Orthogonal Approximation and Classification of Molecules for Zero-Point Energy Shifts Due to H/D Isotope Substitutions

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Synopsis. Dozens of hydrogenous molecules have been classified for the approximation of the H/D isotope shifts in zero-point energies. The classification, based on their molecular structures, has yielded relative approximation errors of better than one percent with a few predictable exceptions. A further refinement of the classification has been suggested.

The zero-point energy (ZPE) of a molecule can be expressed in terms of the traces of the vibrational $\boldsymbol{H}$ ($\equiv\boldsymbol{GF}$) and $\boldsymbol{H}^2$ matrices in a second-order orthogonal approximation[1]

$$\text{ZPE} \simeq \frac{\hbar}{2}[b_0 f + b_1 \text{Tr}(\boldsymbol{H}) + b_2 \text{Tr}(\boldsymbol{H}^2)], \quad (1)$$

where f is the internal degrees of freedom, $\text{Tr}(\boldsymbol{A})$ is the trace of a square matrix $\boldsymbol{A}$ and b_0, b_1, and b_2 are approximation coefficients and are simple functions of approximation parameters involved. The precision of the approximation depends on the choice of the values of approximation parameters, which have been determined by minimizing a weighted integral of the square of the approximation error taken over the range of vibrational eigenvalue λ between zero and its largest value $\lambda_{\max}$. The weighting function $w(\lambda)$ used has the form of

$$w(\lambda) = (k+1)\lambda^k/\lambda_{\max}^{k+1}, \quad (2)$$

where k is the weighting parameter and the approximation parameters have been calculated in the range of $k \geq 0$. Parameter values thus determined are to optimize the approximation for the ZPE itself rather than the approximation for the difference between two ZPE's such as differences between the ZPE's of two isotopic molecules and those between the ZPE's of a molecule in two phases.

In a recent paper,[2] we developed another second-order approximation for the ZPE and on the basis of the approximation established a theoretical foundation for the additivity of the ZPE. In the new approximation, the zeroth-order term, which is the ZPE of an imaginary molecule consisting of completely uncoupled oscillators, i.e., consisting only of diagonal elements of $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices, $\frac{\hbar}{2}\Sigma(f_{ii}g_{ii})^{1/2}$, has been singled out. The approximation parameters in the new approximation were determined by minimizing the weighted integral of the square of the derivative of the error. The weighting function used was the same as that of Eq. 2 in form and parameters were determined in the range of $k > -1/2$. The parameter values thus obtained were expected to give better approximation for ZPE differences than for the ZPE itself since they are designed to optimize the differential ZPE.

In this paper, we report on results of the approximation for the ZPE shifts due to deuterium-for-hydrogen substitutions, using the approximation form of Eq. 1 with parameters obtained in the new approximation. A scheme of classification of molecules based on their molecular structures is presented for satisfactory H/D ZPE shift approximations.

Computation

From Eq. 1, the isotopic difference in the ZPE, δ(ZPE), can be expressed as

$$\delta(\text{ZPE}) \simeq \frac{\hbar}{2}[\beta_1 \delta\text{Tr}(\boldsymbol{H}) + \beta_2 \delta\text{Tr}(\boldsymbol{H}^2)], \quad (3)$$

where $\delta\text{Tr}(\boldsymbol{A})=\text{Tr}(\boldsymbol{A})$(lighter isotope)$-\text{Tr}(\boldsymbol{A})$(heavier isotope), and β_1 and β_2 are the approximation coefficients which were determined in the new procedure for ZPE approximation[2] and are unique at a given k value. The values of the approximation coefficients have been tabulated for various k values.[2]

We examined dozens of hydrogenous molecules. All the isotopic pairs studied were grouped according to the molecular geometries around the site of the H/D substitutions. In a somewhat trial-and-error manner, we first determined the best k value, k_o, at which the error in the δ(ZPE) is almost zero for each pair. We then obtained a group average of k_o's, $\bar{k}_o$ for each group, and calculated percent errors of δ(ZPE) by using the same $\bar{k}_o$ value for all isotopic pairs of the molecules belonging to the same group.

Grouping of molecules is important. We have already shown in a previous paper[3] that for a very limited set of sample molecules the best k value for the approximation of H/D isotope shifts in ZPE can be well correlated with the number of H–X bonds and H–X–Y angles, where X is the site of isotopic substitutions and H is the substituted hydrogen atom (SHA), and with the number of torsional and other plane-wagging motions involving the SHA.

Results and Discussion

The molecular species studied were classified as shown in the first two columns of Table 1. In the second column of the table, (Y), (Z), and (W) represent polyatomic moieties of a species while those letters without parentheses denote single atoms ($\neq$H). Also, X–Y means a direct bonding, which may be a multiple bond, while X···(Y) indicates that there may be more than one bond between X and (Y). The values of $\bar{k}_o$'s are listed in the third column. In the fourth through seventh columns are listed the k_o values and % errors of

Table 1. Classification of Molecules for H/D Isotope Shifts in Zero-Point Energies[a)]

Group	Description	$\bar{k}_o$[b)]	Representative molecule				
			molecule	pair	k_o	% error at $\bar{k}_o$	Ref.
Ia	HX-Y [Linear]	0.277	HCN	d_0/d_1	0.259	−0.72	4
	HX-Y-Z [Linear]:						
Ib1	(Z=H)	0.264	C_2H_2	d_0/d_1	0.266	0.07	5
				d_0/d_2	0.262	−0.07	
Ib2	(Z≠H)	0.197	HCCF	d_0/d_1	0.206	0.37	5
Ic	HX-Y [Bent]	0.427	HOCl	d_0/d_1	0.442	0.40	6
Id	HX···(Y) [Planar]	0.278	C_6H_6	d_0/d_1	0.269	−0.35	7
Ie	HX···(Y) [Nonplanar][d)]	0.322 (0.278)	CHF_3	d_0/d_1	0.409	2.78	8
			$CHCl_3$	d_0/d_1	0.299	−0.90 (0.86)[f)]	5
			$CHBr_3$	d_0/d_1	0.257	−2.56 (−0.84)[f)]	5
IIa	H_2X	1.052	H_2O	d_0/d_1	1.005	−0.28	9
IIb	H_2X-Y [Planar]	0.718	H_2CO	d_0/d_1	0.742	0.31	10
IIc	H_2XY_2 [Nonplanar]	0.441	CH_2F_2	d_0/d_2	0.498	1.38	11
	H_2X-YZ_2 [Planar]:						
IId1	(Z=H)	0.398	CH_2CH_2	CH_2/CD_2	0.401	0.08	12
IId2	(Z≠H)	0.272	CH_2CF_2	d_0/d_2	0.276	0.16	5
IIe	H_2X···(Y) [Nonplanar][g)]	0.400	CH_3CH_2Cl	d_0/d_2	0.390	−0.30	5
			$CH_3CH_2CH_3$	CH_2/CD_2	0.410	0.26	5
IIIa	H_3X	0.723	NH_3	d_0/d_1	0.677	−0.64	13
IIIb	H_3X-Y [Nonplanar][d)]	0.462 (0.437)[e)]	CH_3F	d_0/d_3	0.537	1.69	14
			CH_3Cl	d_0/d_3	0.463	0.46 (0.65)[f)]	5
			CH_3Br	d_0/d_3	0.432	−0.76 (−0.13)[f)]	5
			CH_3I	d_0/d_3	0.415	−1.21 (−0.58)[f)]	5
IIIc	H_3X-Y-Z···(W) [X-Y-Z Linear]	0.528	CH_3CCH	d_0/d_3	0.574	0.91	5
IIId	H_3X-Y···(Z) [Around Y nonlinear][g)]	0.419	CH_3CH_2Cl	CH_3/CD_3	0.436	0.46	5
			$CH_3CH_2CH_3$	CH_3/CD_3	0.442	0.63	5
IV	H_4X	0.686	CH_4	d_0/d_1	0.733	0.64	15
				d_0/d_3	0.646	−0.59	

a) Case B approximation. See Ref. 2 for details. b) The group average of the optimum k. See text. c) The first-named isotopic species is the reference molecules from which λ_{max} was obtained. d) With no possibility of torsion involving the H atom being substituted. e) Alternate $\bar{k}_o$ value obtained by excluding fluoro compounds. f) The numbers in the parentheses are the percent errors obtained by using the alternate $\bar{k}_o$ listed in the parentheses in the third column. g) With possibility of torsions involving the H atom being substituted.

δ(ZPE) at the $\bar{k}_o$ for isotopic pairs of representative molecules of each group. Each group contains more isotopic pairs than listed, but we limit the presentation of the results to the molecules that are used in the discussion hereafter, thus avoiding a lengthy listing of numerical results. In the last column of the table, the origin of the used frequency data is shown.

With a few exceptions, the k_o values within any given group are similar and consequently, the relative errors obtained by using the group average of the k_o's are less than one percent. Any larger error suggests a further subdivision of the classification when it occurs. For instance, Group Ie should be further divided into fluoro compounds and others. Figures 1(a) and 1(b) compare the patterns of the eigenvalue shifts upon the H/D substitutions in fluoroform and chloroform. The high electronegativity of F induces relatively high stretching and bending force constants in CHF_3, which in turn causes the higher frequencies for CHF_3 than for $CHCl_3$, especially in the region below ρ ($\equiv\lambda/\lambda_{max}$)~0.2. Thus one needs different weighting parameters for CHF_3 and for other haloforms. The results of using $\bar{k}_o$=0.278 for the other haloforms are shown in the parentheses in the 7th

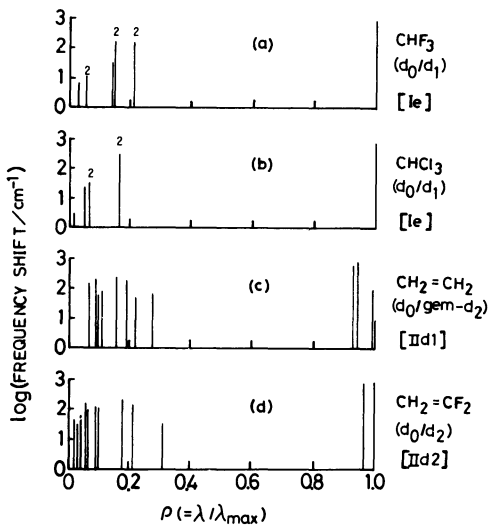

Fig. 1. Examples of differences in eigenvalue shift patterns; (a) vs. (b) for fluoro vs. other halo compounds and (c) vs. (d) for H vs. heavier atoms at β position. A vertical line is positioned at the eigenvalue of the lighter molecule, and its height shows the magnitude of the red-shift in the corresponding frequency due to the indicated H/D substitution. A number at the top of the shift line denotes the degeneracy of the shift.

column of Table 1. Group IIIb is another example of the potential advantage of decoupling fluoro compounds from other halo compounds.

The reason for the necessity for distinguishing between hydrogen atom and non-hydrogen atoms in Group Ib (Ib1 and Ib2) and IId (IId1 and IId2) is illustrated in Figs. 1(c) and 1(d). The substitution of H's by heavy atoms such as F not only reduces the number of H–Y stretching vibrations into half, thus affecting the high frequency population, but also does it decrease the frequencies of angle-bending and out-of-plane vibrations.

In general, the number of hydrogen atoms at the α and β positions relative to the site of H/D substitutions significantly affect the shift pattern. The expectation that molecular structure beyond the β positions would have been negligible effects on δ(ZPE) is in good agreement with the cut off procedure[16] and the general fact that the hydrogen isotope effects are well localized.[17]

As illustrated in acetylene (Ib1) and methane (IV), multiple H/D substitutions at the equivalent hydrogen positions do not significantly affect k_o. On the other hand, the substitutions at nonequivalent positions, such as methylene and methyl hydrogen, do require different k_o values as exemplified by CH_3CH_2Cl and $CH_3CH_2CH_3$ (cf: IIe and IIId).

The evidently satisfactory results obtained on the basis of the present scheme of classification are, in a sense, surprising especially because 1) this classification scheme has been based only on the molecular geometries and has given no consideration to the possible effects of intramolecular forces (except for the discussion on fluorine vs. other halogens), and 2) δ(ZPE) for the H/D effect has been approximated as a difference between two large numbers.

The present groups do not cover all hydrogenous molecules. However, the geometrical aspect of the classification is not far from being complete. Effects of substituents and bond orders can be incorporated in further refinements of the classification without qualitative knowledge of intramolecular forces. The prospect of such a classification is in that an appropriate parameter value may be obtained directly from a molecular structure, which in turn enables one to write δ(ZPE) as an explicit function of the elements of $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices even before knowing the $\boldsymbol{F}$ matrix. Furthermore, coupled with the analytical method for δ(ZPE) presented in a previous paper,[18] the present classification scheme would provide a means for a deeper insight into correlation of the isotopic ZPE shifts with molecular structure and molecular forces.

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