\frac{dT}{T} - \ ,$$

is the diagonal matrix with elements on the diagonal

$$\frac{hc\nu_i}{2T}\,\mathrm{cth}\,\frac{hc\nu_i}{2kT} - k\ln\mathrm{sh}\,\frac{hc\nu_i}{2kT} \ .$$

The corresponding matrix $\hat{A}_{\Delta S_v}$ is easily obtained from the second term in Eqn. (18) in the same was the matrices $\hat{A}_{\Delta U}$ and $\hat{A}_{\Delta C_V}$ were constructed.

We introduce the matrix

$$\hat{A}_{\ln\beta_v} = -\frac{\hat{A}_{\Delta F_v}}{kT} = -\frac{\hat{A}_{\Delta U} - T\hat{A}_{\Delta S_v}}{kT} \quad . \tag{19}$$

The matrix obtained is symmetrical, and the term at the intersection of its ith row and jth column represents the contribution of the interaction of the ith and jth vibrational coordinates to $\ln\beta$. The sum of all the elements of the matrix $\hat{A}_{\ln\beta_v}$ is equal to $\ln\beta_v$, that is

$$\ln\beta = \ln\beta_t + \ln\beta_r - \frac{3}{2}\ln\frac{m^*}{n} + \sum_{i,j} a_{ij}, \tag{20}$$

where a_{ij} denotes the (i,j)th element of the matrix $\hat{A}_{\ln\beta_v}$.

The use of the representation (20) makes it possible to analyse $\ln\beta$, and hence the isotope effect, in terms of the vibrational coordinates, and not the vibrational frequencies. The representation (20) is exact. An example for the case of the molecule of formaldehyde H_2CO (H_2CO/HDCO replacement) is given in Fig. 1.

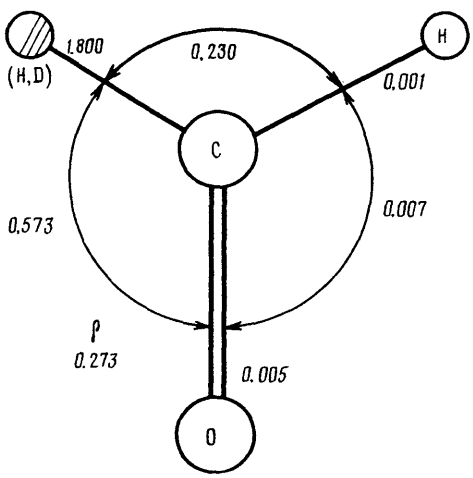


Figure 1. Representation of the vibrational component of $\ln\beta_{D/H}$ for the formaldehyde molecule (H_2CO/HDCO replacement) as the sum of the contributions of the structural elements; $\ln\beta_{dis}$ is the contribution of coordinates at a distance from the replacement centre; $\ln\beta_{n-d}$ is the contribution of the non-diagonal interactions.

$$\ln\beta_{dis} = 0.013 \quad ,$$
$$\ln\beta_{n-d} = 0.006 \quad ,$$
$$\ln\beta = 2.200 \quad ,$$

The natural vibrational coordinates used (see Fig. 1) are the changes in all the valence bonds and angles, and also the coordinate of the out-of-plane vibration ρ (the displacement of a bond from the plane). One of the coordinates (a valence angle) is redundant, and the calculation gives one frequency equal to zero.

4. Matrix representation of the translational–rotational contribution and the total value of $\ln\beta$

The representation examined in the previous paragraph makes it possible to write $\ln\beta$ as the sum of the elements of the matrix $\hat{A}_{\ln\beta_v}$ and the contribution Ω (the Teller–Redlich term), determined by the translational and rotational degrees of freedom of the molecule:

$$\ln\beta = \sum_{ij}{}' a_{ij} + \Omega, \tag{21}$$

where

$$\Omega = \Delta S_t/k + \Delta S_r/k - \frac{3}{2}\ln\frac{m'}{m} = \frac{1}{2}\ln\frac{\det\hat{G}'}{\det\hat{G}} \quad , \tag{22}$$

(m is the mass of the atom being replaced).

The Teller–Redlich term Ω is determined by the geometry and the distribution of the masses in the molecule as a whole. In particular, this contribution cannot be transferred in homologous series.

Nevertheless, there is no difficulty in constructing an accurate representation of the Teller–Redlich term and the total value of $\ln\beta$ as the matrix of the contributions of the interactions of the structural elements of the molecule, analogous to the matrix (19) for $\ln\beta_v$. To construct the required representation,[46,47] it is sufficient to note that the value of $\ln\beta \to 0$ as $T \to \infty$. The Teller–Redlich term is independent of temperature, so that Eqn. (21) gives

$$\lim_{T\to\infty} \ln\beta_v = -\Omega \quad , \tag{23}$$

which leads to the required matrix representation for the term (22) (the matrix $\hat{A}_\Omega$):

$$\hat{A}_\Omega = -\lim_{T\to\infty}\hat{A}_{\ln\beta_v} = \begin{pmatrix} \lim\limits_{T\to\infty} a_{11} & \cdots & \lim\limits_{T\to\infty} a_{1N} \\ \cdots & \cdots & \cdots \\ \lim\limits_{T\to\infty} a_{1N} & \cdots & \lim\limits_{T\to\infty} a_{NN} \end{pmatrix}. \tag{24}$$

Eqns. (24) and (21) readily give the matrix representation for the total value of $\ln\beta$:

$$\hat{A}_{\ln\beta} = \hat{A}_{\ln\beta_v} + \hat{A}_\Omega, \tag{25}$$

where each element of the matrix $\hat{A}_{\ln\beta}$ is the sum of the corresponding elements of the matrices $\hat{A}_{\ln\beta_v}$ and $\hat{A}_\Omega$.

The matrices $\hat{A}_\Omega$ and $\hat{A}_{\ln\beta}$ for the formaldehyde molecule (H_2CO/HDCO replacement) have been published.[46] The principal contributions to the value of $\ln\beta$ are made by the following coordinates: the bond CH* (contribution 1.484), the valence angle H*CO (0.377), the out-of-plane vibration ρ (0.168), and the valence angle H*CH (0.160). The contributions of the other coordinates and of the interactions between the coordinates are small.

Thus in the works cited[46,47] a complete and accurate representation of the logarithm of the β-factor as the sum of the contributions of the structural elements of the molecule was constructed for the first time.

5. The use of the representations of ln β to analyse isotope effects. The analysis of the rule of the geometric mean

If a molecule contains a group of l equivalent atoms, the following rule applies approximately when they are successively replaced by the atoms of an isotope[50–52]

$$\ln\beta = \frac{1}{x}\ln f_{(AD_xH_{l-x}/AH_l)} = \frac{1}{l}\ln f_{(AD_l/AH_l)}, \quad (26)$$

where f is the ratio of the partition functions with respect to the states of the isotopic forms indicated in brackets.

It can be seen from Eqn. (26) that the rule of the geometric mean states that $\ln f$ is linearly dependent on the number of atoms x being replaced or, which is the same thing, that the value of $\ln\beta$ is independent of x.

We can take as a measure of the deviation from the rule (26) the difference between the actual value of $\ln\beta_{AD_xH_{l-x}/AH_l}$, calculated using Eqn. (5), and the estimate of this quantity obtained from the value for the completely substituted form using the rule of the geometric mean:

$$\delta = \frac{1}{x}\ln f_{(AD_xH_{l-x}/AH_l)} - \frac{1}{l}\ln f_{(AD_l/AH_l)}. \quad (27)$$

We define the relative deviation as $\delta_{rel} = \delta/\ln\beta_{(AD_l/AH_l)}$. We can consider a molecule of the type H_2A, where A represents an arbitrary molecular group. Eqn. (9) has been used[53] to obtain the following equation for δ:

$$\delta = \frac{1}{2}\sum_{k=1}^{\infty}\ln\left[1 + \frac{(\varkappa/k)^4(p_2-q_2)+\ldots+(\varkappa/k)^{4N}(p_{2N}-q_{2N})}{1+(\varkappa/k)^2p_1+\ldots+(\varkappa/k)^{4N}p_{2N}}\right], \quad (28)$$

where

$$q_1=\sigma_1^{AH_2}+\sigma_1^{AD_2}, \quad q_2=\sigma_2^{AH_2}+\sigma_1^{AH_2}\sigma_1^{AD_2}+\sigma_2^{AD_2}, \ldots, \quad q_{2N}=\sigma_N^{AH_2}\sigma_N^{AD_2}$$

$$p_1=2\sigma_1^{AHD}, \quad p_2=2\sigma_2^{AHD}+(\sigma_1^{AHD})^2, \ldots, \quad p_{2N}=(\sigma_N^{AHD})^2.$$

In Eqn. (28), account is taken of the fact that in the harmonic approximation we always have $p_1 = q_1$. Since at temperatures which are not too low the series (28) converges rapidly and since it is usually necessary only to estimate the value of δ, we can restrict ourselves, at $T = 300$ K, to the first term of the expansion.

Eqn. (28) shows that the deviation from the rule of the geometric mean is related to the difference in the values of p_i and q_i for $i \geqslant 2$. In other words, in terms of the force field and the geometry of the molecule, fulfilment of the rule of the geometric mean is due to similarity in the values of p_i and q_i.

It should be noted that $p_i - q_i$ for $i \geqslant 2$ depends only on higher powers of the difference in the reciprocal masses $(\Delta\mu)^i$, $i \geqslant 2$. Thus the inaccuracy of the geometric-mean rule is essentially a non-linear effect.

From the form of the expressions for p_i and q_i it is clear that the relative magnitude of the numerator of the terms in the series (28) relative to the denominator is greater, the greater the number of frequencies in the molecule undergoing an appreciable shift on isotopic replacement. This is due to the fact that the numerator of the terms in Eqn. (28) depends on the differences $p_i - q_i$, which are determined by the isotopic shifts of the frequencies, whereas the denominator contains the quantities p_i, which depend only on the absolute magnitude and number of the frequenices. Thus with increase in the number of frequencies in the molecule remaining unchanged or changing only slightly on isotopic replacement, the denominator of the terms of the series (28) will increase much more rapidly than the numerator, with a corresponding decrease in the values of δ and δ_{rel}.

Thus the greatest deviations from the geometric-mean rule should be expected for the H_2 molecule and small molecules of the type H_3B, in which the hydrogen atoms being replaced are joined to one central atom B, so that all the vibrations are vibrational modes of hydrogen and undergo a marked shift on isotopic replacement. The molecules of this type include molecules (H_2O, H_2S, NH_3) of practical interest for chemical exchange.[54] For organic molecules (except CH_4), it is clear that the deviations from Eqn. (26) should be negligible.

6. Localisation of the isotope effect of hydrogen

In the examination of the dependence of $\ln\beta$ on the remoteness of the substituents it should be borne in mind that isotopic replacement is equivalent to a perturbation which can be regarded as small in all cases except the case of the replacement of hydrogen atoms. This perturbation influences the whole molecule, but the influence is different for its different parts, decreasing with increase in the distance between the vibrational coordinates and the atom being replaced. It is possible, however, to have strong interaction between vibrational coordinates separated from one another, as a result of the fact that the frequencies of the vibrations to which these coordinates contribute are similar (resonance interaction).

This raises the question of the accuracy with which the fragmentary model reproduces the value of the β-factor of the whole molecule. The importance of this question follows from the fact that fragmentary models (see Fig. 2) are used to calculate isotope effects, particularly for complex molecules, and frequently this approach is the only one possible. It is therefore necessary to know the magnitude of the errors introduced by this approximation. In particular, it is important to know whether the value of the β-factor is influenced significantly by accidental resonance of the vibrations of the atom being replaced with the vibrations of coordinates at a distance.

This question has been studied in relation to the kinetic isotope effect. For example, a calculation[55] for a number of systems involving comparison with "truncated" models showed that the "removal" of an atom separated by more than two bonds from the atom being replaced introduces practically no error in the calculation of the kinetic isotope effect. No theoretical analysis of the problem has been published, however, and the case of resonance has not been studied.

The representation (9) has been used[56] to analyse the question of the "extent" of the isotope effect. To study this problem, the model four-atom molecule represented in Fig. 2 was examined. The following natural coordinates were introduced: the changes in the bond lengths r_1, r_2, and R, the changes in the valence angles φ_1 and φ_2, and the out-of-plane twisting coordinate χ. The calculation was carried out using force constants and geometric parameters characteristic of saturated hydrocarbons. To obtain the fragmentary model from the original molecule, the matrix of kinematic coefficients $\hat{G}$ was left unchanged, but the rows and columns of the force constant matrix of the original molecule were multiplied by a weighting factor x if these columns and rows corresponded to a natural coordinate including the atom removed.

The calculation was carried out for two cases: in the first case, an atom separated by three bonds ("third neighbour") from the atom being replaced was "removed" (x was taken as zero); in the second case, in addition, an atom separated by two bonds ("second neighbour") from the atom being replaced was also removed.

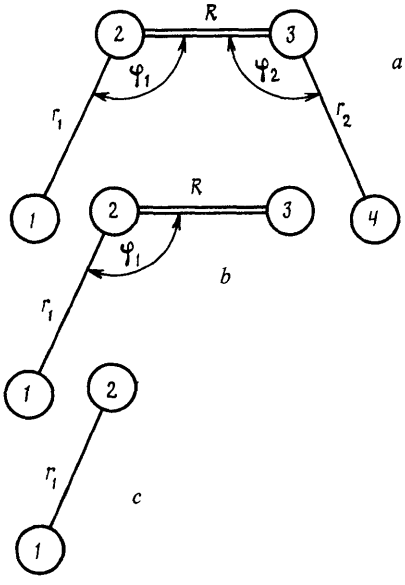


Figure 2. Fragmentary models.

The influences of the removal of the second and third neighbours differ significantly in scale. The removal of an atom separated by three bonds from the atom being replaced introduces a small error. The influence of an atom separated by two bonds from the atom being replaced cannot be neglected, however.

In the multiplication, described above, of the force constants for the coordinates removed by the factor x, the quantities ∂_i in Eqn. (9) can be represented as

$$\sigma_i=\sigma_i^{(0)}+\sigma_i^{(1)}x+\sigma_i^{(2)}x^2+\ldots+\sigma^{(N-m)}x^{N-m}, \qquad (29)$$

where $\sigma_i^{(0)}$ includes only the force constants and geometric parameters relating to the coordinates closest to the atom beign replaced. After substituting Eqn. (29) in Eqn. (9) and reducing similar terms in the numerator and denominator, Eqn. (9) takes the form

$$\ln\beta=\ln\beta_0+\delta(x), \qquad (30)$$

where $\delta(x)$ is a correction. Here, the term $\ln\beta_0$ in the right-hand side includes only the force constants and geometry of the remaining part of the molecule and is therefore the principal component of $\ln\beta$ (the contribution of the immediate environment of the atom being replaced). The second term in the right-hand side of Eqn. (30) depends on x, and for $x = 1$ it is a correction reflecting the contribution of molecular fragments at a distance.

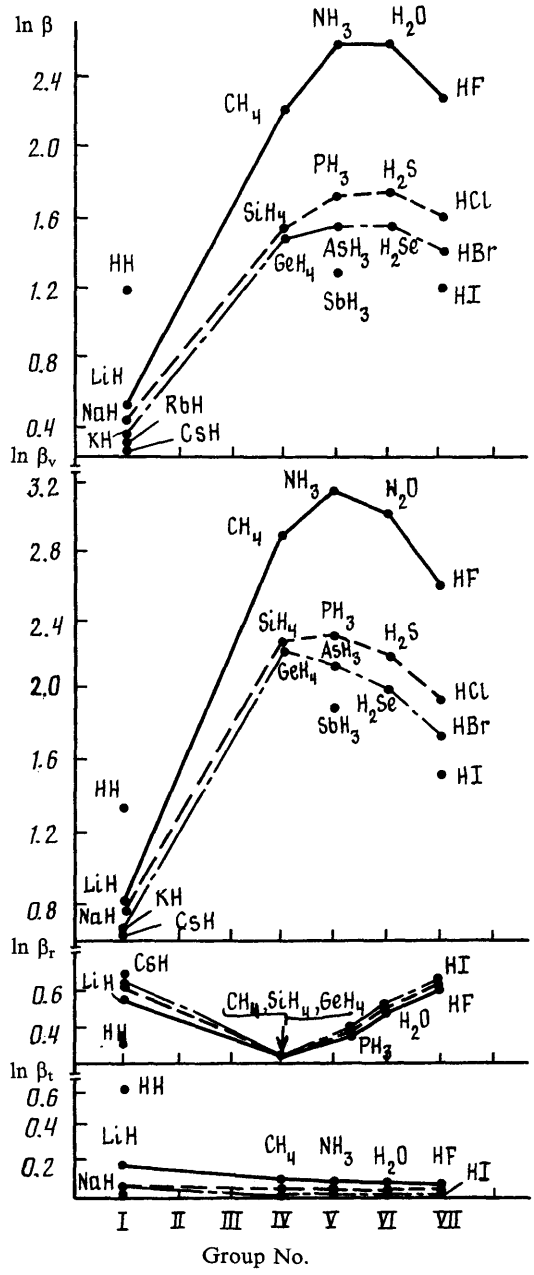


Figure 3. Components of ln β for normal hydrides.

Eqn. (30) has also been analysed.[56] At room temperature the isotope effect is localised at the replacement centre, as shown by the small size of the correction in Eqn. (30). The correction increases with decrease in temperature, however, and at 30 K its value is comparable with that of $\ln\beta_0$. This reflects the increasing delocalisation of the isotope effect with decrease in temperature, revealed by the fact that remote coordinates begin to make a significant contribution to $\ln\beta$.

The representation of Eqns. (29) and (30) also makes it possible to solve the problem of expressing $\ln\beta$ as the sums of the contributions of the first, second, and higher environments of the atom being replaced.[56]

IV. Analysis of quantitative data on the β-factors of hydrogen compounds

1. Dependence of $\ln\beta_{D/H}$ on the nature of the atom directly joined to the hydrogen atom being replaced. Analysis of $\ln\beta_{D/H}$ for normal hydrides

It is known empirically that the values of the ratio of the reduced partition functions (the $\beta_{D/H}$-factor) of the isotopic forms of molecules is determined primarily by the nature of the atom directly joined to the hydrogen atom being replaced. To study this relationship it is natural to consider the large number of so-called normal molecular hydrides of the *s*- and *p*-elements (that is the molecular hydrides of a given element with the general formula EH_n). The normal hydrides can serve as a model for examining more complex compounds, and therefore represent a key group in the chemistry of the isotopes of hydrogen.

Attempts have been made to obtain a phenomenological description of $\ln\beta$ for normal hydrides,[2] and also to interpret $\ln\beta_{D/H}$ in terms of the force field using the approximate methods of interpretation and correlations described above.[57–59]

The values of $\ln\beta_{D/H}$ for normal hydrides were recently re-examined by Bigeleisen.[58] It was concluded that the contribution of each *i*th vibrational coordinate to $\ln\beta$ is proportional to $(f_{ii}\Delta g_{ii})^{1/2}$, where f_{ii} is a diagonal element of the force constant matrix, nd $\Delta g_{ii} = g_{ii} - g_{ii}^{*}$ the difference in the diagonal elements of the matrices of the kinematic coefficients for the H- and D-forms of the molecule. It should be noted, however, that although the contribution made to $\ln\beta$ by the valence bond coordinates is in fact approximately linearly dependent on $(f_{ii}\Delta g_{ii})^{1/2}$, this correlation is not completely satisfactory for the valence angle coordinates, particularly for the normal hydrides of groups IV and V.

The representation (20) described above has been used to analyse the behaviour of $\ln\beta_{D/H}$ for normal hydrides.[59] Figs. 3 and 4 give the force constants and the contributions of different coordinates to $\ln\beta$. In the analysis of these data it should first be noted that the Teller–Redlich term $\ln\beta_t + \ln\beta_r + (^3/_2)\ln(m_D/m_H)$, which depends on the geometry and the masses, changes little and does not determine the behaviour of $\ln\beta$ for normal hydrides. The decisive factor is the variability of the vibrational contribution $\ln\beta_v$. For all normal hydrides, a predominant part is played by the contribution made to $\ln\beta_v$ by the H–E valence bond coordinate, and this contribution increases regularly in each period together with the force constant F_{HE} on going from group I to group VII, and decreases regularly in each group with increase in the atomic number of the element.

The contribution made by the angular coordinates depends both on the magnitude of the contribution of an individual valence angle and on the total number of valence angles. This number is equal to 3 for the hydrides of the group IV elements, 2 for group V, and 1 for group VI. On going from group VI to group IV, the contribution made by one angle (see Fig. 4) decreases, whereas the total contribution from the angular coordinates increases, since the total number of angles increases. The part played by the number of angles is extremely significant, and the total contribution made to $\ln\beta_v$ by the angular coordinates is greatest for the normal hydrides of the elements of group IV. This contribution does not exist for diatomic molecules, and it is for this reason that $\ln\beta$ for the hydrogen halides is smaller than that for the hydrides of the elements of groups V and VI, despite the larger force constant and the corresponding larger contribution of the H–E bond to $\ln\beta$.

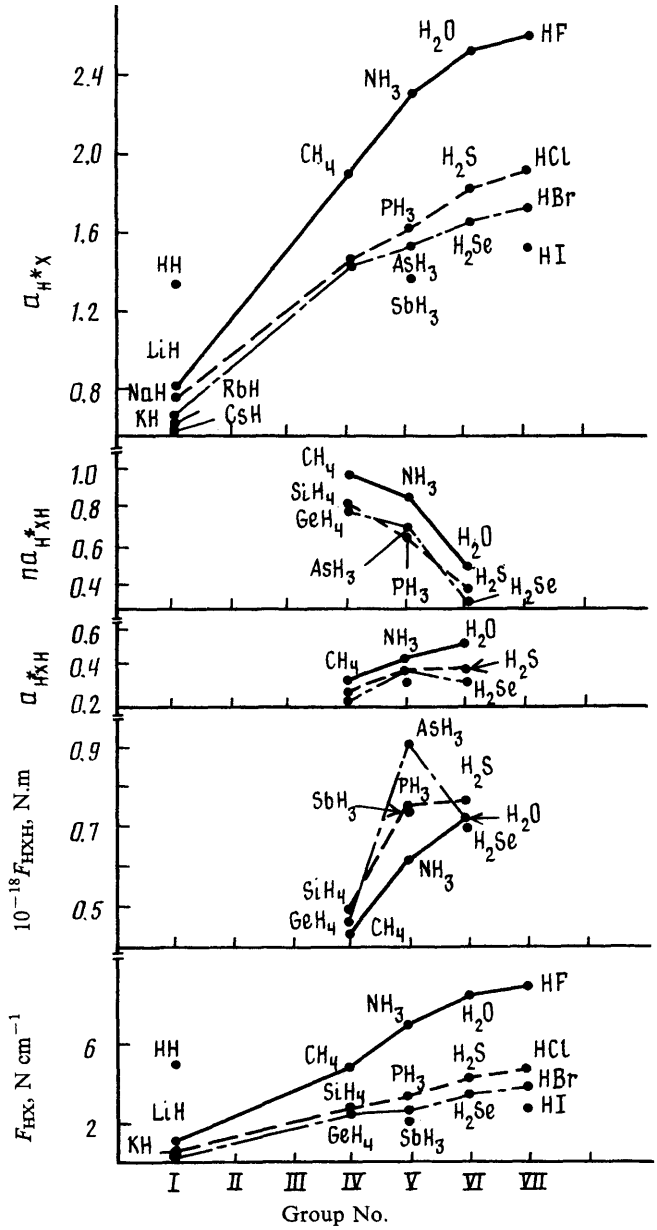


Figure 4. Contributions of different structural elements to $\ln\beta$ for normal hydrides: a_{H^*-X} is the contribution of the H*–X bond, a_{H^*XH} the contribution of the valence angle H*XH, and na_{H^*XH} the contribution of the valence angles with allowance for their multiplicity; F_{HX} and F_{HXH} are the bond and valence angle force constants respectively.

The magnitude of the contribution of the angular coordinates to $\ln\beta$ is not related in simple fashion to the magnitude of the angle force constant F_{HEH}. Here, a significant feature is that the numerical values of F_{HEH} for normal hydrides are comparable with one another. For the hydrides AsH_3 and SbH_3, the values of F_{HEH} and hence the contributions of the angles to $\ln\beta$ are anomalously large, and for AsH_3 this feature is observed when the calculation is carried out using force fields obtained by different authors.[59] Moreover, for these molecules, the values of the non-diagonal elements $F_{(HE,HEH)}$ in the force constant matrix are appreciable. The contribution of the non-diagonal interactions to $\ln\beta_v$ is correspondingly large. In this case the coordinates HE (bond) and HEH (angle) are strongly coupled, and therefore cannot be considered independently. The contributions of coordinates at a distance (bonds and angles not involving the atom being replaced) are small (< 0.06) for the normal hydrides.[59,60]

Thus for the normal hydrides as a class of compound, $\ln\beta_{D/H}$ shows approximately the same dependence on the H—E bond force constant, the contribution of a single angular coordinate, and the number of angular coordinates contributing to $\ln\beta$. As a consequence of the localisation of the isotopic effect, these conclusions apply not only to the normal hydrides themselves, but also to their derivatives.

2. Dependence of $\ln\beta_{D/H}$ on the number, type, and remoteness of the substituents. Compounds of hydrogen with carbon with sp^3-hybridisation

The value of $\ln\beta_{D/H}$ is determined not only by the nature of the hydride-forming element but also by the nature and number of the substituents on the atom joined directly to the hydrogen atom being replaced. The dependence of $\ln\beta_{D/H}$ on the nature and number of the substituents is also large-scale, and comparable with the dependence of $\ln\beta$ on the nature of the hydride-forming atom. For example, for carbon, even without a change in the hybridisation in the compounds CH_3X, the value of $\ln\beta_{D/H}$ may vary from 2.49 (X = $OCOCH_3$) to 2.26 (X = H), which is almost equal to the range of variation of $\ln\beta$ for the normal hydrides from group IV to group VII in period II. The number of substituents has an equally marked influence (see Table 2).

Comparison of the values of $\ln\beta_{D/H}$ for molecules of the type CH_2XY with the values of $\ln\beta$ for CH_2X_2 and CH_2Y_2 molecules shows that for replacement on several different substituents, additivity of $\ln\beta_{D/H}$ may in general not be observed.

The representation (20) has been used[60] to calculate the contributions of vibrational coordinates of different types to $\ln\beta_{D/H}$ for molecules of the form $CH_{4-n-m}Y_nX_m$, where X, Y = F, Cl, Br, I. This set of values of the contributions is sufficiently representative for an analaysis of the relationship being considered. In fact, the range of change in $\ln\beta_{D/H}$ for the methyl group is almost completely covered by the above set. Moreover, this set of molecules can also be regarded as a model set in the general case of isotopic replacement with respect to hydrogen, since the hydrogen effect is localised at ordinary temperatures.

To be definite, and for simplicity, we shall consider the case of the replacement of only one hydrogen atom. Some of the published results[60] are given in Table 2. It can be seen from this Table that the principal contribution to $\ln\beta$ is made by the C—H* bond, and that this contribution remains approximately constant, changing by not more than 5% in the whole set of molecules studied (here and subsequently, the asterisk indicates the atom replaced by the isotope). This range of change is much smaller than the variation in the actual value of $\ln\beta_{D/H}$, but larger than the variation of the force constant F_{CH} in the given set. The explanation is that the vibrational coordinate corresponding to change in the C—H* bond length, subsequently denoted in the text as CH*, shows, particularly for fluorine-containing molecules, considerable dynamic coupling with the coordinates CX and with the valence angle coordinates, so that the magnitude of its contribution to $\ln\beta_{D/H}$ cannot be determined entirely by the force constant of one given coordinate.

Table 2. Values of $\ln\beta_{D/H}$ for halogenomethanes and $CH_2(CN)_2$ (T = 300 K).

Molecule	$\ln\beta_{D/H}$	Translational–rotational contribution	Σ	C—H* bond contribution	Contributions of the angles H*CX
CHF_3			2.67±0.03 (E)		
$CHClF_2$	2.70	0.05	0.07	1.97	2·0.57 (HCF) 0.51 (HCCl)
$CHBrF_2$	2.65	0.05	−0.25	1.93	2·0.67 (HCF) 0.63 (HCBr)
CH_2F_2	2.64	0.15	−0.39	1.94	2·0.79 (HCF) 0.40 (HCH)
$CHCl_2F$	2.64	0.04	−0.03	1.98	0.63 (HCF) 2·0.50 (HCCl)
CH_2Cl_2			2.52±0.02 (E)		
$CHBr_2F$	2.62	0.03	−0.08	1.94	0.76 (HCF) 2·0.50 (HCBr)
CH_2FCl	2.62	0.12	−0.20	1.95	0.74 (HCF) 0.67 (HCCl) 0.38 (HCH)
$CHBrClF$	2.61	0.04	0.03	1.95	0.58 (HCCl) 0.56 (HCF) 0.50 (HCBr)
$CHCl_3$			2.54±0.02 (E)		
CH_2BrF	2.58	0.11	−0.18	1.95	0.80 (HCF) 0.55 (HCBr) 0.38 (HCH)
$CHBrCl_2$	2.56	0.02	−0.03	1.94	2·0.57 (HCCl) 0.52 (HCBr)
$CHBr_2Cl$	2.51	0.02	−0.10	1.93	0.68 (HCCl) 2·0.51 (HCBr)
CH_2BrCl			2.57±0.06 (E) calculated value:		
	2.51	0.10	−0.07	1.95	0.67 (HCCl) 0.55 (HCBr) 0.38 (HCH)
$CHBr_3$			2.55±0.03		
CH_2Br_2			2.47±0.05 (E)		
CH_2ICl	2.48	0.10	−0.07	1.94	0.60 (HCl) 0.60 (HCCl) 0.36 (HCH)
CH_3Br			2.33±0.04 (E)		
CH_2IBr	2.44	0.09	−0.10	1.95	0.62 (HCBr) 0.57 (HCl) 0.35 (HCH)
$CH_2(C{\equiv}N)_2$	2.43 (E)				

Note. The letter "E" denotes a value obtained from the experimental frequencies; the contributions of the vibrational coordinates are given only for those molecules for which the most reliable data on the force constants in natural coordinates are available; Σ is the sum of the contribution of the interaction of coordinates of different kinds and the contribution of bonds and angles not including the atom being replaced.

Alcohols and ethers

Compound	$CH_3^*-O-C(=O)-CH_3$	$CH_3^*-O-C(=O)-H$	$CH_3^*-O-CH_2CH_3$	$CH_3^*-OCH_3$	CH_3^*OH
$\ln\beta_{D/H}$	2.49±0.13	2.48±0.09	2.45	2.44±0.05	2.40±0.05

Nitrogen-containing compounds

Compound	$CH_3^*NH_3^+$	$CH_3^*-N=N-CH_3^*$	$CH_3^*NH_2$	$CH_3^*-N=NH$	CH_3^*-NC
$\ln\beta_{D/H}$	2.42	2.41±0.04	2.39	2.36	2.35±0.02

Compounds with halogens and other elements

Compound	CH_3^*F	CH_3^*Cl	CH_3^*Br	CH_3^*I	CH_3^*-H	$CH_3^*SCH_2CH_3$	$CH_3^*-GeH_3$	$CH_3^*-SnH_3$
$\ln\beta_{D/H}$	2.46±0.05	2.36±0.04	2.33±0.04	2.32±0.05	2.26±0.02	2.35	2.29	2.21±0.03

Compounds with carbon

Compound	$CH_3^*-CH_2CH_3$	$CH_3^*CH_2I$	$CH_3^*-CH_2OCH_3$	$CH_3^*CH_2F$	$CH_3^*CH_3$	$CH_3^*-C\equiv CH$	$CH^*-C\equiv N$	
$\ln\beta_{D/H}$	2.45±0.06	2.40	2.38	2.37	2.36±0.07	2.41±0.05	2.36±0.02	
Compound	$CH_3^*-C(=O)-OH$	$CH_3^*-C(=O)-OCH_3$	$CH_3^*-C(=O)-Cl$	$CH_3^*-C(=O)-NH_2$	$CH_3^*-C(=O)-CH_3$	$CH_3^*-C(=O)-D$	$CH_3^*-C(=O)-F$	$CH_3^*-C(=O)-H$
$\ln\beta_{D/H}$	2.39	2.38±0.13	2.38	2.37	2.36±0.08	2.31±0.03	2.31±0.04	2.30

In general, and in contrast to the normal hydrides, for substituted methanes the interactions of the vibrational coordinates make a significant contribution to $\ln\beta$. This feature means that in this case the coordinates cannot be considered independently, as confirmed by an analysis of the force constant matrices.

The fairly marked scatter and the non-characteristic nature of the contributions of the valence angles to $\ln\beta_{D/H}$ are obvious. For a given molecule, the scatter in these contributions obtained by calculation from the force fields given by different authors, often exceeds even the scatter in the actual values of $\ln\beta$. This is not surprising, since the numerical value of $\ln\beta$ is determined only by the frequencies, which are obtained unambiguously from the force field, while the values of the contributions of specific coordinates are determined by the force field, which is found unambiguously from the experimental frequencies. In other words, slight scatter in the frequencies or in even individual frequencies may correspond to a large scatter in the values of the force constants. The difference in the force fields is also responsible for the scatter in the values of the contributions.

At the same time it is obvious that the physically correct solution for the force field is unique, and, moreover, that from its physical significance the scale of the variation in the contributions in a set of molecules should not exceed the scale of the variation of $\ln\beta$. It is therefore appropriate to solve the inverse problem, that is to find the values of the contributions of the coordinates by solving the over-determined system of linear equations by the least-squares method for a sufficiently representative set of molecules, using the known values of $\ln\beta_v$. The values of the contributions of the vibrational coordinates obtained in this way may serve as a criterion of the physical correctness of the force fields.

Since the solution of the system of linear equations in this case (the replacement of one hydrogen atom) is in principle unique, it is necessary to fix one of the contributions. The contribution of the CH* bond was chosen as this contribution. The accuracy of the additive scheme indicated corresponds to that of the calculation of $\ln\beta$ from the experimental vibrational frequencies.[60]

For the calculation of the β-factor for carbon replacement, Galimov[61] proposed an empirical additive scheme which has been widely applied, chiefly in the study of geochemical effects. In this scheme, the β-factor itself (and not its logarithm) is calculated, as the sum of the increments in the chemical bonds without allowance for the angles; this is quite permissible for carbon. From what has been said above it is clear that the additive representation is also possible and useful for hydrogen effects, but in this case it is more natural to expand the logarithm of the β-factor with necessary allowance for the valence angles.

Moreover, the dependence of $\ln\beta_{D/H}$ on the number and type of substituents for a given hydride-forming element is obviously determined primarily by the contribution of the valence angles H*EX and by the contribution of $\ln\beta_t + \ln\beta_r$. The electronic influences of the substituents on the force constant and hence on the contribution of the E–H* bond play a secondary role. Even if it is assumed that the contributions of the angles and bonds of each type to $\ln\beta_v$ are unchanged and depend only on the number of substituents, it cannot be expected that $\ln\beta$ will vary linearly with respect to the number of substituents, since the linearity breaks down when account is taken of the rotational contribution (it can readily be seen that the rotational contribution changes non-linearly with change in the number of substituents). There is even less reason to expect linearity when account is taken of the contributions of the interactions between the coordinates.

sp$_3$-Hybridisation

Compound	$CH_3^*CH_3$	$CHH^*(CH_3O)CH_3$	$CH_3^*-CH_2CH_3$	$H^*-C(CH_3)_2CH_3$	$CH_2^*CH_3$	CH_3^*-H	CH_3^*F	CH_3^*OH	$CH_3^*NH_2$
$\ln\beta_{D/H}$	2.57±0.09	2.51	2.45±0.06	2.42	2.36±0.07	2.26±0.02	2.46±0.05	2.40±0.05	2.39

sp$_2$-Hybridisation

Carbonyl compounds

Compound	$H^*-C(=O)OCH_2Cl$	$H^*-C(=O)OH$	$H^*-C(=O)OCH_3$	$H^*-C(=O)NH_2$	$H^*-C(=O)F$	$H^*-C(=O)CH_3$	$H^*-C(=O)C(=O)H$	$H^*(H)C=O$
$\ln\beta_{D/H}$	2.42	2.39	2.38±0.16	2.35	2.31	2.30±0.07	2.16±0.07	2.13±0.04

Unsaturated hydrocarbons

Compound	$H^*(F)C=C(H)F$	$H^*(H)C=CCl_2$	$F(H^*)C=C(H)F$	$H^*(H)C=CH_2$	$H^*(Cl)C=C(H)Cl$	$H^*(Cl)C=C(Cl)H$	$CH_2^*=C=CH_2^*$	$H^*(H)C=N=N$	$H^*(H)C=CH-CH=CH_2$
$\ln\beta_{D/H}$	2.43±0.08	2.34±0.07	2.33±0.05	2.33	2.31±0.04	2.28±0.05	2.21	2.16	2.09

sp-Hybridisation

Compound	$H^*-C\equiv CF$	$H^*-C\equiv C-CF_3$	$H^*-C\equiv CH$	$H^*-C\equiv CBr$	$H^*-C\equiv N$	$H^*-C\equiv CCl$	$H^*-C\equiv C-CH_3$	$H^*-C\equiv C\equiv N$
$\ln\beta_{D/H}$	2.11	2.06±0.02	2.06±0.02	2.04	2.035±0.005	2.03	1.97±0.11	1.88

Cyclic compounds

Compound	CH_2-CH_2 (O)	Cyclohexane	Cyclo-butane-D_6	Benzene-D_6	Cyclo-propane D_6	HCH^* (CH=CH)	Cubane-D_1	$CH^*=CH$ (CH_2)
$\ln\beta_{D/H}$	2.44	2.42	2.40	2.38±0.06	2.39±0.04	2.32	2.22	2.10

The new coordinates which appear when substituents are introduced, particularly the coordinates of adjoining angles, make a contribution to $\ln\beta$ which may be either larger than or smaller than the contribution of the coordinates which disappear. Moreover, replacement brings about a change in the contribution of $\ln\beta_t$ + $\ln\beta_r$. Thus with increase in the number of substituents of the same type, the value of $\ln\beta$ may either increase or decrease. The dependence of $\ln\beta_{D/H}$ for the methyl group on the nature of the substituents in compounds of the type CH_3^*R is shown by the data given below (T = 300 K).[57,60,62]

In the analysis of these data it should be borne in mind that they were calculated for the replacement of the three hydrogen atoms in the methyl group, whereas in the calculation for the $CHX_nY_mZ_l$ molecules only one hydrogen atom was replaced. Thus the values of $\ln\beta_{D/H}$ for the compounds CH_3R are 0.5–1% too high, as a result of the inaccuracy of the geometric-mean rule. The variation in $\ln\beta$ for the methyl group for a given substituent X is determined primarily by the rotational contribution and by the value of the force constant of the HCX angle, and to a much smaller extent by the influence of the substituent on the force constants of the C–H and C–X bonds. These factors may act in opposite directions. Thus on going from CH_3F to CH_3I the angle force constant (F_{HCX}/r^2_{CH}) changes from 0.900 N cm^{-1} to 0.651 N cm^{-1}. This also determines the change in $\ln\beta$, which goes from 2.457 to 2.320. On going from F to I, the force constant of the C–X bond also decreases, from 5.535 N cm^{-1} to 2.338 N cm^{-1}, but this factor has less influence on $\ln\beta$. The constant F_{CH}, however, generally changes in the opposite direction in this series, although the change is slight (from 4.878 N cm^{-1} for CH_3F to 5.002 N cm^{-1} for CH_3I).

3. Compounds of carbon with hydrogen with sp^2- and *sp*-hybridisation. Dependence of $\ln\beta$ on the geometry of the molecule

We can compare the logarithms of the $\beta_{D/H}$-factors of compounds with sp^3-, sp^2-, and *sp*-hybridisation of the hydride-forming carbon atom. First of all, the general decrease in the value of $\ln\beta_{D/H}$ for sp^2- and *sp*-hybridisation compared with sp^3-hybridisation should be noted. At the same time, the bond force constants F_{CH} and the corresponding contributions of the bonds to $\ln\beta$ are greatest for *sp*-hybridised and smallest for sp^3-hybridised molecules. The factor responsible for the decrease in $\ln\beta$ on going from sp^3-hybridisation to sp^2- and *sp*-hybridisation can therefore only be the decrease in the number of vibrational coordinates contributing to $\ln\beta$. To confirm this, we can consider the contributions of the vibrational coordinates to $\ln\beta$ for monosubstituted derivatives of ethane, ethylene, and acetylene (see Fig. 5).[63]

Fig. 5 shows that the number of coordinates closest to the atom being replaced decreases in the order ethane–ethylene–acetylene, leading to a decrease in $\ln\beta$, despite the increase in the force constants and hence in the contributions made to $\ln\beta_{D/H}$ by each individual vibrational coordinate.

The values of $\ln\beta_{D/H}$ for substituted ethylenes $HR^1C=CR^2R^3$ are given below [the dependence of $\ln\beta_{D/H}$ (on the carbon atom) on the type of hybridisation of the atom directly joined to the atom being replaced (T = 300 K)].[57,60,62]

It should be borne in mind that for replacement in ethylene the substituents R^2 and R^3 are separated by three bonds from the hydrogen being replaced. The influence of the substituents R^2 and

R^3 is therefore weaker than that of the substituent R^1, but stronger than the corresponding influence for the methyl group.

Fig. 5 shows that for ethylene, an appreciable contribution to $\ln\beta$ is made by the out-of-plane coordinates. In substituted ethylenes, the out-of-plane vibrations depend markedly on the substituent.[5]

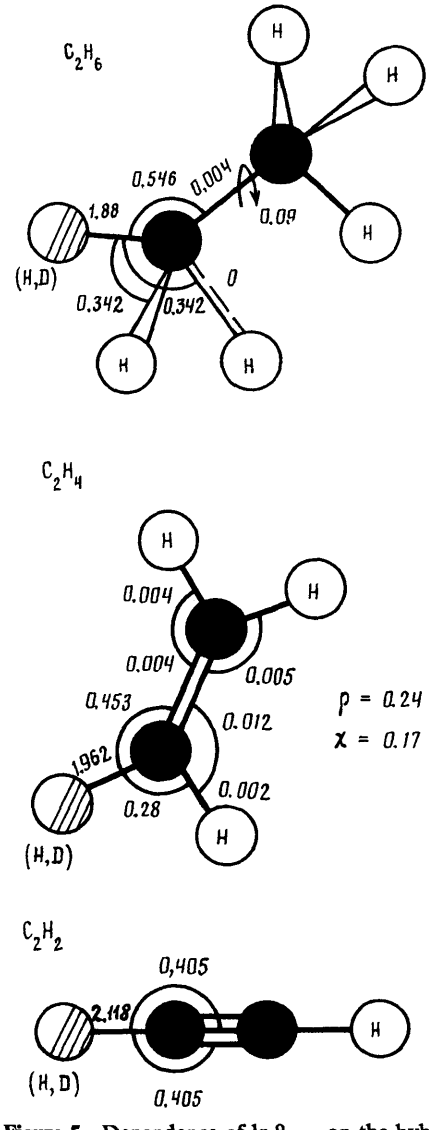
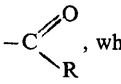


Figure 5. Dependence of $\ln\beta_{D/H}$ on the hybridisation; the change in the contributions of the vibrational coordinates in the series ethane–ethylene–acetylene; only the non-zero contributions are given; the values of $\ln\beta_{D/H}$ are 2.372 (ethane), 2.334 (ethylene), and 2.105 (acetylene); the vibrational components of $\ln\beta_{D/H}$ are 3.222, 3.124, and 2.889 respectively.

The influence of the substituents R^2 and R^3 on $\ln\beta$ is therefore also much stronger than for the methyl group. In fact, the atoms R^2 and R^3 are included in the twisting coordinate χ (rotation of the planes CHR^1 and CR^2R^3 about the C=C bond in different directions) and cannot in this case be regarded as separated neighbours. This must be taken into account in all cases of substitution at a double bond.

Another group of carbon compounds with sp^2-hybridisation consists of compounds of the type , which can be regarded as substituted formaldehydes. All that has been said about the β-factors of ethylenic compounds applies in this case also, except that in the substituted formaldehydes there is no vibrational coordinate χ. The value of $\ln\beta$ for the formaldehyde is therefore low. In carbonyl compounds, an important part is played by the electronic influences of the substituents. The introduction of electron-acceptor groups such as –OH and –F increases the strength of the H–C bond, leading to an increase in its contribution and hence to an increase in $\ln\beta$.

The relative random error in the value of $\ln\beta_{D/H}$ for compounds with a double bond, particularly carbonyl compounds, is extremely large. This makes it impossible to analyse fine effects. This large error is related to the difficulty of obtaining accurate data on the vibrational spectra of these substances, due to the difficulty of purifying the substances, the indeterminacy (in a number of cases) in the number of conformers, and other factors. These factors make it difficult to interpret the spectrum to obtain an unambiguous assignment of the bands to fundamental vibrations even for simple compounds. Thus in the above case of formaldehyde-D_1 the published set of fundamental frequencies for HDCO is clearly erroneous. The case of this molecule also shows that the calculation of $\ln\beta$ can provide an additional criterion for the correctness of the interpretation of an experimental spectrum.

The error in $\ln\beta$ for complex molecules is generally greater than that for simple molecules. This is also related to the inaccuracy of the spectroscopic data for large molecules. At the same time, because of the localisation of the hydrogen effect, the molecular fragments at a distance do not influence the β-factor significantly. The use of small molecules as models therefore acquires particular further importance because of the higher accuracy of their β-factors.

For compounds of the acetylene series, the $\ln\beta$ values change very little with change in the nature of the substituents, due to the remoteness of the latter. At the same time, when heavy substituents are present, $\ln\beta$ for these molecules is smaller as a result of the decrease in the contribution of the angular coordinates.

In view of the fruitfulness and general character of the approach used, the study can be extended by examining different versions of the C–H bond. $\ln\beta_{D/H}$ has its highest values for sp^3-hybridised molecules, and $\ln\beta$ for methylene groups is higher than that for methyl groups. The value of $\ln\beta_{D/H}$ for isobutane-D_1 is apparently too low, because of the incorrect published[5] assignment of the frequencies of the isotopic forms.

The high values of $\ln\beta$ for benzene is related to the rigidity of its structure and to the significant contribution from the large number of out-of-plane coordinates. Many vibrations of the benzene ring cannot be assigned to one definite bond or angle.[5] Thus as in the case of the halogen-substituted methanes considered above, it is appropriate to examine the benzene ring as a whole, without distinguishing "distant" and "nearest" fragments within it.

On the other hand, alicyclic molecules have lower $\ln\beta$ values compared with open-chain molecules, and $\ln\beta$ decreases with increase in the strain in the ring. This is related to the increase in the H*–C–C angles compared with the tetrahedral angle, which leads to a decrease in their strength and a decrease in their contribution to $\ln\beta$.

4. The values of $\ln \beta_{D/H}$ for compounds of hydrogen with nitrogen and oxygen

In the approach being used, the regularities of the change in the $\ln \beta_{D/H}$ values for compounds of nitrogen and oxygen are the same as for carbon compounds. All that has been said above about the dependence of $\ln \beta_{D/H}$ on the type of hybridisation and the number, nature, and remoteness of the substituents is also applicable to these molecules. The number of compounds of nitrogen and oxygen for which experimental spectroscopic data are available, however, is much smaller than that for carbon compounds. The $\ln \beta_{D/H}$ values for some of these compounds are given in Table 3. The $\ln \beta_{D/H}$ values for the corresponding normal hydrides show that the behaviour of $\ln \beta_{D/H}$ for nitrogen compounds with sp^3-hybridisation is similar to the case of the methyl group, but the $\ln \beta$ values for nitrogen compounds are on the average 0.2 unit greater than for the methyl group with identical substituents. For nitrogen compounds with sp^2-hybridsation, the $\ln \beta_{D/H}$ values are lower, as they should be (thus for NH_3, $_{D/H}$ = 2.21).

Table 3. Values of $\ln \beta_{D/H}$ (T = 300 K) for compounds containing NH and OH bonds.[57,60,62]

N–H bond	$\ln \beta_{D/H}$	O–H bond	$\ln \beta_{D/H}$
$NH(CH_3)_2$	2.71	$HO-NO_2$	2.59±0.02
NH_2-NH_2	2.59	$HO-NH_2$	2.59
NH_2-CH_3	2.58±0.03	HO–F	2.54
$NH_2-C(=O)-CH_3$	2.56	$HO-CH_3$	2.51±0.04
		$HO-C(=O)-CH_3$	2.50±0.05
$NH_2-C(=O)-H$	2.49	HO–Cl	2.44±0.02
NH_2-OH	2.45		
NH_3	2.42	$HO-C(=O)-H$	2.42
HN=NH*(cis)	2.40		
HN_3	2.29±0.2	HO–H	2.38±0.02

The $\ln \beta_{D/H}$ values for the O–H bond in oxygen compounds are close to the values for N–H bonds.

Practically all compounds containing NH and OH groups are capable to some extent of forming hydrogen bonds; this leads to a change in the immediate environment of the hydrogen atom being replaced and to a change in the force constants, and also influences $\ln \beta$ (the $\ln \beta$ values given in Table 3 were calculated for the monomers). At the same time, it is known that hydrogen bond formation has only a weak influence on the value of $\ln \beta$. This follows from the low values of the isotope effects of vapour pressure at 300 K. When a hydrogen bond is formed, compensation of the contributions made to $\ln \beta$ by the newly produced degrees of freedom takes place, and this explains the weak influence of association on the β-factor.[64]

In addition to hydrogen bond formation, another specific process is possible for the amino-group, namely protonation, which takes place in practice in aqueous solutions of aminoacids. On protonation of the amino-group, as a result of the increase in the number of vibrational degrees of freedom, $\ln \beta_{D/H}$ increases (2.68 for the ammonium ion, compared with 2.42 for ammonia). It should be emphasised, however, that protonation cannot be regarded simply as the mechanical addition of new structural elements to the molecule, since it is accompanied by a radical rearrangement of the force field. This may change in $\ln \beta$ in either direction. Thus protonation of oxygen and fluorine leads to a considerable decrease in $\ln \beta_{D/H}$. The published[65,66] separation coefficients for the H_3O^+/H_2O system show that $\ln \beta_{D/H}$ for the hydroxonium ion is ~0.3 unit lower thn $\ln \beta_{D/H}$ for H_2O. This is related to the difference in the electronic structures of the O and N atoms, as a result of which the protonation of the water molecule or the removal of an electron from it lead to a decrease in the strength of the bond, a sharp decrease in the force constants, and hence a decrease in $\ln \beta$. These marked changes in $\ln \beta_{D/H}$ on protonation may be significant in isotopic fractionation processes in biological systems.

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