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DEPENDENCE UPON BOND LENGTH

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Abstract

Empirical study of cubic and quartic vibrational force constants for diatomic molecules shows them to be approximately exponential functions of internuclear distance. A family of curves is obtained, determined by the location of the bonded atoms in rows of the periodic table. Displacements between successive curves correspond closely to those in Badger's rule for quadratic force constants (for which the parameters are redetermined to accord with all data now available). Constants for excited electronic and ionic states appear on practically the same curves as those for the ground states. Predictions based on the diatomic correlations agree with the available cubic constants for bond stretching in polyatomic molecules, regardless of the type of bonding involved. Some implications of these regularities are discussed.

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Molecular vibrations must be taken into account in the interpretation of many types of experiments. Often the anharmonicity of the vibrations is an important consideration. For example, in most molecular structure determinations the dominant vibrational corrections arise from anharmonic terms in the potential function. It has been shown¹ that within a practical approximation the difference between the average molecular configuration derived from electron diffraction experiments² and the equilibrium configuration is due solely to the cubic potential terms. The cubic terms also give the largest of the corrections needed to derive equilibrium moments of inertia from observed spectroscopic rotational constants.³ In a large class of isotope effects, especially where hydrogen is involved, anharmonicity plays an important role. Some examples that have been discussed theoretically are various magnetic interactions,⁴ including second moments⁵ and chemical shifts⁶ of nuclear magnetic resonance lines, and optical activity⁷ of compounds of the type RR'CHD. Aside from diatomics, however, very little is known about the anharmonicity of molecular potential functions. Consequently, it has usually been the practice either to ignore the effects of anharmonicity or to rely on rather crude approximations.

Several types of empirical formulas have been proposed to describe the variation of harmonic bond stretching force constants with bond length and with chemical properties of the bonded atoms, and these often give satisfactory results for polyatomic as well as diatomic molecules. One of the simplest is Badger's rule,⁸

$$F_2 = 1.86 (r_e - d_{1j})^{-3} \quad (1)$$

in which r_e is the equilibrium bond length and the constant d_{ij} is fixed for bonds between atoms from rows i and j of the periodic table. We have examined the available data and find that cubic and quartic force constants for diatomic molecules can also be represented as functions of bond length and position in the periodic table (see Fig. 1) and that anharmonic bond stretching constants for a number of polyatomic molecules can be predicted within experimental error by the same functions. This paper gives the relations obtained and a qualitative discussion of the origin of the observed regularities.

Analysis of Diatomic Data

A table⁹ of quadratic, cubic, and quartic force constants for diatomic molecules and ions was calculated from spectroscopic data, using the relations:

$$F_2 = 5.889 \times 10^{-7} \mu \omega_e^2 \quad (2)$$

$$F_3 = - a_1 (F_2 / r_e) \quad (3)$$

$$F_4 = a_2 (F_2 / r_e^2) \quad (4)$$

where

$$- a_1 = 1 + (\alpha_e \omega_e / 6B_e^2) \quad (5)$$

$$a_2 = (5/4)a_1^2 - (2/3)(\omega_e x_e / B_e) . \quad (6)$$

Here the potential function is written as

$$2V(r) = F_2(r-r_e)^2 + F_3(r-r_e)^3 + F_4(r-r_e)^4 + \dots$$

The other notation and units (given under Table I) are standard. For hydride molecules additional terms¹⁰ were included in Eqs. (5) and

(6). Most of the spectroscopic parameters were taken from Herzberg's tabulation,¹¹ but an attempt was made to include all new and revised parameters published up to December, 1960.

The accumulation of data since 1935 has enabled Badger's correlation to be extended to about twice as many families of molecules, and the parameters for most of the others have been revised. Table I lists the values of a_{1j} and d_{1j} which gave the best fit to straight lines,

$$r_e = d_{1j} + (a_{1j} - d_{1j})F_2^{-1/3} . \quad (7)$$

The accuracy of the correlation is discussed in detail in reference 9 and remains about as good as that found by Badger. The parameter a_{1j} might be regarded as a standard bond length ($F_2 = 1$ at $r_e = a_{1j}$) and d_{1j} as a distance of closest approach ($F_2 \rightarrow \infty$ at $r_e = d_{1j}$).

Included for comparison in Table I are the parameters d'_{1j} derived from the original version of Badger's rule, in which $a_{1j} - d_{1j}$ was assigned the constant value $(1.86)^{1/3} = 1.23$; although this is the commonly used form of the rule, it does not allow a satisfactory fit to data for the heavier molecules, as Badger pointed out.⁸ It was also found that the data that have become available for a number of molecules containing transition metals bonded to hydrogen or first row atoms required parameters considerably different from the usual ones, as indicated in Table I.

As illustrated in Fig. 1, the correlations obtained for cubic and quartic constants are about as good as those for the quadratic constants. For some of the families of molecules, the semilogarithmic graphs show noticeable curvature, but for convenience a simple

exponential function,

$$(-1)^n F_n = 10^{-(r_e - a_{1j})/b_{1j}}, \quad (8)$$

($n = 2, 3, 4$) was fitted to all the data. Table II lists the parameters obtained. The experimental uncertainty in many of the anharmonic constants is several percent; data for which the uncertainty is greater than 25% were excluded.

For quadratic constants, the overall agreement with Eq. (8) was somewhat more satisfactory than Badger's rule except for light molecules; in particular, Li_2 and some excited states of LiH and H_2 . For the anharmonic constants various functions analogous to Badger's were also tried with similar results. In Fig. 1 the (solid) lines calculated from Eq. (8) may be compared with the (dashed) curves obtained from the relations of Table III for the H-1 and 1-1 families of molecules, which showed the most noticeable curvature, and for the 2-2 family, which is practically linear.

For excited electronic states and ionic states, the anharmonic constants as well as the quadratic constants are found to conform fairly well to the curves established from data for the ground states, although the scatter is considerably increased. In Fig. 1, open circles indicate excited or ionic states; to avoid overcrowding the figure, these constants were included for hydrides only. However, similar agreement is found for the other families of molecules. Data for these states were included but assigned one-fourth the weight of ground state data in determining the parameters given in Tables I-III.

As a simple rule for order-of-magnitude calculations it may be noted that for about two-thirds of the known molecular states the ratios a_1 and a_2 of Eqs. (5) and (6) fell in the ranges 2 to 4 and

2 to 6, respectively. These quantities were found to be less regular functions of internuclear distance than the force constants, however.

Polyatomic Molecules

For a few polyatomic molecules vibration-rotation interaction constants are available from which cubic bond stretching force constants can be derived, and the results are given in Table IV. The methods used are described elsewhere.^{1,9} A generalized valence force field has been assumed, in which the part of the potential due to the stretching of a particular bond has the form ($n = 2, 3, 4$):

$$2V = \sum_n F_n (r - r_e)^n + \text{interaction terms.}$$

Except for CO_2 and H_2O , the interaction terms had to be neglected in deriving the force constants. In most cases the uncertainty thereby introduced is expected to be less than that due to the experimental error in the vibration-rotation parameters and normal coordinates which enter into the calculations.¹² As seen in Table IV the agreement between the polyatomic values and those predicted from the diatomic curves (using the polyatomic bond lengths) is quite satisfactory, considering the experimental errors and theoretical approximations involved. It thus seems, at least for the available data, that stretching cubic constants for polyatomic molecules can be predicted from diatomic data simply by allowing for the change in bond length. It is hoped that more, accurate vibration-rotation parameters will be forthcoming to provide additional tests.

Cubic constants for bond bending can also be obtained from the appropriate vibration-rotation interaction parameters, but at present there is almost no reliable data available to test any method for estimating them.¹³

Discussion

Some thirty empirical relations have been proposed connecting harmonic force constants and bond length with such properties as bond order, electronegativity, dissociation energy, ionization potential and number of valence electrons.¹⁴ Perhaps ten of these are more or less equivalent in range and accuracy to Badger's rule. As is clear from Fig. 1, many of these relations can be expected to apply also to the anharmonic constants. We have chosen to restrict consideration to Eq. (8), because it can be applied so readily to bonds in polyatomic molecules.

While Eq. (8) gives a satisfactory over-all fit to the data, other relations are somewhat better for some groups of molecules. For example, for several families, including the hydrides and diatomic molecules of the alkali metals, a better correlation is obtained for the constant F_2 by applying Badger's rule to columns rather than to rows of the periodic table;¹⁵⁻¹⁷ we have found that this also holds for F_3 and F_4 . Theoretical considerations¹⁸⁻²⁰ suggest the use of columns rather than rows, but in practice this is a much less convenient way to organize the experimental data.

To obtain the best accuracy of prediction in any particular case, the data employed should be restricted to a series of molecules in which the bond character is similar, or at least suffers no abrupt change along the series.¹⁶ It is also desirable to compare results obtained from several correlation schemes whenever this is feasible.

In addition to the correlations within each family of molecules, it will be noted in Tables I-III that the parameters a_{1j} and d_{1j}

both show fairly regular trends from one family to another, consistent with Badger's observation that "the d_{1j} 's appear to depend on the completeness of the inner shells of the respective atoms, and not much on the outer shells."

A general argument can be given to show that these regularities reflect the extent to which the repulsive forces between the nuclei of the bonded atoms are reduced by electronic shielding. This has been indicated by several authors in connection with perturbation treatments of harmonic force constants.¹⁸⁻²⁰ We shall consider briefly some qualitative aspects and examine how the situation changes as one goes from F_2 to F_3 and F_4 .

Within the accuracy of the Born-Oppenheimer approximation, the vibrational potential function may be written as

$$U(r) = U_N(r) + U_E(r) \quad (9)$$

where $U_N(r) = Z_a Z_b e^2 / r$ is the nuclear repulsive potential and $U_E(r)$ represents an average over the electronic kinetic and potential energy in the field of the fixed nuclei.²¹ At the equilibrium internuclear distance there are the relations

$$-D_e = U_N + U_E \quad (10)$$

$$0 = -U_N/r + \partial U_E / \partial r \quad (11)$$

$$F_2 = 2U_N/r^2 + \partial^2 U_E / \partial r^2 \quad (12)$$

$$F_3 = -2U_N/r^3 + \frac{1}{3} \partial^3 U_E / \partial r^3 \quad (13)$$

$$F_4 = 2U_N/r^4 + (1/12)\partial^4 U_E/\partial r^4 \quad (14)$$

where D_e is the dissociation energy and the derivatives are evaluated at $r = r_e$. The nuclear repulsion, which is outweighed by the electronic contributions in (10), and is balanced by them in (11), is always found to dominate in the force constants.²²

The various derivatives of U_E (at $r = r_e$) turn out to be roughly constant for isoelectronic series of molecules with the same Z_a and Z_b . The derivatives vary regularly for molecules whose atoms belong to the same column of the periodic system (rows usually give a fairly smooth correlation also).

Although Eqs. (9-14) hold strictly only when Z_a and Z_b refer to "bare nuclei," it is of interest to examine also the results obtained when the inner shell electrons are assumed to follow the nuclei exactly during a vibration. Murrell has applied Eq. (12) to some diatomic molecules, taking Z_a and Z_b as the number of electrons outside a completed shell. He noted that $(\partial^2 U_E/\partial r^2)_e$ shows a regular variation in related groups (see his Figs. 2 and 3) which is qualitatively consistent with an expression derived from perturbation theory.^{18,19} With this choice of Z_a and Z_b , the derivative $(\partial^2 U_E/\partial r^2)_e$ has small positive values for the hydrides (except for LiH) and diatomic molecules of alkali metals, while it remains large and negative for other molecules.

Similar correlations appear in an analogous treatment of the anharmonic constants. There is a systematic trend in passing from F_2 to F_3 and F_4 in that the imbalance between the nuclear and electronic contributions steadily increases. (For F_3 and F_4 , graphs similar to

Murrell's Figs. 2 and 3 are rotated counterclockwise.) This is illustrated in Table V, which lists for a few examples $U_E^{(n)}/U^{(n)}$, the ratio of the electronic contributions in Eqs. (12-14) to the total. We shall refer to the electronic contribution as shielding when its sign is opposite to that of the nuclear contribution, and as antishielding when its sign is the same. Thus, negative values of the ratios in Table V correspond to shielding contributions, and the ratios are always²² negative when Z_a and Z_b refer to bare nuclei. It is seen that the shielding decreases as n is increased for a given molecule or as r_e is increased in a series of molecules.

The hydrogen halides illustrate how rapid is the onset of antishielding with decrease in the effective nuclear charges: merely "clamping" the two 1s electrons onto the halogen nucleus causes antishielding to appear in the quartic constants and even in the cubic constant of HI.

This empirical analysis of the electronic contributions can readily be given a qualitative theoretical basis. We shall take the approach used by Bratož, et al., in a united-atom treatment of harmonic force constants for diatomic hydrides.²⁰ However, the conclusions depend only upon general properties of the electronic energy function.

Since $U(r) \rightarrow 0$ for large values of the internuclear distance,

$$\partial^n U_E / \partial r^n \rightarrow -\partial^n U_N / \partial r^n \rightarrow 0, \quad (15)$$

($n = 0, 1, 2, \dots$). For $r \rightarrow 0$, it has been shown²³ that $U_E(r)$ approaches the united atom energy and again

$$\partial U_E / \partial r \rightarrow 0, \quad (16)$$

while the higher derivatives in general approach finite values. At intermediate values of r the first derivative must pass through at least one maximum, since $-\partial U_E/\partial r$ represents an attractive force exerted on the nuclei. For this qualitative discussion, the simple curve shown at the top of Fig. 2 is chosen and the higher derivatives constructed graphically.^{24,25} The minus and plus signs indicate the regions corresponding to shielding and antishielding contributions, respectively. At large enough r there is always shielding, as seen from Eq. (15). The dashed curves in Fig. 2 indicate the negative of the corresponding derivatives of the nuclear repulsive potential.

When $U_E(r)$ is defined by Eq. (9) with Z_a and Z_b the full nuclear charges, the location of the equilibrium internuclear distance is far enough to the right in Fig. 2 (for instance, at point "B") to yield only shielding contributions, as shown by Eqs. (10-14). However, the successive derivatives show a steady outward progression of the boundary between the shielding and antishielding regions. This tends to quench the shielding contributions, and the effect is accentuated as r_e increases.

The way in which antishielding enters when the effective nuclear charges are reduced may also be understood from Fig. 2. If the electronic density is regarded as the sum of various orbital distributions,²⁰ these give additive contributions in Eqs. (11-14). For each orbital the derivative curves are expected to be qualitatively similar to Fig. 2. Since inner shell orbitals have their peak density at small r , for them the location of r_e is well to the right side of the curves, as indicated by the point "C" in Fig. 2. For "larger"

orbitals the position of r_e moves to the left; thus, r_e might be near the point "A" for the valence orbitals. Consider first the quadratic force constant. Since the curve near "C" has practically reached the limiting form of Eq. (15), the inner shell orbitals quite effectively shield an equivalent amount of nuclear charge, whereas the curve near "A" shows that the valence orbitals may contribute relatively little shielding. This is evidently the situation in the hydrides and diatomic alkali metal molecules, whose harmonic force constants are fairly well approximated by simply ignoring the valence orbitals.²⁰ Although point "A" will usually not lie so far to the left in other molecules, the valence orbitals will still shield much less than their share of the nuclear charge. In the same way, the general shape of the higher derivative curves near "A" is seen to account for the tendency of the valence orbitals to become antishielding in the anharmonic constants.

Acknowledgment

We wish to thank Miss Patricia Kurth for preparing the table of diatomic force constants.

Table I. Parameters for Badger's Rule.^a

1	J	a_{1j}	d_{1j}	d'_{1j}
H	H	1.26	0.025	0.025
H	1	1.66	0.30	0.36
H	2	1.84	0.38	0.58
H	3	1.98	0.49	0.65
H	4	2.03	0.51	0.80
H	5	2.03	0.25	0.81
1	1	1.91	0.68	0.68
1	2	2.28	0.74	0.92
1	3	2.35	0.85	1.02
1	4	2.33	0.68	1.12
1	5	2.50	0.97	1.22
2	2	2.41	1.18	1.18
2	3	2.52	1.02	1.28
2	4	2.61	1.28	1.40
2	5	2.60	0.84	1.24
3	3	2.58	1.41	1.35
3	4	2.66	0.86	1.48
3	5	2.75	1.14	1.55
4	4	2.85	1.62	1.62
4	5	2.76	1.25	1.51
H	3T	1.85	0.15	0.53
H	4T	1.84	0.61	0.61
H	5T	1.78	0.97	0.62
1	3T	2.08	1.14	0.97
1	4T	2.34	1.17	1.08

^aUnits employed in the tables and equations of this paper are: r_e , Angstrom units; F_2 , 10^5 dynes cm^{-1} ; μ , g mole $^{-1}$; ω_e , cm^{-1} ; F_3 , 10^{13} dynes cm^{-2} ; F_4 , 10^{21} dynes cm^{-3} .

Table II. Parameters for exponential functions.^a

1	J	F ₂	^a _{1j} -F ₃	F ₄	F ₂	^b _{1j} -F ₃	F ₄
H	1	1.54	1.58	1.57	0.64	0.48	0.43
H	2	1.80	1.85	1.77	0.69	0.59	0.47
H	3	1.98	2.01	1.81	0.95	0.74	0.80
H	4	2.08	2.07	2.04	0.96	0.74	0.66
H	5	2.06	2.12	2.04	0.78	0.90	0.69
1	1	1.73	1.78	1.81	0.47	0.39	0.36
1	2	2.02	2.10	2.06	0.53	0.48	0.41
1	3	2.15	2.26	2.08	0.60	0.55	0.34
1	4	2.36	2.41	2.18	0.76	0.57	0.32
1	5	2.47	2.48	2.54	0.87	0.68	0.68
2	2	2.40	2.48	2.35	0.70	0.61	0.46
2	3	2.54	2.57	2.53	0.94	0.72	0.70
2	4	2.63	2.70	2.64	0.96	0.73	0.51
2	5	2.71	2.81	2.60	1.09	1.09	1.30
3	3	2.70	2.77	2.66	0.75	0.89	1.06
3	4	2.66	2.76		0.98	1.19	
3	5	2.73	2.83		0.88	1.05	
4	4	2.85	2.95		0.94	0.70	
4	5	2.84	2.93		1.09	0.78	
H	3T	1.82	1.92		1.04	0.86	
H	4T	1.59			0.75		
H	5T	1.77			0.44		
1	3T	1.98			0.44		
1	4T	2.15			0.52		

^aDefined by: $r_e = a_{1j} - b_{1j} \log_{10} [(-1)^n F_n]$ for $n = 2, 3, 4$.

Table III. Parameters for inverse power functions.^a

i	j	a _{ij}			d _{ij}		
		F ₂	-F ₃	F ₄	F ₂	-F ₃	F ₄
H	1	1.66	1.68	1.61	0.30	0.32	0.28
1	1	1.91	1.98	2.01	0.68	0.61	0.39
2	2	2.41	2.50	2.41	1.18	1.08	0.99

^aDefined by: $r_e = d_{ij} + (a_{ij} - d_{ij})[(-1)^n F_n]^{-1/(n+1)}$
for $n = 2, 3, 4$.

Table IV. Cubic force constants for bond stretching in polyatomic molecules

Bond	Molecule	Bond Length	-F ₃ , Cubic Constant	
			Expt.	Predicted
CH	CH ₄	1.09	10	10
	HCN	1.06	12	12
	DCN	1.06	11	12
	HCCH	1.06	11	12
	DCCD	1.06	11	12
CC	HCCH	1.20	32	30
	DCCD	1.20	33	30
CN	HCN	1.16	44	39
	DCN	1.16	42	39
CO	CO ₂	1.16	38.5	39
	OCS	1.16	36	39
CS	CS ₂	1.55	14	14
	OCS	1.55	16	14
CSe	OCSe	1.71	10	10
CBr	BrCN	1.79	6.8	7.2
CI	ICN	1.99	4.9	5.5
OH	H ₂ O	0.96	19.8	19.5
NO	N ₂ ¹⁴ O	1.19	33	33
	N ¹⁵ N ¹⁴ O	1.19	33	33
NN	N ₂ ¹⁴ O	1.13	39	46
	N ¹⁵ N ¹⁴ O	1.13	44	46

Table V. Variation of electronic contributions.^a

Molecule	r_e	$n=2$	$n=3$	$n=4$
$Z_a = Z_b = 1$				
Li ₂	2.672	0.047	0.50	0.52
Na ₂	3.079	0.101	0.51	0.25
K ₂	3.923	0.278	0.62	0.99
LiH	1.595	-0.111	0.42	0.54
NaH	1.887	0.017	0.59	0.69
KH	2.244	0.279	0.63	0.62
RbH	2.367	0.320	0.67	0.78
CsH	2.494	0.367	0.71	0.89
$Z_a = Z_b = 5$				
N ₂	1.094	-2.83	-0.33	0.29
PN	1.491	-2.42	-0.05	0.36
P ₂	1.893	-2.03	0.01	0.47
$Z_a = Z_b = 6$				
O ₂	1.207	-7.02	-1.64	-0.38
SO	1.493	-5.30	-0.90	-0.03
S ₂	1.889	-3.88	-0.54	0.24
Se ₂	2.157	-3.57	-0.45	0.10
$Z_a = 1, Z_b = 7$				
HF	0.917	-3.10	-0.98	-0.42
HCl	1.275	-2.02	-0.28	0.18
HBr	1.414	-1.78	-0.13	0.23
HI	1.604	-1.63	0.06	0.45

^aThe tabulated quantity is $(\partial^n U_E / \partial r^n)_e / (\partial^n U / \partial r^n)_e$.

Footnotes

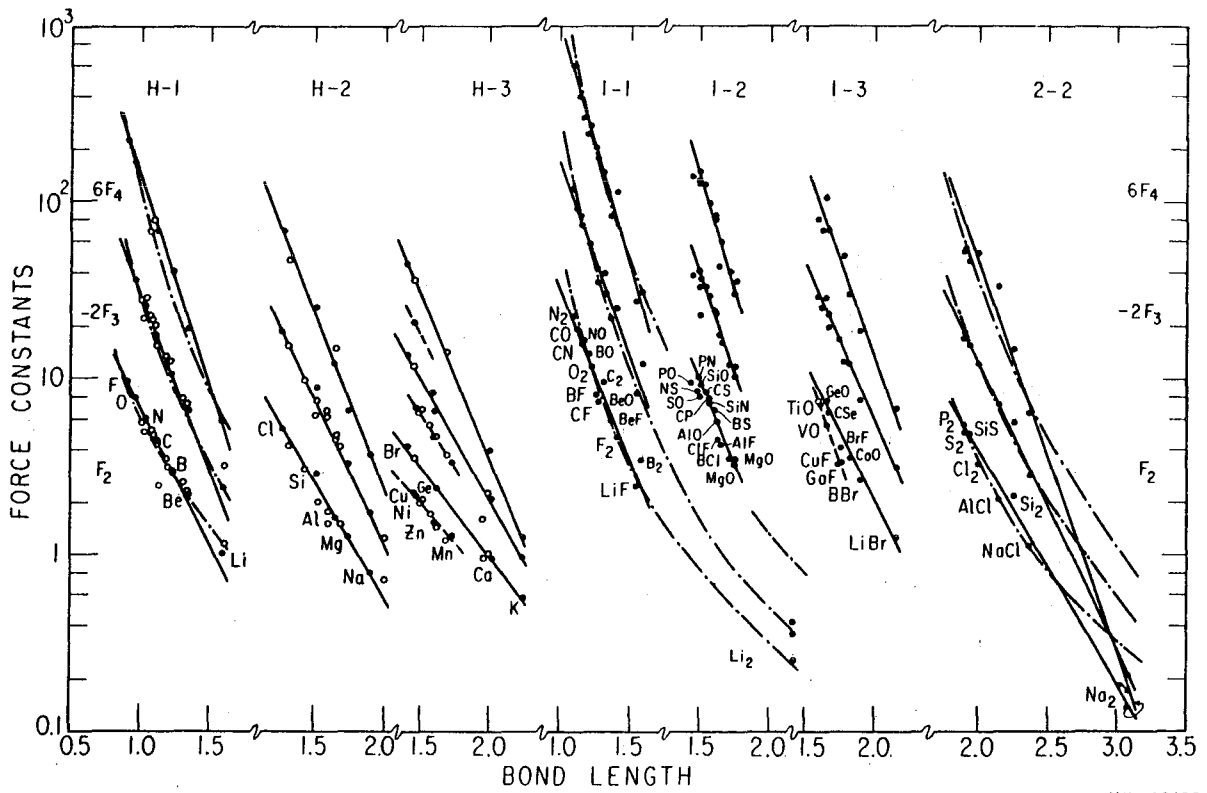
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12. Our results for CO₂, HCN, and H₂O are in good agreement with those obtained by J. Plíva, Coll. Czechoslov. Chem. Commun. 23, 777 (1958). He points out that a treatment based on the usual type of coordinates³ will not yield cubic constants that are isotopically invariant. His correction terms have not been applied in Table IV, however, as they are small compared with the experimental uncertainties.
13. The data for the three triatomic molecules considered by Plíva¹² represent practically all the available information about cubic constants for bends, bend-stretch interactions, and quartic constants of polyatomic molecules.

Footnotes (Continued)

14. For reviews see Y. P. Varshni, Rev. Mod. Phys. 29, 664 (1957) and references 15-18.
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21. See, for example, Hirschfelder, Curtiss, and Bird, Molecular Theory of Gases and Liquids (J. Wiley and Sons, Inc., New York, 1954), p. 921.
22. There are a very few exceptional cases, such as the $A^1\Sigma^+$ excited state of LiH, the only example for which F_3 is positive.
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25. One can use Eq. (9) to construct the derivatives corresponding to any experimental or assumed potential curve $U(r)$. For the Morse function, for example (after correction for its incorrect behavior at $r = 0$), results are qualitatively similar to Fig. 2 except that $\partial U_E/\partial r$ has on the left another maximum and a minimum point so that the higher derivatives show several oscillations at small r .

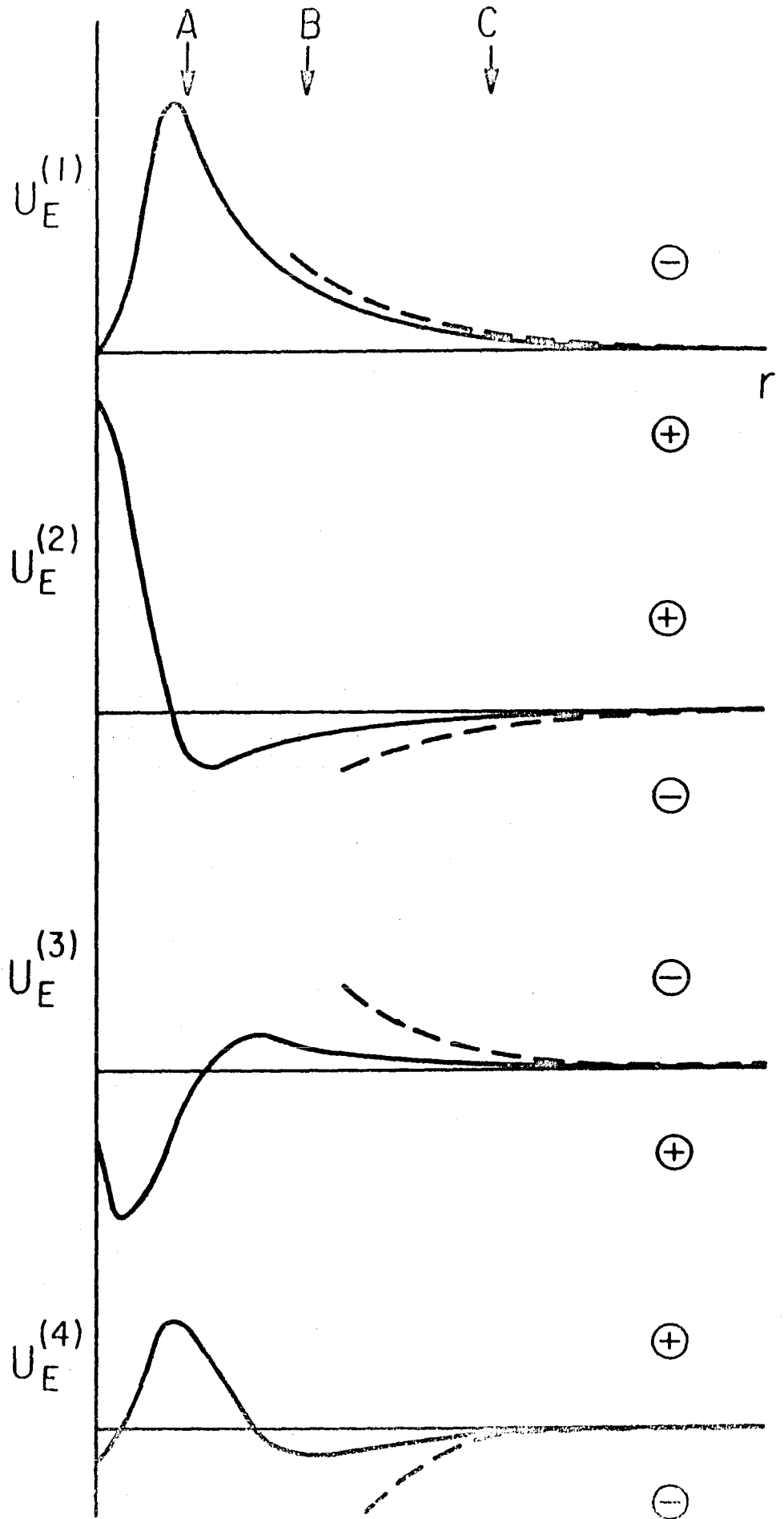
Captions for Figures

- Fig. 1** Comparison of quadratic, cubic, and quartic force constants as functions of bond length. The straight line relations are obtained from Table II. For some of the families the curves (shown dot-dashed) corresponding to Table III are also plotted. Empty circles indicate excited electronic states or ionic states; full ones, ground states.
- Fig. 2** Derivatives of the electronic energy as functions of internuclear distance. The minus and plus signs denote shielding and antishielding regions, respectively. The ordinates of the various curves are not to the same scale.



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Fig. 1



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