product was recrystallized from ether/light petroleum to yield 4-bromo-2′,6′-dinitrobiphenyl as a yellow crystalline solid: mp 100–101 °C; λ_{max} (MeOH) 230 nm (log ϵ 4.43); NMR (acetone-d_6, Hz at 100 MHz referenced to $\nu_2 = 0$, protons numbered as in Figure 1) $\nu_1 = 33.39$, $\nu_2 = 0$, $\nu_5 = -63.09$, $\nu_7 = -30.45$; $J_{12} = 8.29$, $J_{13} = 0.42$, $J_{14}(J_{23}) = 2.23$, $J_{57} = 8.21$. Anal. ($C_{12}H_7BrN_2O_4$) C, H, Br, N.

4-Bromo-2′,6′-dinitrobiphenyl was reduced to the diamine using tin/hydrochloric acid.

4-Bromo-2′,6′-diiodobiphenyl (8) was prepared from the diazonium salt of the diamine using standard techniques and was purified and obtained as a colorless oil: λ_{max} (MeOH) 232 nm (log ϵ 4.44): *m/e* 484:486, calcd for $C_{12}H_7BrI_2$ 100.0:98.7, found 100:99. Anal. ($C_{12}H_7BrI$) C, H, Br, I.

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The Calculation of Isotopic Partition Functions Ratios by a Perturbation Theory Technique. 2. Dissection of the Isotope Effect

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Abstract: Statistical mechanical perturbation theory is applied to the evaluation of molecular partition functions and (reduced) isotopic partition function ratios $[(s_2/s_1)f]$ are calculated. The unperturbed vibrational problem corresponds to noninteracting stretches, bends, torsions, etc. It is demonstrated that an analysis of the unperturbed problem yields important insights into the magnitude of $(s_2/s_1)f$ values and into the isotope effects on chemical equilibria which can be calculated from these quantities. In such an analysis, one does not need to consider normal mode vibrational frequencies but one considers instead the frequencies corresponding to noninteracting individual coordinates. The contributions of the individual coordinates to $(s_2/s_1)f$ values and to isotope effects on equilibrium constants are presented.

Isotope effects on gas phase chemical equilibrium constants can be expressed in terms of ratios of isotopic molecular partition function ratios.[1,2] Consider, for example, the reactions

$$\mathrm{AH} + \mathrm{C} = \mathrm{BH} + \mathrm{E} \tag{1}$$

$$\mathrm{AD} + \mathrm{C} = \mathrm{BD} + \mathrm{E} \tag{2}$$

$$\mathrm{AH} + \mathrm{BD} = \mathrm{AD} + \mathrm{BH} \tag{3}$$

Here AD (BD) refers to a compound in which the deuterium isotope of hydrogen has been substituted for the protium isotope in AH (BH). The molecular species C and E are not isotopically substituted. Then

$$K_1/K_2 = K_3 = (Q_{\mathrm{AD}}/Q_{\mathrm{AH}})/(Q_{\mathrm{BD}}/Q_{\mathrm{BH}}) \tag{4}$$

where Q refers to molecular partition function. Calculations of such isotope effects are usually carried out within the framework of the Born–Oppenheimer approximation so that, for a given molecule in a given electronic state, the equilibrium molecular geometry and force constants for vibrational motion are independent of isotopic substitution.[3] It is usually adequate to consider only ground electronic states at room temperature. It can then be demonstrated that there are no isotope effects on chemical equilibria if the molecules are subject to classical mechanics (K_3[classical] = 1) or, equivalently, in the limit of infinite temperature for quantum mechanical molecules, except for the relevant symmetry number factors which are of little interest. Symmetry number factors will usually be dropped here. The interest is therefore in the reduced isotopic partition function ratio, the ratio of the quantum mechanical partition functions of two isotopic molecules divided by the corresponding ratio of partition functions calculated classically.

While corrections must be taken into account for very precise calculations,[4] isotopic partition function ratios for ideal gas phase molecules are usually evaluated by a model in which the nuclear motion degrees of freedom of an N atomic molecule are 3 classical translations, 3 classical rigid rotations (2 if the molecule is linear), and $3N - 6$ harmonic vibrations ($3N - 5$ for a linear molecule). Bigeleisen and Mayer[1] derived the expression for the reduced isotopic partition function ratio $(s_2/s_1)f$ corresponding to this model,

$$(s_2/s_1)f = \frac{(Q_2/Q_1)}{(Q_2/Q_1)[\mathrm{classical}]} = \frac{(Q_2/Q_1)_{\mathrm{vib}}}{(Q_2/Q_1)[\mathrm{classical}]_{\mathrm{vib}}} = \prod_{i}^{3N-6} \frac{u_{2i}}{u_{1i}} \frac{1 - e^{-u_{1i}}}{1 - e^{-u_{2i}}} e^{(u_{1i} - u_{2i})/2} \tag{5}$$

Here $u = h\nu/kT$; T is the absolute temperature; ν refers to harmonic normal mode vibrational frequency; h and k have their usual meanings. The subscripts 2 and 1 refer to the two isotopic molecules with 2 usually referring to the heavier molecule (e.g., $1 = H_2$, $2 = HD$). Then

$$K_3 = \frac{(s_2/s_1)f(\mathrm{AD/AH})}{(s_2/s_1)f(\mathrm{BD/BH})} \tag{6}$$

With a given harmonic force field (usually obtained from an analysis of spectroscopic data) for a given molecule and corresponding equilibrium geometry, it is straightforward to evaluate[5] by computer the normal mode vibrational frequencies of a pair of isotopically substituted molecules and $(s_2/s_1)f$. Methods of calculating $(s_2/s_1)f$ without evaluating normal mode vibrational frequencies are of interest because they can illuminate the nature of isotope effects. Thus Bigeleisen and Ishida[6] have expressed ln $(s_2/s_1)f$ in terms of sums of even powers of vibrational frequencies. These sums can be expressed directly in terms of harmonic force constants, atomic masses, and geometrical parameters of the molecules. Another method of calculating $(s_2/s_1)f$ was recently discussed by Singh and Wolfsberg,[7] in a publication hereafter referred to as paper 1.

Perturbation Theory

In paper 1, the vibrational Hamiltonian operator for a molecule was partitioned into an unperturbed part H_0 and a perturbed part H_1,

$$H = \tfrac{1}{2} \sum_{i,j=1}^{L} g_{ij} p_i p_j + \tfrac{1}{2} \sum_{i,j=1}^{L} f_{ij} q_i q_j \tag{7}$$

$$H_0 = \tfrac{1}{2} \sum_{i}^{L} g_{ii} p_i^2 + \tfrac{1}{2} \sum_{i}^{L} f_{ii} q_i^2 \tag{8}$$

$$H_1 = \sum_{i<j} g_{ij} p_i p_j + \sum_{i<j} f_{ij} q_i q_j \tag{9}$$

Here the q_i's are the L internal displacement coordinates describing the vibrational motion and the p_i's are the corresponding conjugate momenta. If the problem is set up with coordinates which do not have a redundancy,[7,8] L equals $3N - 6$ ($3N - 5$ for a linear molecule) for the N-atomic molecule. The f_{ij}'s are the harmonic force constants of the molecular force field (described by the **F** matrix) and the g_{ij}'s are the elements of Wilson's **G** matrix.[8] The f_{ij}'s are independent of isotopic substitution (within the framework of the Born–Oppenheimer approximation); the g_{ij}'s do depend on the masses of atoms in coordinates i and j and on isotope independent geometrical parameters. The internal displacement coordinates may be either valence force (vf) coordinates (e.g., stretches, bends, torsions) or symmetry (sym) coordinates which are linear combinations of vf coordinates (forming bases of irreducible representations of the point group of the undistorted molecule to which reference is made). In the present work, only vf coordinates will be employed. *When vf coordinates are used, the unperturbed Hamiltonian corresponds to uncoupled oscillators for stretches, bends, torsions, etc., each with a frequency given in terms of the corresponding force constant f_{ii} and reduced mass $(g_{ii})^{-1}$ by $\nu'_i = (2\pi)^{-1} \cdot (f_{ii}g_{ii})^{1/2}$.* One should note, however, that, in molecules with redundancy, the number of frequencies ν' exceeds the number of normal mode vibrational frequencies ν. Thus, in CH_3Cl the vf coordinates are four stretches and six bends so that there are ten frequencies ν'; however, CH_3Cl only has nine normal mode frequencies ν.

The reduced isotopic partition function ratio was evaluated in paper 1 by a perturbation technique. The unperturbed partition function ratio corresponds to the frequencies ν' and is given by

$$(s_2/s_1)f_0 = \prod_J \frac{V_{2J}}{V_{1J}} \frac{1 - e^{-V_{1J}}}{1 - e^{-V_{2J}}} e^{(V_{1J} - V_{2J})/2} = \prod_J c(J) \tag{10}$$

where $V_J = h\nu'_J/kT$. $(s_2/s_1)f_0$ is identical in form to eq 5 except that the normal mode frequencies have been replaced by the individual coordinate frequencies ν'. The product above is taken over these individual coordinates. Since much of the interest here will be in $(s_2/s_1)f_0$ and since $(s_2/s_1)f_0$ is written as a product of c factors, the properties of these c factors are of interest. Some of these properties are listed in Table I, to which further reference will be made later.

Table I. Some Properties of the c Factors

$$c(J) = \frac{V_{2J}}{V_{1J}} \frac{1 - e^{-V_{1J}}}{1 - e^{-V_{2J}}} e^{(V_{1J} - V_{2J})/2} = \frac{V_{2J}}{V_{1J}} \frac{\sinh (V_{1J}/2)^{a}}{\sinh (V_{2J}/2)}$$

Rule 1. $(g_{JJ})_1 \geq (g_{JJ})_2$ and $c(J) \geq$ unity
Rule 2. If $(g_{JJ})_1 = (g_{JJ})_2$, $c(J) =$ unity
Rule 3.[b] As T increases, $c(J)$ approaches unity
Rule 4.[b] As f_{JJ} is increased, $c(J)$ increases
Rule 5.[b] As $[(g_{JJ})_1 - (g_{JJ})_2]/(g_{JJ})_1$ is increased, $c(J)$ increases

[a] $V_{1J} = h\nu'_{1J}/kT$, $\nu'_{1J} = (2\pi)^{-1}(f_{JJ}(g_{JJ})_1)^{1/2}$, $V_{2J} = h\nu'_{2J}/kT$, $\nu'_{2J} = (2\pi)^{-1}(f_{JJ}(g_{JJ})_2)^{1/2}$. Note that, unless a specific statement is made to the contrary, the subscript 1 here refers to a coordinate in the molecule with all light atoms while the subscript 2 refers to the corresponding coordinate in the heavy isotopically substituted molecule (e.g., (water) $1 = H_2{}^{16}O$, (ethylene) $1 = {}^{12}C_2H_4$, etc.). [b] All parameters in $c(J)$ are constant, except the variation explicitly stated.

It was shown in paper 1 that there are no first-order perturbation corrections to $(s_2/s_1)f_0$. To second order in the perturbation, the following formula was obtained,

$$(s_2/s_1)f = (s_2/s_1)f_0 \times (\mathrm{CORR}) \tag{11}$$

where CORR is a correction factor which depends on the off-diagonal elements of the **F** and **G** matrices. The explicit formula for CORR is given in the Appendix.

In paper 1, evaluations of $(s_2/s_1)f$ with eq 5 and 11 were compared and explicit values of $(s_2/s_1)f_0$ and $(s_2/s_1)f_0 \times$ CORR were given for single and multiple isotopic substitutions in a number of representative molecules over a range of temperatures. Usually, the agreement between eq 5 and 11 improves with increasing temperature. However, already at room temperature the agreement was usually adequate (deviation less than 1.5% for most single D/H substitutions).

In this paper, the contributions to $(s_2/s_1)f_0$ and to CORR will be further dissected for systems studied in paper 1. The emphasis will be on studying the contributions of the individual c factors (eq 10) to $(s_2/s_1)f_0$ and on showing the utility of using these c factors in the interpretation of isotope effects. The individual c factors can be said to be the contributions of the individual coordinates to $(s_2/s_1)f$. Similarly the contribution of each $(\mathrm{CORR})_{ij}$ $(i \neq j)$ to CORR (in the Appendix) can be said to be the contribution of that particular interaction to $(s_2/s_1)f$ although $(\mathrm{CORR})_{ij}$ also depends on f_{ii}, g_{ii}, f_{jj}, and g_{jj}. As pointed out in the Appendix, $(\mathrm{CORR})_{ij}$ can be further dissected into $(\mathrm{CORR\text{-}G})_{ij}$, $(\mathrm{CORR\text{-}F})_{ij}$, and $(\mathrm{CORR\text{-}FG})_{ij}$. While the dissection of CORR has been carried out for all the cases presented in the following section, this dissection has not been found to be very useful at present; presentation and discussion of the dissection is deferred to the future. CORR will, however, be compared with CORR-G (CORR evaluated with all f_{ij} set equal to zero) and CORR-F (CORR evaluated with all g_{ij} set equal to zero). The dissections in this paper are based on given equilibrium molecular geometries and molecular force fields which have been deduced by other workers from spectroscopic data, as indicated. For some molecules, different workers have deduced different geometries and force fields. Since the emphasis of the present paper is the demonstration of the utility of the perturbation approach, discussion of how

Table II. Perturbation Theory Results for D/H Substitution in Water and Ammonia[a]

	HDO/H_2O	$(HDO/H_2O)_{2000K}$	D_2O/H_2O	NH_2D/NH_3	NHD_2/NH_3	ND_3/NH_3
$(s_2/s_1)f$ eq 5	13.48	1.166	188.6	13.92	199.5	2944
$(s_2/s_1)f$ eq 11	13.48	1.166	188.6	13.90	198.7	2923
$(s_2/s_1)f_0$	13.45	1.166	187.7	13.89	198.6	2919
c(M-D)	9.350	1.150	$(9.350)^2$	7.422	$(7.422)^2$	$(7.422)^3$
c(H-M-D)	1.439	1.014		$(1.368)^2$	$(1.368)^2$	
c(D-M-D)			2.146		1.926	$(1.926)^3$
CORR	1.002	1.000	1.005	1.000	1.001	1.001
CORR-G	1.002	1.000	1.004	0.998	0.995	0.991
CORR-F	0.997	1.000	0.994	0.984	0.969	0.954

[a] $T = 298.16$ K except in column 3 where T is explicitly indicated as 2000 K.

Table III. Diagonal Force Constants (in mdyn/Å) and Relevant Geometrical Data.[a]

Molecule	f(M-H)	f(M-M)	f(H-M-H)/ $R(\text{M-H})^2$	f(H-M-M)/ $R(\text{M-H})^2$	f(M-M-M)/ $R(\text{M-M})^2$	f(torsion)/ $R(\text{M-H})^2$
H_2O[b]	8.45 (2)[n]		0.761 (2)			
NH_3[c]	7.05 (3)		0.616 (3)			
CO_2[d]		15.5 (2)			0.570 (2)	
C_2H_6[e]	4.81 (6)	4.44 (1)	0.481 (6)	0.501 (6)		0.0223 (1)
C_3H_8[f]	4.71 (6)	4.33 (2)	0.446 (2)	0.529 (4)	0.506 (1)	0.0211 (2)
	[4.78] (2)		0.447 (4)	0.551 (2)		
			[0.451] (1)	[0.571] (4)		
c-C_3H_6[g]	5.13 (6)	4.16 (3)		0.724 (12)		
C_2H_4[h]	5.11 (4)	9.50 (1)	0.571 (2)			0.228 (1)
CH_3F[i]	5.38 (3)	5.79 (1)	0.492 (3)	0.716 (3)		
CH_3Cl[j]	5.50 (3)	3.42 (1)	0.485 (3)	0.589 (3)		
CH_3Br[k]	5.50 (3)	2.90 (1)	0.476 (3)	0.521 (3)		
CH_3I[l]	5.57 (3)	2.34 (1)	0.472 (3)	0.466 (3)		
CH_4[m]	5.50 (4)		0.472 (6)			

[a] The force fields have been discussed in ref 7; references to the original literature are given there. For bending force constants, the entries in the table refer to the force constants divided by the square of an appropriate equilibrium internuclear distance (R^2) as indicated; the dimensions of these entries are then the same as those for stretching force constants. When comparing magnitudes of bending force constants with those of stretching force constants, and also with each other, one usually compares bending force constants divided by R^2 because of the structure of the elements of the **G** matrix (see Table IV). Contrary to the statement in ref 7, the carbon dioxide force constants were obtained by fitting calculated harmonic frequencies to observed fundamentals. Torsional force constants are listed to show magnitudes; complete specification of torsions requires more information than given here. In the subsequent footnotes, the statement "no redundancy" means that the number of internal coordinates (stretches, bends, etc.) equals the number of normal mode vibrational frequencies, while the statement "redundancy" means that the number of internal coordinates exceeds the number of normal mode vibrational frequencies. The geometries in the subsequent footnotes refer to the equilibrium geometries. [b] H_2O: no redundancy; geometry, $R(\text{OH}) = 0.957$ Å, $\angle\text{HOH} = 105°$. [c] NH_3: no redundancy; geometry, $R(\text{NH}) = 1.01$ Å, $\angle\text{HNH} = 107°$. [d] CO_2: no redundancy; geometry, $R(\text{CO}) = 1.16$ Å, linear molecule. [e] C_2H_6: redundancy; staggered geometry, $R(\text{CH}) = 1.10$ Å, $R(\text{CC}) = 1.53$ Å, angles are tetrahedral; force field II of ref 7 was used. [f] C_3H_8: redundancy; staggered geometry, there are two different types of hydrogens on each methyl group; this fact gives rise to two values of f(HMH) and two values of f(HMM) in the methyl group; force constants referring to the methylene group are given in brackets, $R(\text{CH}) = 1.09$ Å [1.10 Å], $R(\text{CC}) = 1.53$ Å, angles are tetrahedral. [g] c-C_3H_6; no redundancy; geometry, $R(\text{CH}) = 1.09$ Å, $R(\text{CC}) = 1.51$ Å, $\angle\text{CCC} = 60°$, $\angle\text{CCH} = 114°$. [h] C_2H_4: no redundancy; planar geometry, $R(\text{CH}) = 1.09$ Å, $R(\text{CC}) = 1.34$ Å, $\angle\text{HCH} = 117°$. In addition to the coordinates listed in the table, ethylene has two in-plane wags with force constants 1.08 mdyn/Å and two out-of-plane wags with force constants of 0.256 mdyn/Å. Complete specification of these wags requires further information which will not be given here. [i] CH_3F: redundancy; geometry, $R(\text{CH}) = 1.09$ Å, $R(\text{CF}) = 1.39$ Å, $\angle\text{HCH} = 110°$; $f(\text{H-M-M})/R(\text{M-H})^2 = f(\text{H-C-F})/R(\text{C-H})^2$. [j] CH_3Cl: redundancy; geometry, $R(\text{CH}) = 1.09$ Å, $R(\text{CCl}) = 1.78$ Å, $\angle\text{HCH} = 111°$; force field II of ref 7 was used. [k] CH_3Br: redundancy; geometry, $R(\text{CH}) = 1.09$ Å, $R(\text{CBr}) = 1.94$ Å, $\angle\text{HCH} = 111°$. [l] CH_3I: redundancy; geometry, $R(\text{CH}) = 1.09$ Å, $R(\text{CI}) = 2.14$ Å, $\angle\text{HCH} = 111°$. [m] CH_4: redundancy; geometry, $R(\text{CH}) = 1.09$ Å, angles are tetrahedral. [n] All numerical data have been rounded to three significant figures. The numbers in parentheses indicate the number of coordinates corresponding to the force constant.

these different geometries and force fields affect the dissections is deferred to the future.

Bigeleisen, Ishida, and Hom[9] recently have dissected contributions to $(s_2/s_1)f$ by a procedure which involves many solutions of the normal mode vibrational problem for each molecule. They find the contribution to $(s_2/s_1)f$ from a given force constant by setting that force constant equal to zero, then computing the exact value of $(s_2/s_1)f$ for this model, and finally comparing this result with that obtained when the relevant force constant has its actual molecular value; for some force constants it is necessary to employ extrapolation procedures which require the solution of even more normal mode vibrational problems. The Bigeleisen–Ishida procedure represents an alternate way of dissecting $(s_2/s_1)f$ although it does not give some of the insight given by the perturbation approach. While the perturbation approach here and the Bigeleisen–Ishida approach are different ways of dissecting $(s_2/s_1)f$, the results can be compared. In most (but not all) cases where comparison has been made the results are similar; these comparisons will be discussed in a separate publication.

Calculations

In Table II, results of D for H substitutions in water and ammonia are shown. Except for the third column which is explicitly labeled as 2000 K, the results here (as in most other tables) refer to a temperature of 298.16 K. The vf coordinates used here are two OH stretches and one HOH bend in H_2O and three NH stretches and three HNH bends in NH_3. The exact values of $(s_2/s_1)f$ agree well with the perturbation theory values and the latter agree well with $(s_2/s_1)f_0$ since CORR is very close to unity in all cases. $(s_2/s_1)f_0$ is a product of c contributions [eq 10] from the individual internal coordinates and these are listed as M–D for the stretching coordinates, H–M–D for the bending coordinates which are singly substituted in the deuterated compound, and D–M–D for the bending coordinates which are doubly substituted in the deuterated compound. Coordinates which are not isotopically substituted between the two members of a molecule pair correspond to the same values of g_{JJ} in both molecules and consequently c for that coordinate equals unity (Rule 2, Table I). Such c values are not listed in the tables so that the c value for only one oxygen–hydrogen stretching coordinate is listed for the pair HDO/H_2O while for D_2O/H_2O two such c values are included (indicated by the exponent 2 in the table). Similarly for the pair NH_2D/NH_3 one nitrogen–hydrogen stretching coordinate and two bends are listed. From Rule 1 in Table I, the c values are equal to or larger than unity. Since $(s_2/s_1)f$ is given as a product of c factors and of CORR and since an exchange equilibrium constant like K_3 is given as the ratio of $(s_2/s_1)f$ values, the interest here is really in the deviation from unity (DU) of the various factors. Thus when DU of a c factor is zero, this c factor does not contribute to the isotope effect. When DU of K_3 is zero, there is no isotope effect.

The diagonal force constants for stretching and bending coordinates and relevant equilibrium geometrical parameters for water and ammonia are listed in Table III. The details of the calculation of c factors for HDO/H_2O are given in Table IV, as well as general formulas for diagonal G matrix elements for stretches and bends, in order to demonstrate how easy it is to calculate these factors. Note again that the ν' are not normal mode vibrational frequencies but are respectively frequencies for isolated stretching and isolated bending coordinates.

A comparison of c values at 298.16 and 2000 K for HDO/H_2O in Table II demonstrates Rule 3 of Table I. The relative magnitudes of c(O–D) and c(N–D) for HDO/H_2O and NH_3D/NH_3 in Table II reflect the decrease of the stretching force constant from water to ammonia (see Table III and Rule 4, Table I); the stretch G matrix elements are almost the same in water and ammonia. The relative magnitudes of c(H–O–D) and c(O–D) in HDO/H_2O reflect not only the fact that the bending force constant is smaller than the stretching force constant (Rule 4, Table I) but also that the diagonal G matrix element for the stretch is proportionally more sensitive to D/H substitution than is that for the bend (Rule 5, Table I). In the cases here, as in subsequent tables, the largest contribution to $(s_2/s_1)f_0$ arises from c(stretch). The relative magnitudes for c(H–M–D) in HDO/H_2O and NH_2D/NH_3 reflect the lower bending force constant in ammonia (Rule 4, Table I).

It follows from Table II that the square of c(H–O–D) for HDO/H_2O is less than c(D–O–D) for D_2O/H_2O. This is most easily understood by comparing c(H–O–D) with c(D–O–D)/c(H–O–D). The latter fraction is just c(bend) for D_2O/HDO. For the bending coordinate, it follows from Table IV that $g(H_2O) - g(HDO) = g(HDO) - g(D_2O) > 0$. Thus it follows from Rule 5, Table I, that c(bend) for D_2O/HDO must be larger than c(H–O–D) for HDO/H_2O.

The equilibrium constant for the self-exchange equilibrium

$$H_2O + D_2O = 2HDO \tag{12}$$

$$K = \frac{[(s_2/s_1)f(HDO/H_2O)]^2}{(s_2/s_1)f(D_2O/H_2O)} \tag{13}$$

is exactly evaluated through eq 5 at 298.16 K

$$K = (13.48)^2/188.6 = 0.963 \tag{14}$$

Table IV

A. Diagonal **G** Matrix Elements

(a) Stretch between atoms A and B with masses m_A, m_B

$$g(\text{stretch}) = \frac{1}{m_A} + \frac{1}{m_B}$$

(b) Bend of angle A–B–C with R(AB) the equilibrium separation of A and B and α the equilibrium angle A–B–C

$$g(\text{bend}) = \left(\frac{1}{m_A} + \frac{1}{m_B}\right)\frac{1}{R(AB)^2} + \left(\frac{1}{m_B} + \frac{1}{m_C}\right)\frac{1}{R(BC)^2} - \frac{2}{m_B}\frac{\cos\alpha}{R(AB)R(BC)}$$

B. Calculation of c Factors for HDO/H_2O (T = 298.16 K)

$$\nu' = (f_{ii}g_{ii}/5.89141 \times 10^{-7})^{1/2}$$

with units: ν' (cm^{-1}), f_{ii} (mdyn/Å), g_{ii} (inverse amu)

$$V = h\nu'/kT = 1.4387\nu'/T$$

(a) $c(\text{stretch}) = c(\text{O–D})$

$$\nu'(\text{O–H}) = \left[8.454 \times \left(\frac{1}{15.9994} + \frac{1}{1.00782}\right) \Big/ 5.89141 \times 10^{-7}\right]^{1/2} = 3890.40\ \text{cm}^{-1}$$

$$\nu'(\text{O–D}) = \left[8.454 \times \left(\frac{1}{15.9994} + \frac{1}{2.0140}\right) \Big/ 5.89141 \times 10^{-7}\right]^{1/2} = 2832.29\ \text{cm}^{-1}$$

$$V_1 = V(\text{O–H}) = 1.4387 \times 3890.40/298.16 = 18.7722$$

$$V_2 = V(\text{O–D}) = 1.4387 \times 2832.29/298.16 = 13.6665$$

$$c(\text{O–D}) = \frac{V_2}{V_1}\frac{1 - e^{-V_1}}{1 - e^{-V_2}}e^{(V_1 - V_2)/2} = 9.350$$

(b) $c(\text{bend}) = c(\text{H–O–D})$

$$\nu'(\text{H–O–H}) = 1662.93\ \text{cm}^{-1}$$

$$\nu'(\text{H–O–D}) = 1457.74\ \text{cm}^{-1}$$

$$c(\text{H–O–D}) = 1.439$$

Note that, if symmetry numbers were taken into account, the above value is really the value for $K/4$. From the perturbation theory approach

$$K = \frac{[(s_2/s_1)f_0(HDO/H_2O) \times \text{CORR}(HDO/H_2O)]^2}{(s_2/s_1)f_0(D_2O/H_2O) \times \text{CORR}(D_2O/H_2O)}$$
$$= \frac{c^2(\text{O–D})}{c^2(\text{O–D})} \times \frac{c^2(\text{H–O–D})}{c(\text{D–O–D})} \times \frac{\text{CORR}(HDO/H_2O)^2}{\text{CORR}(D_2O/H_2O)}$$
$$= 1 \times \frac{(1.439)^2}{2.146} \times \frac{(1.002)^2}{1.005}$$
$$\simeq (1.439)^2/2.146 = 0.965 \tag{15}$$

Thus K is almost entirely given by the ratio of the appropriate c factors for the bending coordinate and DU of K depends on the previously discussed deviation of the ratio c^2(H–O–D)/c(D–O–D) from unity. The precise value of the deviation depends on the value of the bending force constant in water; the deviation would be zero for vanishing force constant and increases monotonically with increasing magnitude of the force constant. Thus the value of K is determined by the bending force constant. This fact has been previously noted on the basis of model calculations for this reaction.[10] A similar conclusion has been reached by Ishida and Bigeleisen[11] in their elegant study based on the expansion of the reduced partition function ratio in sums of even powers of the vibrational frequencies. It should be pointed out that it has only been demonstrated here

Table V. Perturbation Theory Results for Heavy-Atom Substitution[a]

	$H_2{}^{18}O/H_2{}^{16}O$	$(H_2{}^{18}O/H_2{}^{16}O)_{2000K}$	$C^{18}O^{16}O/C^{16}O_2$	$^{13}CO_2/^{12}CO_2$	$^{15}NH_3/^{14}NH_3$
$(s_2/s_1)f$, eq 5	1.0669	1.0041	1.1162	1.1904	1.0675
$(s_2/s_1)f$, eq 11	1.0670	1.0041	1.1147	1.1945	1.0680
$(s_2/s_1)f_0$	1.0701	1.0043	1.1063	1.2305	1.0761
c(stretch)	$(1.0281)^2$	$(1.0019)^2$	1.0939	$(1.0864)^2$	$(1.0171)^3$
c(bend)	1.0124	1.0005	$(1.0057)^2$	$(1.0211)^2$	$(1.0075)^3$
CORR	0.9972	0.9998	1.0076	0.9708	0.9925
CORR-G	0.9993	1.0000	1.0063	0.9772	0.9987
CORR-F	0.9999	1.0000	0.9999	0.9998	0.9995

[a] $T = 298.16$ K except in column 3 where T is explicitly indicated as 2000 K.

that the CORR terms as a whole make negligible contribution to the value of the equilibrium constant; if the individual $(\mathrm{CORR})_{ij}$ had been included in Table II, it would have been demonstrated that the individual terms also make negligible contribution.

The self-exchange equilibria among the deuterated ammonias (e.g., $NH_3 + NHD_2 = 2NH_2D$) could be similarly discussed on the basis of Table II and the DU of K depends on $c^2(\text{H-N-D})/c(\text{D-N-D})$.

The equilibrium constant for

$$NH_3 + HDO = NH_2D + H_2O \tag{16}$$

is given by

$$K = (s_2/s_1)f(NH_2D/NH_3)/(s_2/s_1)f(HDO/H_2O) \tag{17}$$

From eq 5 and Table II, at 298.16 K,

$$K = 13.92/13.48 = 1.033 \tag{18}$$

From the perturbation theory, with omission of contributions from CORR,

$$K = \frac{c(\text{N-D})c^2(\text{H-N-D})}{c(\text{O-D})c(\text{H-O-D})} = \frac{7.422(1.368)^2}{9.350\ 1.439} = 1.032 \tag{19}$$

Thus, the fact that the equilibrium constant is quite close to unity is a consequence of two competing factors: the contribution of the stretches tends to give a value smaller than unity while the two isotopically substituted bends in NH_2D, compared to the one substituted bend in HDO, give an effect in the opposite direction.

The two examples of analysis of isotopic exchange equilibrium constants in terms of the perturbation method demonstrate how one can use the c factors for individual coordinates to dissect the over-all isotope effect. In cases where CORR factors are more important than in the instances discussed so far, one would have to multiply the c factor result by a CORR factor result which differs from unity.

An analysis of some heavy-atom isotopic substitution $(s_2/s_1)f$ values is presented in Table V. DU of CORR relative to DU of $(s_2/s_1)f$ tends to be larger for these heavy-atom effects than for the cases in Table II. The relatively large DU of CORR for $^{13}CO_2/^{12}CO_2$ follows from the large value of the g_{ij} interaction **G** matrix element between the two stretches and the large isotope effect thereon for central atom isotopic substitution in a linear molecule. To the extent that CORR deviates from unity, CORR-G reproduces the value of CORR more closely than does CORR-F.

The c factors will not be analyzed extensively although such an analysis could be carried out by using the rules in Table I, the force constants in Table III, and the expressions for the **G** matrix elements in Table IV. Carbon dioxide has two stretching coordinates and two perpendicular bending coordinates. It is noted that the DU of c(bend) for $^{13}CO_2/^{12}CO_2$ is considerably larger than that for $C^{18}O^{16}O/C^{16}O_2$ in spite of the fact that the oxygen isotopic substitution involves a change of two atomic mass units. This result arises from the structure of the diagonal **G** matrix element for g(bend), Table IV, which leads to a relatively much larger isotope effect for central atom isotopic substitution in a linear molecule.

The diagonal **G** matrix element for the stretch A-B is $(m_A)^{-1} + (m_B)^{-1}$ from Table IV. Thus $(g_1 - g_2)/g_1$ for $^{18}O/^{16}O$ substitution is much larger for a CO stretch than an OH stretch; c(stretch) is larger in Table V for ^{18}O substitution in carbon dioxide than in water because of Rule 5, Table I, and also because the C-O force constant (Table III) is larger than the O-H force constant (Rule 4, Table I).

The equilibrium constant for

$$C^{16}O_2 + H_2{}^{18}O = C^{18}O^{16}O + H_2{}^{16}O \tag{20}$$

at 298.16 K is, from eq 5,

$$K = \frac{(s_2/s_1)f(C^{18}O^{16}O/C^{16}O_2)}{(s_2/s_1)f(H_2{}^{18}O/H_2{}^{16}O)} = \frac{1.1162}{1.0669} = 1.046 \tag{21}$$

From the perturbation theory, one obtains

$$\begin{aligned} K &= K_{\text{stretch}} \times K_{\text{bend}} \times K_{\text{CORR}} \\ &= \frac{1.094}{(1.028)^2} \times \frac{(1.006)^2}{(1.012)} \times \frac{1.008}{0.997} \\ &= 1.035 \times 0.999 \times 1.011 = 1.045 \end{aligned} \tag{22}$$

Thus, the major contribution to DU of K arises from the stretching coordinates.

In Table VI, results are presented for a number of single D for H substitutions in hydrocarbons. In addition to stretching and bending coordinates, internal coordinates which describe the vibrational motions of these molecules include one or more torsions for most of these molecules; for ethylene there are also in-plane wagging and out-of-plane wagging coordinates (see Table III). The diagonal force constants and geometrical parameters are given in Table III. The agreement between $(s_2/s_1)f$ values calculated by eq 5 and by eq 11 is quite good. However, the small difference between an exact calculation of $(s_2/s_1)f$ and a perturbation theory calculation can lead to a relatively large error in DU of an equilibrium constant when this DU is very small. Thus one obtains

$$C_2H_6 + CH_2DC_2H_5 = C_2H_5D + C_3H_8 \tag{23}$$

$$\begin{aligned} K &= (s_2/s_1)f(C_2H_5D/C_2H_6)/(s_2/s_1)f(CH_2DC_2H_5/C_3H_8) \\ &= 11.22/10.93 = 1.027 \quad \text{(from eq 5)} \\ &= 11.16/11.04 = 1.011 \quad \text{(from eq 11)} \end{aligned} \tag{24}$$

The CORR factors for these molecules show larger deviations from unity than those in Table II. Except for cyclopropane, CORR is "reasonably" well reproduced by CORR-G.

As an example of the application of the data in Table VI, consider

$$C_3H_8 + C_2H_3D = (CH_3)_2CHD + C_2H_4 \tag{25}$$

Table VI. Perturbation Theory Results for D/H Substitution in Ethane, Propane, Cyclopropane, and Ethylene (T = 298.16 K)

	C_2H_5D/C_2H_6	$CH_2DC_2H_5/C_3H_8$[a]	$(CH_3)_2CHD/C_3H_8$	$c\text{-}C_3H_5D/c\text{-}C_3H_6$	C_2H_3D/C_2H_4
$(s_2/s_1)f$, eq 5	11.22	10.93	12.20	11.55	10.38
$(s_2/s_1)f$, eq 11	11.16	11.04	12.26	11.71	10.38
$(s_2/s_1)f_0$	11.48	11.23	12.92	12.25	10.04
c(C-D)	4.907	4.813	4.881	5.227	5.201
c(H-C-D)	$(1.299)^2$	$(1.281)^2$	1.284		1.342
c(D-C-C)	1.377	1.412	$(1.427)^2$	$(1.531)^2$	
c(ip wag)[b]					1.151
c(op wag)[c]					1.135
c(torsion)	1.007	1.006	$(1.006)^2$		1.101
CORR	0.972	0.983	0.949	0.955	1.033
CORR-G	0.982	0.984	0.970	1.004	1.033
CORR-F	0.985	0.998	0.977	0.972	0.998

[a] The isotopically substituted atom is the unique hydrogen in the methyl group. See Table III. [b] In-plane wag in ethylene. [c] Out-of-plane wag in ethylene.

Table VII. Perturbation Theory Results for $^{13}C/^{12}C$ Substitution in Ethane, Propane, Cyclopropane, and Ethylene (T = 298.16 K)[d]

	$^{13}CCH_6/C_2H_6$	$^{13}CH_3CH_2CH_3/C_3H_8$	$CH_3{}^{13}CH_2CH_3/C_3H_8$	$c\text{-}^{13}CC_2H_6/c\text{-}C_3H_6$	$^{13}CCH_4/C_2H_4$
$(s_2/s_1)f$, eq 5	1.1366	1.1411	1.1483	1.1353	1.1351
$(s_2/s_1)f$, eq 11	1.1354	1.1400	1.1461	1.1314	1.1350
$(s_2/s_1)f_0$	1.1557	1.1577	1.1867	1.1695	1.1479
$c(^{13}C\text{-}C)$	1.0340	1.0334	$(1.0334)^2$	$(1.0324)^2$	1.0591
$c(^{13}C\text{-}H)$	$(1.0186)^3$	$(1.0183)^3$	$(1.0185)^2$	$(1.0193)^2$	$(1.0192)^2$
$c(H\text{-}^{13}C\text{-}H)$	$(1.0088)^3$	$(1.0083)^3$	1.0084		1.0108
$c(H\text{-}^{13}C\text{-}C)$[a]	$(1.0079)^3$	$(1.0082),^2$ 1.0085	$(1.0088)^4$	$(1.0110)^4$	
$c(H\text{-}C\text{-}^{13}C)$[b]	$(1.0020)^3$	$(1.0023)^2$	$(1.0021),^4$ $(10022)^2$	$(1.0027)^4$	
$c(^{13}C\text{-}C\text{-}C)$		1.0048			
$c(C\text{-}^{13}C\text{-}C)$			1.0128		
c(ip wag)[c]					1.0128
c(ip wag′)[c]					1.0047
c(op wag)[c]					1.0132
c(op wag′)[c]					1.0012
CORR	0.9824	0.9846	0.9657	0.9675	0.9888
CORR-G	0.9894	0.9888	0.9819	0.9842	0.9918
CORR-F	0.9984	0.9986	0.9967	0.9972	0.9996

[a] In $^{13}CH_3CH_2CH_3$ there are two types of $H\text{-}^{13}C\text{-}C$ bending coordinates, two of one type and one of another. See also Table III. [b] In $CH_3{}^{13}CH_2CH_3$ there are two types of $H\text{-}C\text{-}^{13}C$ bending coordinates, four of one type and two of another. See also Table III. [c] There are two wags of each type which are affected by the isotopic substitution in ethylene (ip = in plane; op = out of plane). [d] Note that C without a superscript is carbon-12.

From eq 5, K = 12.20/10.38 = 1.18. From perturbation theory,

$$K = \frac{(s_2/s_1)f_0[(CH_3)_2CHD/C_3H_8]}{(s_2/s_1)f_0(C_2H_3D/C_2H_4)} \times \frac{\mathrm{CORR}[(CH_3)_2CHD/C_3H_8]}{\mathrm{CORR}(C_2H_3D/C_2H_4)}$$
$$= \frac{c(\mathrm{C\text{-}D})}{c(\mathrm{C\text{-}D})} \times \frac{c(\mathrm{H\text{-}C\text{-}D})}{c(\mathrm{H\text{-}C\text{-}D})} \times \frac{c^2(\mathrm{D\text{-}C\text{-}C})}{c(\text{in-plane wag})c(\text{out-of-plane wag})} \times \frac{c^2(\mathrm{torsion})}{c(\mathrm{torsion})} \times \frac{\mathrm{CORR}[(CH_3)_2CHD/C_3H_8]}{\mathrm{CORR}(C_2H_3D/C_2H_4)}$$
$$= \frac{4.881}{5.201} \times \frac{1.284}{1.342} \times \frac{(1.427)^2}{(1.151)(1.135)} \times \frac{(1.006)^2}{1.101} \times \frac{0.949}{1.033}$$
$$= 0.94 \times 0.96 \times 1.56 \times 0.92 \times 0.92 = 1.18 \qquad (26)$$

Note that quantities in the numerators refer to propane while denominators refer to ethylene even when this is not explicitly stated. The direction of DU is determined by the large value of c for the two D-C-C bends in propane compared to the smaller c values of the two wags in ethylene. The relative magnitudes of these c values could be discussed in terms of force constants and **G** matrix elements on the basis of the rules of Table I as were the magnitudes of c values in Table II.

Another example of the application of perturbation theory is provided by the comparison of deuterium substitution in the methyl and the methylene group of propane through the equilibrium

$$CH_2DC_2H_5 = (CH_3)_2CHD \qquad (27)$$

For this equilibrium

$$K = \frac{(s_2/s_1)f[(CH_3)_2CHD/C_3H_8]}{(s_2/s_1)f(CH_2DC_2H_5/C_3H_8)}$$
$$= 12.20/10.93 = 1.12 \text{ (from eq 5)} \qquad (28)$$

From perturbation theory,

$$K = \frac{c(\mathrm{C\text{-}D})}{c(\mathrm{C\text{-}D})} \times \frac{c(\mathrm{H\text{-}C\text{-}D})}{c^2(\mathrm{H\text{-}C\text{-}D})} \times \frac{c^2(\mathrm{D\text{-}C\text{-}C})}{c(\mathrm{D\text{-}C\text{-}C})} \times \frac{c^2(\mathrm{torsion})}{c(\mathrm{torsion})} \times \frac{\mathrm{CORR}[(CH_3)_2CHD/C_3H_8]}{\mathrm{CORR}(CH_2DC_2H_5/C_3H_8)}$$
$$= \frac{4.881}{4.813} \times \frac{1.284}{(1.281)^2} \times \frac{(1.427)^2}{1.412} \times \frac{(1.006)^2}{1.006} \times \frac{0.949}{0.983}$$
$$= 1.01 \times 0.78 \times 1.44 \times 1.01 \times 0.97 = 1.11 \qquad (29)$$

Table VIII. Perturbation Theory Results for D/H Substitution in CH_3X Compounds (T = 298.16 K)

	CH_2DCl/CH_3Cl	CH_2DF/CH_3F	CH_2DBr/CH_3Br	CH_2DI/CH_3I	CH_2DH/CH_3H	CH_2DD/CH_3D
$(s_2/s_1)f$, eq 5	13.38	13.89	12.86	12.63	11.85	12.09
$(s_2/s_1)f$, eq 11	13.48	13.97	12.95	12.72	12.06	12.29
$(s_2/s_1)f_0$	13.70	14.22	13.14	12.89	12.13	12.38
c(C-D)	5.603	5.476	5.599	5.668	5.596	5.596
c(D-C-H)	$(1.301)^2$	$(1.304)^2$	$(1.296)^2$	$(1.294)^2$	$(1.294)^2$	$(1.294)^2$
c(D-C-X)	1.445	1.527	1.398	1.359	1.294	1.321
CORR	0.984	0.983	0.986	0.987	0.995	0.993
CORR-G	0.978	0.979	0.979	0.980	0.988	0.985
CORR-F	0.996	0.994	0.996	0.996	0.996	0.996

Numerators refer to methylene substitution and denominators to methyl substitution. It is to be noted that c(C-D), c(H-C-D), c(D-C-C) are almost the same for methyl and methylene substitution; this result reflects the fact that geometries and bond distances are almost the same in methyl and methylene groups here and that the relevant force constants also are very similar in these groups (Table III). c(torsion) is also almost the same in both cases except that there are two torsions for the methylene group and only one for the methyl group. It is seen that the major difference between $(CH_3)_2CHD$ and $CH_2DC_2H_5$ arises from the fact that a D-C-C coordinate in the methylene-substituted compound is replaced by a H-C-D coordinate in the methyl-substituted compound. Thus K is closely approximated by c(D-C-C)/c(H-C-D) = 1.42/1.28. The relative magnitudes of these two c factors follow from Rules 4 and 5 of Table I.

In Table VII, data are presented for single ^{13}C for ^{12}C substitutions in the molecules which were discussed in Table VI. One notes that $c(^{13}C\text{-}C)$ is approximately the same for all the molecules except for the doubly bonded molecule ethylene; this result of course just reflects the force constants. Similar statements can be made about $c(^{13}C\text{-}H)$, $c(H\text{-}^{13}C\text{-}H)$, $c(H\text{-}^{13}C\text{-}C)$, and $c(H\text{-}C\text{-}^{13}C)$. For these molecules, DU of c(torsion) either equals zero or is insignificant. The range of variation of $(s_2/s_1)f$ values is quite small in Table VII. $(s_2/s_1)f$ for $^{13}CO_2/^{12}CO_2$ in Table V is considerably larger and it is seen that this results from the high value of $c(^{13}C\text{-}O)$ relative to $c(^{13}C\text{-}C)$. These c values are explainable in terms of the relatively large C-O stretching force constant in CO_2 (Table III). The DU of CORR values for the heavy-atom isotope effects relative to the DU of $(s_2/s_1)f$ values is again seen to be much larger than for the corresponding D/H effects. CORR values are usually reasonably reproduced by CORR-G values.

The data in Table VIII on CH_2DX/CH_3X may be used to study the equilibria

$$CH_3Cl + CH_2DX = CH_2DCl + CH_3X \qquad (30)$$

$$K = \frac{(s_2/s_1)f(CH_2DCl/CH_3Cl)}{(s_2/s_1)f(CH_2DX/CH_3X)} \qquad (31)$$

Table IX demonstrates that the exact K values are quite well reproduced by the perturbation theory, and even by the $(s_2/s_1)f_0$ values, and in particular by the contribution of c(D-C-Cl) relative to c(D-C-X). It is indeed the bending H-C-X force constants that show the large variability among those diagonal force constants of CH_3X compounds which involve hydrogen in Table III. This conclusion for the above equilibria among the methyl halides agrees with the earlier conclusions of Shiner, Rapp, Halevi, and Wolfsberg.[12] The c(D-C-X) values in Table VIII for Cl, F, Br, and I directly reflect the trends in the H-C-X bending force constants (Rule 4, Table I). The c value for CH_2DH/CH_3H is smaller than that for CH_2DI/CH_3I in spite of the fact that the H-C-H bending force constant in CH_3H (CH_4) is larger than the H-C-I bending force constant in CH_3I; this result comes about largely since the relative isotope effect on the diagonal **G** matrix element in CH_3I is much larger because of the high mass of the I atom (Rule 5, Table I). The results for X = D can be similarly explained. Table VIII should not be compared with Table VI because, as was noted in paper 1, the force fields for the methyl halides are based on spectroscopic data corrected for anharmonicity while the force fields for the hydrocarbons in Table VI are based on uncorrected data. Thus the C-H stretching force constants used for the methyl halides are higher than those for the hydrocarbons and the corresponding c factors are also higher.

Table IX. Calculation of the Equilibrium Constant for $CH_3X + CH_2DCl = CH_2DX + CH_3Cl$ by Perturbation Theory (T = 298.16 K)

	X =				
	F	Br	I	H	D
K(exact)(eq 5)[a]	1.038	0.961	0.944	0.886	0.904
K(eq 11)[b]	1.036	0.961	0.944	0.895	0.912
K_0 from $(s_2/s_1)f_0$[c]	1.038	0.960	0.941	0.885	0.904
c(C-D)[d]	0.977	0.999	1.012	0.999	0.999
c^2(D-C-H)[e]	1.006	0.993	0.990	0.990	0.990
c(D-C-X)[f]	1.057	0.967	0.940	0.895	0.914

[a] Exact calculation with use of $(s_2/s_1)f$ from eq 5. [b] Perturbation theory calculation with use of $(s_2/s_1)f$ from eq 11. [c] Zeroth order perturbation theory calculation with use of $(s_2/s_1)f_0$ from eq 10. [d] Contribution to K_0 from the c factors for the isotopically substituted carbon-hydrogen stretching coordinate. [e] Contribution to K_0 from the c factors for the two isotopically substituted D-C-H bending coordinates. [f] Contribution to K_0 from the value of c(D-C-Cl) relative to c(D-C-X).

Table X shows data for $^{13}CH_3X/^{12}CH_3X$. The variation of the $(s_2/s_1)f$ values arises largely from the variation of the $c(^{13}C\text{-}X)$ values and $c(H\text{-}^{13}C\text{-}X)$ values although the variation in the CORR values cannot be ignored. The c variations can be explained in terms of the force constants in Table III; the understanding of the values for X = H and D also requires the recognition of the lightness of the X mass and of Rule 5, Table I.

Application of Perturbation Theory to Model Calculations

The application of perturbation theory to calculating isotope effects on model equilibria is now considered,

$$M_1 = M_1^* \qquad K_1$$

$$M_2 = M_2^* \qquad K_2$$

$$M_1 + M_2^* = M_1^* + M_2 \qquad K = K_1/K_2$$

$$K = (s_2/s_1)f(M_2/M_1)/(s_2/s_1)f(M_2^*/M_1^*) \qquad (32)$$

Here 1 and 2 refer to light and heavy isotopically substituted species as usual and M* is a model molecule which differs from M in that some specified force constant(s) has a value different

Table X. Perturbation Theory Results for $^{13}C/^{12}C$ Substitution in CH_3X Compounds (T = 298.16 K)

	$^{13}CH_3Cl/^{12}CH_3Cl$	$^{13}CH_3F/^{12}CH_3F$	$^{13}CH_3Br/^{12}CH_3Br$	$^{13}CH_3I/^{12}CH_3I$	$^{13}CH_3H/^{12}CH_3H$	$^{13}CH_3D/^{12}CH_3D$
$(s_2/s_1)f$, eq 5	1.1240	1.1457	1.1177	1.1100	1.1192	1.1257
$(s_2/s_1)f$, eq 11	1.1227	1.1443	1.1165	1.1091	1.1201	1.1262
$(s_2/s_1)f_0$	1.1503	1.1758	1.1425	1.1347	1.1403	1.1490
$c(^{13}C\text{-}X)$	1.0301	1.0440	1.0267	1.0222	1.0201	1.0260
$c(^{13}C\text{-}H)$	$(1.0201)^3$	$(1.0198)^3$	$(1.0201)^3$	$(1.0202)^3$	$(1.0201)^3$	$(1.0201)^3$
$c(H\text{-}^{13}C\text{-}H)$	$(1.0090)^3$	$(1.0090)^3$	$(1.0089)^3$	$(1.0089)^3$	$(1.0087)^3$	$(1.0087)^3$
$c(H\text{-}^{13}C\text{-}X)$	$(1.0080)^3$	$(1.0111)^3$	$(1.0069)^3$	$(1.0059)^3$	$(1.0087)^3$	$(1.0093)^3$
CORR	0.9761	0.9732	0.9773	0.9774	0.9823	0.9801
CORR-G	0.9900	0.9875	0.9908	0.9918	0.9936	0.9921
CORR-F	0.9991	0.9989	0.9992	0.9992	0.9998	0.9998

Table XI. $(s_2/s_1)f$ Values for Normal (M_2/M_1) and Model (M_2^*/M_1^*) Molecules and the Isotope Effect Corresponding to $M_1 = M_1^*(K_1)$, $M_2 = M_2^*(K_2)$ (T = 298.16 K)

	$(s_2/s_1)f$			K_1/k_2		
Molecule[a]	Exact	PTBO	PTB2	Exact	PTBO	PTB2
	A: $M_1 = CH_3Cl$; $M_2 = CH_2DCl$					
M = normal molecule	13.384	13.696	13.479			
M* = HCH f.c. + 10%	13.857	14.214	13.975	0.966	0.964	0.965
M* = HCX f.c. − 33.3%	12.149	12.344	12.182	1.102	1.110	1.106
M* = CH f.c. + 10%	14.785	15.124	14.890	0.905	0.906	0.905
M* = all $f_{ij} = 0$[b]	13.213	13.696	13.398	1.013	1.000	1.006
	B: $M_1 = C_2H_4$; $M_2 = C_2H_3D$					
M = normal molecule	10.375	10.041	10.376			
M* = CH f.c. − 10%	9.379	9.082	9.380	1.106	1.106	1.106
M* = HCH f.c. − 25%	9.789	9.505	9.790	1.060	1.056	1.060
M* = CC f.c. − 10%	10.374	10.042	10.375	1.000	1.000	1.000
	C: $M_1 = {}^{12}C^{12}CH_4$; $M_2 = {}^{13}C^{12}CH_4$					
M = normal molecule	1.1351	1.1479	1.1350			
M* = CH f.c. − 10%	1.1327	1.1453	1.1326	1.0021	1.0023	1.0021
M* = HCH f.c. − 25%	1.1332	1.1457	1.1331	1.0017	1.0020	1.0017
M* = CC f.c. − 10%	1.1307	1.1434	1.1306	1.0039	1.0039	1.0039

[a] M = normal molecule means that the calculation of $(s_2/s_1)f(M_2/M_1)$ is carried out for a normal molecule with geometry and force field as indicated in Table III. M* = HCH f.c. + 10% (f.c. = force constant) refers to a model molecule which differs from the normal molecule only in that the HCH bending force constant has been increased by 10% over the normal value. For each M* case, $(s_2/s_1)f(M_2^*/M_1^*)$ values are calculated, as well as K_1/K_2 values. [b] Model molecule in which all off-diagonal force constants have been set equal to zero.

from the value in M, but in all other respects the molecule M* is the same as M. The evaluation of K_1/K_2 demonstrates how an $(s_2/s_1)f$ value is affected by a change in a force constant. The theoretical evaluation of experimental isotope effects on rates interpreted within transition state theory requires, particularly in the case of secondary isotope effects, an insight into how small force constant changes affect $(s_2/s_1)f$; a similar statement can be made about the theoretical evaluation of vapor pressure isotope effects which requires the comparison of $(s_2/s_1)f$ values in the gas and in the condensed phase.

In Table XI, calculations for three model isotope effects are presented

$$\begin{array}{llll} \text{A} & CH_3Cl = (CH_3Cl)^* & K_1 & \multirow{2}{*}{(33)} \\ & CH_2DCl = (CH_2DCl)^* & K_2 & \\ \text{B} & C_2H_4 = (C_2H_4)^* & K_1 & \multirow{2}{*}{(34)} \\ & C_2H_3D = (C_2H_3D)^* & K_2 & \\ \text{C} & {}^{12}C^{12}CH_4 = ({}^{12}C^{12}CH_4)^* & K_1 & \multirow{2}{*}{(35)} \\ & {}^{13}C^{12}CH_4 = ({}^{13}C^{12}CH_4)^* & K_2 & \end{array}$$

For each type of model isotope effect, various models M* have been investigated, as indicated in Table IX. In each case, the exact $(s_2/s_1)f$ value (eq 5) is listed under Exact, the $(s_2/s_1)f_0$ value (eq 10) is listed under PTBO (zeroth order perturbation), and the second-order perturbation theory value $[(s_2/s_1)f_0 \times \text{CORR}$, eq 11] is listed as PTB2 for M_2/M_1 and for M_2^*/M_1^*. For M_2^*/M_1^*, the values of K_1/K_2 from the exact calculation, the zeroth-order perturbation theory calculation, and the second-order perturbation theory calculation are also listed. If one leaves for the moment the last case under A (all off-diagonal force constants equal zero) out of consideration, one sees that the perturbation theory to second order reproduces the exact calculations of K_1/K_2 with quantitative accuracy and that even the zeroth-order perturbation achieves almost the same accuracy. One should be reminded that zeroth-order perturbation calculations, which are based on $(s_2/s_1)f_0$, require in the case of the examples in Table XI the calculation only of the ratio of c factors for M_2/M_1 and M_2^*/M_1^* for the coordinate, the diagonal force constant for which is being changed between M and M*. Thus for the first M* case under A in Table XI,

$$\frac{K_1}{K_2}(\text{PTBO}) = \frac{c^2[\text{D-C-H}, f(\text{H-C-H})/R(\text{C-H})^2]}{c^2[\text{D-C-H}, f(\text{H-C-H})/R(\text{C-H})^2]} = \frac{c^2[0.485\ \text{mdyn/Å}]}{c^2[1.10 \times 0.485\ \text{mdyn/Å}]} \tag{36}$$

On the basis of the calculations in Table XI and others which will be reported in another publication (the effect of the magnitude of the force constant change will also be discussed there), it is recommended that the change of $(s_2/s_1)f$ due to a diagonal force constant change can be very economically calculated through zeroth-order perturbation theory by just calculating the *c* factors for the coordinate, the force constant corresponding to which is being changed.

Table XI includes one case involving off-diagonal force constant changes, the last case under A. The exact DU of *K* is quite small. In zeroth-order perturbation theory, DU of *K* is equal to zero. In second-order perturbation theory, the CORR factors give rise to a small DU for *K* but this cannot be said to reproduce the exact DU quantitatively; both the Exact and the PTB2 DU's are small, however. This type of result appears to be typical when off-diagonal force constants are varied in molecules like methyl chloride where there is a coordinate redundancy. In molecules without redundancy, second-order perturbation theory quantitatively reproduces exact K_1/K_2 values for the cases where off-diagonal force constants are varied. Further discussions of this point are deferred to the future.

Conclusions

We have demonstrated the utility of *c* factors in the analysis of isotope effects on chemical equilibria. The *c* factors arise out of a perturbation theory development and correspond to the zeroth-order perturbation theory result. When one analyzes isotope effects in terms of *c* factors, one thinks of individual bond stretches, bends, torsions, etc., without considering the more complex normal mode vibrational frequencies. A given *c* factor may be taken to represent the contribution of the corresponding coordinate to the reduced isotopic partition function ratio, $(s_2/s_1)f$, in terms of which isotope effects on chemical equilibria may be formulated. Arguments based on *c* factors have underlain the qualitative thinking of many workers about isotope effects; such arguments have usually in the past been frowned upon by the more theoretically minded, including the present authors.

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Appendix

It was shown in paper 1 that

$$\mathrm{CORR} = \prod_{i<j} e^{F_{2ij}-F_{1ij}} = \prod_{i<j} (\mathrm{CORR})_{ij} \qquad \text{(A1)}$$

where the subscripts 2 and 1 refer to the two isotopic molecules. Here

$$F_{ij} = \frac{1}{(kT)^2}\frac{1}{(1-e^{-V_i})(1-e^{-V_j})} \times \left[{B_{ij}}^2 \frac{1-e^{-(V_i+V_j)}}{V_i+V_j} + {C_{ij}}^2 \frac{e^{-V_i}-e^{-V_j}}{V_j-V_i} \right] - \frac{1}{2}\frac{{g_{ij}}^2}{g_{ii}g_{jj}} - \frac{1}{2}\frac{{f_{ij}}^2}{f_{ii}f_{jj}} \qquad \text{(A2)}$$

with

$$B_{ij} = \alpha_{ij} - \beta_{ij}$$

$$C_{ij} = \alpha_{ij} + \beta_{ij}$$

$$\alpha_{ij} = {}^1\!/_2 \hbar f_{ij} \left(\frac{g_{ii}g_{jj}}{f_{ii}f_{jj}}\right)^{1/4}$$

$$\beta_{ij} = {}^1\!/_2 \hbar g_{ij} \left(\frac{f_{ii}f_{jj}}{g_{ii}g_{jj}}\right)^{1/4}$$

Moreover, one can further dissect $(\mathrm{CORR})_{ij}$ into a part $(\mathrm{CORR\text{-}G})_{ij}$ which is obtained by setting f_{ij} equal to zero and a corresponding part $(\mathrm{CORR\text{-}F})_{ij}$, obtained by setting g_{ij} equal to zero. Then

$$(\mathrm{CORR})_{ij} = (\mathrm{CORR\text{-}G})_{ij} \times (\mathrm{CORR\text{-}F})_{ij} \times (\mathrm{CORR\text{-}FG})_{ij} \qquad \text{(A3)}$$

where the last term is the $f_{ij}g_{ij}$ interaction term. We furthermore define

$$\mathrm{CORR\text{-}G} = \prod_{i<j} (\mathrm{CORR\text{-}G})_{ij}$$

$$\mathrm{CORR\text{-}F} = \prod_{i<j} (\mathrm{CORR\text{-}F})_{ij} \qquad \text{(A4)}$$

Note that the evaluation of CORR-G does not require a knowledge of the off-diagonal force constants f_{ij}.

References and Notes

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