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Isotope chemistry and molecular structure. Total deuterium isotope effects*

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A qualitative discussion is given on the relationship between the magnitude of isotope effects in polyatomic systems and bending and stretching force constants. This is followed by a general method for the calculation of the isotope effect which can be ascribed to each force constant in the general quadratic potential energy for the vibration of a polyatomic molecule. The method is applied to deuterium isotope effects in the molecules H_2O , CH_2O , CH_4 , C_2H_4 , C_2H_6 , and C_6H_6 at and above 300°K. It is found that deuterium isotope effects associated with individual internal valence force constants are nearly additive at room temperature. Strict additivity holds in the high temperature limit. Bond stretching force constants account for at least 65% of the total deuterium-to-protium reduced partition function ratio at 300°K and become even more dominant at higher temperatures. The origin of the relative importance of stretching and bending forces as a function of temperature is found in the first two terms of the finite orthogonal polynomial method of Bigeleisen and Ishida. Correlations are established between the magnitude of deuterium isotope effects in different molecules as a function of temperature with stretching and bending force constants.

INTRODUCTION

Within the Born–Oppenheimer (BO) approximation the potential energy surfaces for isotopic molecules are identical. It follows that equilibrium isotope effects exist only for quantum systems within this approximation.^{1,2} Thus the reduced partition function ratio, $(s/s')f$, of isotopic molecules is the appropriate function for the understanding of isotope chemistry. While the early history of isotope chemistry developed within the framework of the detailed analysis of molecular vibrations,³ the expansion of $\ln(s/s')f$ in power series of $(h/kT)^{2j}$ $\times \sum \delta \nu_i^{2j}$, where $\delta \nu_i = \nu'_i - \nu_i$ and ν'_i and ν_i the eigenfrequencies of the light and heavy isotopic molecules, respectively, has led to the theoretical foundations of the rules of isotope chemistry and the formal relationship between isotope chemistry and molecular structure.^{2,4–6} These follow directly from the relations

$$\ln\left(\frac{s}{s'}\right)f = \frac{1}{24} \left(\frac{h}{kT}\right)^2 \sum_{\text{atoms}} \left(\frac{1}{m'_i} - \frac{1}{m_i}\right) \langle \nabla^2 U \rangle + \dots \quad (1)$$

and

$$\ln\left(\frac{s}{s'}\right)f = \sum_{j=1}^n W_j A_j \sum_{i=1}^{3n-6} \delta u_i^{2j} \quad (u'_i \leq \infty). \quad (2)$$

The coefficients A_j in Eq. (2) are the same Bernoulli coefficients as one obtains in the Taylor series expansion, Eq. (1), while the modulating coefficients, W_j , are mathematically explicit functions of n , j , and u_{max} . They have been tabulated at close intervals of u_{max} in the range $0 < u_{\text{max}} < 25$ and $n = 0, 1, \dots, 6$.⁷ The other symbols and notation conform to our usual notation.⁷ The favorable convergence properties of Eq. (2) plus the analytical expressions for the moments of the eigenvalues for a set of coupled harmonic oscillators, $\sum \lambda_i$, where $\lambda = 4\pi^2 \nu^2$, has resulted in the explicit analytical development of the relationship between isotope chemistry and molecular forces for diatomic⁸ and triatomic⁹ molecules in the harmonic oscillator approximation. Analytical so-

lution of the problem for systems of four or more atoms is presently tedious and we have therefore reduced many of the problems of polyatomic molecules to computer calculation. This paper is one of a series of papers relating the isotope chemistry of polyatomic molecules to molecular forces. In this paper we will show how deuterium isotope effects depend on stretching, bending, and other forces for prototype molecules of chemical interest over a wide temperature range. We shall intercompare deuterium isotope effects with the type of chemical bonding. All of these will be done in the harmonic oscillator (BO) approximation.

ISOTOPE CHEMISTRY AND MOLECULAR FORCES

We shall briefly illustrate the one to one correlation of isotope chemistry with molecular structure. Isotope chemistry is related with molecular structure through the molecular forces rather than the geometry per se. In fact isotope effects are a poor criterion of molecular geometry. The relationship with the geometry exists through the correlation of geometry and electronic structure rather than geometric parameters. In Table I we list values of $\ln(s/s')f$ calculated by Spindel, Stern, and Monse¹⁰ for $^{13}\text{C}/^{12}\text{C}$ for two homologous series of carbon

TABLE I. $^{13}\text{C}/^{12}\text{C}$ reduced partition function ratio at 300° K.^a

Molecule	$f_{\text{H stretch}}^b$	$f_{\text{H bend}}$	$\ln(s/s')f$
CO	18.5		0.0920
OCS	16.1, 7.1	0.64(2)	0.1356
CO ₂	15.6(2)	0.77(2)	0.1729
Br ₂ CO	13.6, 2.5(2)	0.83(2), 1.13	0.1283
Cl ₂ CO	13.7, 3.1(2)	0.94(2), 0.95	0.1391
F ₂ CO	15.1, 6.5(2)	1.18(2), 1.52	0.1886

^aReference 10.

^bNumber in parentheses gives the number of equivalent force constants with $g'_{ij} \neq g_{ij}$.

compounds, OC, OCS, OCO, Br₂CO, Cl₂CO, and F₂CO. The reduced partition function ratio for CO, a linear diatomic molecule, is anomalously small because there are no bending forces. We see the progressive increase in $\ln(s/s')f$ in the series OC, OCS, OCO with increase in both the C-X stretching force constant and the O-C-X bending force constant. In the series Br₂CO, Cl₂CO, F₂CO we see the progression of $\ln(s/s')f$ with the X-C stretching force constant.

Varshavsky¹¹ has given a plot of β values, $(s/s')f$, for tritium compounds compared with protium as a function of atomic number of the hydride. The plot has the typical appearance of a Mendeleev periodic property. This is a reflection of the variation of the strength of the M-H bond as one goes across a row in the periodic table and the decrease in the M-H bond strength as one goes down each column.

Recently Hartshorn and Shiner¹² have constructed a large number of self-consistent **F** matrices to fit the vibrational spectra of H and D hydrocarbons. From these **F** matrices and the appropriate **G** matrices they have calculated $\ln(s/s')f$ for the respective compounds. A typical result found by them is that given in Fig. 1 for the methyl halides. Here we plot $\ln(s/s')f$ for CH₂DX/CH₃X for X=I, Br, Cl, and F against the H-C-X bending force constant. The C-H stretching and H-C-H bending force constants show much less variation with X than the H-C-X bending force constant. The almost linear dependence of $\ln(s/s')f$ on $f(\text{H-C-X bend})$ is apparent.

In a series of papers Wolfsberg and Stern¹³⁻¹⁵ have looked for secondary deuterium isotope effects in the absence of force constant changes at the C-D or D-C-X bond. They find small kinetic isotope effects associated with the reaction coordinate but negligible isotope effects associated with the equilibrium between ground state and transition state unless there are changes in the force constants of the C-H, D or H, D-C-X bonds. For the kinetic secondary deuterium isotope effect they have shown a direct relationship between kinetic isotope effect and force constant change in the reaction



The kinetic isotope effect is linear in the difference in the β C-H stretching force constant between the ground state and transition state. Changes in the H-C-H and C-C-H bending force constants at the β carbon also give kinetic isotope effects, but in these cases a slight curvature is to be noted in a plot of $\ln(k_{\text{H}}/k_{\text{D}})$ vs $(f_{\text{H}} - f_{\text{H}}^\ddagger)$ (cf. Fig. 1 of Wolfsberg and Stern¹⁴), where f_{H} and f_{H}^\ddagger are the force constants in the ground and transition states, respectively, associated with a nonzero $(g'_{\text{H}} - g_{\text{H}})$. Wolfsberg and Stern show that a 15% effect at 300°K for D₂ substitution at the β carbon is consistent with (a) $(f_{\text{C-H}} - f_{\text{C-H}}^\ddagger) = 4.5 - 4.2$ mdyn Å⁻¹, (b) $(f_{\text{H-C-H}} - f_{\text{H-C-H}}^\ddagger) = 0.53 - 0.35$ mdyn Å, or (c) $(f_{\text{C-C-H}} - f_{\text{C-C-H}}^\ddagger) = 0.68 - 0.60$ mdyn Å, or an appropriate combination of (a), (b), and (c). Since there are two (C-C-H) bending force constants for each H, D at the β carbon, the effective force constant change $(f_{\text{C-C-H}} - f_{\text{C-C-H}}^\ddagger)$ per D substitution at the β carbon is 0.16 mdyn Å. It is immediately apparent

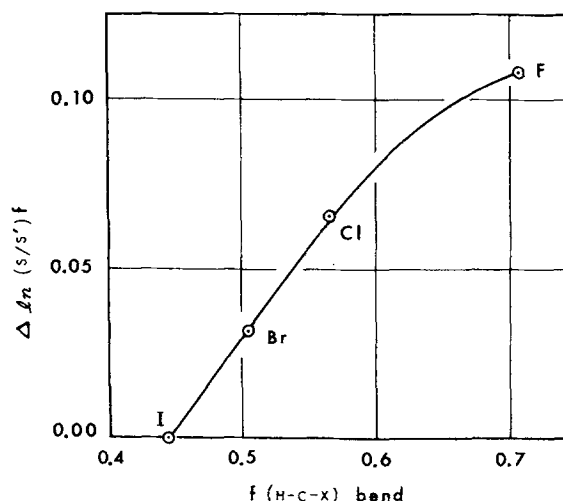


FIG. 1. Plot of $\ln(s/s')f$ for CH₂DX/CH₃X vs the H-C-X bending force constant; X=F, Cl, Br, I.

that, per unit change in force constant, the bending motion gives a larger secondary β deuterium isotope effect than does the stretching motion. The reason for the latter is easy to find from the first term in Eq. (2). If we limit Eq. (2) to the first-order approximation, we obtain

$$\ln\left(\frac{s}{s'}\right)f \approx \left(\frac{W_1}{24}\right) \sum_i^{3n-6} \delta u_i^2 \quad (3)$$

or

$$\ln\left(\frac{s}{s'}\right)f \approx \left(\frac{W_1}{24}\right) \left(\frac{\hbar}{kT}\right)^2 \sum_i \sum_j f_{ij}(g'_{ij} - g_{ij}), \quad (4)$$

from which one obtains by a modification of the $\bar{\gamma}$ method,¹⁶

$$\ln\left(\frac{k_{\text{H}}}{k_{\text{D}}}\right) \approx \ln\left(\frac{\nu_{1L}}{\nu_{2L}}\right)^\ddagger + \left(\frac{W_1}{24}\right) \left(\frac{\hbar}{kT}\right)^2 \sum \sum [f_{ij}(g'_{ij} - g_{ij}) - f_{ij}^\ddagger(g'_{ij} - g_{ij})^\ddagger]. \quad (5)$$

If the only change between the ground and transition states is a change in one force constant, then

$$\ln\left(\frac{k_{\text{H}}}{k_{\text{D}}}\right) \approx \ln\left(\frac{\nu_{1L}}{\nu_{2L}}\right)^\ddagger + \left(\frac{W_1}{24}\right) \left(\frac{\hbar}{kT}\right)^2 (g'_{ij} - g_{ij})(f_{ij} - f_{ij}^\ddagger). \quad (6)$$

In the β secondary deuterium isotope effect, the classical kinetic isotope effect, $\ln(\nu_{1L}/\nu_{2L})^\ddagger$, is 0.014 in Wolfsberg and Stern's model. The classical term accounts for but 10% of the total kinetic isotope effect at 300°K. The classical effect is associated with the rupture of the C-X bond in the model transition state of Wolfsberg and Stern. Wolfsberg and Stern have used the $\bar{\gamma}$ approximation to Eq. (6) to explain the order of the isotope effects found, C-C-H > H-C-H > C-H. We can now make their analysis quantitative through the known dependence of W_1 on u_i' and u_i .⁵ The fact that a plot of $\ln(k_{\text{H}}/k_{\text{D}})$ vs $\sum \sum f_{ij}(g'_{ij} - g_{ij}) - f_{ij}^\ddagger(g'_{ij} - g_{ij})^\ddagger$ is linear or near linear shows that Eq. (6) is a good approximation. From the

condition that the kinetic isotope effect be the same if ascribed solely to changes in either stretching or bending force constants, we get, after consideration of the procedure discussed by Bigeleisen and Ishida for end atom isotope effects,¹⁷

$$W_1(\text{stretch})(g'_{ij} - g_{ij})_{\text{str}}(f_{ii} - f_{ii}^{\dagger})_{\text{str}} = W_1(\text{bend})(g'_{ij} - g_{ij})_{\text{bend}}(f_{ii} - f_{ii}^{\dagger})_{\text{bend}} \quad (7)$$

If we use common units for the stretching and bending force constants, e.g., millidynes/angstrom, then the mass differences on both sides of Eq. (7) are the same and

$$(f_{ii} - f_{ii}^{\dagger})_{\text{str}} / (f_{ii} - f_{ii}^{\dagger})_{\text{bend}} = W(\text{bend}) / W(\text{stretch}). \quad (8)$$

For the left-hand side of Eq. (8) Wolfsberg and Stern find 1.7 for a 15% secondary effect at 300°K. For the right-hand side of Eq. (8) we find 1.7 from the W tables when C-H stretch and H-C-H bend are 3000 and 1200 cm⁻¹, respectively, and the temperature is 300°K. The deviation from linearity in $(f_{ii} - f_{ii}^{\dagger})$ for the bending vibrations arises from the correction to Eq. (6) from the term $W_2 A_2 (\hbar/kT)^4 \sum (\delta u_i^4 - \delta u_i^{\dagger 4})$.

In the remainder of this paper we shall develop a method for the quantitative calculation of the contribution of molecular force constants to the reduced partition function ratio, actually $\ln(s/s')f$, of isotopic molecules and shall apply the method to deuterium substitution in molecules of chemical interest.

OUTLINE OF METHOD

We desire the absolute and relative contributions of each force constant, f_{ij} , in the potential energy,

$$2V = \sum_i \sum_j f_{ij} q_i q_j, \quad (9)$$

to the logarithm of the reduced partition function ratio

$$\ln\left(\frac{s}{s'}\right)f = \sum_i^{3n-6} \ln\left(\frac{u_i}{u_i'}\right) + \frac{u_i' - u_i}{2} + \ln\left(\frac{1 - \exp(-u_i')}{1 - \exp(-u_i)}\right) \quad (10)$$

in the BO harmonic oscillator approximation.

The total contribution or "total effect" of an F -matrix element, f_{ij} , on $\ln(s/s')f$ is defined, consistent with Eq. (4), as a difference between $\ln(s/s')f$ evaluated with the F matrix of the real molecule and an F matrix in which f_{ij} has been replaced by zero. In this modified F matrix all equivalent f_{ij} elements are set equal to zero while all other elements retain their original values. The total effect of f_{ij} on the j th term in the finite polynomial expansion, Eq. (2), is similarly defined as a difference between the j th term corresponding to the real F matrix and the same term evaluated by using the above described modification to the F matrix.

In general the artificial process of setting a diagonal force constant, and sometimes an off-diagonal force constant, equal to zero leads to one or more negative eigenvalues, corresponding to a mechanically unstable molecule. Thus the calculation of the "total effect" of a force constant cannot be obtained simply from the solution of the original set of secular equations plus the modifications with f_{ij} equal to zero and the subsequent

calculations of the respective $\ln(s/s')f$ values. To calculate the "total effect" it is necessary for all the eigenvalues to be real. The difficulty which arises from negative eigenvalues can be overcome by an extrapolation in f_{ii} to zero. The following procedure was developed. We first estimated the smallest value of each f_{ii} , $(f_{ii})_{\min}$, such that all eigenvalues remained positive. A starting test value of $(f_{ii})_{\min}$ was taken to be the largest of $f_{ii}/10$, or f_{ij}^2/f_{jj} for all values of j . The secular equation was now solved with this trial $(f_{ii})_{\min}$ to see whether all eigenvalues were positive. If they were not, the trial $(f_{ii})_{\min}$ was incremented by $f_{ii}/10$. This process was repeated until all eigenvalues became positive. This value of f_{ii} was taken as a working value of $(f_{ii})_{\min}$. The procedure is somewhat arbitrary but adequate for our purpose, inasmuch as we do not need to know the true $(f_{ii})_{\min}$.

Having found $(f_{ii})_{\min}$, we then solved the secular equations for the various isotopic molecules with the original F matrix and then F matrices with $(f_{ii})_{\min}$, $(f_{ii})_{\min} + 0.05 f_{ii}$, $(f_{ii})_{\min} + 0.10 f_{ii}$, and $(f_{ii})_{\min} + 0.15 f_{ii}$. The frequencies for the isotopic molecules calculated from these five F matrices were used to calculate the corresponding $\ln(s/s')f$ as a function of temperature through Eq. (10). The values of $\ln(s/s')f$ calculated from the F matrices with $(f_{ii})_{\min}$ and $(f_{ii})_{\min}$ incremented as described above were used to extrapolate $\ln(s/s')f$ to f_{ii} equal to zero by a fit to an equation of the form

$$\ln(s/s')f = C_0 + C_1 f_{ii} + C_2 f_{ii}^2 + C_3 f_{ii}^3. \quad (11)$$

Finally, the total effect of f_{ii} is the original $\ln(s/s')f$ minus C_0 .

In general this extrapolation procedure was not necessary for off-diagonal elements, f_{ij} . Of the systems investigated only ring bending motions in benzene gave negative eigenvalues when an off-diagonal F -matrix element was put equal to zero. Therefore, with the exception of the ring bending motions in benzene for which the extrapolation procedure was used, the "total effect" of an off-diagonal matrix element was calculated directly as the difference $\ln(s/s')f_0$, the original value, minus $\ln(s/s')f(f_{ij} = 0)$, which was obtained from $f_{ij} = 0$.

RESULTS

We have chosen as prototype molecules the important molecules, H₂O, CH₂O, CH₄, C₂H₄, C₂H₆, and C₆H₆. In the cases of water, methane, and ethylene both mono- and dideutero substitution has been studied to look for noncumulative effects. The F matrices used in the current calculations for H₂O, CH₄, C₂H₄, and C₆H₆ are those we have used previously.¹⁸ We have also studied CH₄ with the Hartshorn-Shiner F matrix.¹² The CH₂O F matrix was the one used by Spindel, Stern, and Monse.¹⁰ The C₂H₆ F matrix was that of Schachtschneider and Snyder,¹⁹ whose matrix diagonalization routine we continue to use. The absolute "total effect" of each force constant in the F matrix was calculated at 300°K, $T = \theta_{\max}/2\pi$, and $T = 2\theta_{\max}/\pi$ where $\theta_{\max} = h\nu_{\max}/k$ and ν_{\max} is the maximum eigenfrequency of the original $F G'$ matrix, which corresponds to the protio form of the molecule. The values of θ_{\max} are rounded upper bound values

TABLE II. Major contributions to $\ln(s/s')f$ in $\text{HDO}/\text{H}_2\text{O}$.^a

	Absolute value	Σ "total effects"	O-H stretch	H-O-H bend
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$			8.454	0.762
$\delta g_{ij}(\text{amu}^{-1})$ and z			0.496(1)	0.496(1)
$T = 300^\circ \text{K}$	2.5829-00	99.8%	85.6%	14.2%
1000	5.0846-01	100.2	90.1	10.1
2000	1.5358-01	100.0	91.2	8.8
∞		100.0	91.7	8.3

^aAll bending coordinates are weighted by $r_{\text{O-H}} = 0.957 \text{ \AA}$.

computed by the RSCS method.⁵ As a result the $\ln(s/s')f$ values and f_{ij} contributions in the different molecules studied at $u_{\text{max}} \approx 2\pi$ are not at exactly equivalent reduced temperatures. In the case of water the values of the temperature chosen were 300, 1000, and 2000 °K for conformity with our previous work on this molecule.⁹ We report only the "total effects" of those force constants which contribute more than 1% of $\ln(s/s')f$ at any of the temperatures studied. The results are reported in the form: absolute value of $\ln(s/s')f$ at the temperature T and the percent of $\ln(s/s')f$ contributed by each f_{ij} . The value of each original f_{ij} element is given along with the value of $\delta g_{ij} = (g'_{ij} - g_{ij})$ and z , the number of equivalent nonzero $\delta g_{ij} (i \leq j)$ elements. For convenience in comparison we tabulate all F-matrix elements in common units of millidynes/angstrom and G-matrix elements in reciprocal atomic mass units. Thus for bending coordinates the conventional Wilson G-matrix elements are weighted by ρ_{XH}^2 and the corresponding F-matrix elements are weighted by ρ_{XH}^2 , where ρ_{XH} is r_{XH}^{-1} , the reciprocal length of the bond between atoms X and H. The results are given in Tables II–XIII. The column labeled absolute value is the value of $\ln(s/s')f$ calculated through Eq. (10) from the F and G matrices cited. The next column Σ "total effects" is obtained by adding the "total effects" of all force constants in the F matrix and is expressed as a percentage of the absolute value. The contributions by each individual force constant, given in successive columns, are tabulated as the "total effect" of that force constant also as a percentage of the absolute value at the corresponding temperature.

Calculations of $\ln(s/s')f$ from molecular force fields are no better than the F matrices used. For the case of methane, we shall consider two of the F matrices in the literature. The first is the well known Jones–McDowell² (JM) F matrix, which reproduces the zero-order frequencies. Jones and McDowell also give the anharmonic potential constants consistent with their F matrix. Our calculations use only the zero order F matrix and do not include effects from the anharmonic constants. The second F matrix is the one derived by Hartshorn and Shiner¹² to give a least squares fit to the CH_4 frequencies with a pseudoharmonic potential. The Hartshorn–Shiner (HS) F matrix is preferable to the JM F matrix if one wishes to compare methane with other hydrocarbons for which only a pseudoharmonic potential is known.

There are differences on the order of 5% between the present calculations and the recently published fraction-

ation factors of Hartshorn and Shiner¹² for the exchange equilibria,



near room temperature. A comparison is given in Table XIV. The differences are readily correlated with the F matrices developed by Hartshorn and Shiner and the ones we have used. Hartshorn and Shiner do not give the absolute values of $\ln(s/s')f$; they merely give fractionation factors, $[(s/s')f_A/(s/s')f_B]$. Part of the utility of the present study is the ability to compare $\ln(s/s')f$ values calculated with one F matrix with that from another F matrix. For the absolute value of $\ln(s/s')f$ for $\text{C}_2\text{H}_5\text{D}/\text{C}_2\text{H}_6$ we conclude that Hartshorn and Shiner's value is larger than our value of $\ln(s/s')f$ by 0.04 at 300 °K; the values of $\ln(s/s')f$ for ethylene agree within 0.01 at 300 °K. In the case of ethylene, the major difference between the F matrix used by Hartshorn and Shiner and the widely accepted ones of SVHW²¹ are in the out-of-plane wag and Crawford's torsional coordinates. The frequencies for the out-of-plane coordinates calculated by HS¹² are in poor agreement with experiment, whereas the SVHW calculations are in excellent agreement with experiment. The HS F matrix for C_2H_6 has 24 distinct nonzero off-diagonal elements compared with 6 in the Schachtschneider–Snyder F matrix. This difference accounts for the differences (cf. Table XIV) in the fractionation factors given by Hartshorn and Shiner and those calculated by us. At this time we reserve any conclusions concerning a change in fractionation factor with substituent of the order of ± 0.05 when the fractionation factor is a calculated one. The calculations are presently limited by incomplete F matrices, anharmonic corrections, BO approximation, and rotational corrections. Only direct experiment can yield more precise fractionation factors presently.

The infinite temperature values reported in Tables II–XIII are just $lzf_{ij}(g'_{ij} - g_{ij})/\Sigma f_{ij}(g'_{ij} - g_{ij})$, where $l = 1$ when $i = j$ and $l = 2$ when $i \neq j$.

DISCUSSION

For all of the molecules studied we note that the stretching force constant is of major importance to the total deuterium isotope effect; it ranges from a low of 66% in ethane and formaldehyde at 300 °K to a high of

TABLE III. Major contributions to $\ln(s/s')f$ in $\text{D}_2\text{O}/\text{H}_2\text{O}$.^a

	Absolute value	Σ "total effects"	O-H stretch	H-O-H bend
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$			8.454	0.762
$\delta g_{ij}(\text{amu}^{-1})$ and z			0.496(1)	0.991(1)
$T = 300^\circ \text{K}$	5.2028-00	99.7%	84.9%	14.8%
1000	1.0180-00	100.2	90.0	10.2
2000	3.0725-01	100.0	91.2	8.8
∞		100.0	91.7	8.3

^aAll bending coordinates are weighted by $r_{\text{O-H}} = 0.957 \text{ \AA}$.

TABLE IV. Major contributions to $\ln(s/s')f$ in HDCO/H₂CO.^a

	Absolute value	Σ "total effects"	C-H stretch	H-C-H bend	H-C-O bend	H ₂ C=O Out-of-plane wag
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$			4.311	0.314	0.691	0.268
$\delta g_{ij}(\text{amu}^{-1})$ and z			0.496(1)	0.496(1)	0.496(1)	0.551(1)
$T = 300^\circ \text{K}$	2.1999-00	96.9%	67.2%	5.9%	16.0%	7.8%
700	6.4472-01	99.2	72.8	6.0	14.1	6.3
2800	5.0921-02	99.9	76.4	5.6	12.5	5.4
∞		100.0	76.7	5.6	12.4	5.3

^aAll bending coordinates are weighted by $r_{\text{C-H}} = 1.09 \text{ \AA}$.TABLE V. Major contributions to $\ln(s/s')f$ in CH₃D/CH₄.

	Absolute value JM ^b	Absolute value HS ^c	Σ "total effects" JM	Σ "total effects" HS	C-H stretch JM	C-H stretch HS	H-C-H bend ^a JM	H-C-H bend ^a HS	Adjacent bend x bend HS
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$					5.495	4.918	0.475	0.370	-0.078
$\delta g_{ij}(\text{amu}^{-1})$ and z					0.496(1)	0.496(1)	0.496(3)	0.496(3)	-0.248(6)
$T = 300^\circ \text{K}$	2.4562-00	2.3119-00	101.5%	96.5%	71.2%	69.2%	30.3%	23.4%	3.9%
760	6.6096-01	6.1083-01	100.3	99.3	75.8	74.9	24.5	20.4	4.0
3020	5.3756-02	4.8780-02	100.0	100.0	79.1	78.2	20.9	18.0	3.8
∞			100.0	100.0	79.4	78.5	20.6	17.7	3.7

^aF-matrix elements weighted by $(1.094)^{-2}$; G-matrix elements weighted by $(1.094)^2$.^bColumns headed by JM are calculated from the harmonic force constants of Jones and McDowell.²⁰^cColumns headed by HS are calculated with the Hartshorn-Shiner F matrix.¹²TABLE VI. Major contributions to $\ln(s/s')f$ in CH₂D₂/CH₄.

	Absolute value JM ^b	Absolute value HS ^c	Σ "total effects" JM	Σ "total effects" HS	C-H stretch JM	C-H stretch HS	H-C-H bend ^a JM	H-C-H bend ^a HS	Adjacent bend x bend HS
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$					5.495	4.918	0.475	0.370	-0.078
$\delta g_{ij}(\text{amu}^{-1})$ and z					0.496(2)	0.496(2)	0.496(4)	0.496(4)	-0.248(12)
$T = 300^\circ \text{K}$	4.9321-00	4.6411-00	101.4%	96.4%	70.8%	68.9%	30.6%	23.6%	3.9%
760	1.3232-00	1.2227-00	100.3	99.4	75.7	74.9	24.6	20.5	4.0
3020	1.0752-01	9.7566-02	100.0	100.0	79.1	78.2	20.9	18.0	3.8
∞			100.0	100.0	79.4	78.5	20.6	17.7	3.7

^aF-matrix elements weighted by $(1.094)^{-2}$; G-matrix elements weighted by $(1.094)^2$.^bColumns headed by JM are calculated from the harmonic force constants of Jones and McDowell.²⁰^cColumns headed by HS are calculated with the Hartshorn-Shiner F-matrix.¹²TABLE VII. Major contributions to $\ln(s/s')f$ in CHDCH₂/C₂H₄.^a

	Absolute value	Σ "total effects"	C-H stretch	H-C-H bend	H ₂ C-C in plane wag	H ₂ C-C out-of-plane wag	CH ₂ =CH ₂ Crawford's torsion
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$			5.026	0.598	1.133	0.802	0.626
$\delta g_{ij}(\text{amu}^{-1})$ and z			0.496(1)	0.496(1)	0.124(1)	0.124(1)	0.124(1)
$T = 300^\circ \text{K}$	2.3206-00	106.2%	72.2%	15.3%	8.7%	5.7%	4.3%
820	5.3605-01	101.6	77.5	11.3	5.6	3.9	3.0
3270	4.1736-02	100.1	80.0	9.7	4.6	3.3	2.5
∞		99.9	80.2	9.5	4.5	3.2	2.5

^aThe H-C-H bend and H₂C-C in-plane wag are weighted by $r_{\text{C-H}} = 1.094 \text{ \AA}$. The out-of-plane wag is weighted by $r_{\text{C-H}} \cos \alpha$, and the torsion is weighted by $r_{\text{C-H}} \sin \alpha$, where α is one-half the equilibrium angle H-C-H.

TABLE VIII. Major contributions in $\ln(s/s')f$ in *cis*-C₂H₂D₂/C₂H₄.^a

	Absolute value	Σ "total effects"	C-H stretch	H-C-H bend	H ₂ C-C in-plane wag	H ₂ C-C out-of-plane wag	CH ₂ =CH ₂ Crawford's torsion
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$			5.026	0.598	1.133	0.802	0.626
$\delta g_{ij}(\text{amu}^{-1})$ and z			0.496(2)	0.496(2)	0.124(2)	0.124(2)	0.248(1)
$T = 300^\circ \text{K}$	4.6474-00	106.2%	71.2%	15.3%	8.7%	5.7%	4.3%
820	1.0729-00	101.1	77.3	11.3	5.6	3.9	3.0
3270	8.3479-02	100.0	80.0	9.7	4.6	3.3	2.5
∞		99.9	80.2	9.5	4.5	3.2	2.5

^aThe H-C-H bend and H₂C-C in-plane wag are weighted by $r_{\text{C-H}} = 1.094 \text{ \AA}$. The out-of-plane wag is weighted by $r_{\text{C-H}} \cos \alpha$, and the torsion is weighted by $r_{\text{C-H}} \sin \alpha$, where α is one-half the equilibrium angle H-C-H.

TABLE IX. Major contributions to $\ln(s/s')f$ in *gem*-C₂H₂D₂/C₂H₄.^a

	Absolute value	Σ "total effects"	C-H stretch	H-C-H bend	H ₂ C-C in-plane wag	H ₂ C-C out-of-plane wag	CH ₂ =CH ₂ Crawford's torsion
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$			5.026	0.598	1.133	0.802	0.626
$\delta g_{ij}(\text{amu}^{-1})$ and z			0.496(2)	0.992(1)	0.248(1)	0.248(1)	0.248(1)
$T = 300^\circ \text{K}$	4.6492-00	104.5%	71.5%	15.2%	8.1%	5.6%	4.1%
820	1.0727-00	101.1	77.4	11.3	5.5	3.9	3.0
3270	8.3477-02	100.1	80.0	9.7	4.6	3.3	2.5
∞		99.9	80.2	9.5	4.5	3.2	2.5

^aThe H-C-H bend and H₂C-C in-plane wag are weighted by $r_{\text{C-H}} = 1.094 \text{ \AA}$. The out-of-plane wag is weighted by $r_{\text{C-H}} \cos \alpha$, and the torsion is weighted by $r_{\text{C-H}} \sin \alpha$, where α is one-half the equilibrium angle H-C-H.

TABLE X. Major contributions to $\ln(s/s')f$ in *trans*-C₂H₂D₂/C₂H₄.^a

	Absolute value	Σ "total effects"	C-H stretch	H-C-H bend	H ₂ C-C in-plane wag	H ₂ C-C out-of-plane wag	CH ₂ =CH ₂ Crawford's torsion
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$			5.026	0.598	1.133	0.802	0.626
$\delta g_{ij}(\text{amu}^{-1})$			0.496(2)	0.496(2)	0.124(2)	0.124(2)	0.248(1)
$T = 300^\circ \text{K}$	4.6488-00	105.6%	71.5%	15.3%	8.7%	5.7%	4.4%
820	1.0725-00	101.2	77.4	11.3	5.6	3.9	3.0
3270	8.3475-02	100.1	80.0	9.7	4.6	3.3	2.5
∞		99.9	80.2	9.5	4.5	3.2	2.5

^aThe H-C-H bend and H₂C-C in-plane wag are weighted by $r_{\text{C-H}} = 1.094 \text{ \AA}$. The out-of-plane wag is weighted by $r_{\text{C-H}} \cos \alpha$, and the torsion is weighted by $r_{\text{C-H}} \sin \alpha$, where α is one-half the equilibrium angle H-C-H.

TABLE XI. Major contributions to $\ln(s/s')f$ in C₂H₃D/C₂H₆.^a

	Absolute value	Σ "total effects"	C-H stretch	H-C-C bend	H-C-H bend
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$			4.703	0.506	0.452
$\delta g_{ij}(\text{amu}^{-1})$ and z			0.496(1)	0.496(1)	0.496(2)
$T = 300^\circ \text{K}$	2.3534-00	98.1%	66.1%	12.3%	19.7%
720	6.6195-01	99.6	72.6	9.9	17.1
2850	5.3506-02	99.8	76.4	8.4	15.0
∞		99.9	76.8	8.3	14.8

^aAll bending coordinates are weighted by $r_{\text{C-H}} = 1.094 \text{ \AA}$.

TABLE XII. Major contributions to $\ln(s/s')f$ C₆H₅D/C₆H₆ (planar).^a

	Absolute value	Σ "total effects"	C-H stretch	H-C-CC in-plane wag
$f_{ij}(\text{mdyn} \cdot \text{\AA}^{-1})$			5.063	0.870
$\delta g_{ij}(\text{amu}^{-1})$ and z			0.496(1)	0.496(1)
$T = 300^\circ \text{K}$	2.1441-00	102.8%	76.1%	26.7%
810	5.1405-01	100.5	82.5	18.0
3230	4.0470-02	100.0	85.1	14.9
∞		100.0	85.3	14.7

^aThe in-plane wag coordinate is weighted by $r_{\text{C-H}} = 1.08 \text{ \AA}$.

TABLE XIII. Major contributions to $\ln(s/s')f$ in C_6H_5D/C_6H_6 (nonplanar).^a

	Absolute value	Σ "total effects"	H-C-CC out-of-plane wag	(wag) \times (CC torsion) ^b
f_{ij} (mdyn $\cdot \text{\AA}^{-1}$)			0.378	-0.087
δg_{ij} (amu ⁻¹) and z			0.496(1)	0
$T = 290^\circ\text{K}$	2.6559-01	111.3	106.4%	4.9%
300	2.5092-01	110.8	106.0	4.8
1140	2.0768-02	101.1	100.4	0.7
∞		100.0	100.0	0

^aThe out-of-plane wag coordinate is weighted by $r_{C-H} = 1.08 \text{ \AA}$. The torsional coordinate is weighted by $r_{C-C} = 1.39 \text{ \AA}$.

^bThe interaction between two coordinates, with three carbon atoms in common.

91.7% in water at high temperature. The bending forces and off-diagonal force constants are more important at low temperatures than at high temperatures. The reason for the latter can be understood from an argument limited to a consideration of the first two terms in Eq. (2). We have²²

$$\begin{aligned} \ln(s/s')f = & W_1(T)A_1(\hbar/kT)^2 \sum \delta g_{ij} f_{ij} \\ & - W_2(T)A_2(\hbar/kT)^4 \left[\sum \delta g_{ii}^2 f_{ii}^2 \right. \\ & + 2 \sum_{i \neq j} \delta(g_{ii}g_{jj}) f_{ij}^2 + 2 \sum_{i \neq j} \delta g_{ij}^2 (f_{ii}f_{jj} + f_{ij}^2) \\ & + 4 \sum_{i \neq j} \delta(g_{ii}g_{ij}) f_{ii}f_{ij} + 4 \sum_{i \neq j \neq k} \delta(g_{ii}g_{jk}) f_{ij}f_{ik} \\ & + 4 \sum_{i \neq j \neq k} \delta(g_{ij}g_{ik}) (f_{ij}f_{ik} + f_{ii}f_{jk}) \\ & \left. + 24 \sum_{i \neq j \neq k \neq l} \delta(g_{ij}g_{kl}) f_{ii}f_{kk} \right], \quad (13) \end{aligned}$$

where $\delta(g_{ij}g_{kl}) = g'_{ij}g'_{kl} - g_{ij}g_{kl}$. The summations in Eq. (13) run over all different values of the distinct subscripts as shown. Since hydrogen is always an end atom, δg_{ij} is zero except for adjacent, bend-related coordinates. The last term of Eq. (13) requires at least a 4×4 H matrix. It does not exist for triatomic molecules in the representation in internal coordinates. We shall neglect terms of the form f_{ij}^2 and $f_{ij}f_{ik}$ when $i \neq j$. The ratio of the "total effect" of a diagonal force constant element f_{ii} at low temperature to the high temperature limiting value, $W_1A_1(\hbar/kT)^2 f_{ii} \delta g_{ii}$, is then

$$1 - \frac{W_2(T)A_2(\hbar/kT)^2}{W_1(T)A_1} \left[\frac{f_{ii}^2 \delta g_{ii}^2 + 4f_{ii} \sum_{j \neq i} \delta(g_{ii}g_{ij}) f_{ij}}{f_{ii} \delta g_{ii}} \right]. \quad (14)$$

TABLE XV. "Total effects" at 300°K from off-diagonal force constants and coupling of internal coordinates.

Type of force constant	Isotopic pair					
	HDO-H ₂ O	HDCO-H ₂ CO	CH ₃ D-CH ₄	C ₂ H ₃ D-C ₂ H ₄	C ₂ H ₅ D-C ₂ H ₆	C ₆ H ₅ D-C ₆ H ₆
stretch-stretch	-2.04-04		5.59-04	-9.10-04	1.85-04	6.16-04
bend-bend			-1.20-03		3.07-03	
C=C stretch				7.88-03		-3.38-03
C-C stretch					2.31-03	9.48-03
C-C-C bend						2.54-02
stretch-bend	3.22-04	2.64-03	5.20-03	1.61-03	1.36-03	2.52-03

TABLE XIV. Calculated deuterium isotope exchange equilibria for C₁ and C₂ hydrocarbons: $RH + CH_3CH_2D = RD + CH_3CH_3$.

R	α_{298° HS ^a	α_{300° This paper
CH ₃	0.916	1.108 (JM) ^b 0.959 (HS) ^c
CH ₃ -CH ₂	1.000	1.000
CH ₂ =CH	0.924	0.968

^aReference 20.

^bJones-McDowell CH₄ F matrix.²⁰

^cHS CH₄ F matrix.¹²

It is immediately apparent that the "total effect" changes relative to the high temperature limiting value as T^{-2} and $f_{ii}(\delta g_{ii}^2/\delta g_{ii})$. Since diagonal force constants for stretching modes are some 10 times those of bending modes, the "total effect" for stretching force constants falls off relatively more rapidly with decreasing temperature than does the "total effect" for bending modes. Recall the absolute value of $\ln(s/s')f$ decreases with increase in temperature.

Since all the $(g'_{ij} - g_{ij})$ elements are zero for $i \neq j$ except for adjacent bending coordinates when isotopic substitution is at an end atom,²³ the contributions from off-diagonal F-matrix elements at high temperatures are a second-order correction to the contributions from diagonal elements. From the first term in Eq. (13) we see that $\ln(s/s')f$ will be strictly additive in the "total effects" from the different force constants at high temperatures. Terms of the type $\delta g_{ij} \sum g_{jk} f_{ij} f_{jk}$ in Eq. (13) as well as terms from δH^2 , δH^4 will introduce nonadditivity of the "total effects" of individual force constants to $\ln(s/s')f$ as one goes to lower temperatures. We use the notation $\delta H^j = (G'F)^j - (GF)^j$.

For all of the molecules studied we see that there is remarkable additivity of the individual force constant effects to give a total effect close to the absolute value even at 300°K. This is a special result for hydrogen-deuterium isotope effects. A similar result is naturally to be expected for tritium. It has three origins. First the masses of hydrogen isotopes are smaller than any atoms to which they are bonded in a molecule. Thus most of the kinetic energy of the vibration is in the hydrogen atom and there is little kinetic energy coupling. In the absence of kinetic energy coupling, the statistical mechanics of an assembly of oscillators is additive in the force constants.⁸ The F matrices themselves have small off-diagonal elements, which leads to small cou-

pling between the internal coordinates. Hydrogen appears in chemical compounds as a terminal atom, except for the interesting cases of hydrogen bonding. For a terminal atom, there is no isotope effect in the coupling between stretching and bending coordinates. Thus the internal coordinates become a good approximation to the normal coordinates for the calculation of $\ln(s/s')f$ for such systems. The consequences of this simplification have been presented previously.¹⁷

All the values of $\ln(s/s')f$ at 300 °K in Tables II–XIII lie in the range 2–2.5. The contributions of off-diagonal elements and from coupling of internal coordinates, not given in those tables, are given in Table XV for representative off-diagonal elements and those internal coordinates which do not involve motion of H(D). The effects are small as we have indicated. The contributions from coordinates such as C–C stretch in ethane or C–C–C bend in benzene come from the small coupling between internal coordinates.

Linear molecules have smaller values of $\ln(s/s')f$ than planar or nonplanar molecules. This is a consequence of the fact that bending forces are either absent (diatomic molecule) or smaller in linear molecules than in planar or nonplanar molecules. Thus Hartshorn and Shiner¹² find a preference of deuterium for ethane over acetylene by a factor of (1/0.735) at 25 °C. The latter arises primarily from the fact that there are two H–C≡C bends in acetylene with force constant 0.22 mdyne Å which have nonzero ($g'_{ii} - g_{ii}$), while in ethane there is one H–C–C bend with $f = 0.567$ mdyne Å and two H–C–H bends with $f = 0.491$ mdyne Å with nonzero ($g'_{ii} - g_{ii}$).²⁴

At low temperatures, e.g., 300 °K for deuterium substitution, the logarithm of the reduced partition function ratio is no longer linear in F -matrix elements. Effects from coupling of the internal coordinates, Boltzmann excitation factors, and the interplay of the zero-point energy term and the temperature independent classical term in Eq. (10), $\sum \ln(u_i/u'_i)$, become important. Nevertheless, the strong correlation between $\ln(s/s')f$ with the diagonal force constant persists. In Table XVI we compare $\ln(s/s')f$ (300 °K) for the molecules studied with $\sum f_{ii}(g'_{ii} - g_{ii})/0.496$. The factor 0.496 normalizes the δg_{ii} elements to that of hydrogen (H/D) bond stretch. The one to one correlation is evident even at 300 °K; however, small differences in $\ln(s/s')f$ values such as

TABLE XVI. Correlation of $\ln(s/s')f$ with $\sum f_{ii}(g'_{ii} - g_{ii})$ for monodeutero substitution.

Molecule	$\ln(s/s')f$ ^a 300 °K	$\sum f_{ii}(g'_{ii} - g_{ii})/$ 0.496 ^a
H ₂ O	2.583	9.22
CH ₄ (Jones–McDowell F matrix)	2.456	6.92
C ₆ H ₆ total	2.395	6.31
C ₂ H ₆	2.353	6.11
C ₂ H ₄	2.321	6.26
CH ₄ (Hartshorn–Shiner F matrix)	2.312	6.51
H ₂ CO	2.200	5.62
C ₆ H ₆ planar	2.144	5.93

^aThese are exact values from Tables II–XIII.

^bIn units of millidyne angstrom⁻¹ · atomic mass units⁻¹.

TABLE XVII. Contributions of stretching and bending forces to $\ln(s/s')f(D/H)$ at 300 °K.

Coordinate	CH ₂ O	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₆ H ₆
C–H stretch	1.478	1.600	1.556	1.675	1.632
f (mdyn Å ⁻¹)	(4.31)	(4.92)	(4.70)	(5.03)	(5.06)
HCH bend ^a	0.130(1)	0.631(3)	0.464(2)	0.355(1)	
HCH bend (p) ^b	0.352		0.289	0.202	0.572
HCH bend (op)	0.172			0.132	0.266
HCH bend (t)				0.100	
Σ "bend"	0.654	0.631	0.753	0.789	0.838
Total Σ	2.132	2.231	2.309	2.364	2.470
Exact	2.200	2.312	2.353	2.321	2.395

^aNumber in parentheses is the number of bending coordinates affected by the isotopic substitution.

^bp, planar; op, out-of-plane; t, torsion.

between ethylene and ethane become quite sensitive to the coupling in the internal coordinates. A discussion of these features goes beyond the scope of the present study.

It is of interest to compare the contributions of bending and stretching forces in a homologous series. This comparison is made in Table XVII, where we intercompare the H/D isotope effects for the molecules CH₂O, CH₄, C₂H₆, C₂H₄, and C₆H₆. We can readily see the one to one correspondence of the contribution of the C–H stretching force constant to $\ln(s/s')f$ with the magnitude of the C–H stretching force constant. In all cases the stretching force constant accounts for more than 65% of the isotope effect even at room temperature. There is also a close parallelism of the sum of the contributions of the bending force constants to $\ln(s/s')f$ with either the magnitude of the C–H stretching force constant or the sum of the bending force constants. It is well known that stretching and bending force constants in a molecule are correlated. Small deviations from an exact linear relationship between force constants and contribution to $\ln(s/s')f$ are associated with coupling effects, higher order terms, and geometrical effects in the case of some bending coordinates. The study of such questions requires a detailed analysis of contribution of each force constant, f_{ij} , to each of the terms $W_j A_j \sum_i^{3n-6} \delta u_i^{2j}$ in Eq. (2). These will be the subjects of future studies in this series.

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