Correlation of Vibrational Zero-Point Energy Shifts of Hydrides upon H/D Isotope Substitutions with Electronegativity

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Correlation of the contribution of the stretching motion ($\delta(\mathrm{ZPE})_{\mathrm{str}}$) to the zero-point energy shift upon H/D mono isotope substitution in $\mathrm{H}_n\mathrm{A}$ (n=1—4) type hydrides with the electronegativity (χ) of the $-\mathrm{H}_{n-1}\mathrm{A}$ moiety was investigated. It is possible to represent all the $\delta(\mathrm{ZPE})_{\mathrm{str}}$-$\chi$ data by a single crude linear line. The line, however, is too crude to make precise estimation of the $\delta(\mathrm{ZPE})_{\mathrm{str}}$ value of a hydride from the χ value or to make precise estimation of the χ value from the $\delta(\mathrm{ZPE})_{\mathrm{str}}$ value. Much more accurate linear relation between $\delta(\mathrm{ZPE})_{\mathrm{str}}$ and χ can be obtained for each of HA, $\mathrm{H_2A}$, $\mathrm{H_3A}$, and $\mathrm{H_4A}$ groups.

The vibrational zero-point energy (ZPE) of a molecule, an important quantum mechanical quantity, appears and is discussed quite frequently in various problems of statistical mechanics and thermodynamics. In the field of isotope chemistry, the term of the isotopic ZPE shift (δ(ZPE)), i.e., the ZPE of the lighter isotopic molecule minus that of the heavier one, is predominant in the isotopic reduced partition function ratio (RPFR), the most fundamental quantity for evaluation of isotope effects, at and below ordinary temperatures.

In a previous paper,[1)] we presented a periodic property of the δ(ZPE) of hydrides of the elements upon the H/D isotope substitutions. We suggested for diatomic molecules, HA, that this periodicity of the δ(ZPE) is attributable in most part to that of the electronegativity of the atom A. Similar periodicity was reported for the H/D isotopic RPFR by J. Bigeleisen.[2)]

In this paper we investigate correlation of the δ(ZPE) portion attributable to the stretching motion ($\delta(\mathrm{ZPE})_{\mathrm{str}}$) upon H/D mono substitutions with electronegativity for hydrides of the 14—17 group elements, $\mathrm{H}_n\mathrm{A}$ (n=1—4), in the periodic table. It will be shown that the concept of electronegativity can be applied to the systematization of the $\delta(\mathrm{ZPE})_{\mathrm{str}}$ as it has successfully been used to understand systematically various properties of the elements.[3)] The hydrides examined in this study are HF-HI, $\mathrm{H_2O}$-$\mathrm{H_2Se}$, $\mathrm{NH_3}$-$\mathrm{SbH_3}$, and $\mathrm{CH_4}$-$\mathrm{SnH_4}$. The sources of their vibrational data have been given in the previous paper.[1)]

Theory and Computation

In 1958, Wilmshurst[4)] claimed that the plot of electronegativity (χ) of X against the stretching frequency, ν_{str}, between H and X, where X is an atom or a group, is linear. The empirical equation of the line is given in the form

$$\chi_{\mathrm{W}} = g\,(1 + M_{\mathrm{H}}/M_{\mathrm{X}})^{-1/2}\,\nu_{\mathrm{str}} - h, \qquad (1)$$

where χ_{W} is the Wilmshurst's electronegativity of X, g and h constants and M_{H} and M_{X} the masses of H and X, respectively. Since χ must be isotope-independent from the viewpoint of the Born-Oppenheimer approximation, the first term on the right-hand side of Eq. 1 and h must be independent of H/D substitutions. Therefore, Wilmshurst's g should be proportional to $M_{\mathrm{H}}{}^{1/2}$;

$$g = g_0 M_{\mathrm{H}}{}^{1/2}, \qquad (1\mathrm{a})$$

with an understanding that M_{H} in Eqs. 1 and 1a be replaced with M_{D} for the deuterated compounds. Then, plot of χ_{W} against $\Delta\nu_{\mathrm{str}}$,

$$\Delta\nu_{\mathrm{str}} = \nu_{\mathrm{str}}(\mathrm{H{-}X}) - \nu_{\mathrm{str}}(\mathrm{D{-}X}) \qquad (2)$$

is also expected to be linear;

$$\chi = g_{\mathrm{A}}\Delta\nu_{\mathrm{str}} - h_{\mathrm{A}}, \qquad (3)$$

where g_{A} and h_{A} are constants.

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

$$\mathrm{ZPE} = (1/2)h\sum^{f}\nu_i, \qquad (4)$$

where h is the Planck constant, ν_i the i-th harmonic frequency and f the number of internal degrees of freedom. δ(ZPE) is simply given as

$$\delta(\mathrm{ZPE}) = (1/2)h\sum^{f}\left(\nu_i' - \nu_i\right), \qquad (5)$$

where the primed quantities refer to the lighter isotope and the non-primed ones to the heavier isotope. When the molecule is a hydride of an element A, $\mathrm{H}_n\mathrm{A}$ (n= 1—4), δ(ZPE) can be divided into the contribution of the H–A stretching motion, $\delta(\mathrm{ZPE})_{\mathrm{str}}$, that of the H–A–H bending motion, $\delta(\mathrm{ZPE})_{\mathrm{bend}}$ and the correction term, CORR, consisting of small contributions from various kinds of interactions;[1,5)]

$$\delta(\mathrm{ZPE}) = \delta(\mathrm{ZPE})_{\mathrm{str}} + \delta(\mathrm{ZPE})_{\mathrm{bend}} + \mathrm{CORR}. \qquad (6)$$

Since there is only one H–A bond directly affected by a mono H/D substitution, the following linear relation between χ and $\delta(\mathrm{ZPE})_{\mathrm{str}}$ is then expected from Eqs. 3, 5, and 6;

$$\chi = p\delta(\mathrm{ZPE})_{\mathrm{str}} - q \tag{7}$$

or

$$\delta(\mathrm{ZPE})_{\mathrm{str}} = r\chi + s \tag{7a}$$

where p, q, r, and s are constants. In general, p and q are proportional to the sums of g_A and h_A, respectively, over all stretching frequencies affected by the H/D substitution. Since the electronegativity relations such as Eq. 1 hold only with respect to the stretching frequencies, Eqs. 7 and 7a are independent of magnitudes of the $\delta(\mathrm{ZPE})_{\mathrm{bend}}$ and CORR terms of Eq. 6.

Since the first introduction of the concept of electronegativity by Pauling[3] in the 1930's, various researchers proposed different definitions of electronegativity and/or modifications over old electronegativity definitions. In this paper, we chose to examine electronegativities given by Wilmshurst (χ_W),[4] by Inamoto and Masuda (χ_I),[6] and by Boyd and Edgecombe (χ_B),[7] and the unshielded core potential (V_B), a measure of electronegativity, by Luo and Benson.[8]

Wilmshurst's electronegativities of atoms are the same as those by Gordy[9] who determined electronegativity values of atoms from the numbers of electrons in the valence shells and the single bond covalent radii of the atoms. Wilmshurst[10] extended Gordy's formula to include the electronegativity calculations for groups. χ_W values for the atoms were cited from Gordy's paper,[9] and those for the groups from Wilmshurst's papers[4,10] except for those of $-SiH_3$, $-GeH_3$, and $-SnH_3$ whose χ_W values were calculated by the present authors using his formula.[10] Inamoto and Masuda's electronegativity is a modified version of the one by Wilmshurst. All the χ_I values were calculated using their equation,[6] except for atomic electronegativities which are by definition the same as those of Gordy (The χ_I value for F was recalculated using the new covalent radius value of F[11] by us.). Boyd and Edgecombe[7] obtained atomic and group electronegativity values based on the topological properties of the electron density distribution of molecules. All the χ_B values except for those of I, $-SbH_2$ and $-SnH_3$ were cited from their paper;[6] values for I, $-SbH_2$, and $-SnH_3$ were not given. The unshielded core potential, first proposed by Yuan[12] as a measure of electronegativity of the elements, was extended to groups and was successfully applied to correlation study of heats of formation by Luo and Benson.[8,13] All the V_B values were cited from their paper.[13]

The decomposition of $\delta(\mathrm{ZPE})$ into $\delta(\mathrm{ZPE})_{\mathrm{str}}$, $\delta(\mathrm{ZPE})_{\mathrm{bend}}$, and CORR is performed as follows.

For the HA type hydrides, there is only one vibrational frequency, and consequently, $\delta(\mathrm{ZPE})=\delta(\mathrm{ZPE})_{\mathrm{str}}$.

For polyatomic H_nA (n=2—4) type hydrides, the ZPE is first expressed in terms of the first and second order traces of the $\boldsymbol{H}$ (=$\boldsymbol{GF}$) matrix, $\boldsymbol{F}$ and $\boldsymbol{G}$ being the vibrational force constant matrix and the effective inverse mass matrix, respectively, by the finite orthogonal polynomial approximation[14] as

$$\mathrm{ZPE} \fallingdotseq (\hbar/2)\left[b_0 f + b_1 \mathrm{Tr}(\boldsymbol{H}) + b_2 \mathrm{Tr}(\boldsymbol{H}^2)\right], \tag{8}$$

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

$$\delta(\mathrm{ZPE}) \fallingdotseq (\hbar/2)\left[b_1 \delta\mathrm{Tr}(\boldsymbol{H}) + b_2 \delta\mathrm{Tr}(\boldsymbol{H}^2)\right], \tag{9}$$

where

$$\begin{aligned}\delta\mathrm{Tr}(\boldsymbol{H}) &= \mathrm{Tr}(\boldsymbol{H}') - \mathrm{Tr}(\boldsymbol{H})\\ &= \sum\sum\left(g'_{ji} - g_{ji}\right) f_{ij} = \sum\sum \delta\left(g_{ji}\right) f_{ij}\end{aligned} \tag{10}$$

and

$$\begin{aligned}\delta\mathrm{Tr}(\boldsymbol{H}^2) &= \mathrm{Tr}(\boldsymbol{H}'^2) - \mathrm{Tr}(\boldsymbol{H}^2)\\ &= \sum\sum\sum\sum\left(g'_{kj}g'_{li} - g_{kj}g_{li}\right) f_{ik}f_{jl}\\ &= \sum\sum\sum\sum \delta\left(g_{kj}g_{li}\right) f_{ik}f_{jl}\end{aligned} \tag{11}$$

In Eqs. 10 and 11, f_{ij} and g_{ij} are the i, j elements of the $\boldsymbol{F}$ and $\boldsymbol{G}$ matrices, respectively, $\delta(g_{ji})=g'_{ji}-g_{ji}$ and $\delta(g_{kj}g_{li})=g'_{kj}g'_{li}-g_{kj}g_{li}$. The degree of approximation to be achieved in Eq. 9 can be set at any level, depending on the choice of the values of the coefficients b_1 and b_2. In this work, the b_1 and b_2 values for each hydride were chosen such that the right-hand side of Eq. 9 agrees with the left-hand side within 0.1% error. In Eq. 9, $\delta(\mathrm{ZPE})$ is expressed in terms of elements of the $\boldsymbol{F}$ matrix. 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,[15] it follows that $\delta(\mathrm{ZPE})$ is divided into the contributions of the individual elements of the $\boldsymbol{F}$ matrix. Finally, adding up the contributions of equivalent f_{ij}'s as the contribution of one kind of force constant, $\delta(\mathrm{ZPE})$ is given as the sum of the contributions of different kinds of force constants, and consequently the decomposition of $\delta(\mathrm{ZPE})$ expressed by Eq. 6 results.

We decomposed $\delta(\mathrm{ZPE})$ into $\delta(\mathrm{ZPE})_{\mathrm{str}}$, $\delta(\mathrm{ZPE})_{\mathrm{bend}}$, and CORR for the above listed hydrides and examined validity of Eq. 7 or Eq. 7a.

Results and Discussion

In Table 1, we summarized the results of decomposition of $\delta(\mathrm{ZPE})$ into $\delta(\mathrm{ZPE})_{\mathrm{str}}$, $\delta(\mathrm{ZPE})_{\mathrm{bend}}$, and CORR, along with the atomic and group electronegativity values. All the ZPE values are given in units of cm^{-1}. $\delta(\mathrm{ZPE})_{\mathrm{str}}$, the largest contributor to $\delta(\mathrm{ZPE})$ among the three terms, accounts for 68—100% of $\delta(\mathrm{ZPE})$. The relative significant of $\delta(\mathrm{ZPE})_{\mathrm{bend}}$ increases while that of $\delta(\mathrm{ZPE})_{\mathrm{str}}$ decreases as n (in H_nA) becomes large. This is because the number of coordinates directly affected

Table 1. Results of Decomposition of δ(ZPE) into Contributions of $\delta(\mathrm{ZPE})_{\mathrm{str}}$, $\delta(\mathrm{ZPE})_{\mathrm{bend}}$, and CORR,[a)] and the Atomic and Group Electronegativity Values

Molecule	δ(ZPE)	$\delta(\mathrm{ZPE})_{\mathrm{str}}$	$\delta(\mathrm{ZPE})_{\mathrm{bend}}$	CORR	Atom or group	χ_{W}	χ_{I}	χ_{B}	V_{B}
HF	568.9	568.9			F	3.94	3.99	4.00	9.915
HCl	422.9	422.9			Cl	3.00	3.00	3.05	7.04
HBr	381.8	381.8			Br	2.68	2.68	2.75	6.13
HI	334.6	334.6			I	2.36	2.36		5.25
H_2O	632.5	545.9	87.5	−0.9	-OH	3.86	3.72	3.64	8.11
H_2S	463.3	393.8	69.5	0.0	-SH	2.61	2.66	2.63	5.77
H_2Se	407.6	349.5	69.2	−11.1	-SeH	2.37	2.36	2.47	5.13
NH_3	659.0	500.0	156.7	2.3	$-NH_2$	3.40	3.02	3.10	6.67
PH_3	485.0	355.7	133.0	−3.7	$-PH_2$	2.20	2.19	2.17	4.55
AsH_3	450.4	338.0	156.7	−44.3	$-AsH_2$	2.03	2.05	2.26	4.20
SbH_3	396.4	304.6	116.3	−24.5	$-SbH_2$	1.76	1.86		3.55
CH_4	645.4	440.4	203.7	1.3	$-CH_3$	2.63	2.47	2.56	5.19
SiH_4	474.3	343.0	131.5	−0.2	$-SiH_3$	1.76	1.91	1.91	3.41
GeH_4	464.3	337.8	127.2	−0.7	$-GeH_3$	1.69	1.88	2.05	3.24
SnH_4	405.0	308.0	97.8	−0.8	$-SnH_3$	1.51	1.71		2.83

a) All the δ(ZPE), $\delta(\mathrm{ZPE})_{\mathrm{str}}$, $\delta(\mathrm{ZPE})_{\mathrm{bend}}$, and CORR values are given in units of cm^{-1}.

by mono H/D substitutions is only one for the stretching motion while that number is $n-1$ for the bending motion. Contributions of the CORR terms are small. Their magnitudes are in most cases less than 4 cm^{-1}, with the maximum being 44.3 cm^{-1} for AsH_3.

We plotted $\delta(\mathrm{ZPE})_{\mathrm{str}}$ against χ_{W}, χ_{I}, χ_{B}, and V_{B} in Figs. 1a, 1b, 1c, and 1d, respectively. The following observations can be made in Fig. 1a.

(i) It is possible to present all the data by a single linear relation having relatively large deviations. This line is much cruder than the relation Wilmshurst[4)] presented. Especially, the points for H_4A species deviate substantially from a linear relation for the other H_nA ($n=1-3$) species. Thus, the relation seems to be too crude to estimate the χ_{W} value of a hydride from its $\delta(\mathrm{ZPE})_{\mathrm{str}}$ value or to estimate the $\delta(\mathrm{ZPE})_{\mathrm{str}}$ from χ_{W}.

(ii) A linear line with much smaller deviations can be drawn for each of HA (A=F−I), H_2A (A=O—Se), H_3A (A=N—Sb) and H_4A (A=C—Sn). For a fixed χ_{W} value, $\delta(\mathrm{ZPE})_{\mathrm{str}}$ increases in general in the order of $HA<H_2A<H_3A<H_4A$.

Similar qualitative observations can also be made in the other figures. That is, a single crude linear line can be drawn to represent all the data, but classifying the hydrides into HA, H_2A, H_3A, and H_4A groups yields lines with much smaller deviations. The reversion is found only for χ_{B} between PH_3 and AsH_3 and between GeH_4 and SiH_4.

The observed shifts in the linear plots for the HA, H_2A, H_3A, and H_4A groups are due to the periodicities of the electronegativity and the A–H bond-stretching force constant, $f_{\mathrm{A-H}}$: In a given row in the periodic table, both $f_{\mathrm{A-H}}$ and χ increase toward Group 17, while both $f_{\mathrm{A-H}}$ and χ decrease as one goes down in a given group.[1,3)] Referring to Eqs. 9, 10, and 11, in $\delta(\mathrm{ZPE})_{\mathrm{str}}$ for the H/D substitution, the only non-vanishing term of $\delta\mathrm{Tr}(\boldsymbol{H})$ is $f_{\mathrm{A-H}}(g_{\mathrm{A-H}}-g_{\mathrm{A-D}})$ where $g_{\mathrm{A-H}}$ and $g_{\mathrm{A-D}}$ are the $\boldsymbol{G}$ matrix elements of the A–H and A–D bond-strertching coordinates, respectively, and the most dominant of all terms of $\delta\mathrm{Tr}(\boldsymbol{H}^2)$ is $f_{\mathrm{A-H}}^2(g_{\mathrm{A-H}}^2-g_{\mathrm{A-D}}^2)$. Therefore, the periodicity in $f_{\mathrm{A-H}}$ is directly reflected in a periodicity in $\delta(\mathrm{ZPE})_{\mathrm{str}}$. The observed shifts in the plots of Figs. 1a, 1b, 1c, and 1d thus do not represent a breakdown of the theory. They are a manifestation of the periodicities.

The values of the least-squares-fitted coefficients to the functional form of Eq. 7a are listed in Table 2. The solid lines in the figures are drawn by using these values. The average and maximum deviations for each line in each relation are summarized in Table 3. Although the data in Table 3 suggest that the goodness of the linearity of the $\delta(\mathrm{ZPE})_{\mathrm{str}}-\chi$ relation is in the order of $\chi_{\mathrm{I}}>V_{\mathrm{B}}>\chi_{\mathrm{W}}>\chi_{\mathrm{B}}$, it would be a right conclusion at this point that χ_{I}, V_{B}, and χ_{W} give equivalently good results, considering that the number of data points is very limited. χ_{B} evidentally gives poorer estimate of $\delta(\mathrm{ZPE})_{\mathrm{str}}$ than the other electronegativities.

If electronegativity is the power of an atom in a molecule to attract electrons to itself, as defined by Pauling,[3)] it is quite natural to expect that $\delta(\mathrm{ZPE})_{\mathrm{str}}$ converges to zero as the atomic electronegativity value approaches zero. It is also a reasonable expectation that the same holds even for group electronegativity. In this respect, χ_{I} is superior to the other electronegativities examined in this paper. The intersect values (values of s given in Table 2) of the $\delta(\mathrm{ZPE})_{\mathrm{str}}-\chi_{\mathrm{I}}$ relation are all very close to zero, compared to those of the other relations. In fact, least-squares-fit calculations in the functional form of

$$\delta(\mathrm{ZPE})_{\mathrm{str}} = r_{\mathrm{I}}\chi_{\mathrm{I}}, \tag{12}$$

where r_{I} is a constant, yield only a little larger deviation

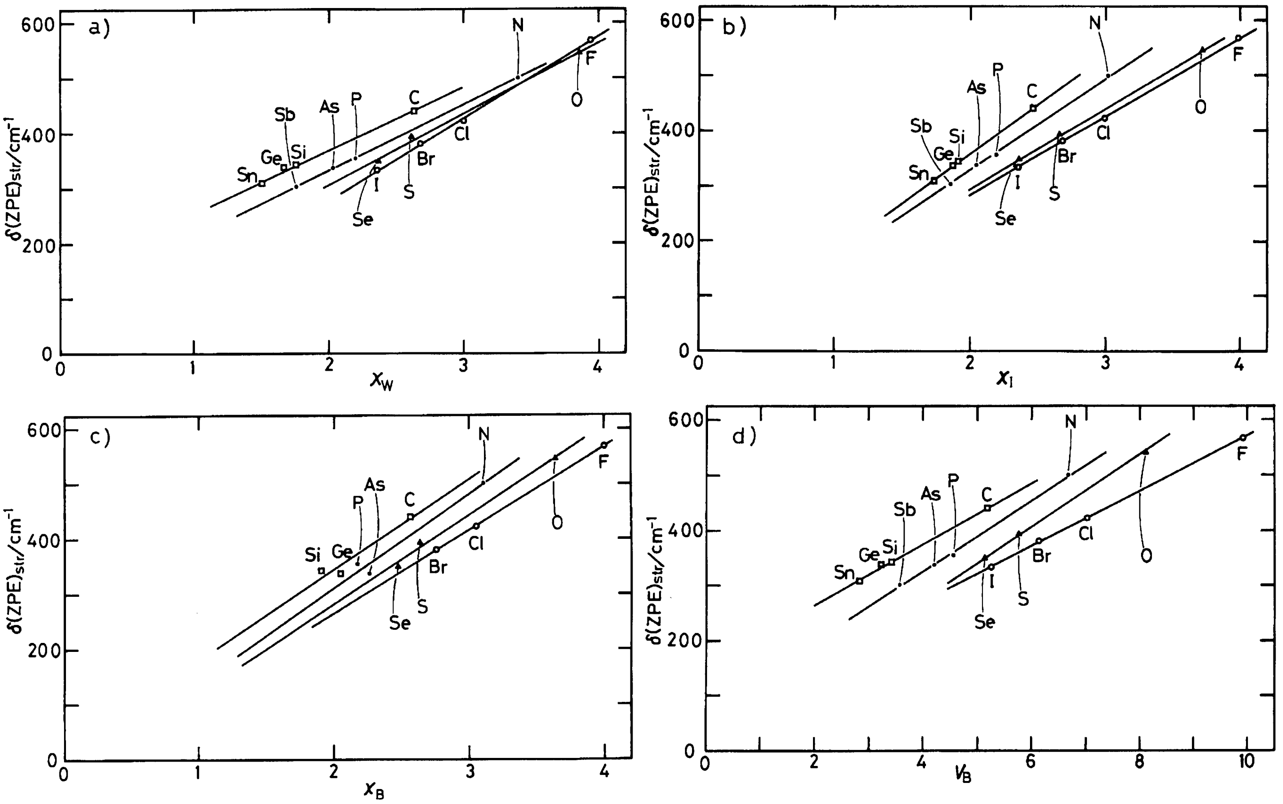

Fig. 1. Plots of $\delta(\mathrm{ZPE})_{\mathrm{str}}$ against a) Wilmshurst's electronegativity (χ_{W}), b) Inamoto's electronegativity (χ_{I}), c) Boyd's electronegativity (χ_{B}), and d) Benson's unshielded core potential (V_{B}). ○'s, △'s, ●'s and □'s denote the results for the HA, H_2A, and H_4A hydrides, respectively. The solid linear lines are drawn by using the least-squares-fitted coefficient values in Table 2.

Table 2. Values of Coefficients When $\delta(\mathrm{ZPE})_{\mathrm{str}}-\chi$ Relations are Least-Squares-Fitted to the Functional Form of Eq. 7a.

Eletro-negativity	Hydrides (H_nA)							
	n=1		n=2		n=3		n=4	
	r	s	r	s	r	s	r	s
χ_{W}	148.4	17.3	128.5	51.2	119.1	95.0	114.9	139.4
χ_{I}	143.6	−4.6	144.2	9.7	168.6	−10.0	188.5	0.3
χ_{B}	150.6	−33.9	161.7	−41.4	170.3	−29.7	163.7	18.1
V_{B}	50.0	72.8	65.7	13.7	63.8	72.0	55.0	155.5

Table 3. The Average and Maximum Deviations of $\delta(\mathrm{ZPE})_{\mathrm{str}}$ from the Least- Squares- Fitted Relations[a)]

Electro-negativity	HA		H_2A		H_3A		H_4A	
	ave	max	ave	max	ave	max	ave	max
χ_{W}	2.4	−4.9	5.0	7.4	0.7	−1.4	2.9	−4.9
χ_{I}[b)]	1.5	−3.0	0.5	0.7	1.9	−3.8	1.9	−3.0
	1.8	−3.2	2.0	2.4	2.6	4.6	1.9	−2.9
χ_{B}	1.6	2.4	6.7	10.0	11.5	−17.2	10.4	−15.6
V_{B}	1.4	2.6	0.9	1.4	4.3	−6.7	2.1	4.2

a) All the values are given in units of cm^{-1}. The maximum deviations are given with signs. b) The second entry is for the case in which linear relations are presented in the form of Eq. 12.

as a whole than that in the form of Eq. 7a; the maximum deviation becomes 4.6 cm^{-1} for PH_3 which should be compared to the maximum deviation of 3.8 cm^{-1} for PH_3 in the case of Eq. 7a (cf. Table 3). r_1 values for HA, H_2A, H_3A, and H_4A are 284.2, 294.8, 328.8, and 357.4, respectively.

Close correlations between $\delta(\mathrm{ZPE})_{\mathrm{str}}$ and electronegativity found in this paper suggest that the H/D RPFR of hydrides could be estimated without any knowledge on its structure and molecular vibration, because $\delta(\mathrm{ZPE})$ is a predominant contributor to PRFR at and below ambient temperatures and $\delta(\mathrm{ZPE})_{\mathrm{str}}$ is the most significant term in $\delta(\mathrm{ZPE})$. It is interesting to examine whether the relations between $\delta(\mathrm{ZPE})_{\mathrm{str}}$ and χ observed for stable H_nA molecules can be extended to other hydrides and molecules (including radicals and ions) and furthermore whether similar relations hold for isotope substitutions of other elements.

In conclusion, a single crude linear relation was found between χ and $\delta(\mathrm{ZPE})_{\mathrm{str}}$ for H_nA ($n=1-4$) species. A linear relation with much less deviations was found between χ and $\delta(\mathrm{ZPE})_{\mathrm{str}}$ for each of HA, H_2A, H_3A, and H_4A. Among the electronegativities examined, one by Inamoto and Masuda,[6)] χ_{I}, seems most appropriate to study relation between χ and $\delta(\mathrm{ZPE})_{\mathrm{str}}$ quantitatively.

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