Zero-Point Energy Shifts in Hydrides of the Elements upon H/D Isotope Substitutions and Their Periodicity

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Periodicities are established among the zero-point energy shifts, δ(ZPE), of AH_n ($n = 1-4$) type hydrides of the elements upon mono H/D isotope substitutions. δ(ZPE) for diatomic hydrides is correlated with the position of the element A in the periodic table. The contribution of the A-H stretching force constant to δ(ZPE) is to a good approximation a linear function of the square root of the force constant, irrespective of the molecular type. A similar correlation is also found between the square root of the H-A-H bending force constant and its contribution to δ(ZPE).

Key words: zero-point energy, H/D isotope substitutions, force constants, periodic table, hydrides of the elements.

Introduction

The vibrational zero-point energy, ZPE, of a molecule is a fundamental quantity in various thermodynamic functions formulated in statistical mechanics. The ZPE term alone is sometimes a good approximation for some thermodynamic functions. In the field of chemistry of isotopes, the isotopic ZPE shift, δ(ZPE), term is predominant in the isotopic reduced partition function ratio, RPFR, at and below ordinary temperatures.

A few years ago we developed an approximation for the ZPE [1] in which the ZPE is expressed in terms of the elements of vibrational **G** and **F** matrices. Based on the approximation and subsequent improved approximations, we have proved the approximate linear frequency sum rule [2], have established the theoretical foundation for the additivity of the ZPE [3], and have derived an approximate expression for the ZPE shift upon H/D isotope substitutions [4].

Hydrogen forms binary compounds with most of the elements in the periodic table. The nature of the bonding between the element and hydrogen is diverse; ionic, metallic, covalent, etc., and different hydrides possess different ZPE's. Inspired by a paper by Bigeleisen [5] on the periodicity in the hydrogen

isotope chemistry, we calculated the δ(ZPE)'s of many AH_n ($n = 1-4$) type hydrides of the elements in group I through VIII of the periodic table for mono H/D isotope substitutions and correlated them with molecular structure and molecular forces. This paper reports the results of such a correlation study and intends to contribute to the systematization of the isotope chemistry of hydrogen.

This is a part of our long-term theoretical study on the ZPE. One of the major goals is to establish a method to calculate the ZPE or δ(ZPE) without solving vibrational secular equations with the help of computers.

Theory and Computation

The ZPE of a molecule is defined, ignoring the anharmonic correction terms, as

$$\text{ZPE} = \tfrac{1}{2} h c \sum_{i}^{f} \omega_i, \qquad (1)$$

where h is the Planck constant, c the velocity of light, ω_i the ith harmonic wave number and f the number of internal degrees of freedom. The isotopic difference in ZPE, δ(ZPE), is simply

$$\delta(\text{ZPE}) = \tfrac{1}{2} h c \sum_{i}^{f} (\omega_i' - \omega_i), \qquad (2)$$

where the primed quantities refer to the lighter isotope and the non-primed ones to the heavier isotope.

δ(ZPE) can be divided into contributions of individual force constants (**F** matrix elements) in the following way:

For the diatomic AH type hydrides, there is only one vibrational frequency, and consequently δ(ZPE) is assigned to the A-H stretching force constant.

For polyatomic AH_n $(n = 2 - 4)$ type hydrides, the ZPE is first expressed in terms of the first and second order traces of the $\mathbf{H}(\equiv \mathbf{GF})$ matrix by the finite orthogonal polynomial approximation [1] as

$$ZPE \simeq \frac{\hbar}{2}[b_0 f + b_1 \text{Tr}(\mathbf{H}) + b_2 \text{Tr}(\mathbf{H}^2)], \qquad (3)$$

where b_0, b_1 and b_2 are the approximation coefficients and $\text{Tr}(\mathbf{B})$ is the trace of the square matrix $\mathbf{B}$. Then, using the same b_0, b_1 and b_2 values for the two isotopic species, δ(ZPE) can be given as

$$\delta(ZPE) \simeq \frac{\hbar}{2}[b_1 \delta \text{Tr}(\mathbf{H}) + b_2 \delta\text{Tr}(\mathbf{H}^2)], \qquad (4)$$

where

$$\delta\text{Tr}(\mathbf{H}) = \text{Tr}(\mathbf{H}') - \text{Tr}(\mathbf{H})$$
$$= \sum\sum(g'_{ji} - g_{ji})f_{ij} = \sum\sum\delta(g_{ji})f_{ij} \qquad (5)$$

and

$$\delta\text{Tr}(\mathbf{H}^2) = \text{Tr}(\mathbf{H}'^2) - \text{Tr}(\mathbf{H}^2)$$
$$= \sum\sum\sum\sum(g'_{kj}g'_{li} - g_{kj}g_{li})f_{ik}f_{ji}$$
$$= \sum\sum\sum\sum\delta(g_{kj}g_{li})f_{ik}f_{jl}. \qquad (6)$$

In (4), δ(ZPE) is expressed in terms of elements of the **F** matrix. By assigning $\hbar b_1 \delta(g_{ji})f_{ij}/2$ to the contribution of f_{ij}, and $\hbar b_2 \delta(g_{kj}g_{li})f_{ik}f_{jl}/2$ to the contributions of f_{ik} and f_{jl} evenly [6], it follows that δ(ZPE) is divided into the contributions of the individual elements of the **F** matrix. Finally, adding up the contributions of equivalent f_{ij}'s as the contribution of one kind of force constant, δ(ZPE) is given as the sum of contributions of different kinds of force constants.

Values of the approximation coefficients in (4) (more accurately, the value of the approximation parameter k, for a given value of which the coefficients are uniquely determined [3]) were determined in a somewhat trial-and-error manner for each hydride so that δ(ZPE) calculated by (4) is within 0.01% of the exact δ(ZPE). If we accept larger errors in the approximation, i.e., 1% or so, we can use the k-values listed in a previous paper [7] without extra trial and error calculations.

Fifty-seven AH type diatomic molecules, three AH_2 type triatomic bent molecules, three AH_3 type tetra-

atomic pyramidal molecules and four AH_4 type pentaatomic tetrahedral molecules were examined. Data on most diatomic hydrides were taken and derived from the tabulation of Huber and Herzberg [8]; they are all obtained from experimental vibrational data. ScH data were taken from [9], TiH and VH from [10], FeH from [11], and those of YH, ZrH, NbH, MoH, TcH, RuH and RhH were taken from [12]; they are the results of theoretical calculations. Origins of spectroscopic, **F** matrix and structural data on polyatomic molecules are as follows; H_2O from [13], H_2S from [14], H_2Se from [15], NH_3 from [16], PH_3 and SbH_3 from [17], and CH_4, SiH_4, GeH_4 and SnH_4 from [18]. All the data are based on or derived from experimental results.

The δ(ZPE)'s are expressed in units of cm^{-1}. Bending coordinates were weighted by the equilibrium A-H bond lengths. Consequently, all force constants have the same dimension; we used the conventional unit, mdyn/Å. Correspondingly, we used the conventional unit for the elements of **G** matrices.

Throughout this paper, we considered only mono H/D isotope substitutions and only hydrides at the electronic ground states.

Periodicity in H/D ZPE Shift of Diatomic Hydrides

In Fig. 1 we plotted δ(ZPE) against the atomic number, Z, for 57 diatomic hydrides of the elements, from hydrogen $(Z = 1)$ to bismuth $(Z = 83)$, in their ground states. The hydrides whose frequency data are experimentally obtained are indicated by open circles (46 hydrides) and the hydrides whose frequency data are obtained only by theoretical calculations are shown by diamonds (11 hydrides). The missing hydrides are either non-existent or at present very poorly characterized; for example, the inert gas elements do not form stable diatomic hydrides at the ground state.

The plot shows the typical variation of any physical or chemical property which is a periodic function of Z. Bigeleisen [5] plotted against Z the H/D isotopic RPFR at 300 K, in which δ(ZPE) is the main term, for 39 diatomic hydrides and obtained a similar periodic variation. δ(ZPE) increases for typical elements as one goes from left to right in any period in the periodic table (e.g., Li, Be, B, C, N, O, F). It decreases for typical elements as one goes down any group in the periodic table (e.g.; H, Li, Na, K, Rb, Cs; F, Cl, Br, I). These features are associated with the s and p elec-
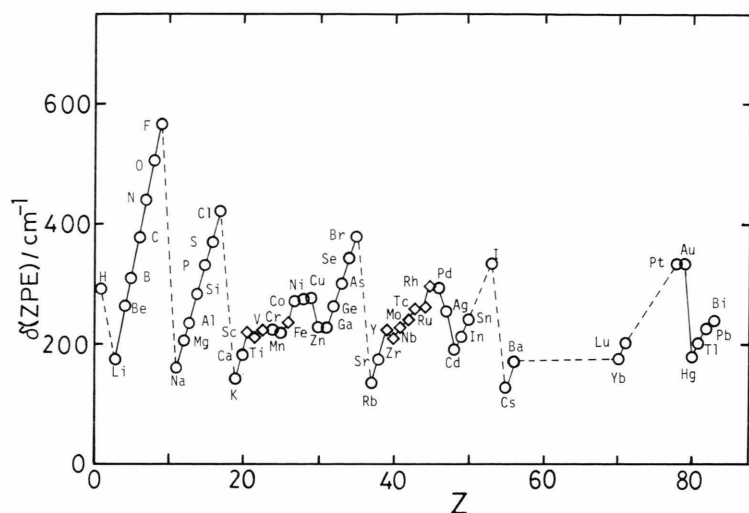
Fig. 1. Plot of δ(ZPE) in diatomic hydrides against Z.

trons of the elements combined with hydrogen. Also, as exhibited by the hydrides of the third and fourth period transition elements, there are fine structures associated with the d electrons. We may further encounter other fine structures associated with the f electrons in the hydrides of the lanthanide and the actinide elements.

δ(ZPE) of the diatomic hydride of an element A is

$$\delta(\text{ZPE}) = \frac{\hbar}{2} \delta(g_{ii})^{1/2} f_{ii}^{1/2}, \tag{7}$$

where

$$\delta(g_{ii})^{1/2} = g_{ii}'^{1/2} - g_{ii}^{1/2}, \tag{8}$$

$$g_{ii}' = 1/m_A + 1/m_H, \ g_{ii} = 1/m_A + 1/m_D, \tag{9a, 9b}$$

m's are atomic masses and f_{ii} is the A-H stretching force constant. Since m_A is much larger than m_H and m_D except for the case of A = H, $g_{ii}'^{1/2}$, and $\delta(g_{ii})^{1/2}$ are very slow functions of m_A. For instance, $\delta(g_{ii})^{1/2}$ is equal to 0.2659 (on ^{12}C scale) for A = Li, 0.2828 for A = Na and 0.2905 for A = Bi (for the elements in the third and later periods in the periodic table, the differences in $\delta(g_{ii})^{1/2}$ values are within 3%). Thus the periodicity observed in Fig. 1 reflects the periodic property of f_{ii}, the stretching force constant, from molecule to molecule.

The bond stretching force constant, f_{ii}, is in principle determined by the electronic structure of the molecule. For the common bonding partner H, the magnitude of f_{ii} will as a first approximation be determined by the power of the atom A to attract the electron of hydrogen to itself. Thus, the electronegativity of the atom A will be most heavily related to f_{ii}. In fact, the

electronegativity shows a variation similar to that of f_{ii} in the periodic table, and it was pointed out [19] for a smaller number of diatomic hydrides than that of this paper that there is a strong correlation between the square of electronegativity and f_{ii}. The sharp drops in the δ(ZPE) value at Cu-Zn, Ag-Cd and Au-Hg in Fig. 1 reflect the similar variations of the electronegativity in the respective sequences in the periodic table.

A-H Stretching Force Constant and Its Contribution to δ(ZPE) in AH_n $(n = 1 - 4)$ Hydrides

δ(ZPE) in diatomic hydrides is to a good approximation a linear function of $f_{ii}^{1/2}$, since the kinetic energy part, $\delta(g_{ii})^{1/2}$, is almost independent of the atomic masses of the elements combined with hydrogen.

For polyatomic hydrides, only one among n A-H stretching coordinates is affected by the mono H/D substitution. If a hydride consists of completely uncoupled oscillators, i.e., consists only of the diagonal elements of the **F** and **G** matrices, then $\text{ZPE} = \hbar \sum (g_{ii} f_{ii})^{1/2}/2$ and $\delta(\text{ZPE}) = \hbar \delta(g_{ii})^{1/2} f_{ii}^{1/2}/2$, where $\delta(g_{ii})^{1/2}$ is given by (8) and the relationship between the square root of f_{ii} and its contribution to δ(ZPE) in polyatomic hydrides is the same as that in diatomic hydrides. Although in real molecules there exist interaction force constants and there are interactions among f_{ii}'s and f_{ij}'s, the analysis by the above mentioned method (cf. (4)) showed that the contribution of f_{ii} to δ(ZPE) through interaction terms is small; For example, in H_2O, NH_3 and CH_4, the contribution of f_{ii} (A-H stretching force constant) through

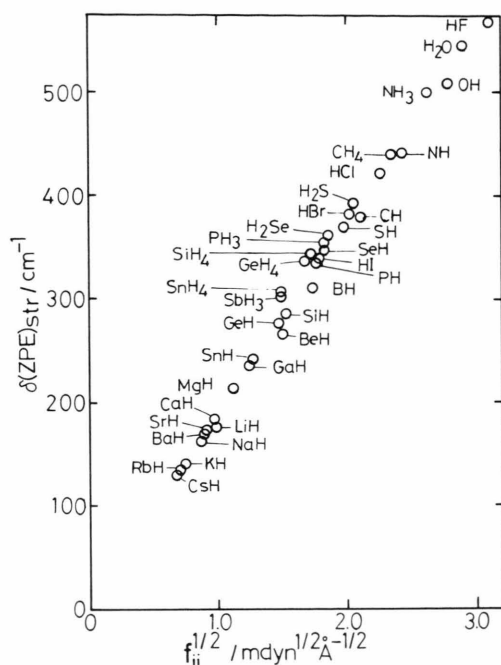Fig. 2. Correlation between stretching force constant and its contribution to δ(ZPE).

observe, for the saturated hydrides in the second and third periods of the periodic table, the sequencies; $CH_4 < NH_3 < H_2O < FH$ (2nd period) and $SiH_4 < PH_3 < H_2S < HCl$ (3rd period). Similarly, for polyatomic hydrides, we note the sequences in the groups of the periodic table; $H_2O > H_2S > H_2Se$ (group VIB), $NH_3 > PH_3 > SbH_3$ (group VB) and $CH_4 > SiH_4 > GeH_4 > SnH_4$ (group IVB). In addition it is seen in the figure that the A-H stretching force constant and consequently its δ(ZPE)$_{str}$ is larger for the saturated molecules than for the corresponding diatomic radicals (e. g., $CH_4 > CH$, $NH_3 > NH$, $H_2O > OH$). Although a complete explanation of these sequences based on theoretical MO calculations is beyond the scope of this paper, they certainly reflect the relationship between the bond stretching force constant, the electronegativity of the element combined with hydrogen and the bonding molecule orbitals in the hydride.

interaction terms between f_{ii} and other kinds of force constant is, respectively, 0.18%, 0.14% and 0.13% of the total contribution of f_{ii}. This is because g_{ij} (i = A-H stretch, j = bend) = 0 and δg_{ij} (i = A-H, $j \neq i$) = 0 for the end atom substitution which is the case with all the hydrides studied. Thus, even for polyatomic hydrides, a similar linearity is expected between $f_{ii}^{1/2}$ and its contribution to δ(ZPE).

In Fig. 2, we plotted δ(ZPE)$_{str}$, i.e., δ(ZPE) attributed to the A-H stretching force constant, against $f_{ii}^{1/2}$. For simplicity and clarity of the figure, the diatomic hydrides of the transition elements were omitted. Their $f_{ii}^{1/2}$ values are mostly around 1.3 mdyn$^{1/2}$/Å$^{1/2}$. As expected, δ(ZPE)$_{str}$ is to a good approximation a linear function of $f_{ii}^{1/2}$ with some variations, irrespective of molecular type. For diatomic hydrides, the plots of the lighter hydrides slightly deviate downward due to the mass effect.

A number of sequences can be identified in Figure 2.

As discussed previously, for the diatomic hydrides of the typical elements, δ(ZPE)$_{str}$ increases as one goes from left to right in any period in the periodic table, and it decreases as one goes down any column in the periodic table. Not a single exception to this rule is observed in Figure 2. In a similar way, we

H-A-H Bending Force Constant and Its Contribution to δ(ZPE) in AH$_n$ ($n = 2 - 4$) Hydrides

Bending coordinates appear only in polyatomic hydrides. Unlike the case of stretching coordinates in which mono H/D isotope substitution affects only one stretching coordinate, the same isotope substitution affects ($n - 1$) bending coordinates of AH$_n$ type polyatomic hydrides of the elements. Analogously to the case of stretching coordinates, if we assume that a hydride consists of completely uncoupled oscillators, the contribution of the bending force constant, f_{ii}, to δ(ZPE), δ(ZPE)$_{bend}$, is

$$\delta(\text{ZPE})_{bend} = \frac{\hbar}{2}(n - 1)\,\delta(g_{ii})^{1/2}\,f_{ii}^{1/2}, \qquad (10)$$

where $\delta(g_{ii})^{1/2} = g_{ii}'^{1/2} - g_{ii}^{1/2}$,

$$g_{ii}' = 2/m_H + 2(1 - \cos\alpha)/m_A, \qquad (11\,a)$$

$$g_{ii} = 1/m_H + 1/m_D + 2(1 - \cos\alpha)/m_A, \qquad (11\,b)$$

and α is the H-A-H angle. Thus, the kinetic energy part depends not only on the atomic mass of A but also on the H-A-H angle. However, it is a slow function of m_A and it is also a slow function of α, and we may expect an approximately linear relationship between $f_{ii}^{1/2}$ and $\delta(\overline{\text{ZPE}})_{bend}$, i.e., δ(ZPE)$_{bend}$ per bending coordinate affected by mono H/D isotope substitution ($\equiv \delta$(ZPE)$_{bend}/(n - 1)$).
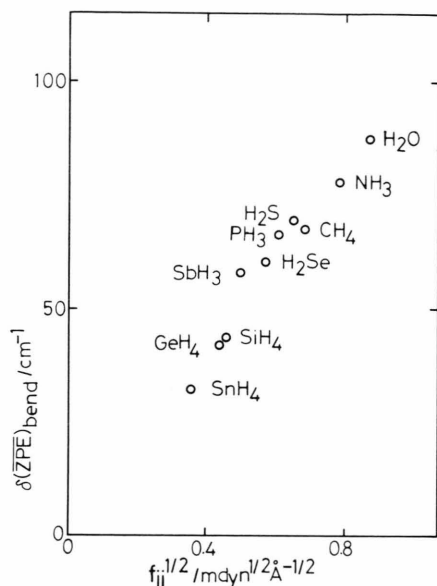
Fig. 3. Correlation between bending force constant and its contribution to $\delta(\text{ZPE})$.

In Fig. 3, we plotted $\delta(\overline{\text{ZPE}})_{\text{bend}}$ against the square root of the bending force constant. We can again observe a good linear relationship in the figure.

In Fig. 3, we can identify a number of sequences by row and column in the periodic table, though the number of hydrides collected is limited. $\delta(\overline{\text{ZPE}})_{\text{bend}}$ increases as one goes from left to right in the periodic table ($H_2O > NH_3 > CH_4$ and $H_2S > PH_3 > SiH_4$). Note that, if we compare $\delta(\text{ZPE})_{\text{bend}}$ instead of $\delta(\overline{\text{ZPE}})_{\text{bend}}$, then the sequences are reversed. $\delta(\overline{\text{ZPE}})_{\text{bend}}$ and also $\delta(\text{ZPE})_{\text{bend}}$ decrease as one goes downward in the periodic table ($H_2O > H_2S > H_2Se$, $NH_3 > PH_3 > SbH_3$, and $CH_4 > SiH_4 > GeH_4 > SnH_4$).

We can identify some fine structures in the sequences by column in the periodic table that are most probably attributable to the slow dependences of $\delta(g_{ii})^{1/2}$ on the atomic mass (m_A) and the molecular structure (α). In the family of H_2O, H_2S and H_2Se, the H-A-H angle is $104.52°$, $92.06°$ and $90.17°$, respectively. The magnitude of the $2(1 - \cos\alpha)/m_A$ term in (11 a) and (11 b) is larger for larger α ($180° \geq \alpha \geq 90°$) and for smaller m_A. That is, $\delta(g_{ii})^{1/2}$ is larger for smaller α and for larger m_A. Thus, in the plot of $\delta(\overline{\text{ZPE}})_{\text{bend}}$ vs. $f_{ii}^{1/2}$, H_2O is located below the line combining H_2S and H_2Se. A similar fine structure is observed in the sequence $NH_3 > PH_3 > SbH_3$. NH_3 is located below the line combining PH_3 and SbH_3; the H-A-H angles for NH_3, PH_3 and SbH_3 are, respectively, $106.7°$, $93.83°$ and $91.50°$. For AH_4 type hydrides, α is tetrahedral and common to all the members. Consequently, the fact that CH_4 is located slightly below the line combining SnH_4 and GeH_4 is due to the mass effect.

It is true that the present method of dividing $\delta(\text{ZPE})$ into contributions of individual force constants is only as good as the $\mathbf{F}$ matrices used. Some fluctuations in Figs. 1, 2, and 3 must be attributable to inadequateness of the $\mathbf{F}$ matrices. Nevertheless, we believe we have shown in this paper several essential features of the zero-point energy shifts in hydrides of the elements upon H/D isotope substitutions.

Acknowledgements

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