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Valence Coordinate Contributions to Zero-Point Energy Shifts Due to Hydrogen Isotope Substitutions

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The orthogonal approximation method for the zero-point energy (ZPE) developed previously has been applied to analyze the shifts in the ZPE, δ(ZPE), due to monodeuterium substitutions in methane, ethylene, ethane and benzene in terms of elements of ***F*** and ***G*** matrices. The δ(ZPE) can be expressed with a reasonable precision as a sum of contributions of individual valence coordinates and correction terms consisting of the first-order interactions between the coordinates. A further refinement in the precision is achieved by a set of small number of second-order terms, which can be estimated by a simple procedure.

The zero-point energy, ZPE, of a molecule is of fundamental interest since it represents the minimum energy of the vibrating system with respect to the minimum in the potential energy surface. In the field of chemistry of isotopes, the ZPE differences between isotopically substituted molecules, δ(ZPE), are very important in the theoretical consideration of isotope effects on equilibria and also on reaction rates.

In a previous paper,[1] we developed an approximation for the ZPE expressed in terms of the first-order and second-order traces of the vibrational ***H*** matrix (***H***≡***FG***), i.e., Tr(***H***) and Tr(***H***^{2}), on the basis of a method of orthogonal expansion,

$$\mathrm{ZPE} = \frac{\hbar}{2}\lambda_{\max}^{1/2}[f\beta_0 + (\beta_1/\lambda_{\max})\mathrm{Tr}(\boldsymbol{H}) + (\beta_2/\lambda_{\max}^2)\mathrm{Tr}(\boldsymbol{H}^2)], \tag{1}$$

where $\lambda_{\max}$ is the largest vibrational eigenvalue of the molecule, f is the number of internal degree of freedom, and the coefficients β_0, β_1, and β_2 are simple functions of λ_0, a reference eigenvalue for a normalization purpose (Sometimes, $\eta \equiv \lambda_0/\lambda_{\max}$ is used in place of λ_0.), and ξ, the range of λ_i/λ_0 for the purpose of expansion. An advantage of this approximation method is that contributions of individual elements of the ***F*** and ***G*** matrices to the ZPE and/or to the δ(ZPE) can be explicitly estimated, and thus the method can provide an analytical means to study correlation of the ZPE and δ(ZPE) with molecular structures and molecular forces.

The method was since tested for the ZPE's of normal paraffins[2] and for the δ(ZPE) due to the deuterium-for-hydrogen substitutions in some molecules,[3] and a linear frequency sum rule was derived.[3] Now it seems to be a due course to apply the method to study in detail relationships between δ(ZPE) and the elements of ***F*** and ***G*** matrices.

In this paper we report on an analysis of correlation between internal valence coordinates and the ZPE shifts for monodeuterium substitutions, i.e., the d_1/d_0 pairs, in methane, ethylene, ethane and benzene. A simple equation is presented which yields the δ(ZPE) with a reasonable precision.

Computation

The isotope shift in ZPE, δ(ZPE), is defined as the ZPE of the lighter of two isotopic species of the pair minus the ZPE of the heavier. Thus, δ(ZPE) for the pair, d_1/d_0, is ZPE(d_0)−ZPE(d_1). In this paper we will treat the contributions of various valence coordinates and interactions between them to the shift in the sum of the frequencies, expressed in units of wavenumbers, $\delta\sum\omega_i$. From Eq. 1, we have

$$\delta\sum\omega_i \simeq \omega_{\max}[\beta_1\delta\sum(\lambda_i/\lambda_{\max}) + \beta_2\delta\sum(\lambda_i/\lambda_{\max})^2], \tag{2}$$

where $\omega_{\max} = \lambda_{\max}^{1/2}/2\pi c$, and δ denotes the difference in the quantity that follows it between the two isotopic molecules, d_0 and d_1. If one uses the conventional units for the elements of ***F*** and ***G*** matrices so that the eigenvalues are in units of mdyn Å^{-1}amu^{-1} (1 mdyn=1×10^{-8}N, 1 Å=1×10^{-10}m, and 1 amu=1.66057×10^{-27}kg), Eq. 2 becomes

$$\delta\sum\omega_i \simeq \beta_1'\delta\sum\lambda_i + \beta_2'\delta\sum\lambda_i^2, \tag{3}$$

where

$$\beta_1' \equiv \beta_1/\sigma\omega_{\max},\quad \beta_2' \equiv \beta_2/\sigma^2\omega_{\max}^3, \tag{4a,b}$$

and

$$\sigma \equiv 4\pi^2c^2/10^5N_0 \tag{5}$$

in which c is the speed of light in cm/s and N_0 the Avogadro's number.

The term of $\sum\lambda_i$ is the first-order term and that of $\sum\lambda_i^2$ is the second-order term. Each can be explicitly written in terms of the elements of ***F*** and ***G*** matrices, which forms the basis of our present study. Due to the Born-Oppenheimer approximation, an ***F*** matrix of a chemical species is common to all isotopic molecules. Because hydrogen is always a terminal atom (with exceptions of hydrogen-bonded structures), any motion of a hydrogen atom in a molecule does not vary many valence coordinates. Thus, many ***G*** matrix elements in $\sum\lambda_i$ and $\sum\lambda_i^2$ cancel between the isotopic pair d_1/d_0.

Let us denote the first-order term by S_1. Then,

$$S_1 \equiv \beta_1'\delta\sum\lambda_i = \beta_1'[\sum_i f_{ii}\delta g_{ii} + 2\sum_{i>j}\sum f_{ij}\delta g_{ij}], \tag{6}$$

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Table 1. Second-Order Terms of $\delta\sum\lambda_i^2$, $A_m \equiv a_m\sum\bar{F}\delta\bar{G}$ [a)]

Type(m)	a_m	$\delta\bar{G}$	$\bar{F}$	Summation [b)]
1	1	$\delta(g_{ii}^2)$	f_{ii}^2	Over all coordinate number i
2	2	$\delta(g_{ii}g_{jj})$	f_{ij}^2	Over all distinct combinations of different coordinate numbers i and j
3	4	$\delta(g_{ii}g_{ij})$	$f_{ii}f_{ij}$	(same as above)
4a	2	$\delta(g_{ij}^2)$	$f_{ii}f_{jj}$	(same as above)
4b	2	$\delta(g_{ij}^2)$	f_{ij}^2	(same as above)
5	4	$\delta(g_{ii}g_{jk})$	$f_{ij}f_{ik}$	Over all distinct combinations of different coordinate numbers i, j, and k
6	4	$\delta(g_{ij}g_{ik})$	$f_{ii}f_{jk}+f_{ij}f_{ik}$	(same as above)
7	4	$\delta(g_{ij}g_{kl})$	$f_{il}f_{jk}+f_{ik}f_{jl}$	Over all distinct combinations of different coordinate numbers i, j, k, and l

a) $\sum_m A_m = \delta\sum\lambda_i^2$. b) When more than one subscript are involved, all permutations of the same combination are counted once, except for Type 3 terms for which both $\delta(g_{ii}g_{ij})f_{ii}f_{ij}$ and $\delta(g_{jj}g_{ij})f_{jj}f_{ij}$ have to be separately considered.

where f_{ii} and g_{ii} are the diagonal elements of $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices, respectively, for the i-th coordinate, while f_{ij} and g_{ij} are the off-diagonal elements of $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices, respectively, representing the interactions between the i-th and j-th coordinates. δg_{ii} and δg_{ij} are the isotopic differences in g_{ii} and g_{ij}, respectively, i.e., the lighter (g_{ii} and g_{ij}) minus the heavier (g_{ii} and g_{ij}). The double summation in Eq. 6 is taken over all different combinations of different coordinates i and j.

Similarly, the second-order term S_2 is

$$S_2 \equiv \beta_2'\delta\sum\lambda_i^2 = \beta_2'\sum_{m=1}^{7}A_m, \tag{7}$$

where each A_m[4] is in the form of a product of a force constant factor, $\bar{\boldsymbol{F}}$, and a geometric factor, $\delta\bar{\boldsymbol{G}}$ as defined in Table 1.

At this point, let us define the kinds (or the types) of coordinate and the kinds (or the types) of interaction between coordinates. What follows is more or less generally presumed in papers on chemistry of isotopes, but it is essential for the present work to spell it out. A valence coordinate system of a molecule consists of a set of groups of equivalent coordinates. Then, each of such groups is a kind (or a type). Due to the isotope-independence of $\boldsymbol{F}$ matrix, the equivalence of coordinates for the present purpose is considered unaffected by a change of molecular symmetry by an isotopic substitution. A complete set of kinds of coordinate of a given chemical species is, therefore, found by examining the most symmetric isotopic species. Thus, ethane may be said to consist of five kinds (or types) of coordinates if redundancies are freely built into the coordinate system to preserve the highest possible symmetry; C–H stretching, C–C stretching, H–C–H bending, H–C–C bending, and HC–CH torsion. We will denote the kinds (or types) of coordinate with subscripts p and q, in order to distinguish them from the coordinate numbers for which the subscripts i, j, k, and l will be used.

The interaction (pq) between two kinds of coordinate, p and q, is the sum of all equivalent interactions between all coordinates i of kind p and all coordinates j of kind q. p may be equal to q in an interaction (pq), while i cannot be equal to j in an interaction (ij). It should be noted that not all interactions between the coordinates of kind p and those of kind q are necessarily identical. In such cases, an appropriate notation will be used to uniquely define the relative positions of two coordinates involved.

To examine the various terms included in Eqs. 6 and 7 from the viewpoint of the kinds of coordinate and of interaction, it may be useful to decompose these equations into the quantities, T, defined below.

$T_1(p)$: Sum of all terms of the form $f_{ii}\delta g_{ii}$, where i is a coordinate of kind p, multiplied by β_1'. $f_p \equiv f_{ii}$.

$T_1(pq)$: Sum of all terms of the form $2\beta_1' f_{ij}\delta g_{ij}$, $i>j$, where i is a coordinate of kind p and j is a coordinate of kind q. $f_{pq} \equiv f_{ij}$.

$T_2^m(p)$: Take the sum of all second-order terms of type m (cf: Table 1) involving the diagonal force constant f_{ii}, where i is a coordinate of kind p, and multiply the sum with β_2'. Then, $T_2^m(p)$ for $m=1$ is equal to the product, and $T_2^m(p)$ for all other terms containing another force constant beside f_{ii} is one-half of the product.

$T_2^m(pq)$: Take the sum of all second-order terms of type m involving the interaction constant f_{ij}, where i is a coordinate of kind p and j is a coordinate of kind q, and multiply the sum with β_2'. $T_2^m(pq)$ is equal to the product for types 2 and 4b, and one-half the product for all other types containing another constant beside f_{ij}. For $m=6$ and 7, the rule applies to each term of force constant product.

$T_2(p)$: Total second-order contribution of the coordinates of kind p to $\delta\Sigma\omega_i$.

$T_2(pq)$: Total second-order contribution of the interactions of kind pq to $\delta\Sigma\omega_i$.

$T_2(m)$: Total contribution of the second-order interactions of type m to $\delta\Sigma\omega_i$.

$T(p)$: Total contribution of the coordinates of kind p to $\delta\Sigma\omega_i$.

$T(pq)$: Total contribution of the interactions of kind pq to $\delta\Sigma\omega_i$.

Relationships among $\delta\Sigma\omega_i$, S_1, S_2, and various T's are easily understood. Whenever a second-order term contains a product of two different force constants, each half of the term is attributed to each of the participating force constants.

The various contributions, T, to $\delta\Sigma\omega_i$ were calculated for the d_1/d_0 pairs of methane, ethylene, ethane and benzene. The $\boldsymbol{F}$ matrices and the approximation parameters used are noted in the footnotes of Tables 2—6. The expansion coefficients β_1' and β_2' were computed from Eqs. 4a,b. The parameters ξ and η

Table 2. Major Contributions to $\delta\sum\omega_i$ in CH_3D/CH_4[a]

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Coordinate type (p) or Interaction type (pq)	f_p or f_{pq} /mdyn Å^{-1}	n_p or n_{pq}	$T_1(p)$[b] or $T_1(pq)$	$T_2(p)$[b] or $T_2(pq)$	$T(p)$[b] or $T(pq)$	$\frac{(4)^{c)}}{(2)\times(3)}$	$T_2^1(p)$[b]	$T_2^m(p)$ or $T_2^m(pq)$, $m \neq 1$[f]	(4)+(8)[b]
C–H stretch	4.918	1	1137.4 (92.4)	−202.1 (−16.4)	935.3 (76.0)	231.3	−202.4 (−16.4)		935.1 (75.9)
HCH bend[g]	0.370	3	256.7 (20.8)	−11.8 (−1.0)	244.9 (19.9)	231.3	−8.1 (−0.7)	[3]=−3.4; [4]=−1.5 (−0.3) (−0.1)	248.5 (20.2)
(HCH)×(HCH); adjacent[g]	−0.0779	3	54.1 (4.4)	−2.9 (−0.2)	51.2 (4.2)	−231.3	0.0 (0.0)	[2]=−1.5; [3]=−3.2; [5]=2.2 (−0.1) (−0.3) (0.2)	54.1 (4.4)
Total (approx)[d]			1448.2 (117.6)	−216.8 (−17.6)	1231.4 (100.0)		−210.5 (−17.1)		1237.7 (100.5)
Total (exact)[e]			1448.2 (117.6)	−216.4 (−17.6)	1231.8 (100.0)		−210.5 (−17.1)		1237.7 (100.5)

a) **F** matrix is taken from Hartshorn and Shiner.[5] The *cl* approximation[1] is used; k=0.77, ξ=3.614329, η=1.274406, ω_{max}=3022.31 cm^{-1} and $\delta\sum\omega_i$(exact)=1231.45 cm^{-1}. b) All T terms are in cm^{-1}. The numbers in parentheses below the wavenumber values are percent of $\delta\sum\omega_i$(exact). c) In units of Å mdyn^{-1}cm^{-1}. d) The sum of the contributions tabulated. e) The sum of all contributions, both tabulated and not tabulated. Contributions whose absolute magnitudes are less than 0.1% of $\delta\sum\omega_i$(exact) are not tabulated. f) Number in the brackets is the type of interaction, m. See Table 1 for the definition of interaction types. g) All bending coordinates are weighted by the equilibrium C–H bond length. The adjacent bends are two bends which share a C–H bond.

Table 3. Major Contributions to $\delta\sum\omega_i$ in $CHD{=}CH_2/CH_2{=}CH_2$ (All Vibrations)[a]

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Coordinate type (p) or Interaction type (pq)	f_p or f_{pq} /mdyn Å^{-1}	n_p or n_{pq}	$T_1(p)$[b] or $T_1(pq)$	$T_2(p)$[b] or $T_2(pq)$	$T(p)$[b] or $T(pq)$	$\frac{(4)^{c)}}{(2)\times(3)}$	$T_2^1(p)$[b]	$T_2^m(p)$ or $T_2^m(pq)$, $m \neq 1$[f]	(4)+(8)[b]
CH stretch	5.026	1	1311.9 (102.0)	−322.8 (−25.1)	989.1 (76.9)	261.0	−322.7 (−25.1)		989.2 (76.9)
HCH bend	0.598	1	156.1 (12.1)	−9.5 (−0.7)	146.6 (11.4)	261.0	−11.0 (−0.9)		145.1 (11.3)
H_2CC pw[g]	1.133	1	73.9 (5.7)	−2.4 (−0.2)	71.6 (5.6)	65.3	−3.1 (−0.2)		70.8 (5.5)
H_2CC op[g]	0.802	1	52.3 (4.1)	−1.4 (−0.1)	51.0 (4.0)	65.3	−1.5 (−0.1)		50.8 (3.9)
$H_2C{-}CH_2$ t[g]	0.626	1	40.8 (3.2)	−1.3 (−0.1)	39.6 (3.1)	65.3	−1.4 (−0.1)		39.4 (3.1)
(CH)×(pw); w/ common CH	±0.300	0	0.0 (0.0)	−3.7 (−0.3)	−3.7 (−0.3)	—	0.0 (0.0)	[2]=−1.5; [3]=−2.4 (−0.1) (−0.2)	0.0 (0.0)
(CH)×(pw); w/o common CH	±0.608	0	0.0 (0.0)	−3.5 (−0.3)	−3.5 (−0.3)	—	0.0 (0.0)	[2]=−7.0; [3]=3.0 (−0.5) (0.2)	0.0 (0.0)
Total (approx)[d]			1635.1 (127.1)	−344.4 (−26.8)	1290.7 (100.3)		−339.6 (−26.4)		1295.4 (100.7)
Total (exact)[e]			1635.1 (127.1)	−348.2 (−27.1)	1286.9 (100.0)		−339.6 (−26.4)		1295.4 (100.7)

a) **F** matrix is taken from Stern, Van Hook and Wolfsberg.[6] The *cl* approximation[1] is used; k=0.24, ξ=2.756151, η=1.392833, ω_{max}=3110.79 cm^{-1} and $\delta\sum\omega_i$(exact)=1286.64 cm^{-1}. b)—f) See the footnotes b)—f) of Table 2, respectively. g) Two HCH bends and two H_2CC in-plane wags (pw) are each weighted by the equilibrium C–H bond length, R_{CH}, two out-of-plane wags (op) are each weighted by $R_{CH}\cos\alpha$, and the torsion (t), as defined by Arnett and Crawford,[7] is weighted by $R_{CH}\sin\alpha$, where α is one half the equilibrium angle H–C–H.

used for each chemical species correspond to the value of the weighting parameter k[1] that makes the approximation, Eq. 3, almost exact for the d_1/d_0 pair of the molecule.

Results and Discussion

Results of calculations have been summarized in

Table 4. Major Contributions to $\delta\sum\omega_i$ in C_2H_5D/C_2H_6[a)]

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Coordinate type (p)	f_p /mdyn Å^{-1}	n_p	$T_1(p)$[b)]	$T_2(p)$[b)]	$T(p)$[b)]	$\frac{(4)^{c)}}{(2)\times(3)}$	$T_2^1(p)$[b)]	$T_2^m(p)$, $m\neq1$[f)]	(4)+(8)[b)]
C-H stretch	4.704	1	1251.5	−295.5	956.0	266.1	−295.6		955.9
			(94.9)	(−22.4)	(72.5)		(−22.4)		(72.5)
HCH bend[g)]	0.451	2	240.5	−15.4	225.1	266.5	−12.9	[4]=−2.8	227.6
			(18.2)	(−1.2)	(17.1)		(−1.0)	(−0.2)	(17.3)
HCC bend[g)]	0.532	1	141.9	−5.8	136.0	266.5	−4.4	[4]=−1.5	137.5
			(10.8)	(−0.4)	(10.3)		(−0.3)	(−0.1)	(10.4)
HC-CH τ[g)]	0.00672	1	2.0	−0.1	1.9	299.7	−0.0	[4]=−0.1	2.0
			(0.2)	(−0.0)	(0.1)		(−0.0)	(−0.0)	(0.2)
Total (approx)[d)]			1635.9	−316.8	1319.1		−312.9		1322.9
			(124.0)	(−24.0)	(100.0)		(−23.7)		(100.3)
Total (exact)[e)]			1635.9	−316.6	1319.3		−312.9		1322.9
			(124.0)	(−24.0)	(100.0)		(−23.7)		(100.3)

a) ***F*** matrix used is Schachtschneider and Snyder's VFF(V).[8)] The *cl* approximation[1)] is used; k=0.30, ξ=2.901508, η=1.370426, ω_{max}=2968.70 cm^{-1} and $\delta\sum\omega_i$(exact)=1319.28 cm^{-1}. b)—f) See the footnotes b)—f) of Table 2, respectively. g) All bending coordinates and the torsion (τ) are weighted by the equilibrium C-H bond length. The torsion is as defined by Wilson, Decius, and Cross.[9)]

Table 5. Major Contributions to $\delta\sum\omega_i$ in Benzene-d_1/Benzene-d_0 (Planer Vibrations Only)[a)]

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Coordinate type (p)	f_p /mdyn Å^{-1}	n_p	$T_1(p)$[b)]	$T_2(p)$[b)]	$T(p)$[b)]	$\frac{(4)^{c)}}{(2)\times(3)}$	$T_1^2(p)$[b)]	$T_2^m(p)$, $m\neq1$[f)]	(4)+(8)[b)]
C-H stretch[g)]	5.063	1	1202.3	−236.3	966.1	237.5	−235.7		966.7
			(103.3)	(−20.3)	(83.0)		(−20.2)		(83.0)
HCC$_2$ pw[g)]	0.870	1	206.5	−6.3	200.1	237.5	−7.8	[3]=1.5	198.7
			(17.7)	(−0.5)	(17.2)		(−0.7)	(0.1)	(17.1)
Total (approx)[d)]			1408.8	−242.6	1166.2		−243.5		1165.3
			(121.0)	(−20.8)	(100.2)		(−20.9)		(100.1)
Total (exact)[e)]			1408.8	−244.5	1164.3		−243.5		1165.3
			(121.0)	(−21.0)	(100.0)		(−20.9)		(100.1)

a) ***F*** matrix is taken from Crawford and Miller.[10)] The *cl* approximation[1)] is used; k=0.55, ξ=3.332543, η=1.309823, ω_{max}=3083.78 cm^{-1} and $\delta\sum\omega_i$(exact)=1164.06 cm^{-1}. b)—f) See the footnotes b)—f) of Table 2, respectively. g) The coordinate system consists of six C-H stretchings, six C-C stretchings, six CCC bendings and six in-plane wags (pw). The pw's are weighted by the equilibrium C-H bond length and CCC bends are weighted by the equilibrium C-C bond length.

Tables 2—6. Each entry of the terms T, i.e., the columns 4, 5, 6, 8, 9, and 10 in these tables, shows the magnitude of the term in cm^{-1} and, in parentheses, percent of the exact value of $\delta\Sigma\omega_i$, $\delta\Sigma\omega_i$(exact). The exact value was calculated from the eigenvalues obtained by solving vibrational secular equations. For clarity, only the coordinate and interaction types (column 1) for which the magnitude of the first-order or second-order term (column 4 or 5) is more than 0.1% of the $\delta\Sigma\omega_i$(exact) have been tabulated. Columns 4 and 5 tabulate the totals of the first-order and second-order terms, respectively, and column 6 is the sum of columns 4 and 5. Columns 7—10 will be used for detailed examination of individual contributions contained in columns 4—6.

From their definitions, $T_1(p)$ and $T_1(pq)$ may be written as

$$T_1(p) = \beta_1' n_p f_p \delta g_p, \tag{8}$$

and

$$T_1(pq) = 2\beta_1' n_{pq} f_{pq} \delta g_{pq}, \tag{9}$$

where n_p and n_{pq} are, respectively, the numbers of non-vanishing δg_{ii}, in which i is a member of p, and the number of non-vanishing δg_{ij} in which (ij) is a member of the interaction type (pq) (column 3). Because hydrogen is a terminal atom, n_p is usually unity. The larger value of n_p is possible only when two or more coordinates of the same kind share the substituted hydrogen atom (SHA).

The "Total" under the columns 4, 5, 6, 8, and 10 are, respectively, S_1 (Eq. 6), S_2 (Eq. 7), $\delta\Sigma\omega_i$(Eq. 3), $T_2(1)$, and $S_1+T_2(1)$. A difference between "Total (approx)" and

Table 6. Major Contributions to $\delta\sum\omega_i$ in Benzene-d_1/Benzene-d_0 (Out-of-plane Vibrations Only)[a]

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Coordinate type (p) or Interaction type (pq)	f_p or f_{pq} /mdyn Å^{-1}	n_p or n_{pq}	$T_1(p)$[b] or $T_1(pq)$	$T_2(p)$[b] or $T_2(pq)$	$T(p)$[b] or $T(pq)$	$\frac{(4)^{c)}}{(2)\times(3)}$	$T_2^1(p)$[b]	$T_2^m(p)$ or $T_2^m(pq)$, $m \neq 1$[f]	(4)+(8)[b]
HCC$_2$ op[g]	0.378	1	243.9	−32.6	211.3	645.2	−42.3	[3]=9.7	201.6
			(114.2)	(−15.3)	(98.9)		(−19.8)	(4.6)	(94.3)
(op)×(t);[g]	±0.0875	0	0.0	4.0	4.0	—	0.0	[2]=−3.6; [3]=−10.1;[5]=−2.4	0.0
sharing 3C's			(0.0)	(1.9)	(1.9)		(0.0)	(−1.7) (4.7) (−1.1)	(0.0)
(op)×(op);[g]	−0.0570	0	0.0	−2.3	−2.3	—	0.0	[2]=−2.3; [3]=−3.0; [5]=3.0	0.0
sharing 2C's			(0.0)	(−1.1)	(−1.1)		(0.0)	(−1.1) (−1.4) (1.4)	(0.0)
(op)×(t);[g]	±0.0430	0	0.0	0.7	0.7	—	0.0	[2]=−0.9; [3]=2.7; [5]=−1.2	0.0
sharing 2C's			(0.0)	(0.3)	(0.3)		(0.0)	(−0.4) (1.3) (−0.5)	(0.0)
Total (approx)[d]			243.9	−30.2	213.7		−42.3		201.6
			(114.2)	(−14.1)	(100.0)		(−19.8)		(94.3)
Total (exact)[e]			243.9	−30.2	213.7		−42.3		201.6
			(114.2)	(−14.1)	(100.0)		(−19.8)		(94.3)

a) ***F*** matrix is taken from Miller and Crawford.[11] The *cl* approximation[1] is used; k=1.4, ξ=4.193083, η=1.209680, ω_{max}=993.44 cm^{-1} and $\delta\sum\omega_i$(exact)=213.67 cm^{-1}. b)—f) See the footnotes b)—f) of Table 2, respectively. g) The coordinate system consists of six HCC$_2$ out-of-plane wags (op) and six CC–CC torsions (t) as defined in Wilson, Decius, and Cross.[9] The op's are weighted by the equilibrium C–H bond length and t's are weighted by the equilibrium C–C bond length.

"Total (exact)" is a sum of the small contributions which were individually not tabulated due to the 0.1% criterion.

In the following we will first itemize important observations one would make on these tables and then discuss each feature separately.

Observations. (1) On $\delta\Sigma\omega_i$: $\delta\Sigma\omega_i$ is within 0.1% of $\delta\Sigma\omega_i$(exact) if all contributions are counted. It is within 0.1% for all molecules, except ethylene (100.3%) and the planar vibrations of benzene (100.2%), when only those tabulated in these tables are summed up.

(2) On few entries for interaction types (pq) in column 1: Except for methane, ethylene and benzene (out-of-plane vibrations), there is no entry for the interactions in column 1, which means that $T_1(pq)$ and $T_2(pq)$ for the interaction forces do not individually contribute more than 0.1% of $\delta\Sigma\omega_i$(exact) in most cases.

(3) On the relative magnitudes of entries in columns 4, 5, and 6: By far the largest contributor is the H-X stretching coordinate. The following inequalities generally hold on the absolute magnitudes among various terms; a) $T_1(p) \gg T_2(p)$ and $T_1(pq) \gg T_2(pq)$, b) T_1(H-X stretch)$\gg T_1$(bend)$\gg T_1$(out-of-plane motion), c) many $T_1(pq)$'s vanish, and when they do not, T_1(bend)$\gg T_1(pq)$, and d) T_2(HX stretch)$\gg T_2$(p$\neq$HX-stretch).

(4) On the "Totals" for the columns: a) The S_1 and $T_2(1)$ entries (columns 4 and 8) for "approx" are respectively identical to the "exact", and b) the difference between "approx" and "exact" of S_2 (column 5) is equal to that of $\delta\Sigma\omega_i$ (column 6).

(5) On column 10: $S_1+T_2(1)$ is within 0.7% of $\delta\Sigma\omega_i$(exact) except for the out-of-plane vibrations of benzene. The sources of the errors for all molecules are identified in column 9.

First-Order Terms. Every type of coordinate that includes the SHA in the coordinate definition makes a positive contributions, $T_1(p)$, to the first-order term. The number n_p of non-vanishing δg_p (Eq. 8) is more than unity only when more than one equivalent bending coordinate share the SHA, as exemplified by methane and ethane. Expressions for $T_1(p)$ can be easily obtained. It is seen that column 7 in Tables 2—6 gives $\beta_1^\prime\delta g_p$ (Eq. 8) and, $\beta_1^\prime$ being common to all coordinate types of a given molecule, the difference in $T_1(p)/n_pf_p$ is the difference in δg_p. For every molecule studied, all bending coordinates except CCC bends in benzene are weighted by the equilibrium C–H bond length. For stretching and angle-bending coordinates, therefore, the numbers under column 7 are equal to $\beta_1^\prime\delta\mu_H$. For the wagging and torsional coordinates in ethylene, 65.3 for the coordinate types pw, op, and t is simply 261/4. The value for the out-of-plane wag for benzene seems to be out of place at a first glance, but actually it is not. The unusually large value is due to the artifact that the out-of-plane vibrations have been isolated for the purpose of this analysis, thus making ω_{max} for this group of motions small (993 cm^{-1}). In fact, the products of these values of $\beta_1\delta\mu_H/(\sigma\omega_{max})$ and ω_{max} fall in a relatively narrow range between 7 and 8 in units of 10^5 Å mdyn^{-1} for all molecules tested, and variation of the values is due to the difference in the k-values used for the different molecules.

The first-order contribution of an interaction type (pq) does not vanish only if 1) there is at least one member coordinate i of kind p and at least one member coordinate j of kind q, such that $s_{i\mathrm{H}}\cdot s_{j\mathrm{H}}\neq 0$, where $s_{i\mathrm{H}}$ is the s-vector[9] for the motion of the SHA in the coordinate i, and 2) f_{ij} for such a pair ij is non-zero. Thus, δg_{pq} vanishes whenever one of p and q is a stretching coordinate.

The most common interaction type that makes a finite contribution to the first-order term is one between two bending coordinates that share the SHA.

The fact that the "Total (approx)" and "Total (exact)" for S_1 are identical for all molecules studied is accidental due to two major reasons. The first is lack of appropriate f_{ij} in the $\boldsymbol{F}$ matrix used. For instance, the interactions such as (HCH)×(in-plane wag)$_{\mathrm{adj.}}$, in ethylene, (HCH)×(HCC)$_{\mathrm{adj.}}$, in ethane do not contribute to the first-order term simply because the corresponding interaction constants are, somewhat strangely, missing from the particular $\boldsymbol{F}$ matrices used. The second reason is lack of adjacent bending coordinates. For example, there is no entry for the (HCC)×(HCC)$_{\mathrm{adj.}}$ interaction in column 1 for the in-plane vibrations of benzene, due to the fact that coordinate system used happens to include six wags rather than, say, twelve HCC bends. However, the difference between the "approx" and "exact" can be made assuredly negligible as long as one includes all the important interactions for which f_{pq}'s are large.

Second-Order Contributions by Diagonal Elements of *F* Matrix. It is clear from Table 1 that the diagonal elements of $\boldsymbol{F}$ matrix may contribute to the second-order terms only through Types 1, 3, 4a, and 6. Further, it can be shown that $\delta(g_{ii}^2)$ does not vanish if and only if the corresponding δg_{ii} is non-zero and that $\delta(g_{ij}^2)$ does not vanish if and only if the corresponding δg_{ij} is non-zero. Therefore, the number of non-vanishing $\delta(g_{ii}^2)$ is n_p, where p is the kind of coordinate of which i is a member. The number of non-vanishing $\delta(g_{ij}^2)$ is n_{pq}, where pq is the kind of interaction of which ij is a member.

It is thus evident that $T_2^1(p)$ is always non-zero for every p which has a member involving the SHA. Furthermore, they are the largest second-order term, because both of its geometric and force constant factors involve the diagonal elements only. Because the bond-stretching force constants are larger than the bending force constants, usually by one order of magnitude, T_2^1(H–X stretch) is by far the most important contributor of all $T_2^1(p)$'s. $T_2^1(p)$ is always nagative, because β_2' is negative.

As explained earlier, many g_{ij} $(i\neq j)$ are zero, and many $\delta(g_{ij})$ vanish for monodeuterium substitutions. $T_2^3(p)$ is non-zero, only if g_{ij} and f_{ij} are both non-zero at least one coordinate i of kind p that contains the SHA and for at least another coordinate j $(i\neq j)$. Note that j may be another member of p. $T_2^{4\mathrm{a}}(p)$ does not vanish, only if there is another coordinate j sharing the SHA with i, such that $s_{i\mathrm{H}}\cdot s_{j\mathrm{H}}\neq 0$. Again, j may be another member of p. The probability of non-zero $T_2^6(p)$ due to any f_{ii} is so low that we can safely disregard this term.

The sum of S_1 and $\Sigma T_2^1(p)$ (column 10 of Tables 2—6) is within 0.7% of $\delta\Sigma\omega_i$(exact) for all molecules studied with the exception of out-of-plane vibration of benzene. This offers a possibility of a means for a quick approximate calculation for δ(ZPE). A further refinement can be made if one is able to locate all major correction terms to this approximation, namely, all large terms among $T_2^m(p)$ and $T_2^m(pq)$, $m\neq 1$ (column 9, Tables 2—6).

Second-Order Contributions by Off-Diagonal Elements of *F* Matrix. From Table 1, it is seen that an off-diagonal element f_{ij} may make a non-vanishing contribution in all but those for m=1 and 4a. Due to the stringent requirements for the existence of non-zero $T_2^6(pq)$ and $T_2^7(pq)$, we can safely ignore these terms. Similarly, the likelihood of occurrence of non-zero $T_2^5(pq)$ is small and, even if it does occur, its magnitude will be small due to the fact that it contains a product of two off-diagonal force constants and one off-diagonal $\boldsymbol{G}$ matrix element. This leaves us with three types: $T_2^2(pq)$, $T_2^3(pq)$, and $T_2^{4\mathrm{b}}(pq)$.

For a given (non-zero) f_{pq}, the process of finding major contributing terms among $T_2(m)$, $m\neq 1$, is a rather simple task once $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices become available, because one can eliminate a major portion of all possible second-order terms on the basis of vanishing δg_{ii} and δg_{ij}: When a δg_{ii} or a δg_{ij} vanishes, the corresponding $\delta(g_{ii}^2)$ or $\delta(g_{ij}^2)$ also does.

Among the non-vanishing terms of $T_2^2(pq)$, $T_2^3(pq)$ and $T_2^{4\mathrm{b}}(pq)$, the term $T_2^3(pq)$ tends to be the largest, especially when the members i and j share the SHA because, then, the geometric factors g_{ii} and g_{ij} would become comparable. One should note that Type 3 (m=3) terms contains both $f_{ii}f_{ij}\ \delta(g_{ii}g_{ij})$ and $f_{jj}f_{ij}\ \delta(g_{jj}g_{ij})$ which are different from each other. For a given (ij) both possibilities should be explored.

A Simple Correlation Formula

As noted earlier in this paper, column 10 in Tables 2—6 suggests that an approximation,

$$\delta\sum\omega_i \simeq S_1 + T_2(1), \tag{10}$$

gives a precision of 0.7% or better in all molecules tested except the out-of-plane vibrations of benzene. The error for the latter is unusually large simply because the major contribution for this case, $T(op)$, comes from the weak out-of-plane motion, thus making other small second-order terms $T_2(m)$, $m\neq 1$, relatively significant. The foregoing example shows that the process of estimating such a correction term is not a laborious task, even for the relatively large correction.

We made similar correlation study for some other molecules, which we did not report here, and obtained the result that Eq. 10 is a good approximation of Eq. 3.

Equation 10 may be rewritten as

$$\delta(\mathrm{ZPE}) \simeq \frac{\hbar c}{2}\{[\beta_1'\sum_i f_{ii}\delta g_{ii} + \beta_2'\sum_i f_{ii}^2\delta g_{ii}^2] + 2\beta_1'\sum_{i>j}\sum f_{ij}\delta g_{ij}\}. \tag{11}$$

The terms within the brackets represent the contribution of various valence coordinates (diagonal elements), and the last term under the double sum is the contribution of interactions between the coordinates. It has been shown that the first-order interaction terms usually vanish, unless there are more than one adjacent bending coordinates sharing the SHA and the corresponding interaction force constant is non-zero.

Equation 11 thus implies that, usually, a fair result can be obtained only by considering the diagonal elements of $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices. This result is consistent with the result by Wolfsberg's perturbation approximation.12) His approximation for ZPE consists of a zeroth-order term, $\hbar(f_{ii}g_{ii})^{1/2}/2$, and a correction term which consists of the off-diagonal elements as well as the diagonal ones. This zeroth-order term gives an excellent approximation, and the correction term is usually very small.

The fact that the second-order terms $T_2(m)$, $m \neq 1$ in our present approximation are relatively small can be understood from Eq. 2. Every ratio $\lambda_i/\lambda_{\max}$ in Eq. 2 is much smaller than unity, except for the H-X stretching eigenvalues. The ratios for all bending modes usually lie in the range below $0.25\lambda_{\max}$.2,3) The squares of such ratios are much smaller quantities than $\lambda_i/\lambda_{\max}$. As we have shown in this paper, a large majority of the non-vanishing terms $T_2(m)$, $m \neq 1$, may be regarded as correction terms for the eigenvalues of bending modes. Since the stretching modes are well accounted for within S_1 and $T_2(1)$, the terms of $T_2(m)$, $m \neq 1$, are thus second-order corrections for the small eigenvalues, and one expects such corrections to be very small. One may also reason for the smallness of these terms on the basis of relative magnitudes of $\delta\overline{\boldsymbol{G}}$ and $\overline{\boldsymbol{F}}$ tabulated in Table 1.

It is thus reasonable to make a general statement that Eq. 11 is a simple way to correlate the δ(ZPE) for the monodeuterium substitution and the molecular structures and forces.

Conclusion

The shift in the zero-point energy due to monodeuterium substitutions can be expressed, with the precision which is usually better than 1%, by the relation,

$$\delta(\mathrm{ZPE}) \simeq \frac{\hbar c}{2}\{[\beta_1'\sum_i f_{ii}\delta g_{ii} + \beta_2'\sum_i f_{ii}^2\delta g_{ii}^2] + 2\beta_1'\sum_{i>j}\sum f_{ij}\delta g_{ij}\}.$$

A further refinement in the precision can be achieved by a relatively simple process of estimating major correction terms among the second-order terms of Types 3, 4, and 2.

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