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Valence States in Molecules. 3. Transferable Vibrational Force Constants from Homonuclear Data

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A recently introduced valence-state potential energy function (von Szentpály, L. *Chem. Phys. Lett.* **1995**, *245*, 209.) and its dissociation energy (D_{VS}) serve to establish an arithmetic combining rule for scaled force constant increments, $\lambda = kR_e/D_{VS}$. λ is transferable from homo- to heteronuclear molecules at an accuracy of 1.6% average absolute error in harmonic vibrational wavenumbers, $\tilde{\nu}_e$, of 42 diatomic molecules covering a force constant range of factor 30. The parallel to combining rules for repulsive potentials in solid-state and atomic physics is shown, and the reasons for the failure of previous attempts to obtain transferable force constant increments are examined.

Introduction

The problem of transferable spectroscopic constants is of decisive importance in force-field calculations of unknown systems. Starting from a small reference data set, combining rules are required to calculate spectroscopic constants to a reasonable accuracy. Vibrational force constants (FCs) have been found to be transferable only within special classes of molecules of similar polarity.[1] Except for a recent and, as shown below, inaccurate claim,[2] FC increments expressed by effective nuclear charges[3] and/or electronegativity (EN)[1] are nontransferable from homo- to heteronuclear molecules. Since the harmonic force constant, k, vibration−rotation coupling constant, α_e, and spectroscopic dissociation energy, D_e, of diatomic molecules span over 3 orders of magnitude, the quest for their transferability has translated into a search for the universal scaling properties of the potential energy (PE) curves[4−11] and quantitative relations between the constants.[12−16] A universal PE curve with transferable bond energies and FCs would be most valuable for (i) a huge data reduction in empirical force-field/molecular mechanics parameters, (ii) the interpretation of vibrational spectra, and (iii) a unified rationalization of the complexity of chemical bonds.

Method

In part 1[17] and part 2,[11] I used Ruedenberg's definition of the valence state (VS)[18] (i) to derive the valence-state electronegativity (VSEN, χ_{VS})[17] characterizing the atom in the molecule (AIM) and expressed as a function of the partial charge, δ,

$$\chi_{VS} = {}^1/_2[I + A + (I - A)\delta] = \chi^0 + \eta\delta \qquad (1)$$

where I is the ionization energy, A the electron affinity of the active valence orbital, χ^0 the Mulliken EN, and η the chemical hardness, and (ii) to introduce a universal VS potential energy (VSPE) function with the reference zero energy ($U(\infty)$) being the VS energy of the molecule:[11]

$$U(R)R = -D_{VS}(R_e + \lambda^{-1}) + D_{VS}\lambda^{-1} \exp[\lambda(R_e - R)] \qquad (2)$$

$$\lambda = kR_e/D_{VS} \qquad (3)$$

R_e is the equilibrium bond length. The VS dissociation energy $D_{VS} = U(\infty) - U(R_e)$ refers to the dissociation into promoted VS atoms. The molecule is characterized by its electron density ($\rho(\mathbf{r})$) and electron-pair density ($\pi(\mathbf{r}_1, \mathbf{r}_2)$), i.e., the diagonal elements of the spinless first- and second-order density matrices. Both ρ and π are partitioned into interference contributions (ρ^i and π^i) and interference-free densities (ρ^{VS} and π^{VS}) assigned to the AIMs.[18] The VSs are reached upon dissociating the molecule with frozen ρ^{VS} and π^{VS}. The VS is essentially molecular, especially as the VS atoms maintain the interference-free part of the electron-pair density of the AIMs after breaking the bond(s). For a VS atom A, obtained from the homonuclear molecule A_2, the repulsion energy due to the frozen on-site pair population amounts to $\sum J_i/4$. $J_i = I_i - A_i$ models the two-electron one-center repulsion energy of the ith atomic orbital, and the summation goes over all bonding valence orbitals.[11] For a single-bonded polar molecule AB, we calculate

$$D_{VS} = D_e + \sum[E_{hy} + (J/4)] - \Delta\chi^2/(J_A + J_B) = D_e + \sum E_{hy} + (1 - \delta^2)\sum(J/4) \qquad (4)$$

E_{hy} is the hybridization energy, including the promotion energy to the barycenter of the spin−orbit split states; $\sum J/4 - \Delta\chi^2/(J_A + J_B)$ is the sum of the on-site pair repulsion energies resulting from the frozen π^{VS} of the polar molecule. The derivation of the latter contribution is dealt with in detail in ref 11.

The purpose of this paper is to demonstrate that the exponential factor (λ) of the universal VSPE curve is transferable and obeys the simple arithmetic mean combining rule

$$\lambda_{AA} + \lambda_{BB} = 2\lambda_{AB} \qquad (5)$$

Note that $\lambda R_e = z$, the only species-dependent parameter in the reduced VSPE function, $u = U/D_{VS}$, is a dimensionless FC and the generalized Sutherland parameter. The question of transferable bond energies will be treated in a forthcoming paper. At present, it is assumed that R_e is known experimentally or interpolated by one of the well-known schemes,[2,19−21] while D_{VS} is calculated by adding the appropriate promotion energies to the observed D_e. For the diatom AB, the resulting FC is

$$k_{AB} = (\lambda_{AA} + \lambda_{BB})D_{VS}(AB)/2R_e(AB) \qquad (6)$$

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TABLE 1: Homonuclear Data for $\lambda = kR_e/D_{VS}$, Spectroscopic and Valence-State Dissociation Energies, D_e and D_{VS}, Bond Lengths, R_e, and Harmonic Force Constants, k[a]

A_2	D_e, eV	D_{VS}, eV	R_e, Å	k,[a] eV/Å^2	λ, Å^{-1}	λ(p), Å^{-1}
H_2	4.747	11.169	0.7413	35.94	2.385	
Li_2	1.056	3.443	2.673	1.576	1.223	
Na_2	0.735	3.042	3.080	1.071	1.084	
K_2	0.52	2.44	3.925	0.615	0.973	
Rb_2	0.492[b]	2.338	4.18	0.521	0.931	
Cs_2	0.45	2.16	4.648	0.434	0.934	
Cu_2	2.08	5.33	2.220	8.222	3.42	
Ag_2	1.67	4.81	2.469[c]	7.31	3.75	
Cl_2	2.514	11.18[d]	1.987	20.15	3.581	4.627
Br_2	1.991	10.39[d]	2.281	15.36	3.371	4.354
I_2	1.556	8.73[d]	2.666	10.74	3.279	4.197
F_2	1.66	7.35[d]	1.412	29.51	5.67	(5.21)[e]

[a] Unless otherwise indicated, D_e, R_e, and k from refs 22 and 23. Conversion factor: 1 eV/Å^2 = 0.1602 mdyn/Å. [b] Caldwell, C. D.; Engelke, F.; Hage, H. *Chem Phys.* **1980**, *54*, 21. [c] Brown, C. M.; Ginter, M. L. *J. Mol. Spectrosc.* **1978**, *69*, 25. [d] Operational $D_{VS} = hcB_e\tilde{\nu}_e/\alpha_e$; conversion factor, 8065.5 cm^{-1} = 1 eV. [e] See text for explanation.

Results and Discussion

Table 1 lists the homonuclear input data for the λ_{AA} of single-bonded diatoms; R_e and $k = \mu(2\pi c\tilde{\nu}_e)^2$ are from ref 22. Equation 4 is used with experimental D_e,[22,23] while E_{hy} and J are interpolated from Bratsch's tabulation of promotion energies and EN.[24,11] The degree of hybridization in homonuclear molecules enters into the reference D_{VS} values. Based on pertinent analyses,[25] hybridization is assumed to be negligible for the homonuclear diatoms of groups 1 and 11. For Cl_2, Br_2, and I_2, the analyses attribute a decrease from 15% to 10% of s character in bonding hybrid orbitals on going to heavier elements in the group. In this paper, an intrinsic hybridization criterion particular to the VSPE function (eq 2) is presented. The vibration−rotation coupling constant is[11]

$$\alpha_e = (6B_e^{\,2}/\tilde{\nu}_e)z/3 = 2B_e^{\,2}\lambda R_e/\tilde{\nu}_e \tag{7}$$

With

$$z = hc\tilde{\nu}_e^{\,2}/2B_eD_{VS} \tag{8}$$

we get an operational definition for

$$D_{VS}(\mathrm{sp}^m) = hcB_e\tilde{\nu}_e/\alpha_e \tag{9}$$

The spectroscopic constants representing the first, second, and third derivatives of U at R_e, viz., B_e, ν_e, and α_e, determine not only D_{VS} but also the entire three-parameter VSPE curve of any diatom. For homonuclear molecules, eqs 4 and 8 combine to an expression for the promotion energy to the VS

$$2E_{hy} + (J/2) = (hcB_e\tilde{\nu}_e/\alpha_e) - D_e \tag{10}$$

Using tabulated E_{hy} and J data[11,24] with eq 10 yields 13% s character for Cl_2 and Br_2, while 10% is found for I_2, in excellent agreement with theoretical analyses.[25]

The F−F bond has been found to be exceptional according to most methods.[7c,26] In ref 11, the effect of interacting lone pairs on λ and z has been absorbed into an ad hoc $z = \alpha_e\tilde{\nu}_e/2B_e^{\,2}$. Because of the antibonding effects of lone pairs, D_{VS} = 7.35 eV is significantly smaller, thus, λ = 5.67 larger than those for the other halogen diatoms. The % s character in the F_2 bond cannot be determined using eq 10, due to the superposition of the bond-weakening lone-pair effects.

TABLE 2: Spectroscopic and Valence-State Dissociation Energies, D_e and D_{VS}, Bond Lengths, R_e, Calculated and Experimental Force Constants, $k_{cal} = (\lambda_{AA} + \lambda_{BB})D_{VS}/2R_e$, and k_{obs}

AB	D_e, eV	D_{VS}, eV	R_e, Å	$[\lambda_{AA} + \lambda_{BB}]/2$ Å^{-1}	k_{cal},[a] eV/Å^2	k_{obs}, eV/Å^2
LiCI	4.86	6.45	2.021	2.925	9.33	8.90
NaCI	4.29	5.68	2.361	2.855	6.87	6.87
KCl	4.40	5.08	2.667	2.800	5.33	5.31
RbCl	4.39	4.91	2.787	2.779	4.89	4.88
CsCl	4.59	4.83	2.906	2.780	4.62	4.67
CuCI	3.95	7.15	2.051	4.025	14.05	14.44
AgCI	3.24	6.32	2.281	4.19	11.61	11.58
LiBr	4.37	6.15	2.170	2.789	7.90	7.43
NaBr	3.82	5.40	2.502	2.719	5.87	5.83
KBr	3.94	4.86	2.821	2.664	4.59	4.61
RbBr	4.01	4.79	2.945	2.643	4.30	4.32
CsBr	4.09	4.60	3.072	2.644	3.96	4.08
CuBr	3.45	6.71	2.173	3.89	12.01	12.76
AgBr	3.00	6.20	2.393	4.05	10.5	10.36
LiI	3.57	5.61	2.392	2.710	6.35	6.00
NaI	3.18	5.03	2.711	2.641	4.90	4.76
KI	3.40	4.60	3.048	2.585	3.90	3.82
RbI	3.44	4.50	3.177	2.564	3.63	3.60
CsI	3.48	4.28	3.315	2.566	3.31	3.39
CuI	<3.27	<6.73	2.338	3.81	<10.97	10.85
AgI	2.6	6.0	2.545	4.01	9.2	9.15
LiH	2.52	5.93	1.596	1.804	6.70	6.41
NaH	1.97	5.26	1.887	1.735	4.84	4.88
KH	1.83	4.64	2.240	1.679	3.48	3.52
RbH	1.81	4.52	2.367	1.658	3.17	3.21
CsH	1.84	4.37	2.494	1.660	2.91	2.92
CuH	2.85	7.31	1.463	2.90	14.5	13.75
AgH	2.39	6.78	1.618	3.07	12.8	11.38
HCI	4.62	10.54	1.275	3.506	28.99	32.23
HBr	3.92	9.75	1.414	3.370	23.24	25.67
HI	3.20	8.99	1.609	3.293	18.40	19.59
BrCl	2.24	10.94	2.136	3.476	17.80	17.59
ICl	2.18	9.91	2.321	3.431	14.66	14.89
IBr	1.84	9.46	2.469	3.325	12.74	12.91
LiF	6.00	7.82	1.564	3.22	16.08	15.48
NaF	4.98	6.59	1.926	3.15	10.8	10.99
KF	5.14	6.05	2.171	3.09	8.62	8.62
RbF	5.20	5.96	2.270	3.07	8.07	8.04
CsF	5.32	5.80	2.345	3.07	7.59	7.60
CuF	4.43	8.31	1.745	4.32	20.6	20.79
AgF	3.64	7.08	1.983	4.48	16.0	15.64
HF	6.12	13.55	0.9168	4.03	59.76	60.24

[a] D_e, R_e, and k_{obs} values from refs 22 and 23; conversion factor: 1 eV/Å^2 = 0.1602 mdyn/Å.

The λ values in column 6 of Table 1 can be directly tested for transferability if the bonding orbitals retain their reference hybridization while forming polar bonds. A hybridization of the halogens in highly ionic alkali-metal halides and group 11 halides does not pay off;[25c] thus, 100% p character is assumed for their electron configuration.[17] In order to be consistent with the AIMs in these halides, the change in hybridization from X_2 to AX has to be incorporated into the λ_{XX} increments. The Pauling−Sherman relation[27] serves to calculate D_{VS}(p) for the unhybridized halogens from the $D_{VS}(\mathrm{sp}^m)$ found from eqs 9 and 10:

$$D_{VS}(\mathrm{p})/D_{VS}(\mathrm{sp}^m) = 3(m + 1)/[(3m)^{1/2} + 1]^2 \tag{11}$$

Dividing kR_e in eq 3 by D_{VS}(p) instead of the operational $D_{VS}(\mathrm{sp}^m)$ of eq 9 increases λ:

$$\lambda(\mathrm{p}) = [(3m)^{1/2} + 1]^2(3m + 3)^{-1}\lambda(\mathrm{sp}^m) \tag{12}$$

Pauling−Sherman factors of 1.292 for 13% s character in $C1_2$ and Br_2 and 1.280 for 10% s character in I_2 have been used for obtaining the λ(p) in the last column of Table 1, which serve to

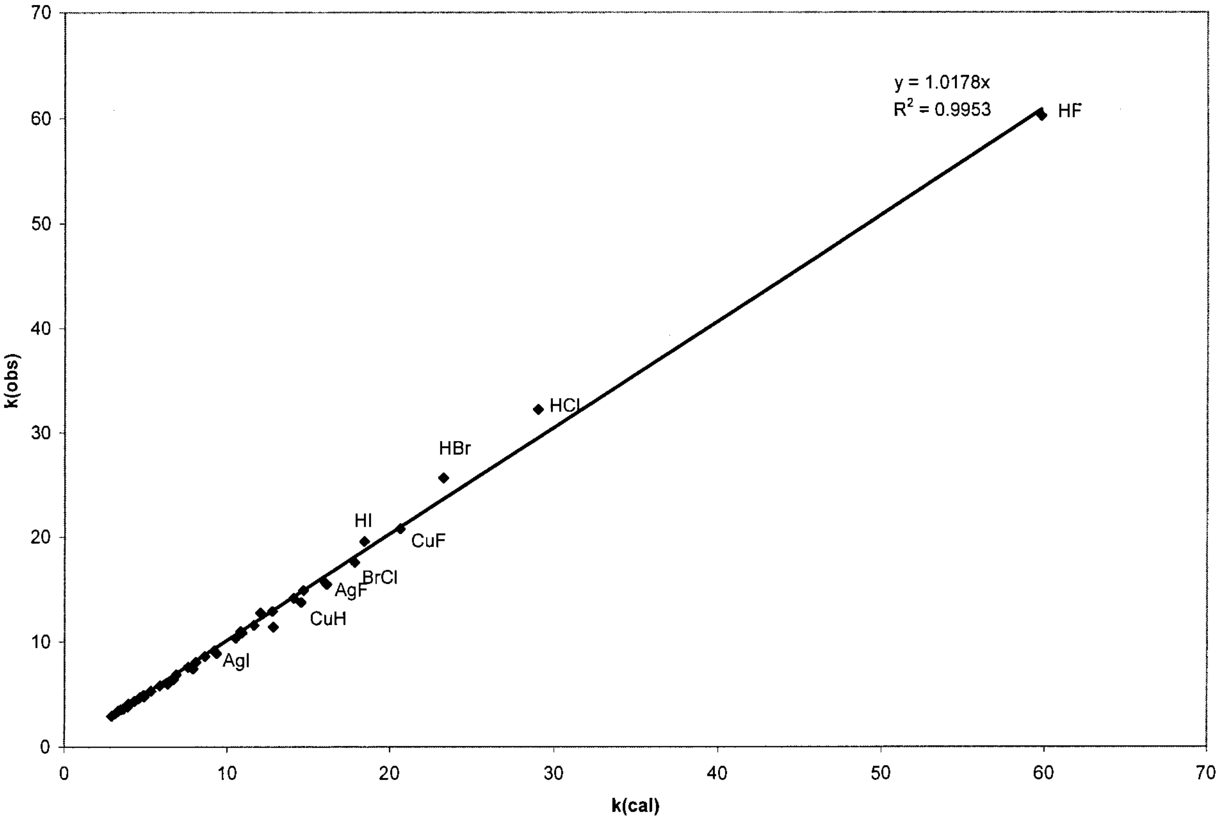

Figure 1. Plot of the observed against calculated harmonic force constants (in eV/Å^2) of 42 heteronuclear diatomic molecules. The correlation coefficient for the best zero-intercept line is $R = 0.9976$.

calculate the FCs of alkali-metal halides. Incidentally, the Pauling−Sherman formula reduces the operational $D_{VS}(sp^m)$ to $D_{VS}(p)$ values which are quite similar to the sum of dissociation energy D_e and promotion energy ($\Sigma P(p)$) needed to reach the unhybridized p VS.[11] The FC increment for the fluorides will be discussed below.

Figure 1 and Table 2 show a comparison of the calculated and observed FCs for 42 single-bonded molecules. The VS promotion energy, $D_{VS} - D_e$, is obtained from refs 11, 17, and 24. Heteronuclear data for D_{VS} and R_e are combined with $[\lambda_{AA} + \lambda_{BB}]/2$ according to eq 6 in order to calculate FC, k_{cal}, in column 6, and compared it with the observed, k_{obs}, in the last column. Still excluding the fluorides shown at the end of Table 2, the average absolute error of 34 calculated FCs amounts to 3.3%, i.e., 1.8% in calculated harmonic wavenumbers, $\tilde{\nu}_e$. The FCs of lithium-containing molecules are systematically too high by about 5%; excluding them reduces the absolute error of k to 2.7%. There is an option to improve the results by choosing LiH as the reference molecule in order to calculate the transferable λ increment for the lithides. Remarkably, the copper and silver halides are as well described as the alkali-metal halides. Although the former are less ionic, d-orbital participation on Cu and Ag does not seem to affect the VS reference energy. The situation is somewhat different for the hydrides. The FCs of the alkali-metal hydrides are calculated to an accuracy of 1.7%, whereas they are 5.5% and 12.5% too high for CuH and AgH, respectively. This may be attributed to a change in the reference VS energy due to sd mixing in the group 11 hydrides,[28] an effect not included in this study. Note also the increased experimental uncertainty in the D_e values for CuH and AgH.[23]

For the reasons given above and in ref 11, the VSPE curve of the fluorine molecule is not suitable for extracting the $\lambda(p)$ increment for the FCs of ionic fluorides. However, an empirical $\lambda(p) = 5.21$ is found to fit the fluoride FCs with an accuracy comparable to that of the whole set of diatoms studied here. The hydrogen fluoride molecule may serve as the example for an alternative way of extracting information from the VSPE function and combining rule. The higher spectroscopic constants α_e and $\tilde{\nu}_e x_e$ of HF are well matched, assuming 5% s character in F and, thus, $D_{VS}(HF) = 13.55$ eV.[11] (The s character has not been specified in ref 11.) This value together with the experimental R_e and operational $\lambda(F_2) = 5.67$ yield an excellent $k(HF) = 59.67$ eV Å^{-2} just 0.8% short of the experimental FC. In agreement with ref 25, this indicates that the s character in F_2 is around 5%. For all of the 42 molecules shown in Table 2, the absolute average error of k is <2.8%, equivalent to 1.6% error in $\tilde{\nu}_e$, whereas a 5% error in $\tilde{\nu}_e$ has been considered to be a useful accuracy.[1,3]

On the whole, λ is found to be remarkably transferable over the whole range of bond polarity. This relates to an interesting parallel with regard to empirical potentials between closed-shell systems. The repulsive interaction between atoms, ions, and molecules with closed-shell structure has long been known to obey simple combining rules.[29,30] Most commonly, the repulsive potential (U_{AB}) is estimated from that of like atoms by geometric averaging:

$$U_{AB} = (U_{AA}U_{BB})^{1/2} \qquad (13)$$

For the exponential factor in such potentials, this is equivalent to the combining rule (eq 5) of this paper. However, combining rules have been previously reported for purely repulsive potentials only. For the first time, a combining rule (i) is applicable for a PE function of the bonding type and (ii) allows us to calculate the harmonic FC to a useful accuracy.

The product between k and powers of R_e has been repeatedly tested in searching for transferable combinations of spectroscopic constants.[1−3,31,32] Pearson has examined the correlation

$$kR_e = aN\chi_A\chi_B + b \tag{14}$$

with $N = 1{-}3$ as the integral bond order:[1] the slope, a, and intercept, b, of regression vary wildly for different classes of compounds, e.g., $a = 180$ and $b = -160$ for the alkali-metal halides, in contrast to $a = 77$ and $b = +117$ for homonuclear molecules. Bergmann and Hinze have recently replaced $\chi_A\chi_B$ by the sum of chemical hardness, $\eta_A + \eta_B$;[2] however, their claim to have improved on earlier correlations is poorly documented and further hampered by their choice of an experimental FC data set published in 1963[20] that contains errors above 10% compared to standard compilations.[22] Probes into the Bergmann and Hinze equation (cf. eq 48 of ref 2)

$$kR_e = 0.50\ \mathrm{mdyn}\ (\eta_A + \eta_B)\ \mathrm{V}^{-1}\ \mathrm{e} \tag{15}$$

reveal systematic errors of >+150% (!) for the alkali-metal hydrides and +50% for alkali-metal halides. This seems to call once more for separate regression lines for different classes of compounds.

The reason for different regression lines is explainable in the framework of the valence-state concept. The FC of ionic molecules results from ionic interactions, while that of nonpolar molecules is due to covalent bonding. The former are better described by special ionic PE functions using the ionic dissociation limit, i.e., $D_i = D_e + I_A - A_B$;[6] the latter are commonly treated with reference to dissociation into free atoms, i.e., using D_e.[4,5,7−10] The two reference energies differ by $I_A - A_B$, whereas a common reference zero of energy is necessary in order to achieve the maximum degree of universality.[11,16] The VSPE function describes the *in situ* covalent and ionic interactions in a unified way[11] by introducing semiempirical elements and simplifying the formalism developed by Ruedenberg.[18] D_{VS} is again shown as a parameter with a high information content, and R_e/D_{VS}, in contrast to R_e/D_e or R_e/D_i, acts as a scaling factor for k in generating transferable force constant increments.

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