full length, we take it as the new initial point and start over. If this point is outside of the stated interval, we temporarily halve or double the initial steplength and start over at the initial point. If either of these procedures is performed in the course of two consecutive iterations the characteristic quantity is either halved or doubled as appropriate. Suitable optional courses of action are built in to allow for the possibility of a negatively concave approximation parabola. The iteration is terminated when the "characteristic quantity" has been reduced to less than $2^{-10}RT$.

The square of the density self-consistency constraint is weighted by 10^3 and those of each of the remaining constraints by 10^2. In order for these quantities to be meaningful, we must specify the exact algebraic forms of the constraints which we employed. The first one we specify by the statement: the filled fraction of all first neighbor sites in all basic cells is equal to the filled fraction of all second neighbor sites in all basic cells. The overlap configuration consistency constraints we specify as: the number of times a given overlap configuration occurs per molecule in one orientation is equal to the number per molecule in the other orientation. We began the first minimization (for 303 K) with the "step length" set equal to RT and each of the basic cell probabilities set equal to $^1/_{374}$th. Obtaining the first result required about 450 iterations and 4 min. Subsequent runs employed the results obtained at a neighboring temperature as starting point and were initiated with the "step length" set at $0.25RT$. They each required no more than about 20 iterations, *i.e.*, about the minimum number required to reduce the "step length" by eight factors of 2. In each case the magnitudes of the errors in the self-consistency conditions were in the range 8×10^{-4}–8×10^{-3}. These errors could, of course, have been reduced by employing larger weighing factors, but only at the cost of much longer minimization runs.

We also wish to note that the reason we were limited to an eight moment formulation of our frequency spectrum approximation technique is that the Hilbert matrices required for larger moment number formulations are not possible to invert accurately using the double precision arithmetic available on the IBM 360/65. This problem might be avoided by using a non-Hilbert matrix dependent formulation or by carrying out the necessary inversions by means of pure integer or multiple precision techniques.

Calculation of H/D, $^{12}C/^{13}C$, and $^{12}C/^{14}C$ Fractionation Factors from Valence Force Fields Derived for a Series of Simple Organic Molecules

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Abstract: The computer programs of Schachtschneider and Snyder have been used to fit force fields to published, observed fundamental frequencies of vibration for a series of small organic molecules and their deuterated analogs. These force fields have been used to calculate H/D, $^{12}C/^{13}C$, and $^{12}C/^{14}C$ fractionation factors for specific positions in each molecule. The fractionation factors of H attached to carbon are affected in a regular way by variations in the nature of the other groups attached to the same carbon but within the accuracy of the calculations do not seem to be significantly affected by the nature of substituents one atom further removed. Similarly the carbon fractionation factors are affected by the nature of the atoms directly attached but are hardly influenced by more remote structural changes. The use of these factors in the interpretation of equilibrium and kinetic isotope effects is illustrated for several reactions.

The calculation of fractionation factors for isotope exchange reactions has been of interest to chemists for a number of years and has had important applications in the development of isotope separation technology and in the study of geological and biological processes.[2,3]

Since the elucidation of the fundamental theory by Bigeleisen and Mayer[4] and by Melander,[5] the calculation of these factors has been a straightforward problem for molecular species for which the values of the fundamental vibration frequencies were known. However, until the recent development of computer programs for the Wilson FG matrix method of molecular vibrational analysis, only a relatively few molecules could be treated with sufficient accuracy for the results to be of interest. In recent years, complete vibrational analyses of an increasing variety of small organic molecules have been published. It therefore appeared useful to us to use the generalized programs developed by Schachtschneider and Snyder[6] for the vibrational analysis problem and the Wolfsberg and Stern program[7] for the calculation of isotope effects *via* the Bigeleisen equa-

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tion[4] to develop tables of fractionation factors for the hydrogen/deuterium, $^{12}C/^{13}C$, and $^{12}C/^{14}C$ exchange equilibrium constants for a variety of simple organic molecules containing a representative sample of the usual substituents and functional groups. Our interest was to assess the molecular structural features which affect such fractionation factors and to use the tables to predict, by structural analogy, what magnitude of secondary isotope effects might be expected for various chemical reaction rate and equilibrium constants. For example, the detailed comparison of isotope effects in two or more rate processes requires the estimation of isotope fractionation factors between the initial states of different reactants.[8] This use of calculated equilibrium exchange fractionation factors has a number of advantages.

(a) Fractionation factors may be calculated for exchange reactions for which it would be difficult, or even impossible to obtain an experimental value.

(b) The fractionation factors refer to equilibria involving real molecules and can be used to predict isotope effects in rate processes through the kind of reasoning based on structural analogies commonly used by mechanistic organic chemists. While this is not a precise use it has some advantage over the more specialized and rigorous approach commonly used which involves the development of a full force field for the transition state. The latter procedure includes too many unknown or adjustable parameters to allow a unique solution.

(c) The computer calculations are reasonably straightforward, and if the force fields are good they can lead, in our opinion, to results as reliable as those determined experimentally.

The hydrogen/deuterium fractionation factors to be discussed are illustrated by the equilibrium shown in eq 1, in which X and Y can be any atom or functional

$$CH_2DX + CH_3Y \rightleftharpoons CH_3X + CH_2DY \qquad (1)$$

group. Deuterium will tend to concentrate in the molecule in which the zero point energy is largest and the hydrogen will tend to concentrate in the molecule in which the zero point energy is smallest. Thus, if the zero point energy of CH_3Y is greater than that of CH_3X, the constant for the equilibrium in eq 1 will be greater than unity, and we shall refer to the binding of H in CH_3Y as being "stiffer" than the binding of H in CH_3X. This term is used in preference to "tighter" because the latter term generally refers to bond dissociation energies, and the two terms need not be synonymous. For example, the binding of H in ethane is "stiffer" than it is in acetylene (see later) even though acetylene has the greater C–H bond dissociation energy.

The fractionation factor (*i.e.*, the equilibrium constant, K_{HD}) for the equilibrium shown in eq 1 may be expressed in terms of a ratio of complete partition functions, Q's, of the species involved in the equilibrium, eq 2. The problem of calculating K_{HD} therefore reduces

$$K_{HD} = \frac{Q_{CH_3X}Q_{CH_2DY}}{Q_{CH_2DX}Q_{CH_3Y}} \qquad (2)$$

to one of being able to calculate accurately ratios of complete partition functions.

Calculation of Fractionation Factors

To calculate fractionation factors it is necessary to have the complete sets of fundamental frequencies of all the molecules taking part in the equilibria. In some cases these are available, but in many cases the relevant frequencies are either unknown or only incompletely known. In this work complete sets of calculated frequencies were used, all calculations being performed with the computer programs of Schachtschneider and Snyder, and that of Wolfsberg and Stern.[9] The program of Wolfsberg and Stern[7] employs the Wilson FG matrix method[10] to calculate the necessary sets of frequencies, and then uses these frequencies to calculate the ratio of complete partition functions automatically. The input data necessary for the evaluation of eq 2, therefore, consist of molecular geometries, nuclidic masses, and force constants.

Good force fields were available in the literature for a few of the molecules studied in this work and these have been used in the present calculations (see Appendix). For the remaining molecules, force fields were obtained by fitting calculated to observed frequencies (see below). This has led, in a number of cases, to a duplication of some normal coordinate calculations, but this was felt to be justified since force fields for molecules of the same symmetry have been obtained based on a common potential energy expression. It is hoped thereby that comparisons of fractionation factors for molecules of the same symmetry are made more meaningful.

Evaluation of Force Constants

When suitable force fields were not available they were evaluated using the following general method. Starting from an assumed set of force constants the Wilson FG matrix method was used to calculate a set of frequencies within the harmonic approximation. The force constants were then adjusted by a least-squares technique to give the closest agreement between the calculated and the observed frequencies. The initial problem in each calculation was to select a set of force constants that would reproduce the observed frequencies with sufficient accuracy for the least-squares fitting to converge. Enough data were usually available from previous normal coordinate calculations to enable good initial values to be selected.

The elements of the G matrix were calculated on the basis of a set of internal valence coordinates, the choice of coordinates being made to agree with the descriptions of Schachtschneider and Snyder.[6] For the least-squares fitting, the G matrix was usually symmetrized by using the linear transformation relating the internal coordinates to the corresponding symmetry coordinates. This factored the G matrix into a number of nonmixing symmetry blocks which were handled separately. When the force constants for each symmetry block of a given molecule had been determined, they were transformed into the corresponding valence force constants and these were used to calculate fractionation factors.

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Only a few of the force constants in a general valence force field may be determined by this vibrational perturbation technique, and in this work only the diagonal and some of the off-diagonal terms of the F matrix have been determined. Following the usual practice, we have given the value zero to most of the off-diagonal terms and have assigned nonzero values to only a few of the more important terms. Even with these restrictions it was not always possible to allow all of the off-diagonal terms to vary in the least-squares fitting. The procedure adopted was to transfer interaction force constants from previous treatments of the same, or similar, molecules and allow them to vary in the least-squares fitting. The converged force constants and their estimated errors were then inspected, and if an interaction force constant had a reasonable value and if the estimated error was smaller than that value, then the force constant was assumed to be reasonably well determined. If, on the other hand, the value of the force constant was unreasonable, or if it was smaller than the estimated error, then the converged value was not used. Instead the transferred value was used and this was not allowed to vary in the least-squares fitting. In other cases it was found necessary to include interaction terms by a process of trial and error in order to obtain a reasonably good frequency fitting. Whenever possible, the values for such constants were selected so as to agree as closely as possible with the values of similar terms used in previous calculations.

Although the method of selecting interaction force constants has been somewhat arbitrary, we have tried to be consistent in these calculations by including similar types of interaction terms in all molecules of the same symmetry. No claims are made about the uniqueness of the force constants so derived, and it is not the purpose of this paper to deal with this problem since calculations have indicated that fractionation factors are not very sensitive to the types of interaction terms included in the force fields. The criterion of choosing a set of force constants has been, therefore, that the correctly converged set should enable the calculated frequencies to reproduce the observed frequencies as closely as possible. In all cases, the average error in the calculated frequencies, for simultaneous fitting to the hydrogen compounds and their deuterated analogs, was $<1\%$. Brief notes on each of the molecules studied in this work are included in the Appendix.

Errors Involved in the Calculations

Before presenting the main body of results, it is necessary to discuss the errors involved in the calculation of fractionation factors, and to estimate the likely uncertainty to be attached to a given value of K_{HD}. There is the obvious limitation that values of K_{HD} calculated by eq 2 will be subject to the usual approximations inherent in the calculation of complete partition functions. To be explicit, the translational and rotational contributions are evaluated assuming classical behavior, and the vibrational contribution is evaluated using frequencies that have been calculated within the harmonic approximation. It is to be expected, therefore, that the most reliable results will be obtained for gas-phase equilibria, and in those cases for which fractionation factors have been measured experimentally,[11] it is found that eq 2 leads to values in very close agreement with the experimental values. This agreement indicates that the approximations inherent in eq 2 do not introduce any sizable error into the values of K_{HD} for these equilibria. For equilibria in solution there is the added problem that solvent–solute interactions may modify the gas-phase partition functions, and such effects will not be allowed for in the calculated values. However, the errors so introduced will tend to cancel out when the ratios of partition functions for the various isotopic pairs are calculated, so that K_{HD} should remain a reliable estimate of the fractionation factor.

Within the formulation of eq 2 the largest error in K_{HD} arises from the uncertainties in the frequencies used to evaluate the partition function ratio, *i.e.*, from the uncertainties in the spectroscopic measurements. This error in K_{HD} may be minimized by using calculated frequencies for an isotopic pair of molecules based on a common force field.[12] By this procedure any errors in the calculated frequencies tend to cancel when the ratio of partition functions is formed, because the enforced theoretical relationships between the frequencies of the isotopic pairs minimize the errors in the frequency shifts caused by the isotopic substitution. Such a cancellation is not possible if the observed frequencies are used to calculate K_{HD} directly by means of the Bigeleisen equation.[4]

This effect is illustrated by the fractionation factors reported in Table I.[13–20] For calculation I, the observed frequencies[13] for HCCH and HCCD were used to evaluate a force field which was then used to calculate frequencies for HCCH and HCCD. Likewise, the observed frequencies for HCCF and DCCF reported by Brown and Tyler[14] were used to evaluate a force field and thence calculate frequencies for HCCF and DCCF. The first column in Table I gives the

Table I. Comparison of Fractionation Factors Calculated from Observed and Calculated Frequencies (25°)

Equilibrium	K_{HD} Obsd freq	K_{HD} Calcd freq	Ref
$HCCD + HCCF \rightleftharpoons HCCH + DCCF$	I 1.028	0.987	13, 14
	II 1.071	0.974	13, 15
$CH_2DCH_3 + CH_3CCl_3 \rightleftharpoons CH_3CH_3 + CH_2DCCl_3$	III 1.079[a]	1.027	16–19
	IV 1.010[a]	1.041	16–18, 20

[a] Calculated from equilibrium $CH_3CD_3 + CH_3CCl_3 \rightleftharpoons CH_3CH_3 + CD_3CCl_3$.

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value of K_{HD} obtained using the observed frequencies and the second column the value of K_{HD} obtained using the calculated frequencies. In calculation II, the observed and calculated frequencies for HCCH and HCCD were those used in calculation I, but the observed frequencies for HCCF and DCCF were those reported by Hunt and Wilson.[15] A new force field (and a new set of calculated frequencies) was, therefore, evaluated for HCCF and DCCF. By comparing the results of calculations I and II it can be seen that the value of K_{HD} is more sensitive to changes in the observed frequencies when it is calculated directly from these frequencies than when it is calculated from the calculated frequencies. Similarly calculations III and IV show the effect of using different assignments for the observed frequencies of CH_3CCl_3 on the values of K_{HD} calculated by the two methods.

Although the use of calculated instead of observed frequencies can minimize the uncertainty in K_{HD}, there will, nevertheless, still be some uncertainty attached to the value of K_{HD} arising from errors in the calculated frequencies. All frequencies were calculated within the harmonic approximation, and no corrections were made for anharmonicity. The results discussed later in the paper indicate that this neglect of anharmonicity corrections does not introduce any significant error into calculations of K_{HD}. The more important sources of error in the calculation of fundamental frequencies appear to be the following.

a. **Definition of the Force Field.** As mentioned in the preceding discussion, it is not possible to determine all the elements of the F matrix; *i.e.*, it is not possible in general to define a unique force field.[21] There will always be some uncertainty, therefore, in the calculated frequencies; however, as illustrated in Table II[6,17,22–24] this does not appear to be a serious problem in the calculation of fractionation factors. Calculations II and III show the effect of using the same observed frequencies for CH_3NO_2 and CD_3NO_2 to obtain a force field, but with a different choice of interaction force constants. The two descriptions of the force field differ in the method of representing the stretch–bend interactions for the C–H vibrations (see Appendix for details). The different interaction force constants cause small changes in the diagonal force constants, but the overall frequency fit remains about the same. The effect on K_{HD}, given in the column under Total, is seen to be small. Calculation I uses the same description of the force field used in II, but with a different set of observed frequencies for CH_3NO_2 in the least-squares fitting. The uncertainties in the observed frequencies, in this example, thus have a larger effect on the calculated value of K_{HD} than the uncertainties in the description of the force field.

Table II. Comparison of Fractionation Factors Calculated for the Equilibrium (25°)
$CH_3CH_2D + CH_3NO_2 \rightleftharpoons CH_3CH_3 + CH_2DNO_2$

	K_{HD}			
	MMI[a]	EXC[a]	ZPE[a]	Total
I[b,c]	1.038	0.974	1.078	1.090
II[b,d]	1.038	0.974	1.067	1.081
III[b,d]	1.038	0.975	1.065	1.078

[a] Reference 24. [b] Observed frequencies for ethane: ref 16, 17. [c] Observed frequencies for CH_3NO_2 and CD_3NO_2: ref 22. [d] Observed frequencies for CH_3NO_2: ref 23; for CD_3NO_2: ref 22.

b. **Reliability of Experimental Data.** It has been emphasized that uncertainties in K_{HD} due to errors in the observed frequencies may be minimized by using calculated frequencies to calculate values of K_{HD}. Reference to Tables I and II, however, shows that even when calculated frequencies are used the value of K_{HD} is still dependent upon the values of the observed frequencies. The uncertainty to be attached to any given value of K_{HD} will obviously depend upon the accuracy with which the relevant frequencies have been determined, so each calculation should be treated separately. However, our calculations so far have indicated that the value of K_{HD} shows only a small variation when evaluated using force fields based on different observed frequencies, and we take as an upper limit for the uncertainty in K_{HD} ±0.02.

It is convenient to include here the case of a misassignment of an observed frequency. It is reasonably straightforward to ensure that a calculated frequency corresponds to the same molecular vibration assigned to the observed frequency. If the observed frequency has been misassigned, however, the calculated and observed frequencies refer to different molecular vibrations. The uncertainty so caused in K_{HD} can be included as a spectroscopic uncertainty, and so is included in the above error limits of ±0.02.

c. **Calculation of the G Matrix.** An additional potential source of error in the calculation of K_{HD} arises in the evaluation of the elements of the G matrix. These are computed for a given molecule by standard methods[6] from the molecular geometry and the nuclidic masses, for a suitable coordinate system. The largest uncertainty would appear to arise when an assumed geometry has to be used. For the molecules reported in this work, this source of error appears to be unimportant, at least to the accuracy to which the results are reported.

Results and Discussion

Provided the necessary frequency data are available, it is possible to calculate fractionation factors for any combination of molecules. We have chosen to report our calculated values of K_{HD} relative to a given reference molecule for molecules of a given symmetry (Tables III–VIII).[25,26] The values of K_{HD} for the equilibria relating the various reference compounds are given in Table IX, and these values enable K_{HD} to be calculated for any combinations of the molecules appearing in the different Tables III–VIII.

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(21) For a given set of interaction force constants it may be possible to define a "unique" force field in the sense that the converged set of values of the force constants is the same for different initial values of the constants in the least-squares fitting. If a different choice of interaction force constants is now made, the force constants in the converged force field will have different values and may well define another "unique" force field.

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(23) W. J. Jones and N. Sheppard, *Proc. Roy. Soc., Ser. A*, **304**, 135 (1968);

(24) MMI gives the contribution to K_{HD} made by the translational and rotational partition functions, and EXC·ZPE is the contribution made by the vibrational partition function. ZPE is the zero point energy term; for details see ref 7.

(25) The reference molecule need not have the same symmetry as that of the other molecules in a given table. Thus, ethane, D_{3d} symmetry, is used as the reference for molecules of C_{3v} symmetry.

(26) R. C. Lord and I. Nakagawa, *J. Chem. Phys.*, **39**, 2951 (1963).

Table III. Fractionation Factors at 25° for Molecules of C_{3v} Symmetry Relative to Ethane
$CH_3CH_2D + CHY_2X \rightleftharpoons CH_3CH_3 + CDY_2X$

X	Y	MMI	EXC	ZPE	Total
F	H	1.058	0.963	1.057	1.077
Cl	H	1.052	0.969	1.013	1.033
Br	H	1.042	0.975	0.982	0.998
I	H	1.037	0.981	0.951	0.967
C≡N	H	1.027	0.986	0.996	1.009
C≡CH	H	1.025	0.992	0.977	0.993
CF_3	H	0.883	1.068	1.112	1.049
CCl_3	H	0.860	1.089	1.097	1.027
SiH_3	H	0.963	1.027	0.924	0.914
GeH_3	H	0.957	1.030	0.951	0.937
NH_3^+	H	1.006	0.974	1.080	1.058
F	F	0.881	0.968	1.718	1.465
Cl	Cl	0.852	0.986	1.449	1.217
Br	Br	0.839	0.998	1.331	1.114

Table IV. Fractionation Factors at 25° for Molecules of C_{2v} Symmetry Relative to Ethylene
$CH_2CHD + CH_2X \rightleftharpoons CH_2CH_2 + CHDX$

X	MMI	EXC	ZPE	Total
CF_2	0.859	1.052	1.109	1.002
CBr_2	0.826	1.075	1.105	0.981

Table V. Fractionation Factors at 25° for Molecules of $C_{\infty v}$ Symmetry Relative to Acetylene
$HCCD + HCCX \rightleftharpoons HCCH + DCCX$

X	MMI	EXC	ZPE	Total
F[a]	0.914	1.054	1.025	0.987
F[a]	0.914	1.055	1.009	0.974
Cl	0.894	1.059	1.050	0.994
Br	0.883	1.062	1.060	0.995

[a] Two force fields obtained, see text.

Table VI. Fractionation Factors at 25° for Molecules of C_s Symmetry Relative to Ethane
$CH_3CH_2D + CH_3X \rightleftharpoons CH_3CH_3 + CH_2DX$

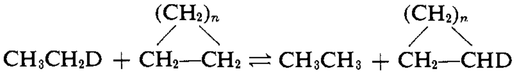
X	MMI	EXC	ZPE	Total
NH_2	1.025	0.985	1.026	1.036
NO_2	1.038	0.976	1.067	1.081
CH_2Cl[a]	0.918	1.048	1.025	0.986
CH_3CH_3[a]	0.925	1.054	0.998	0.973

[a] Average values for the different methyl positions.

Table VII. Fractionation Factors at 25° for Ethyl Chloride and Propane
$CH_3CH_2D + CH_3CH_2X \rightleftharpoons CH_3CH_3 + CH_3CHDX$

X	MMI	EXC	ZPE	Total
Cl	0.925	0.985	1.212	1.104
CH_3	0.927	0.989	1.203	1.103

Table VIII. Fractionation Factors at 25° for Cyclopropane and Cyclobutane



$CH_3CH_2D + \overset{(CH_2)_n}{CH_2{-}CH_2} \rightleftharpoons CH_3CH_3 + \overset{(CH_2)_n}{CH_2{-}CHD}$

n	MMI	EXC	ZPE	Total
1	0.942	0.991	1.102	1.029
2[a]	0.898	1.009	1.136	1.029

[a] Calculated frequencies from ref 26 were used for C_4H_8 and C_4D_8. The results listed were obtained using the rule of the geometric mean to calculate the effect per D.

Table IX. Fractionation Factors at 25° Relative to Ethane
$CH_3CH_2D + X \rightleftharpoons CH_3CH_3 + X'$

X′[a]	MMI	EXC	ZPE	Total
CH_3D	1.227	0.956	0.781	0.916
CH_3CH_2D	1.000	1.000	1.000	1.000
CH_2CHD	1.062	0.976	0.892	0.924
HCCD	1.041	1.038	0.680	0.735

[a] X and X′ represent an isotopic pair of molecules with the heavier isotope in the position indicated in X′.

It is not intended that the values of K_{HD} reported necessarily represent experimentally observable equilibria. The main purpose behind this work has been to examine the various errors involved in the calculation of precise isotope effects, and, of greater interest, to evaluate the effects of substituents on such isotope effects. To this end we have not dealt with kinetic isotope effects, but have concentrated attention on equilibria, where it is possible to obtain accurate data for all of the molecular species involved.

The results for molecules of C_{3v} symmetry are given in Table III. The values shown under Total are to be taken as precise estimates of K_{HD} for the various equilibria, in the sense that the ratios of complete partition functions have been evaluated with accurate frequency data. The other columns show the separate terms in the partition function ratios.[24]

Tables IV–VI give the results for molecules of C_{2v}, $C_{\infty v}$, and C_s symmetries, respectively. It has been noted before[7] in isotope effect calculations that the MMI and EXC terms often tend to cancel, leaving the ZPE term as the most important one in determining the isotope effect. The same trends are noted in the above tables, but the ZPE term alone tends to overestimate K_{HD}. It is, therefore, essential in all comparisons to use the values given under Total for K_{HD} (Total = MMI·EXC·ZPE).

Table VII gives fractionation factors for the CH_2 groups of ethyl chloride and propane relative to ethane, and Table VIII gives fractionation factors for cyclopropane and cyclobutane relative to ethane.

Table IX gives the fractionation factors for methane, ethylene, and acetylene relative to ethane. This table enables the calculation of K_{HD} for any pair of molecules appearing in the Tables III–VIII.

In Table X, the H/D fractionation factors at 25° for

Table X. H/D Fractionation Factors Relative to Acetylene (25°)

FC≡CD	0.987	CH_3CH_2D	1.361
ClC≡CD	0.994	N≡CCH_2D	1.373
BrC≡CD	0.995	Cl_3CCH_2D	1.397
HC≡CD	1.000	$(CH_2)_2CHD$	1.400
$Br_2C{=}CHD$	1.233	$(CH_2)_3CHD$	1.400
H_3SiCH_2D	1.243	$ClCH_2D$	1.405
HCH_2D	1.246	CF_3CH_2D	1.427
$H_2C{=}CHD$	1.257	$H_3N^+CH_2D$	1.439
$F_2C{=}CHD$	1.259	FCH_2D	1.465
H_3GeCH_2D	1.275	O_2NCH_2D	1.471
ICH_2D	1.316	CH_3CHDCH_3	1.501
$CH_3CH_2CH_2D$	1.324	CH_3CHDCl	1.502
$ClCH_2CH_2D$	1.341	CBr_3D	1.516
HC≡CCH_2D	1.351	CCl_3D	1.656
$BrCH_2D$	1.358	CF_3D	1.993

all of the CH bonds listed in Tables III–VIII are reexpressed relative to acetylene, and are listed in order of increasing stiffness of binding. Acetylene is chosen as the common reference molecule since it is the hydrocarbon with the loosest (least stiff) binding of hydrogen and most of the fractionation factors relative to it are greater than unity. The following trends are apparent.

(1) Increasing the coordination number of the C atom bearing the hydrogen increases the HD fractionation factor, *e.g.*, in the series, $HC{\equiv}CD$ (1.000), $H_2C{=}CHD$ (1.257), $CH_3{-}CH_2D$ (1.361).

(2) For $X{-}CH_2D$ compounds the stiffness of binding increases for X groups in the order H_3Si, H, H_3Ge, I, CH_3CH_2, $ClCH_2$, $HC{\equiv}C$, Br, CH_3, $N{\equiv}C$, Cl_3C, Cl, CF_3, H_3N^+, F, NO_2. The range covered is 1.243 to 1.471. These effects of variations of an α-substituent atom appear to be directly related to force constants affecting the H–C–X bending motion.[8]

(3) For a variety of attached X atoms the fractionation factors in $X{-}CH_2D$ compounds roughly parallels bond strength and electronegativity; H is a notable exception (probably because of its small mass) and Si and Ge are out of order.

(4) For $C_\beta C_\alpha H_2D$ compounds the fractionation factor is not appreciably dependent on the coordination number of C_β or on the nature of groups attached at C_β. This result confirms the effectiveness of the "cut-off procedure" of Wolfsberg and Stern.[27] Thus, it appears that one can estimate to a fair degree of accuracy the effects of structural changes on H/D fractionation factors in stable molecules (but not carbonium ions)[28] by taking into account only the changes in groups attached to the α-carbon atom. The compounds CCl_3CH_2D and CF_3CH_2D do show slight increases in K_{HD} over CH_3CH_2D which are in the direction and order expected for the operation of a small inductive effect from the substituents at the β-carbon atom.

(5) Since α C binds more stiffly than α H the fractionation factors are larger for CCXDC groups than for XCH_2D groups.

(6) CCHDC groups in cyclopropane and cyclobutane rings show fractionation factors in between those for $H_2C{=}CHD$ and CH_3CHDCH_3.

(7) The effect of a given change for a group attached at the α-carbon atom is roughly independent of the other groups attached at that atom. For example, between CH_3D and CH_2DCl there is a fractionation factor of 1.405/1.246 or 1.128 while between CH_3CH_2D and CH_3CHDCl there is a factor of 1.502/1.361 or 1.104. The two estimations of the effect of the change from α H to α Cl on the CH/CD fractionation factor are the same within the combined limits of error of the calculations in the four molecules compared; however, the small difference might be real (see (5)) and indicative of the accuracy of this approximation. A corollary of this general relationship is that the effect of each successive replacement of α H by a given atom should be the same. For example, between CH_3D and CH_3CH_2D the factor is 1.361/1.246 or 1.092 while between CH_3CH_2D and CH_3CHDCH_3 it is 1.501/1.361 or 1.102.

The trends noted in (7) are particularly important from a practical point of view, since they greatly extend the utility of the tables of fractionation factors. However, some caution is necessary when using the tables in this way, because the effects of α substituents may not always be cumulative. The fractionation factor of CH_2DF relative to CH_3D is 1.465/1.246 or 1.176. Assuming the effect of α F to be cumulative, the expected fractionation factor of CDF_3 relative to CH_3D is $(1.176)^3$ or 1.626; the fractionation factor calculated directly is 1.993/1.246 or 1.600. On the other hand, K_{HD} for CH_2DCl relative to CH_3D is 1.128, which leads to an expected value of K_{HD} for $CDCl_3$ relative to CH_3D of 1.435; the value of K_{HD} calculated directly for $CDCl_3$ is 1.329. Similarly for $CHBr_3$, K_{HD} calculated from the value of K_{HD} for CH_3Br assuming cumulative behavior is 1.295; the direct calculation gives 1.217.

All the values of K_{HD} reported in the tables refer to equilibria at 25°, but in many calculations it will be desirable to use results referring to other temperatures; for this purpose eq 3 may be used,[29] in which T is

$$\log (K_{HD})_T = \log (K_{HD})_{298} + \left(\frac{298 - T}{T}\right) \log (\text{ZPE}) \quad (3)$$

the absolute temperature. This equation provides a satisfactory temperature correction for the compounds listed in tables over limited ranges of temperature; for example, the average error in K_{HD} for an extrapolation over a 20° range is ± 0.002. It should be emphasized, however, that such a method of correction is only approximate; the actual temperature dependence of isotope effects is known to be more complicated.[30–32]

Although the fractionation factors reported here refer to equilibria, it is possible to use the results to gain information about kinetic isotope effects. Suppose the secondary deuterium isotope effect (k_H/k_D) for the reaction, eq 4, is known, and it is required to estimate a

$$CH_3X \longrightarrow (\ddagger) \longrightarrow \text{products} \quad (4)$$

value $(k_{H'}/k_{D'})$ for the reaction, eq 5. From isotope

$$CH_3Y \longrightarrow (\ddagger') \longrightarrow \text{products} \quad (5)$$

effect theory we may obtain eq 6 and 7, from which

$$\frac{k_H}{k_D} = \frac{Q_{\ddagger H}}{Q_{CH_3X}} \frac{Q_{CH_2DX}}{Q_{\ddagger D}} \frac{\nu_{H\ddagger}}{\nu_{D\ddagger}} \quad (6)$$

$$\frac{k_{H'}}{k_{D'}} = \frac{Q_{\ddagger' H}}{Q_{CH_3Y}} \frac{Q_{CH_2DY}}{Q_{\ddagger' D}} \frac{\nu_{H\ddagger'}}{\nu_{D\ddagger'}} \quad (7)$$

may be obtained eq 8. The first term on the right-hand

$$\frac{k_{H'}}{k_{D'}}\Big/\frac{k_H}{k_D} = \left(\frac{Q_{CH_2DY}}{Q_{CH_3Y}} \frac{Q_{CH_3X}}{Q_{CH_2DX}}\right)\left(\frac{Q_{\ddagger' H}}{Q_{\ddagger' D}} \frac{Q_{\ddagger D}}{Q_{\ddagger H}}\right)\left(\frac{\nu_{H\ddagger'}}{\nu_{D\ddagger'}} \frac{\nu_{D\ddagger}}{\nu_{H\ddagger}}\right) \quad (8)$$

side of eq 8 is the fractionation factor for the types of equilibria reported in this work. The second term refers to a similar fractionation factor for the corresponding transition states, and the last term represents the isotope effect on the frequencies corresponding to the reaction coordinate. Provided that some estimate can be made for the second and third terms on the right-hand side, the required isotope effect can be estimated

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(27) M. J. Stern and M. Wolfsberg, *J. Chem. Phys.*, 45, 4105 (1966).

(28) J. C. Evans and G. Y. S.-Lo, *J. Amer. Chem. Soc.*, 88, 2118 (1966).

(29) This is derived from the Arrhenius equation assuming that only the ZPE term is temperature dependent.

(30) M. Wolfsberg and M. J. Stern, *Pure Appl. Chem.*, 8, 325 (1964).

(31) M. J. Stern, W. Spindel, and E. U. Monse, *J. Chem. Phys.*, 48, 2908 (1968).

(32) W. Spindel, M. J. Stern, and E. U. Monse, *ibid.*, 52, 2022 (1970).

from the known value by calculating the ground-state fractionation factor.

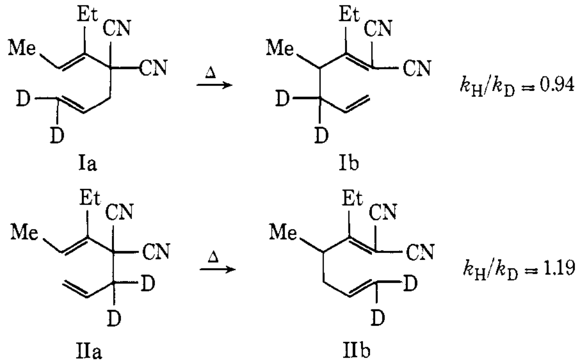
This approach is useful when eq 4 and 5 represent dissociative processes in which X and Y may be separated from CH_3 in the transition states. In such cases the transition state fractionation factor is unity, and the reaction coordinate terms can be expected to be little different from unity;[8] the difference in isotope effects is then a ground-state effect, and can be readily calculated.

When the group X (or Y) is still bound to CH_3 in the transition state the difference in isotope effects is given by the complete expression, eq 8, and the ground state fractionation factor alone is unable to predict the magnitude of this effect. If the structures of the relevant transition states are considered to be similar, however, then it might be possible to assume that although the individual partition functions will be different from those of the corresponding ground-state molecules, their ratios might be almost the same. Equation 8 then predicts that there will be little difference in the isotope effects for reactions 4 and 5.

Applications

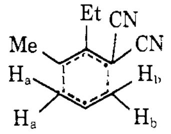
Some specific examples will now be considered to illustrate the uses of the tables of fractionation factors. It is known experimentally that α-deuterium isotope effects in SN1 solvolysis reactions are about 3% smaller when bromide is the leaving ion than when chloride is the leaving ion.[33] It has been shown that this effect can be accounted for almost entirely on the basis of differences in H–C–halogen bending force constants in the reactant molecules.[8] We should, therefore, be able to calculate this leaving group effect directly from the results included in Table III. The fractionation factors relative to ethane for the methyl halides are 1.077, 1.033, 0.998, and 0.967 for F, Cl, Br, and I, respectively. These effects may be calculated relative to Br by dividing by 0.998. If the α-isotope effect for Br is now taken as 1.125, then the α-isotope effects for F, Cl, and I are calculated as 1.214, 1.164, and 1.090, in very good agreement with the previous estimates[8] of 1.22, 1.164, and 1.09. Moreover, anharmonicity corrections were included in the calculation of the latter results, so that this close agreement indicates that the neglect of anharmonicity in the present calculations does not introduce any significant error.

Sunko, Humski, Strelkov, and Borčić have published isotope effects for the rearrangements of Ia and IIa at 85°.[34]



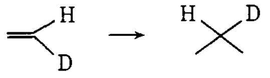
It is very interesting that the reciprocal of the inverse isotope effect for reaction of I is smaller than the normal effect for reaction of II. There are two possible explanations for this. The first, offered by the earlier authors, supposes that the isotope effect is more sensitive to changing bond order when a bond is near fully formed than when it is nearly broken. The second is to suppose that in the transition state bond breaking (on the right-hand side of the formula, Ia or IIa) has proceeded to a greater extent than bond making (on the left), a reasonable expectation since the reaction has an appreciable activation energy. Either of these situations could obtain with a transition state either more nearly like reactants than products or symmetrically disposed between reactants and products.[35]

If the transition state III were symmetrical, in the sense that the bond orders on the left and right sides were equal and the fractionation factors for H_a and H_b were equal, then the experimental results enable the isotope fractionation factor between the ground states to be calculated, *i.e.*, the fractionation between $I_a \rightleftharpoons II_a$, or $I_b \rightleftharpoons II_b$. The fractionation factor is 1.19 × 1/0.94 or 1.266. To calculate a theoretical value, it is necessary to chose a suitable model, and for this we can use the exchange equilibrium between ethylene and the central carbon atom of propane.



III

$$I_a \xrightarrow{0.94} [\text{transition state}] \xleftarrow{1.19} IIa$$



From Tables VII and IX, the fractionation factor for this change is 1.103 × 1/0.924, or 1.194 per D at 25°. Correcting to 85°, by the method described, eq 3, the resulting fractionation factor is 1.069 × 1/0.942 or 1.135 per D. This figure must be squared to give the effect for two deuteriums, 1.288, in good agreement with the experimental value. The calculation was repeated to give the fractionation factor directly at 85°, to avoid the extrapolation from 25°. This value was 1.289, in agreement with the extrapolated value, and both estimates agree closely with the experimental value. Therefore, we do not think that the results of ref 34 necessarily argue for an α-D isotope effect which is nonlinear with respect to bond order.

Malojčić, Humski, Borčić, and Sunko[36] have measured the isotopic fraction in the degenerate Cope rearrangement of biallyl-*1,1,6,6-d*$_4$ (IV), and they report the

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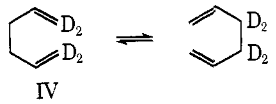
[33] V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Amer. Chem. Soc.*, 90, 418 (1968).

[34] (a) K. Humski, T. Strelkov, S. Borčić, and D. E. Sunko, *Chem. Commun.*, 693 (1969); (b) K. Humski, R. Malojčić, S. Borčić, and D. E. Sunko, *J. Amer. Chem. Soc.*, 92, 6534 (1970).

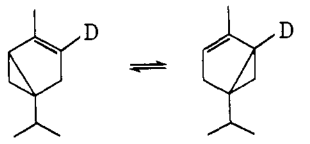
[35] A transition state "more like reactants than products" would have a bond order on the left less than the bond order on the right; a transition state symmetrical with respect to starting materials and products would have the two partial bond orders equal. Independent of this relationship, bond making could have proceeded to a smaller extent than bond breaking if the sum of the two partial bond orders is less than unity.

[36] R. Malojčić, K. Humski, S. Borčić, and D. E. Sunko, *Tetrahedron Lett.*, 25, 2003 (1969).


IV

isotope effect at 200° to be 1.23. Again using the ethylene to propane model it is possible to calculate the fractionation factor for this equilibrium, and at 200° the result is (1.030 × 1/0.964)^4 or 1.301, in only fair agreement with the experimental value. A direct calculation at 200° gives a value 1.366, which indicates the extent of errors involved in correction over large temperature ranges. The discrepancy between the experimental and theoretical values may not be significant because of the uncertainties in the experimental value.[36]

A similar degenerate rearrangement, that of deuterated α-thujene (V) at 250°, shows no isotope effect,


V

within the accuracy of the nmr method used.[37] The exchange between ethylene and cyclopropane should provide a reasonable model for calculating the isotope

effect in the above equilibrium. The fractionation factor calculated at 250° has the value 0.987 × 1/0.970 or 1.018, which is not appreciably different from unity.

Saunders and Katz[38] have published calculations of isotope effects in elimination reactions. Their calculations indicate that the deuterium isotope effects at the β position are not strongly affected by the changes occurring at the α position. This is in accord with the present conclusions (see item 4 above). A change in hybridization of the α-carbon atom from sp^3 to sp, for example, causes only a 0.7% difference in isotope effects observable at the β position.

Fractionation Factors for Equilibria Involving Carbon Isotopes

Thus far in our discussion of fractionation factors only H/D fractionation has been considered. The same methods of calculation already described may be used to calculate $^{12}C/^{13}C$ and $^{12}C/^{14}C$ fractionation factors (or indeed fractionation factors for any isotopic pair). In this section results for carbon isotopic fractionation will be reported. In most cases the force fields used were those derived for the H/D fractionation calculations. The two exceptions were CO_2 and $CO_3{}^{2-}$, for which force fields were derived fitting to frequency data for $^{12}CO_2$, $^{13}CO_2$, and $^{14}CO_2$ in the case of carbon dioxide and for $^{12}CO_3{}^{2-}$ only in the case of carbonate ion. The results are summarized in Table XI.

Table XII gives $^{12}C/^{13}C$ fractionation factors for the different molecules of Table XI reexpressed relative to acetylene in analogy with the H/D fractionation factors of Table X. The same trends can be noted for $^{12}C/^{13}C$ factors as previously noted for H/D factors. Thus, the largest fractionation factors occur when the

Table XI. Fractionation Factors for ^{13}C at 25°

^{13}X	MMI	EXC	ZPE	Total
$^{13}CO_2 + {}^{12}X \rightleftharpoons CO_2 + {}^{13}X$				
$^{13}CO_3{}^{2-}$	0.9911	0.9952	1.0206	1.0066
$^{13}CH_4$	1.0589	0.9922	0.8974	0.9429
$^{13}CH_3CH_3$	1.0386	0.9930	0.9256	0.9546
$^{13}CH_2CH_2$	1.0430	0.9928	0.9207	0.9534
$^{13}HCCH$	1.0483	0.9944	0.9000	0.9382
$^{13}CH_3CH_3 + {}^{12}X \rightleftharpoons CH_3CH_3 + {}^{13}X$				
$^{13}CH_3F$	0.9985	0.9999	1.0099	1.0083
$^{13}CH_3Cl$	0.9961	1.0021	0.9904	0.9885
$^{13}CH_3Br$	0.9920	1.0042	0.9892	0.9855
$^{13}CH_3I$	0.9909	1.0062	0.9813	0.9784
$^{13}CH_3CN$	0.9939	1.0012	1.0041	0.9991
$^{13}CH_3CH_2CH_3$	0.9893	1.0036	1.0115	1.0043
$CH_3{}^{13}CH_2CH_3$	0.9750	1.0054	1.0313	1.0109
$^{13}CH_2CH_2 + {}^{12}X \rightleftharpoons CH_2CH_2 + {}^{13}X$				
$CH_2{}^{13}CH_2CH_2$	0.9837	1.0015	1.0152	1.0001
$^{13}CH_2CBr_2$	0.9627	1.0160	1.0168	0.9946
$^{13}CH_2CF_2$	0.9798	1.0045	1.0142	0.9982
$H^{13}CCH + {}^{12}X \rightleftharpoons HCCH + {}^{13}X$				
$H^{13}CCF$	0.9877	1.0041	1.0071	0.9988
$H^{13}CCCl$	0.9826	1.0063	1.0079	0.9966
$H^{13}CCBr$	0.9782	1.0085	1.0096	0.9960
Fractionation Factors for ^{14}C at 25°				
$^{14}CO_2 + {}^{12}X \rightleftharpoons CO_2 + {}^{14}X$				
$^{14}CO_3{}^{2-}$	0.9826	0.9908	1.0397	1.0122
$^{14}CH_4$	1.1161	0.9849	0.8141	0.8948
$^{14}CH_3CH_3$	1.0757	0.9864	0.8632	0.9140
$H^{14}CCH$	1.0949	0.9888	0.8194	0.8871
$^{14}CH_3CH_3 + {}^{12}X \rightleftharpoons CH_3CH_3 + {}^{14}X$				
$^{14}CH_3F$	0.9970	0.9999	1.0187	1.0155
$^{14}CH_3Cl$	0.9922	1.0042	0.9823	0.9787
$^{14}CH_3Br$	0.9843	1.0084	0.9803	0.9730
$^{14}CH_3I$	0.9821	1.0123	0.9657	0.9601
$^{14}CH_3CN$	0.9882	1.0023	1.0080	0.9984
$^{14}CH_3CH_2CH_3$	0.9796	1.0070	1.0220	1.0082
$CH_3{}^{14}CH_2CH_3$	0.9525	1.0105	1.0604	1.0206
$^{14}CH_2CH_2 + {}^{12}X \rightleftharpoons CH_2CH_2 + {}^{14}X$				
$CH_2{}^{14}CH_2CH_2$	0.9690	1.0029	1.0291	1.0001
$^{14}CH_2CBr_2$	0.9290	1.0315	1.0331	0.9900
$^{14}CH_2CF_2$	0.9615	1.0087	1.0278	0.9968
$H^{14}CCH + {}^{12}X \rightleftharpoons HCCH + {}^{14}X$				
$H^{14}CCF$	0.9766	1.0077	1.0140	0.9979
$H^{14}CCCl$	0.9668	1.0120	1.0156	0.9937
$H^{14}CCBr$	0.9585	1.0164	1.0189	0.9926

Table XII. $^{12}C/^{13}C$ Fractionation Factors Relative to Acetylene (25°)

$$H^{13}C{\equiv}CH + {}^{12}X \overset{K}{\rightleftharpoons} HC{\equiv}CH + {}^{13}X$$

^{13}X	K	^{13}X	K
$^{13}CH_3I$	0.9955	$^{13}CH_2{=}CF_2$	1.0144
$H^{13}C{\equiv}CH$	(1.0000)	$^{13}CH_3CH_3$	1.0175
$^{13}CH_3Br$	1.0027	$CH_2{}^{13}CH_2CH_2$	1.0163
$^{13}CH_4$	1.0050	$^{13}CH_3CH_2CH_3$	1.0219
$^{13}CH_3Cl$	1.0058	$^{13}CH_3F$	1.0259
$^{13}CH_2{=}CBr_2$	1.0107	$CH_3{}^{13}CH_2CH_3$	1.0286
$^{13}CH_2{=}CH_2$	1.0162	$^{13}CO_2$	1.0659
$^{13}CH_3CN$	1.0166	$^{13}CO^{2-}$	1.0729

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(37) W. von E. Doering and J. B. Lambert, *Tetrahedron*, **19**, 1989 (1963).

(38) A. M. Katz and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **91**, 4469 (1969).

atoms or groups directly attached to the isotopic carbon atom are varied. Smaller factors are observed when changes occur at adjacent carbon atoms. As the fractionation factors are reported, values greater than unity indicate stiffer binding of the carbon atom than in the reference compound. Of the hydrocarbons, acetylene thus has the least stiffly bound carbon in this sense, as was found in the H/D fractionations. It is also of interest to note that the fractionation between ethylene and cyclopropane is essentially unity, indicating that the carbon atoms are equally stiffly bound in the two molecules. The carbon dioxide/carbonate fractionation has been calculated previously and there has also been an experimental determination of this quantity.[39] The number reported here agrees exactly with the earlier calculation.

One problem of long standing interest which figures from Table XII help one to understand is the general occurrence of low carbon isotope effects in SN1 reactions[40a] and in the equilibrium ionization of triphenylmethyl chloride in liquid sulfur dioxide.[40b] The early qualitative expectation was that since these processes involve transition states in which an initial state bond to carbon has been substantially broken, the carbon isotope effects should be large. The qualitative rationalization of the observed low effects has been that bond breaking to the leaving group must be compensated for by increased stiffness of binding, through conjugation, hyperconjugation and/or inductive effects, to the other attached "internal" groups.[33] It is quite a striking confirmation of this view that the fractionation factors of Table XII show that the equilibrium conversion of a tetrahedral to a trigonal carbon is associated with only a small carbon isotope effect. (This is different from the situation which obtains with the α-H *vs.* α-D effect.) Thus, the following exchange reaction is calculated to have an equilibrium constant of only 1.0175/1.0162 or 1.001.

$$CH_3CH_3 + {}^{13}CH_2{=}CH_2 \rightleftharpoons {}^{13}CH_3CH_3 + CH_2{=}CH_2$$

Although the fractionation factor for ethyl chloride is not included in the table we can estimate that the equilibrium constant for exchange of its α carbon with ethylene-^{13}C would be only 1.006. Thus, reactions having transition states with trigonal carbon would be expected from these examples to show low carbon isotope rate effects if carbon atom motion is not strongly involved in movement along the reaction coordinate in the transition state. Studies of deuterium isotope effects have independently led to the conclusion that the transition state motion for many typical SN1 reactions does not directly involve C–X bond cleavage but rather diffusion apart of the carbonium ion and leaving group counterion in an intermediate ion pair,[41] a motion not expected to have strong carbon atom involvement. Carbon isotope effects in SN2 reactions can be quite large despite the fact that binding between the central carbon and incoming and leaving groups is strong, because reaction coordinate motion in the transition state *does* strongly involve the central carbon atom.[42]

Acknowledgment. This research was supported in part by Grant No. AT(11-1)-1008 from the United States Atomic Energy Commission (Document No. COO-1008-11) and in part by Grant GP 32854 from the National Science Foundation. Electronic computations were performed with the facilities of the Indiana Research Computing Center.

Appendix

Because of the excessive amount of space required, we have not included details of the calculations. This information, which includes geometries, masses, internal valence coordinates, symmetry coordinates, valence force constants, symmetry force constants, and observed and calculated frequencies for each of the molecules studied, will be available as supplemental material in the annual microfilm edition of the journal.[43] We include in this appendix short notes on each of the molecules studied, together with the relevant references. The tables mentioned in parentheses refer to tables to be found in the supplemental material.

Ethane. The fundamental frequencies of C_2H_6 and C_2D_6 are well known, and force constants have been calculated.[16] We have repeated the calculations so as to include the A_{1u} torsional frequencies which have now been directly observed.[44a] The A class redundancies have been removed (here, and in other cases) by the method of ref 44b (Table XIII).

Methylacetylene and Methyl Cyanide. For both molecules the data of ref 16 were used to calculate fundamental frequencies. It was possible in both cases to reproduce exactly the results reported in ref 16 (Tables XIV and XV).

Methyl Fluoride. This molecule has been extensively studied in the past and there are several normal coordinate calculations available; ref 45 reviews the earlier work. For the present calculations we have taken bond lengths from ref 46, and have assumed tetrahedral angles. Our results agree well with the earlier work (Table XVI).

Methyl Chloride, Methyl Bromide, and Methyl Iodide. These molecules have all been thoroughly studied and normal coordinate calculations are available.[44b, 47] We have repeated the calculations using force constants based on a common potential energy expression (see calculation of fractionation factors) and have obtained results in good agreement with previous work (Tables XVII–XIX).

Methylsilane. The fundamentals have been reported for all vibrations of CH_3SiH_3 and CH_3SiD_3 ex-

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(39) H. G. Thode, M. Shima, C. E. Rees, and K. V. Krishnamurty, *Can. J. Chem.*, 43, 582 (1965).

(40) (a) For a summary of the data with references see A. Fry in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, Princeton, N. Y., 1970, p 381; (b) A. J. Kresge, N. N. Lichtin, K. N. Rao, and R. E. Weston, Jr., *J. Amer. Chem. Soc.*, 87, 437 (1965).

(41) V. J. Shiner, Jr. in ref 33, p. 107.

(42) (a) L. B. Sims, A. Fry, L. T. Netherton, J. C. Wilson, K. D. Reppond, and S. W. Crook, *J. Amer. Chem. Soc.*, 94, 1364 (1972); (b) A. V. Willi and C. M. Won, *J. Phys. Chem.*, 76, 427 (1972).

(43) This supplementary material will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-9002. Remit check or money order for $7.00 for photocopy or $2.00 for microfiche.

(44) (a) S. Weiss and G. E. LeRoi, *J. Chem. Phys.*, 48, 962 (1968); (b) W. T. King, I. M. Mills, and B. L. Crawford, Jr., *ibid.*, 27, 455 (1957).

(45) J. Aldous and I. M. Mills, *Spectrochim. Acta*, 18, 1073 (1962).

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cept the A_2 torsional frequencies.[48] Since a complete set of $3N - 6$ frequencies is required in the calculation of fractionation factors, the torsional frequency of CH_3SiH_3 was estimated from the known potential barrier restricting internal rotation about the C–Si bond (V_3 = 1700 cal mol^{-1}),[49] by the method of Fateley and Miller.[50] The corresponding A_2 symmetry force constant was then calculated from this estimated value for the torsional frequency. The only other uncertainty in the observed fundamentals concerns the value of the E class CH_3 deformation at ~1403 cm^{-1} for CH_3SiH_3. This frequency was not, therefore, used in the least-squares fitting. A partial normal coordinate calculation has been reported[51] for the E block of CH_3SiH_3, and a complete treatment, except for the A_2 torsional mode, has more recently also been reported.[52] It is not possible to compare our results directly with those of ref 49, but there is reasonable agreement with the partial data reported in ref 48 (Table XX).

Methylgermane. Observed fundamentals are available, except for the A_2 torsional frequency, for the molecules CH_3GeH_3, CD_3GeH_3, and CH_3GeD_3.[53] A value for the torsional frequency was estimated from the potential barrier restricting internal rotation about the C–Ge bond in CH_3GeH_3 (1239 cal mol^{-1}).[53] This value, 158 cm^{-1}, is in good agreement with the value of 155 cm^{-1} that has been estimated from combination bands[53] (Table XXI).

1,1,1-Trichloroethane. A normal coordinate calculation has been reported for CH_3CCl_3,[20] but more recent work[19] has assigned new values to some of the fundamentals, and the fundamentals for CD_3CCl_3 have been observed.[18] We have, therefore, been able to repeat the calculation using the more accurate data. Our results agree reasonably well with those of ref 20; the differences in valence force constants observed probably arise because we have used slightly different frequencies for CH_3CCl_3 from those used in ref 20, and we have fitted to two sets of frequencies, CH_3CCl_3 and CD_3CCl_3 (Table XXII).

1,1,1-Trifluoroethane. A normal coordinate calculation, based on a Urey-Bradley potential function, has been reported for CH_3CF_3 and CD_3CF_3.[54] We have repeated the calculation in terms of a valence force field and have included the A_2 torsional frequency; the torsional frequency for CH_3CF_3 has been obtained from microwave measurements[55] (Table XXIII).

Methylammonium Ion. The infrared spectra of the solid methylammonium halides have been reported,[56] but there does not appear to have been a previous normal coordinate calculation. The frequency data for the room temperature (α) phase of the chloride have been used to fit valence force constants. The calculated frequencies confirm the assignments of Theoret and Sandorfy, although there is some difficulty in assigning the E block rocking frequencies ν_{11} and ν_{12}, because of the strongly mixed nature of these vibrations. It was found necessary to include an extra interaction force constant in order to produce a reasonable fit of frequencies in the E block. An assumed geometry was used, except for the C–N bond length which has been measured[57] (Table XXIV).

Methylamine. A normal coordinate calculation has been reported.[58] In the present work we have used the frequency assignments of ref 58 and the observed frequencies for three isotopic molecules to devise a set of valence force constants. There seems to be some doubt about the assignment of the A'' NH_2 twisting frequency and we have used the values calculated in ref 58 as "observed" values in the present fitting. The values used for the torsional frequencies are those from the barrier to free internal rotation[59] (Table XXV).

Nitromethane. The fundamentals for both CH_3NO_3 and CD_3NO_2, and a normal coordinate calculation have been reported.[22] We have repeated the calculation using more recent assignments for the fundamentals of CH_3NO_2.[23] Because of the very low value of the sixfold rotational barrier (6 cal mol^{-1}),[60] we have treated one internal degree of freedom as a free internal rotation for the purpose of calculating partition functions. There are, therefore, only 14 fundamental frequencies. Two sets of force constants were evaluated: one set is given in the supplementary information, the other set contained some different interaction force constants. Thus, terms of the type f_{rd_1} were omitted; and terms of the type $f_{d_1d_2}$, $f_{d_1\alpha_2}$, $f_{d_1\alpha_2}$, $f_{d_1\beta_2}$ and $f_{\alpha_1\alpha_2}$ were included (see main text) (Table XXVI).

Ethyl Chloride. The fundamentals of this molecule and those of its partially deuterated analogs have been observed, and a normal coordinate calculation has been reported.[61] Our own results agree in all essential details with those reported in ref 61 (Table XXVII).

Propane. Several normal coordinate calculations have been reported; the earlier results[6,62] used data for $CH_3CH_2CH_3$ together with data for other n-paraffins to define a general valence force field transferrable among the paraffins. The more recent work[63] has used data for the partially deuterated propanes to obtain force constants for propane by fitting to fundamentals corrected for anharmonicity. We have calculated valence force constants by fitting to observed fundamentals (Table XXIIX).

Cyclopropane. The fundamentals for C_3H_8 and C_3D_8[64] were used to obtain a set of force constants. The symmetry coordinates used in the calculation were constructed by the method of Wilson[10] (Table XXIX).

Ethylene. The extensive work on ethylene has been reviewed.[65] We have used the assignments of ref 67 for C_2H_4 and C_2D_4 to obtain a set of force constants (Table XXX).

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1,1-Dibromoethylene and 1,1-Difluoroethylene. A partial normal coordinate calculation is available for both molecules;[66] we have repeated the calculations so as to include the out of plane vibrations. The observed frequencies of ref 67 were used (Tables XXXI and XXXII).

Acetylene. Valence force constants were obtained for this molecule by fitting to the observed fundamentals for C_2H_2, C_2HD, and C_2D_2 reported by Herzberg[13] (Table XXXIII).

Monohaloacetylenes. Valence force constants for the monohaloacetylenes have been calculated from the frequency data of ref 15. For monofluoroacetylene a second set of force constants was evaluated, fitting to the slightly different assignments of ref 14; see main text (Tables XXXIV–XXXVI).

Methane. We have taken the observed frequencies of ref 68 to obtain a set of force constants (Table XXXVII).

Fluoroform. We have used the relevant force constants reported in ref 69 as starting values in our least-squares fitting (Table XXXVIII).

Chloroform and Bromoform. Although a good Urey-Bradley force field is available for both molecules,[70] we have repeated the calculations in terms of valence force fields, using the same types of interaction force constants that were used for fluoroform. All fittings converged well except for the A_1 block of bromoform, which would not converge. We have chosen the set of force constants for this symmetry block which gives the closest agreement between observed and calculated frequencies (Tables XXXIX and XL).

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Vibrationally Induced Stabilization of the Vertically Excited States of Benzene

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Abstract: This paper examines the vibrationally induced stabilization of the lowest singlet and triplet vertically excited states of the benzene molecule. The nuclear motions which lead to a favorable (at least initially) stabilizing path are selected both qualitatively and quantitatively. The resulting potential energy surfaces of the excited states are discussed in relation to the spectroscopical and photochemical behavior of the benzene molecule.

In 1944 Lewis and Kasha[1] concluded after an investigation of the benzene phosphorescence spectrum that the molecule in its triplet state was contracted along the 1.4 axis. Even though it appeared later that the study of the phosphorescence intensity alone was not a very sensitive way of determining such distortions,[2] and, indeed, Shull[3] has shown that the phosphorescence spectrum can be interpreted in terms of a hexagonal D_{6h} configuration, more convincing experimental results are now available which support a very slight distortion away from hexagonal symmetry.[4] They indicate that the lowest triplet state, ${}^3B_{1u}$, is distorted into a nonplanar structure with two long bonds and four short ones. It is very important to note that these results have been obtained for the C_6H_6 molecule in a crystalline environment (usually in a C_6D_6 crystal). Therefore the nuclear displacements may result from the crystal field itself rather than being intrinsic properties of the free single molecule. Notwithstanding it is shown in this paper, by using a second-order perturbation method, that the nuclear motions which might stabilize the vertically excited triplet state ${}^3B_{1u}$ of the free molecule are precisely those which distort the triplet molecule in the crystal.

I. Qualitative Selection of the Stabilizing Vibrations

The problem we are looking at here is the selection of the nuclear motions which may be particularly efficient in the process of stabilizing a vertically excited species. One approach to this problem is the Herzberg–Teller expansion of the Hamiltonian in a Taylor series in normal coordinates of the ground electronic state.[5] If this development is restricted to only one coordinate, Q, we may write the correct Hamiltonian to second order in nuclear displacements

$$H = H_0 + (\partial H/\partial Q)_0 Q + {}^1/_2(\partial^2 H/\partial Q^2)_0 Q^2 + 0(Q^3) \quad (1)$$

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[5] This set of normal coordinates is well adapted to the study of vibronic problems in *absorption* where the originating state is the ground state; in *emission* problems it is more appropriate to use the normal coordinates of the excited electronic state from whose equilibrium nuclear configuration emission takes place. In the problem at hand neither one is perfect; it would be better to simply use a set of symmetry coordinates. In the benzene case, however, some matrix elements are readily evaluated in terms of the ground state's normal coordinates. It is hoped that such a convenient choice entails only slight impairment of our description.