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derived on the assumption that the distribution of molecules is sufficiently dilute to make intermolecular interaction negligible. A lack of agreement, therefore, between the scattered intensity calculated from the theoretical formulae and that actually found may be caused by a close packing of the molecules. This effect has already been suggested.⁴

When making calculations for contour maps of the intensity, it is very helpful to know the region in which the main maxima occur. The formulae for the intensity, conveniently expressed in terms of the plate coordinates, x and y , may then be considered in fairly restricted areas.¹⁵ Such calculations are being made at present in this laboratory for future publication.

¹⁵ The following useful tables are available: (a) Tables of Sines and Cosines for Radian Arguments, Federal Works Agency Work Projects Administration, Project No. 765-97-3-10, New York, 1940. (b) Hague, Proc. Phys. Soc. **29**, 211 (1917). (c) Gray, Mathews, and MacRobert, *A Treatise on Bessel Functions* (The Macmillan Company, New York, 1931), p. 286.

An improvement in interpretation can be expected from a method of photographing which would allow for quantitative measurements of the intensity. P. P. Debye¹⁶ has suggested the use of a rotating sector in gas diffraction to eliminate the effect of the scattering factors. In our case only one occurs, f_c . It would appear that hydrocarbon films are unusually suited for use by the sector method since one sector would suffice for all films, the radiation allowed to pass through being inversely proportional to $(6 - F_c)^2/s^4$. In addition the difficulty of vapors diffusing into the camera on long exposure, as occurs in gas diffraction, does not arise.

For his interest I wish to thank Professor Lawrence O. Brockway who has directed the work performed in the Chemistry Department of the University of Michigan under contract with the Naval Research Laboratory.

¹⁶ P. P. Debye, Physik. Zeits. **40**, 66 and 404 (1939).

A Relation between Bond Force Constants, Bond Orders, Bond Lengths, and the Electronegativities of the Bonded Atoms

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(Received February 7, 1946)

A relation of the form

$$k = aN(x_A x_B/d^2)^{\frac{1}{2}} + b$$

has been found to hold accurately for a large number of diatomic and simple polyatomic molecules in their ground states. (The average deviation of k calculated from k observed for seventy-one cases is 1.84 percent.) Here k is the bond-stretching force constant, d the bond length, N the bond order, and x_A and x_B are the electronegativities of the bonded atoms. If k is measured in dynes/cm $\times 10^{-5}$ and d in Angstrom units, a and b have the values 1.67 and 0.30, respectively, for stable molecules exhibiting their normal covalencies, except those in which both bonded atoms have only one electron in the valence shell; for diatomic molecules of the alkali metals, Na₂, NaK, etc., a and b are 1.180 and -0.013 , respectively; for hydrides of elements having a single electron in the valence shell, 1.180 and 0.040, respectively; and for diatomic hydrides of elements having two to four electrons in the valence shell, 1.42 and 0.08, respectively. Numerous applications of the relation are made and certain exceptions are pointed out.

DESCRIPTION OF THE RELATION

SEVERAL relations^{1,2} between force constants or vibrational frequencies and bond distances

¹ P. M. Morse, Phys. Rev. **34**, 57 (1929); D. Clark, Phil. Mag. **18**, 459 (1934); H. S. Allen and A. K. Longair, Phil. Mag. **19**, 1032 (1935); M. L. Huggins, J. Chem. Phys. **3**, 473 (1933); **4**, 308 (1936); J. J. Fox and A. E.

have been found to hold approximately for a limited number of molecules. They, in general,

Martin, J. Chem. Soc. **884** (1939); G. B. B. M. Sutherland, J. Chem. Phys. **8**, 161 (1940); J. W. Linnett, Trans. Faraday Soc. **36**, 1123 (1940); C. K. Wu and Chang-Tsing Yang, J. Phys. Chem. **48**, 295 (1944).

² R. M. Badger, J. Chem. Phys., **2**, 128 (1934); **3**, 710 (1935).

have two or more parameters that depend on the atoms forming the bond, or their position in the periodic table. The most widely used of these seems to be that of Badger,²

$$k_e = (c_{ij}/r_e)^{\frac{1}{2}} + d_{ij},$$

where c_{ij} and d_{ij} are the parameters and r_e and k_e the equilibrium bond distance and bond-stretching force constants, respectively.

Remick³ has correctly ascribed the increasing force constants of the series $\text{CH} < \text{NH} < \text{OH} < \text{FH}$ partly to the increasing electronegativities of the series $\text{C} < \text{N} < \text{O} < \text{F}$, on the basis that the displacement of H would in turn cause a displacement of the valence electrons in the potential field of the heavier atom. In a vibratory link $\text{A}-\text{B}$ both A and B are displaced with respect to the center of gravity of the bonding electron cloud, and it seems that the bond-stretching force constant k would vary with the electronegativities of both A and B and could be expressed as some function of their product,

$$k = f(x_A x_B).$$

It is well known that k increases with bond order, that, other things being equal, a double bond is stronger than a single bond, a triple bond stronger than a double bond; and the bond order, which I shall designate as N , may be regarded as a relative measure of the electronic cloud effective in holding the two atoms together.

Thus k varies with all the quantities— N , $x_A x_B$, and d —and it should be possible therefore to express it as a combined function,

$$k = f(N, x_A x_B, d).$$

Though the assumption of such a relationship may be justified by qualitative considerations, a theoretical derivation of the function may not be possible. In the present study the function is evaluated empirically by the correlation of the quantities involved for a large number of molecules in their ground states. It is not possible to check it for the different excited states of one and the same molecule because values for N and x are available for ground states only. The form of the function is:

$$k = aN(x_A x_B/d^2)^{\frac{1}{2}} + b, \quad (\text{I})$$

³ A. E. Remick, *Electronic Interpretations of Organic Chemistry* (John Wiley & Sons, Inc., New York, 1943), p. 170.

where a and b are constants for certain broad classes of molecules; N , k , and d are the bond order, bond-stretching force constant, and bond distance, respectively; and x_A and x_B are the electronegativities of the atoms A and B.

The constants a and b in the above equation have the same values for stable bonds of atoms exhibiting their normal covalencies, except those in which both atoms have a single electron in the valence shell. Most of the simple molecules with bonds of this type, for which k , N , and d are known with reasonable accuracy, are listed in Table I. Their experimentally observed bond-stretching force constants are compared with those computed from the equation,

$$k = 1.67N(x_A x_B/d^2)^{\frac{1}{2}} + 0.30. \quad (\text{IA})$$

Here k is measured in dynes/cm $\times 10^{-5}$ and d in Angstrom units. Specific values of N , k , and d which were used for the calculations are listed in Tables I and VI. The electronegativity values are those found in column 3 of Table VIII.

An examination of the types of molecules in Table I will be helpful in judging for what other molecules Eq. (IA) may be expected to apply. It may not be applied to polyatomic molecules in which there are appreciable interactions between non-bonded atoms, as it assumes a characteristic bond-stretching constant which depends wholly on the properties of the two atoms forming the bond. Polyatomic molecules for which the valence force field function is inadequate may not, in general, be expected to fit the rule. Odd molecules or molecular links of atoms with unsatisfied valencies also seem to be exceptions. Certain classes of these may, nevertheless, be made to fit approximately the more general relation (I) with a proper choice of values for a and b .

For diatomic molecules of the alkali metals, Na_2 , NaK , etc., relation (I) has the form,

$$k = 1.180(x_A x_B/d^2)^{\frac{1}{2}} - 0.013. \quad (\text{IB})$$

Table II will illustrate how accurately it holds.

Diatomic hydrides having one electron in the valence shell fit accurately relation (I) in the form,

$$k = 1.180(x_A x_B/d^2)^{\frac{1}{2}} + 0.040. \quad (\text{IC})$$

See Table III.

TABLE I. Observed and calculated bond-stretching force constants.

Molecule	Link	Bond order <i>N</i>	Bond-stretching force constant in dynes/cm $\times 10^{-3}$ <i>k</i> obs.	<i>k</i> calc. ^a by Eq. (1A)	Gordy <i>k</i> calc. from <i>k</i> obs. % dev.	<i>k</i> calc. by Badger's rule	Badger <i>k</i> calc. from <i>k</i> obs. % dev.
AsH ₃	AsH	1.00	2.81 ^a	2.84	1.1	2.47	12.1
B ₂ H ₆	BH	1.00	3.9 ⁱ	4.0	2.6	3.1	20.5
BeO	BeO	2.00	7.50 ^a	7.57	.9	6.75	10.0
Br ₂	BrBr	1.00	2.46 ^a	2.50	1.6	2.48	.8
CH ₃ Br	CBr	1.00	3.13 ^b	3.03	3.2	2.04	34.8
C ₂ H ₂	CC	3.00 ^b	15.7 ⁱ	15.7	.0	13.0	17.2
C ₂ H ₄	CC	2.12 ^b	9.79 ⁱ	9.70	.9	6.78	30.8
C ₂ H ₆	CC	1.11 ^b	4.50 ^j	4.21	6.4	2.87	36.2
CH ₃ CCH	CC	2.89 ^b	15.6 ^k	15.1	3.2	12.5	19.8
CH ₃ CCH	C*C	1.23 ^b	5.18 ^k	5.28	1.9	3.92	24.3
C ₆ H ₆	CC	1.78 ^b	7.58 ^l	7.69	1.5	5.20	31.4
CH ₃ Cl	CCl	1.00	3.64 ^b	3.54	2.7	2.68	26.4
CH ₃ F	CF	1.00	5.96 ^b	6.02	1.0	5.07	14.9
CH ₄	CH	1.00	5.45 ^m	5.51	1.1	4.27	21.6
HCN	C*H	1.00	6.20 ⁿ	6.22	.3	4.94	20.3
C ₂ H ₂	C*H	1.00	6.24 ⁿ	6.22	.3	4.94	20.8
CH ₃ NH ₂	CN	1.00	4.86 ^o	4.60	5.3	3.78	22.2
HCN	CN	3.00	18.1 ^p	18.8	3.9	17.5	3.3
H ₂ CO	CO	2.00	13.4 ⁱ	13.1	2.2	12.5	6.7
CH ₃ OH	CO	1.00	5.00 ^q	5.28	5.6	4.44	11.2
C ₂ H ₆ S	CS	1.00	3.05 ^r	3.05	.0	2.25	26.2
CS ₂	CS	2.00	7.47 ^a	7.37	1.3	7.09	5.1
C ₂ H ₆ Se	CSe	1.00	2.59 ^r	2.70	4.2	1.84	29.0
Cl ₂	ClCl	1.00	3.29 ^a	3.35	1.8	2.92	11.2
GeH ₄	GeH	1.00	2.78 ^s	2.73	1.8	3.26	17.3
HBr	HBr	1.00	4.11 ^a	4.06	1.2	4.24	3.2
HCl	HCl	1.00	5.15 ^a	4.94	4.1	5.66	9.9
HF	HF	1.00	9.67 ^a	9.70	.3	9.43	2.5
HI	HI	1.00	3.14 ^a	3.14	.0	d	
IBr	IBr	1.00	2.07 ^a	2.10	1.9	d	
ICl	ICl	1.00	2.39 ^a	2.39	.0	2.17	9.2
I ₂	II	1.00	1.72 ^a	1.77	2.9	1.58	8.1
KBr	KBr	1.00	(.83) ^g	.90	(8.4) ^o	.42	(49.4) ^o
KCl	KCl	1.00	(.85) ^g	.99	(16.5) ^o	d	
KI	KI	1.00	.79 ^a	.78	1.3	d	
NaBr	NaBr	1.00	1.04 ^a	1.07	2.9	d	
NaCl	NaCl	1.00	1.18 ^a	1.18	.0	.59	50.0
NaI	NaI	1.00	.94 ^a	.91	3.2	.45	52.1
N ₂	NN	3.00	22.9 ^a	22.7	.9	26.0	13.6
NH ₃	NH	1.00	6.86 ^o	6.81	.7	5.94	13.3
H ₂ O	OH	1.00	8.23 ^u	8.24	.1	7.69	6.5
OF ₂	OF	1.00	7.67 ^v	7.38	3.8	4.79	37.6
OCl ₂	OCl	1.00	4.82 ^w	4.69	2.7	3.78	21.6
PH ₃	PH	1.00	3.33 ^o	3.24	2.7	2.87	13.8
H ₂ S	SH	1.00	4.25 ^a	4.14	2.6	4.43	4.2
H ₂ Se	SeH	1.00	3.37 ^v	3.30	2.1	2.73	19.0
H ₂ S ₂	SS	1.00	2.52 ^r	2.59	2.8	2.30	8.7
SiH ₄	SiH	1.00	2.95 ^a	2.92	1.0	2.88	2.4
Average % deviation					2.0	Average % deviation	17.8

* The effects of triple bond character on the electronegativity of C are taken into account. See discussion in section on electronegativity.

^a Bond distances used in calculations are listed in Table VI, column 3; electronegativities in Table VIII, column 3; bond orders in column 3 of this table.

^b From R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.* **63**, 41 (1941).

^c Omitted in computing average deviation.

^d Badger gives no constants for this combination of period and row of the atomic table.

^e J. Howard, *J. Chem. Phys.* **3**, 208 (1935). The value given is increased 8 percent to correct for anharmonicity.

^f See reference 29 in text.

^g Computed from the ω_s values selected by G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 483.

^h B. L. Crawford and S. R. Brinkley, Jr., *J. Chem. Phys.* **9**, 69 (1941).

ⁱ G. B. B. M. Sutherland and D. M. Dennison, *Proc. Roy. Soc. A*, **148**, 250 (1935).

^j F. Stitt, *J. Chem. Phys.* **7**, 297 (1939).

^k B. L. Crawford, *J. Chem. Phys.* **8**, 526 (1940).

^l R. C. Lord and D. H. Andrews, *J. Phys. Chem.* **41**, 149 (1938).

^m Computed from the ω_1 given by D. M. Dennison (*Rev. Mod. Phys.* **12**, 175 (1940)) using the formula $\omega_1 = (1/2\pi)(k/MH)$.

ⁿ T. A. You Wu and A. T. Kiang, *J. Chem. Phys.* **7**, 178 (1938).

^o J. T. Edsall, *J. Chem. Phys.* **5**, 225 (1937).

^p P. F. Bartunek and E. F. Barker, *Phys. Rev.* **48**, 516 (1935).

^q See reference 10 in text.

^r K. W. F. Kohlrausch, *Raman Spectra* (Akademische Verlagsgesellschaft Becker and Erler, Leipzig, 1943), p. 184.

^s G. Glockler and T. Y. Tung, *J. Chem. Phys.* **13**, 388 (1945).

^t J. W. Straley, C. H. Tindal, and H. H. Nielsen, *Phys. Rev.* **62**, 161 (1942). The value given is increased 8 percent to correct for anharmonicity.

^u L. G. Bonner, *Phys. Rev.* **46**, 458 (1934).

^v Computed from the valence force field formula,

$$\nu_3 = (1/2\pi) [k(1/M_A) + ((1 - \cos \alpha)/M_B)]^{1/2},$$

taking ν_3 as 1280 cm⁻¹ and the vertex angle α measured by electron diffraction, 100°.

^w Computed as described in footnote v of Table I, taking ν_3 as 973 cm⁻¹ and the vertex angle α measured by electron diffraction, 115°.

^x C. R. Bailey, J. W. Thompson, and J. B. Hale, *Phys. Rev.* **49**, 777 (1936).

^y D. M. Cameron, W. C. Sears, and H. H. Nielsen, *J. Chem. Phys.* **7**, 994 (1942). The value given is increased 8 percent to correct for anharmonicity.

^z C. H. Tindal, W. H. Straley, and H. H. Nielsen, *Phys. Rev.* **62**, 151 (1942). The value given is increased 8 percent to correct for anharmonicity.

TABLE II. Observed and calculated force constants and bond distances of alkali metals.

Molecule	Force constant in dynes/cm $\times 10^{-5}$ k obs. ^a	Bond distance d obs. in Å	k calc. by Eq. (IB)	k calc. from k obs. % dev.	d calc. by Eq. (IB)	d calc. from d obs. % dev.
Cs ₂	0.069	4.50 ^b	0.067	2.9	4.44	1.3
K ₂	.099	3.923 ^c	.096	3.0	3.845	2.0
Li ₂	.254	2.672 ^c	.238	(6.3) ^e	2.558	(4.3) ^e
LiCs	.109	3.75 ^d	.113	3.7	3.83	2.1
LiK	.148	3.30 ^d	.147	.7	3.29	.3
LiRb	.129	3.50 ^d	.131	1.6	3.53	.9
Na ₂	.172	3.079 ^e	.173	.6	3.096	.6
NaCs	.108	3.76 ^d	.108	.0	3.75	.3
NaK	.130	3.50 ^d	.128	1.5	3.47	.9
NaRb	.120	3.59 ^d	.120	.0	3.59	.0
Rb ₂	.081	4.22 ^b	.081	.0	4.22	.0
RbCs	.075	4.36 ^d	.074	1.3	4.31	1.1
Average % deviation			1.39	Average % deviation		
				0.86		

^a Computed from the ω_e values of G. Herzberg, reference 5 in text.
^b Added radii. See V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941).

^c From G. Herzberg, reference 5 in text.

^d Determined by Schomaker and Stevenson (J. Am. Chem. Soc. 63, 37 (1941)) from Badger's rule with its parameters fitted to the similar molecules—Li₂, Na₂, and K₂.

^e Omitted in computing average deviation.

Diatomic hydrides of elements having two to four electrons in the valence shell may be grouped together and fitted approximately to

$$k = 1.42(x_A x_B / d^2)^2 + 0.08. \quad (\text{ID})$$

Results are shown in Table IV.

In all the above forms of relation (I), k is in dynes/cm $\times 10^{-5}$, d in Angstroms, and the x values those of column 3, Table VIII. These units are used throughout the paper.

FORCE CONSTANTS

One use of relation (I) is for the determination of force constants and thus for the estimation of fundamental frequencies associated with the stretching of bonds. Frequently it is a difficult or impossible task to decide which of the many frequencies of a polyatomic molecule are the fundamentals associated with the stretching of bonds. From x-ray and electron diffraction measurements the bond distances in a large number of polyatomic molecules are now known with an accuracy of 1 percent to 3 percent. The bond distances of many others can be estimated with a fair degree of certainty from the additivity rule.⁴ Electronegativity values of nearly all the

⁴ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), p. 153;

common elements are available. Perhaps the chief difficulty in using the relation to estimate k is the uncertainty of the bond order N for many bonds which are of fractional order.

Accuracy of the Relation

Table I gives a comparison of the force constants calculated from Eq. (IA) with those obtained directly from the observed spectra. Tables II to IV show similar comparisons for k 's computed from Eqs. (IB)–(ID), respectively. The differences of the two values, k computed and k observed, are for most of the cases listed in Tables I–IV no greater than the probable error in the observed k 's, the average deviation for the seventy-one bonds being only 1.84 percent. Only three of the seventy-five computed k 's, those for KBr, KCl, and SiH, deviate more than 6.4 percent from the observed values, and it seems probable that the wide deviation in these may be due to errors in the observed k 's. For example, the ratios of the observed k 's of KI, KBr, and KCl are not of the proper magnitude when compared to those of NaI, NaBr, and NaCl; whereas the computed values have the expected ratios. The ω_e value used to compute SiH is listed as uncertain by Herzberg.⁵

Though Badger's rule² is of advantage in the estimation of bond distances, force constants computed from it differ so much from the ob-

TABLE III. Observed and calculated force constants and bond distances of diatomic hydrides of elements with one electron in the valence shell.

Molecule	Force constant in dynes/cm $\times 10^{-5}$ k obs. ^a	Bond distance d obs. ^b in Å	k calc. by Eq. (IC)	k calc. from k obs. % dev.	d calc. by Eq. (IC)	d calc. from d obs. % dev.
CsH	0.467	2.494	0.466	0.2	2.488	0.2
RbH	.514	2.368	.514	.0	2.368	.0
H ₂	5.759	.741	5.791	.6	.744	.4
KH	.560	2.244	.564	.7	2.254	.4
LiH	1.026	1.596	1.033	.7	1.602	.4
NaH	.779	1.888	.781	.3	1.892	.2
Average % deviation			0.42	Average % deviation		
				0.27		

^a Computed from ω_e values of G. Herzberg, reference 5 in text.

^b From G. Herzberg, reference 5 in text.

V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941).

⁵ G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939), p. 483.

served values as to make it of questionable value in the computation of unknown k 's. This fact has been pointed out previously by Penney and Sutherland.⁶ Other rules, such as the Clark relation,¹ in which k is expressed as an inverse 5th or 6th power of d cannot be accurate for the computation of k because the errors in d are multiplied several times in the evaluation of k . The advantage of the present relation for the computation of k is that none of the quantities involved in the expression for k are raised to high powers.

Observed Force Constants Used for Comparison

Some discussion of the observed force constants used for testing the relation is justified. Those of all diatomic molecules and of all M—H bonds in polyatomic molecules are for vibrations of infinitesimal amplitudes. Since vibration constants involving the light hydrogen atoms are appreciably affected by anharmonicity, it was necessary to estimate a correction term for these when the values found in the literature were not for vibrations of infinitesimal amplitude. The correction of +8 percent was determined by averaging the anharmonic effects in the M—H bonds of the molecules for which the correct constants are known.

The simplest molecule containing a given bond of known constants was chosen as representative of that bond, and the same link with the same bond order in other molecules was not repeated except for the case of acetylenic CH. Single bonds to acetylenic carbon, $\equiv\text{C}-$, were regarded as different from other single bonds to carbon because of the effective difference in the electronegativity of the carbon in the two cases.

The force constants of the diatomic molecules were computed with the simple harmonic formula,

$$\omega_e = (1/2\pi)(k/\mu)^{1/2},$$

from the ω_e values selected by Herzberg.⁵ The k 's of polyatomic molecules were chosen from the literature referred to in the table and were computed by the various authors on the assumption of a valence force field function, or a slightly

TABLE IV. Observed and calculated force constants and bond distances of diatomic hydrides of elements with two to four electrons in the valence shell.

Molecule	Force constants in dynes/cm $\times 10^{-8}$ k obs. ^a	Bond distance d obs. ^b in Å	k calc. by Eq. (1D)	k calc. from k obs. % dev.	d calc. by Eq. (1D)	d calc. from d obs. % dev.
AlH	1.62	1.646	1.69	4.3	1.693	2.9
BH	3.04	1.233	3.04	.0	1.233	.0
BaH	.81	2.232	.78	3.7	2.184	2.1
BeH	2.26	1.343	2.20	2.7	1.321	1.6
CH	4.37	1.120	4.34	.7	1.115	.4
CaH	.98	2.002	.97	1.0	1.978	1.1
MgH	1.28	1.731	1.34	4.7	1.789	3.3
SiH	(2.48)	1.521	2.15	(13.3)	(1.380)	(9.3)
SrH	.85	2.146	.88	3.5	2.195	2.3
			Average % deviation 2.58		Average % deviation 1.71	

^a Computed from ω_e values of G. Herzberg, reference 5 in text.

^b From G. Herzberg, reference 5 in text.

modified form of this function. This treatment assumes that the fundamental vibrations of the molecules are controlled entirely by the stretching and bending of the chemical bonds, that the interactions between non-bonded atoms are negligible. Constants for several of the polyatomic molecules have been computed by more than one researcher. In general the agreement of the different values is sufficiently close for the accuracy required here. Those for such complex molecules as CH_3OH , CH_3NH_2 , $\text{C}_2\text{H}_6\text{S}$, $\text{C}_2\text{H}_6\text{Se}$ cannot be regarded as very accurate. Rather wide disagreement exists in the literature for OCl_2 and OF_2 , because of the fact that different workers have assigned the fundamentals differently. Sutherland and Penney⁷ have criticized the assignments of Hettner, Pohlman, and Schumacher⁸ and have suggested an alternative assignment. Relation (1A) agrees with the Sutherland and Penney values for OCl_2 but with the Hettner, Pohlman, and Schumacher assignment for ν_3 of OF_2 . There is sufficient interaction between the hydrogens of the two CH_3 groups of ethane that a modified form of the valence force field is required to compute the observed frequencies satisfactorily.⁹ This interaction no doubt causes some deviation from

⁷ G. B. B. M. Sutherland and W. G. Penney, Proc. Roy. Soc. 156, 678 (1936).

⁸ G. Hettner, R. Pohlman, and H. I. Schumacher, Zeits. f. Physik. 96, 203 (1935).

⁹ F. Stitt, J. Chem. Phys. 7, 297 (1939).

⁶ W. G. Penney and G. B. B. M. Sutherland, Proc. Roy. Soc. 156, 654 (1936).

TABLE V. Predicted force constants and vibrational frequencies.

Molecule	Link	Bond length in Å <i>d</i> obs.	Bond-stretching force constant calculated* from Eq. (IA) in dynes/cm $\times 10^{-5}$	Expected frequency cm^{-1}
CsBr	CsBr	3.14 ^c	0.82	168
CsCl	CsCl	3.06 ^c	.87	226
CsI	CsI	3.41 ^c	.72	137
F ₂	FF	1.435 ^d	7.93	1190
Ge ₂ H ₆	GeGe	2.41 ^c	1.29	238
RbBr	RbBr	2.94 ^c	.89	192
RbCl	RbCl	2.89 ^c	.94	248
RbI	RbI	3.26 ^c	.76	159
SCl ₂	SCI	2.00 ^c	2.98	564
SbH ₃	SbH	1.71 ^c	2.35	
SiH ₃ Cl	SiCl	2.06 ^c	2.29	480
SnH ₄	SnH	1.70 ^c	2.28	1960 ^b
TeBr ₂	TeBr	2.49 ^c	1.88	
TeCl ₂	TeCl	2.36 ^c	2.12*	
H ₂ Te	TeH	1.67 ^c	2.68	2300 ^b

* After this paper was submitted for publication Dr. H. Sponer called to my attention a recent measurement of the spectrum of TeCl₂ by W. Spinnler (Helv. Phys. Acta 18, 297 (1945)), who obtains 2.18×10^5 dynes/cm for the bond-stretching constant.

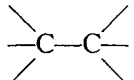
^a A normal single bond is assumed for each line.

^b The observed frequency should be about 4 percent lower because of anharmonicity.

^c L. R. Maxwell, J. Opt. Soc. Am. 30, 374 (1940).

^d M. T. Rogers, V. Schomaker, and D. P. Stevenson, J. Am. Chem. Soc. 63, 2610 (1941).

^e Added covalent radii, see reference 4 in text.

relation (IA). It is interesting that k of 4.30 computed from the  valence vibration (1034 cm^{-1}) alone¹⁰ agrees closely with that computed from relation (IA).

Prediction of Some Unknown Force Constants

Table V lists a few molecules to which relation (IA) may be expected to apply. To my knowledge the force constants of these have not been determined from their spectra. Their bond-stretching constants are computed from relation (IA) and are listed in column 5. Vibrational frequencies obtained from these are given in the last column.

In computing the vibrational frequencies the molecules Ge₂H₆ and H₃SiCl were treated as diatomic molecules with the masses of the hydrogen atoms added to the heavier atoms to which they are bonded. The valence force field formula for the bond-stretching frequency, ν_1 , of tetrahedral molecules, AB₄, is the simple harmonic formula with the reduced mass, μ_{AB} , being replaced by m_B , the mass of B. This allows a direct calculation of the symmetrical frequency

¹⁰ L. G. Bonner, J. Chem. Phys. 5, 293 (1937).

of SnH₄ from k_{SnH} alone. The parallel frequencies, ν_3 , of the triatomic molecules, SCl₂ and H₂Te, were computed from the valence force formula¹¹

$$\nu_3 = \frac{1}{2\pi} \left[\kappa \left(\frac{1}{m_A} + \frac{1 - \cos \alpha}{m_B} \right) \right]^{\frac{1}{2}}$$

assuming the vertex angle α to be 100° in each case. Here m_A and m_B are the masses of the central and end atoms, respectively.

BOND LENGTHS

Table VI compares bond distances calculated from relation (IA) and from Badger's rule² with the experimentally observed values. Lengths of other type bonds, computed with Eqs. (IB)–(ID), are listed in Tables II–IV.

Observed Values Used for Comparison

The experimentally observed bond lengths taken from the literature have, on the average, an accuracy of the order of 1 percent. Those for diatomic molecules and for bonds of the polyatomic molecules which are between hydrogen and a heavier atom were with few exceptions determined from measurements of spectra. The probable error for most of them is well below 1 percent. Other bond lengths, determined by electron diffraction, may deviate as much as 1 percent to 3 percent from the correct value.

The values used for IBr and for the C—Se bond of C₂H₆Se are assumed to be the sum of the covalent radii of the bonded atoms. Some of the "observed" d 's listed in Table III were, as indicated, determined from the vibrational frequencies by Schomaker and Stevenson¹² using a special form of Badger's rule fitted to the similar molecules Li₂, Na₂, and K₂. These, therefore, do not provide an independent test but merely show that Eq. (IB) agrees closely with Badger's rule for this type of molecule. The fact that the Schomaker-Stevenson rule also agrees closely, except for LiCs, lends credence to these values. As pointed out by Schomaker and Stevenson, the disagreement with their rule by LiCs may indicate an error in ω_e for this molecule.

¹¹ J. H. Hibben, *The Raman Effect and Its Chemical Applications* (Reinhold Publishing Corporation, New York, 1939), p. 94.

¹² V. Schomaker and D. P. Stevenson, J. Am. Chem. Soc. 63, 37 (1941).

Accuracy of the Relation for Calculation of Bond Lengths

The agreement of the bond lengths calculated from relation (I) with the observed values for the bonds listed in Tables II–IV and VI is almost as good as the accuracy of the observed values. The average deviation of d calculated from d observed for the seventy-one bonds is 1.34 percent. If C_2H_6 , CH_3OH , CH_3NH_2 , and C_2H_6Se are omitted, the average deviation becomes 1.29 percent for the remaining forty-two molecules of Table IV and 1.18 percent for the sixty-seven remaining ones in all four tables. It will be noticed that the agreement for the molecules of Table IV is hardly as good as that for the molecules in the other tables.

Comparison with Badger's Rule

Though the agreement with the experimentally observed bond lengths, on the average, is markedly better for relation (IA) than for Badger's rule, the advantage is not nearly so great for the computation of bond lengths as for the prediction of force constants. A comparison of the forms of the two relations will reveal why this is true.

The bond lengths and force constants predicted by Badger's rule in Tables I and VI are predominately too small. The average deviation, d calculated from d observed, can be reduced by approximately 1 percent through a different choice of the parameters, c_{ij} and d_{ij} . Apparently Badger selected these parameters to give the best over-all fit for molecules in certain excited states as well as in ground states. The comparisons of Table IV imply that whenever Badger's rule is used with the original c_{ij} and d_{ij} values, the predicted bond lengths should be increased by about 1 percent.

BOND ORDERS

The bond order N as used here represents the effective number of covalent (electron pair) or electrovalent (ionic) bonds acting between the two atoms considered. Bonds like HCl and HF which have partial ionic and partial covalent character¹³ are regarded as normal single bonds.

¹³ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), Ch. II.

TABLE VI. Observed and calculated bond lengths.

Molecule	Link	Bond lengths in Å <i>d</i> obs.	<i>d</i> calc. ^a by Eq. (IA)	Gordy <i>d</i> calc. from % obs. % dev.	<i>d</i> calc. by Badger's rule	Badger <i>d</i> calc. from % obs. % dev.
AsH ₃	AsH	1.56 ^d	1.57	0.6	1.52	2.6
B ₂ H ₆	BH	1.18 ^e	1.21	2.5	1.12	5.1
BeO	BeO	1.331 ^f	1.340	.7	1.308	1.7
Br ₂	BrBr	2.284 ^f	2.317	1.4	2.286	.1
CH ₃ Br	CBr	1.91 ^g	1.86	2.6	1.80	5.8
C ₂ H ₂	CC	1.204 ^h	1.206	.2	1.171	2.7
C ₂ H ₄	CC	1.330 ⁱ	1.322	.6	1.255	5.6
C ₂ H ₆	CC	1.55 ^j	1.48	4.5	1.43	7.7
CH ₃ CCH	CC	1.21 ^k	1.18	2.5	1.17	3.3
CH ₃ CCH	C*C	1.46 ^k	1.48	1.4	1.39	4.8
C ₆ H ₆	CC	1.39 ^l	1.40	.7	1.31	5.8
CH ₃ Cl	CCl	1.77 ^g	1.73	2.3	1.69	4.5
CH ₃ F	CF	1.396 ^m	1.407	.6	1.359	2.7
CH ₄	CH	1.093 ⁿ	1.100	.6	1.033	5.5
HCN	C*H	1.057 ^h	1.058	.1	1.004	5.0
C ₂ H ₂	C*H	1.057 ^h	1.054	.3	1.003	5.1
CH ₃ NH ₂	CN	1.47 ⁿ	1.41	4.1	1.41	4.1
HCN	CN	1.154 ^b	1.184	2.6	1.149	.4
H ₂ CO	CO	1.21 ^o	1.19	1.6	1.20	.8
CH ₃ OH	CO	1.43 ^p	1.49	4.2	1.40	2.1
C ₂ H ₆ S	CS	1.82 ^q	1.82	.0	1.74	4.4
CS ₂	CS	1.54 ^r	1.53	.6	1.53	.6
C ₂ H ₆ Se	CSe	1.94 ^q	2.00	3.1	1.84	5.1
Cl ₂	ClCl	1.989 ^t	2.014	1.3	1.960	1.5
GeH ₄	GeH	1.48 ^r	1.46	1.3	1.52	2.7
HBr	HBr	1.410 ^s	1.397	0.9	1.419	0.6
HCl	HCl	1.275 ^t	1.236	3.2	1.299	1.9
HF	HF	.917 ^t	.919	.2	.914	.3
HI	HI	1.600 ^u	1.603	.2	°	°
IBr	IBr	2.47 ^q	2.50	1.2	°	°
ICl	ICl	2.321 ^f	2.323 ^v	.1	2.294	1.2
I ₂	II	2.667 ^t	2.730	2.4	2.641	1.0
KBr	KBr	2.94 ^u	3.18	(8.2) ^b	2.64	(10.2) ^b
KCl	KCl	2.79 ^u	3.23	(15.7) ^b	°	°
KI	KI	3.23 ^u	3.17	1.9	°	°
NaBr	NaBr	2.64 ^u	2.71	2.6	°	°
NaCl	NaCl	2.51 ^u	2.51	.0	2.25	10.4
NaI	NaI	2.90 ^u	2.81	3.1	2.59	10.7
N ₂	NN	1.095 ^f	1.082	1.2	1.113	1.6
NH ₃	NH	1.014 ^m	1.012	.2	.983	3.1
H ₂ O	OH	.958 ^m	.959	.1	.944	1.5
OF ₂	OF	1.41 ^g	1.37	2.8	1.31	7.1
OC ₂	OC	1.68 ^g	1.65	1.8	1.62	3.6
PH ₃	PH	1.45 ^v	1.42	2.1	1.41	2.8
H ₂ S	SH	1.334 ^w	1.308	1.9	1.344	.7
H ₂ Se	SeH	1.53 ^x	1.51	1.3	1.47	3.9
H ₂ S ₂	SS	2.05 ^g	2.09	1.9	2.03	1.0
SiH ₄	SiH	1.45 ^v	1.44	.7	1.44	.7
		Average % deviation	1.53	Average % deviation	3.38	

* x value for ethylenic C is taken as 2.83.

^a Force constants used for the calculation are listed in Table I, column 4; bond orders in Table I, column 3; electronegativities in Table VIII, column 3.

^b Omitted in computing the average deviation.

^c Badger gives no constants for this combination of period and row of the atomic table.

^d G. B. M. Sutherland, E. Lee, and C. K. Wu, *Trans. Faraday Soc.* **35**, 1374 (1939).

^e See reference 43 in text.

^f See reference 5 in text.

^g See reference c in Table V.

^h H. Verleger, *Physik. Zeits.* **38**, 83 (1937).

ⁱ E. H. Eyster, *J. Chem. Phys.* **6**, 580 (1939).

^j L. Pauling and L. O. Brockway, *J. Am. Chem. Soc.* **59**, 1223 (1937).

^k L. Pauling, H. D. Springhill, and K. J. Palmer, *J. Am. Chem. Soc.* **61**, 927 (1939).

^l V. Schomaker and L. Pauling, *J. Am. Chem. Soc.* **61**, 1769 (1939).

^m D. M. Dennison, *Rev. Mod. Phys.* **12**, 175 (1940).

ⁿ R. G. Owens and E. F. Barker, *J. Chem. Phys.* **8**, 229 (1940).

^o D. P. Stevenson, J. E. LuValle, and V. Schomaker, *J. Am. Chem. Soc.* **61**, 2922 (1939).

^p A. Borden and E. F. Barker, *J. Chem. Phys.* **6**, 553 (1938).

^q See reference e in Table V.

^r J. W. Straley, C. H. Tindal, and H. H. Nielsen, *Phys. Rev.* **62**, 161 (1942).

^s E. K. Plyler and E. F. Barker, *Phys. Rev.* **44**, 984 (1933).

^t A. H. Nielsen and H. H. Nielsen, *Phys. Rev.* **47**, 585 (1935).

^u L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, *Phys. Rev.* **52**, 968 (1937).

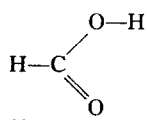
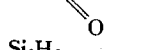
^v C. C. Stephenson and W. F. Giaque, *J. Chem. Phys.* **5**, 149 (1937).

^w G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. van Nostrand Company, Inc., New York, 1945), p. 489.

^x H. H. Nielsen, privately communicated.

^y G. Herzberg, reference w of Table VI, p. 456.

TABLE VII. Predicted bond orders.

Molecule	Link	Bond-stretching force constants in dynes/cm $\times 10^{-5}$ <i>k</i> obs.	Bond length in Å <i>d</i> obs.	Bond order predicted from Eq. (1A) <i>N</i>
BrCN	BrC*	4.2 ^a	1.79 ^a	1.2
	CN	16.9 ^a	1.15 ^a	2.7
CH ₃ CN	CC*	5.3 ^b	1.49 ^b	1.2
	CN	17.5 ^b	1.15 ^b	2.8
CH ₃ NC	CN	5.45 ^b	1.43 ^c	1.1
	NC	16.3 ^b	1.18 ^c	2.7
ClCN	ClC*	5.2 ^a	1.67 ^a	1.3
	CN	16.7 ^a	1.15 ^a	2.7
	C—O	5.4 ^c	1.42 ^g	1.0
	C=O	11.8 ^c	1.24 ^g	1.9 ⁱ
Si ₂ H ₆	SiSi	1.7 ^d	2.32 ^e	1.2

* α value for acetylenic carbon is taken as 2.83.

^a See reference 6 in text.

^b J. W. Linnett, *J. Chem. Phys.* **8**, 91 (1940).

^c L. G. Bonner and R. Hofstadter, *J. Chem. Phys.* **6**, 531 (1938).

^d T. F. Anderson and A. B. Burg, *J. Chem. Phys.* **6**, 586 (1938).

^e See reference 6 of Table VI.

^f W. Gordy and L. Pauling, *J. Am. Chem. Soc.* **64**, 2952 (1942).

^g J. Karle and L. O. Brockway, *J. Am. Chem. Soc.* **66**, 574 (1944).

Bonds of higher order having some ionic character are treated in a similar manner—i.e., electrovalent and covalent bonds are considered equivalent and additive in assigning the bond orders.

Considering their chemical properties and the valencies of their constituent atoms, the bond orders of most of the molecular links listed in Table I, except those of fractional order, can be assigned with a fair degree of certainty.

Bonds of Fractional Order

Pauling, Brockway, and Beach¹⁴ treat molecules having bonds of fractional order as made up of different resonating structures whose bonds are all of integral order, the bond character being then determined by averaging the integral orders of the bonds between the same pair of atoms in the different contributing structures. Thus the CC bond of benzene would be halfway between a single and a double bond, assuming the two equivalent resonating Kékulé structures to be the only significant ones. Penney¹⁵ has proposed a treatment which, though still based upon the valence-bond method, gives fractional orders which are linearly related to bond energies.

¹⁴ L. Pauling, L. O. Brockway, and J. Y. Beach, *J. Am. Chem. Soc.* **57**, 2705 (1935).

¹⁵ W. G. Penney, *Proc. Roy. Soc.* **158A**, 318 (1937).

For the CC bond of benzene he obtains an order of 1.623.

Coulson,¹⁶ who employs the molecular orbital method, defines the order of a bond in an unsaturated molecule as $1+p$, where the unit value is contributed by the σ electrons which are regarded as localized between the two atoms forming the bond, and where p is the summation of the contribution of all the mobile or unsaturation electrons. He obtains 1.67 for the bond order of the CC benzene bond.

Mulliken, Rieke, and Brown,¹⁷ using the molecular orbital method, have recently shown that hyperconjugation—conjugation with or between saturated groups—has an appreciable effect upon the orders of bonds in hydrocarbons. They predict that normal C—C bonds have about 11 percent double bond character and that normal C=C bonds such as are found in ethylene have about 12 percent triple bond character. For the CC bonds of fractional order in Table I, I have used the bond order values given by these researchers. The agreement of their results with

TABLE VIII. Electronegativities.

Atom	Pauling's ^a value	Value used here	Atom	Pauling's ^a value	Value used here
Ag	—	1.9	K	0.8	0.80
Al	1.5	1.5	Li	1.0	.95
As	2.0	2.0	Mg	1.2	1.2
Au	—	3.1	N	3.0	2.98
B	1.9	1.9	Na	.9	.90
Ba	.9	.9	O	3.5	3.45
Be	1.5	1.45	P	2.1	2.1
Bi	—	1.8	Pb	—	1.5
Br	2.8	2.75	Rb	.8	.78
C	2.5	2.55	S	2.5	2.53
C*	—	2.83	Sb	1.8	1.8
Ca	1.0	1.0	Sc	1.3	—
Cd	—	1.1	Se	2.4	2.4
Cl	3.0	2.97	Si	1.8	1.8
Cs	.7	.75	Sn	1.7	1.7
Cu	—	2.2	Sr	1.0	1.0
F	4.0	3.95	Te	2.1	2.1
Ga	—	1.4	Ti	1.6	1.6
Ge	1.7	1.7	Tl	—	1.3
H	2.1	2.13	Y	1.3	—
Hg	—	1.0	Zn	—	1.2
I	2.4	2.45	Zr	1.6	1.6
In	—	1.4			

^a L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1939), p. 64.

* Single bond to acetylenic carbon.

¹⁶ C. A. Coulson, *Proc. Roy. Soc.* **169A**, 413 (1939); J. E. Lennard-Jones and C. A. Coulson, *Trans. Faraday Soc.* **35**, 811 (1939).

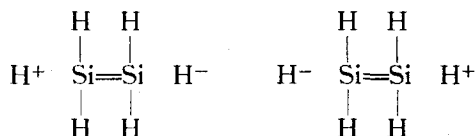
¹⁷ R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Am. Chem. Soc.* **63**, 41 (1941).

relation (IA) is pleasing since it lends confirmation to the somewhat surprising hyperconjugation predicted by them. It is unfortunate that bond orders computed by their method are available only for certain CC bonds.

Prediction of Some Bond Orders

Table VII lists several bonds for which stretching constants and interatomic distances are known, but for which bond orders are regarded as uncertain. Relation (IA) is used with the known constants to predict the bond orders listed in column 7. At present there is no check on these other than the method of Pauling, Brockway, and Beach¹⁴ of estimating bond character, which is applicable to some. As is evident from the above discussion, the fractional order predicted by the relation is not strictly equal to the bond character as defined by these authors but is more nearly equivalent to the bond order as computed by Mulliken, Rieke, and Brown.¹⁷

From its close similarity to ethane, Si₂H₆ may be expected to have some hyperconjugation which would make the order of the SiSi bond somewhat above unity. The order predicted, though not accurate, strongly suggests some double bond character for SiSi. From the electron pair theory the fractional bond order could be explained by postulating structures of the type



to contribute significantly to the ground state.

Resonance between structures of the types



giving XC some double bond character, and CN a bond order somewhat less than 3, could explain the bond orders predicted for CH₃CN, ClCN and BrCN. For methyl isocyanide the predicted orders indicate some contribution to the ground state by structures II and III in addition to the principal structure I,

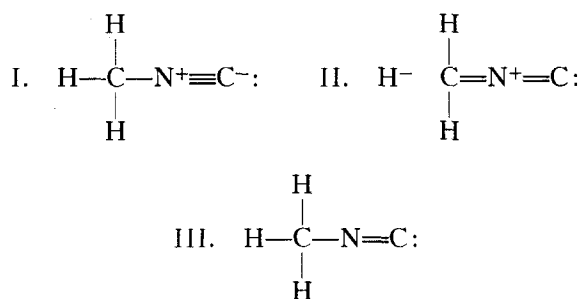
TABLE IX. Calculation of electronegativities.

Molecule AB	Force constant in dynes/cm $\times 10^{-5}$ k obs. ^a	Bond length in Å d obs. ^b	Electronegativity from relation (I) x_A	Equation used
AgCl	1.83	2.42	1.76	(IA)
AgBr	1.68	2.59	1.89	(IA)
AgI	1.45	2.81	1.96	(IA)
AuCl	2.56	2.48	3.10	(IA)
AlCl	2.08	2.12	1.53 ^c	(IE)
AlBr	1.71	2.29	1.53 ^c	(IE)
AlI	1.31	2.50	1.50 ^c	(IE)
BCl	3.40	1.77	1.91 ^c	(IE)
BBr	2.69	1.94	1.90 ^c	(IE)
BiH	1.70	1.809	1.83	(ID)
CdH	1.21	1.762	1.07	(ID)
CuCl	2.29	2.24	2.14	(IA)
CuBr	2.03	2.42	2.24	(IA)
CuI	1.72	2.63	2.28	(IA)
GaCl	1.83	2.11	1.31	(IE)
GaBr	1.52	2.28	1.33	(IE)
GaI	1.24	2.50	1.41	(IE)
HgH	1.14	1.741	.97	(ID)
InCl	1.58	2.29	1.29	(IE)
InBr	1.36	2.46	1.35	(IE)
InI	1.11	2.69	1.44	(IE)
PbH	1.45	1.839	1.51	(ID)
TiCl	1.45	2.31	1.19	(IE)
TiBr	1.26	2.48	1.39	(IE)
TiI	1.07	2.71	1.40	(IE)
TiH	1.15	1.870	1.13	(ID)
ZnH	1.51	1.595	1.20	(ID)

^a Computed from ω_e values of G. Herzberg, reference 5 in text.

^b The bond lengths for hydrides are from G. Herzberg, reference 5 in text. For the halogens they are determined from the additivity rule using the Schomaker-Stevenson corrections. See reference 4 in text.

^c These values are included to demonstrate applicability of Eq. (IE). Pauling gives x values for Al and B as 1.5 and 1.9. See Table VIII.



ELECTRONEGATIVITIES

Electronegativity represents the attraction of an atom for the electrons which bind it in a stable molecule. Mulliken¹⁸ has shown that the average of the first ionization energy and the electron affinity of an element is a measure of this quantity. Though his is a rather straightforward measure, it has not proved applicable to a very large number of elements.

¹⁸ R. S. Mulliken, J. Chem. Phys. 2, 782 (1934); 3, 573 (1935).

Pauling¹⁹ has derived a more widely applicable method based upon the heats of formation of compounds. He shows empirically that

$$x_A - x_B = 0.208\Delta^{\frac{1}{2}},$$

where x_A and x_B are the electronegativities of the elements A and B ; and where Δ , the energy above that expected for a normal covalent bond, expressed here in electron volts, is determined from the bond energy D of the bonds $A-B$, $A-A$ and $B-B$, thus,

$$\Delta = D(A-B) - \frac{1}{2}\{D(A-A) + D(B-B)\},$$

by postulation of the arithmetic mean.²⁰ Mulliken's values and certain other considerations are used to set the origin of the Pauling scale.

The relation which is the subject of this paper offers a means of determining electronegativity from molecular spectra. The method is widely applicable and appears to be of worthwhile accuracy.

Comparison with Pauling's Values

The electronegativity values used to establish the relation are those of Pauling.²¹ When a given element was involved in more than one bond its x value was adjusted to give the best over-all fit to relation (I). The values were extended to the third place where the accuracy of the data justified it. In no instance was it necessary to alter the last significant figure given by Pauling—that is, to change the x value by more than 0.05. This is remarkable, since Pauling's values were determined in a different manner from other bond properties. A comparison is given in Table VIII.

Determination of Some New Values

Relation (I) was used to determine a number of x values not given by Pauling. These are also listed in Table VIII. The molecular constants and particular form of relation (I) used for computing them are shown in Table IX.

The only molecules involving Ga and In for which force constants are available are certain diatomic halides. These have unsatisfied valencies which make relation (IA) inapplicable, and their

interatomic distances have not been measured. Consequently, I have chosen the parameters a and b of relation (I) so as to give the best fit for the similar halides of B and Al (elements of the same valence) with all interatomic distances determined from the Schomaker-Stevenson rule,¹² and have used the resulting equation,

$$k = 2.25(x_A x_B / d^2)^{\frac{1}{2}} - 0.20, \quad (1E)$$

to determine the x values for Ga, In, and Tl. The consistency of the results (see Table IX) appears to justify the procedure.

The x values for Ag and Cu and especially that for Au seem rather high in comparison to those of other metals. The extrapolation of Eq. (IA) to these elements is certainly questionable. Some double bond character may exist in the halides used, and the bond lengths which were determined from the additivity rule¹² may not be sufficiently accurate. Nevertheless, the x values for Ag obtained from three different halides agree reasonably well. The results are likewise consistent for Cu. Values determined from the hydrides were not used in assigning x for these elements because their polyvalent character makes it uncertain which form of the relation applies. However, it seems that the correct values should be somewhere between those given by Eqs. (IC) and (ID): 1.6 and 2.1 for Ag, 1.7 and 2.3 for Cu, 3.0 and 3.9 for Au. The values assigned are in qualitative agreement with other properties.²² Elements of sub-group I—Cu, Ag, and Au—have much higher ionization potentials, higher boiling points, form oxides that are less basic, etc., than do elements of the main group I—Li, Na, etc.

Effects of Bond Type

Carbon bound by a triple and a single bond shows a significantly higher electronegativity in the direction of the single bond than does carbon held by bonds of lower order. Possible causes of this are the less effective shielding of the nucleus by the electrons involved in the triple bond and the smaller than normal²³ single bond radius which allows a closer approach of the bonding

¹⁹ L. Pauling, reference 13, p. 58.

²⁰ L. Pauling, reference 13, p. 48.

²¹ L. Pauling, reference 13, p. 64.

²² W. M. Latimer and J. H. Hildebrand, *Reference Book of Inorganic Chemistry* (The Macmillan Company, New York, 1940), p. 101.

²³ L. Pauling, H. D. Springhill, and K. J. Palmer, *J. Am. Chem. Soc.* **61**, 927 (1939).

electrons to the nucleus. This higher value of x in $\equiv\text{C}-$ is revealed in other phenomena. Hydrogens joined to acetylenic carbon are known to be more acidic²⁴ and to participate in hydrogen bonding more effectively than do those of a more saturated hydrocarbon.²⁵ In this work the x value for $\equiv\text{C}-$ was chosen which provided the best fit for the CH bond of HCN and of C_2H_2 , and this value was used for other single bonds to a triple bonded carbon.

Other variations in bond character—bond type, degree of hybridization of the atomic orbitals—no doubt influence the effective electronegativities. Their effects, which do not seem as pronounced as that of acetylenic C, are neglected.

Effects of Electric Charges

The x values listed in Table VIII do not hold for charged atoms. However, Pauling²⁶ has given simple rules, based on changes in nuclear screening, for correcting these values for the effects of electric charges. If x^+ represents the electronegativity of an element with a +1 charge, then

$$x^+ = x + \frac{2}{3}(x_r - x)$$

approximately, where x is the value for the neutral atom and x_r is the value for the atom immediately to the right of it in the atomic table. Similarly for a negative unit charge,

$$x^- = x - \frac{2}{3}(x - x_l),$$

where x_l is the electronegativity of the element immediately to the left in the atomic table. These rules are used to correct for the effects of formal charges in ionic groups treated in this paper.

For most applications of relation (I), the effects of partial ionic character of a bond on the x values may be neglected as the electronegativity product tends to remain constant when the x value of one of the bonded atoms is increased at the expense of the other.

SPECIAL APPLICATIONS

(MH)⁺

Assuming a normal bond order of unity for these ions, higher force constants would be pre-

²⁴ J. B. Conant and G. W. Wheland, J. Am. Chem. Soc. **54**, 1212 (1932).

²⁵ S. C. Stanford and W. Gordy, J. Am. Chem. Soc. **63**, 1094 (1941).

²⁶ L. Pauling, reference 13, p. 65.

dicted for them, because of their greater electronegativity product, than for the corresponding neutral group. When M^+ has a large x value compared to H, however, contributions of the form, M H^+ , with zero bond order, could reduce the bond order enough to more than counterbalance the effects of the greater electronegativity product. Thus, understandably, force constants for $(\text{HCl})^+$ and $(\text{OH})^+$ are lower than those of the corresponding neutral group, whereas those for $(\text{BH})^+$ and $(\text{BeH})^+$ are higher.

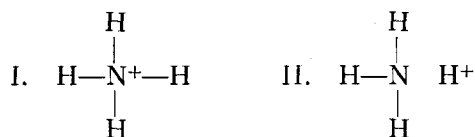
From relation (I), the bond order of M^+-H is approximately

$$N' = (k'/k)(x_{\text{M}}d'^2/x_{\text{M}'}d^2)^{\frac{1}{2}},$$

where the primed constants are for M^+-H . This assumes that a and b have the same value for $\text{M}-\text{H}$ and M^+-H and that b is small compared to k or k' . The former assumption is certainly questionable in some instances, and the computed N 's should be regarded as only approximate predictions. The bond orders for $(\text{OH})^+$, $(\text{HCl})^+$, $(\text{BH})^+$, and $(\text{BeH})^+$ computed in this way, using Herzberg's⁵ constants, are 0.6, 0.8, 0.9, and 1.0, respectively.

(NH₄)⁺ and (H₃O)⁺

The principal structures contributing to the ground state of $(\text{NH}_4)^+$ would be I and the four equivalent forms of II.

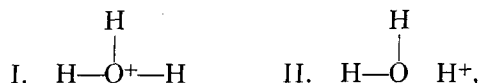


Pauling²⁷ has predicted 20 percent ionic character for NH. I shall assume equal resonance between I and each of the forms of II. This would mean that a particular NH is bonded only 80 percent of the time—since no effective bond exists in N H^+ —and that $\text{N}=\frac{4}{5}$. The x value of N is increased by about .1 since it has a + charge $\frac{1}{4}$ of the time that a given NH is bonded. The NH distance will not be greatly different from that in NH_3 , and I shall take it to be 1.02Å. With these assumptions relation (IA) gives $k_{\text{NH}}=5.64$. If this value is decreased 8 percent to correct for anharmonicity and the simple har-

²⁷ L. Pauling, reference 13, p. 72.

monic formula applied, the predicted vibration frequency is 3070 cm^{-1} . This is in good agreement with the absorption of the ammonium halides²⁸ in the region of 3100 , which presumably arises from the valence vibration of $(\text{NH}_4)^+$.

A similar treatment can be given $(\text{H}_3\text{O})^+$. Assuming equal resonance between I and each of the three equivalent forms of type II,



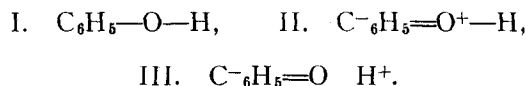
the bond order is effectively $\frac{3}{4}$, and the average electronegativity of O is increased about 0.1 by the $+$ charge. With $d_{\text{OH}}=0.97$, the estimated k_{OH} is 5.96. The ion should absorb in the region of 3120 cm^{-1} or 3.2μ . This, as it should be, is a little beyond the position to which the H_2O band is shifted by the strong hydrogen bonds existing in pure water. These ions would exist in a solution of a strong acid in water, but it would hardly be possible to resolve their absorption from that of liquid water and ions of the type $(\text{H}_4\text{O})^{++}$. A strong acid should, however, tend to broaden the 3μ water band on the long wavelength side.

CH-NH₂, CH₃OH, C₆H₅OH, and C₆H₅SH

Linnett²⁹ regards the NH and OH stretching force constants which he computes for these compounds as lower than normal. If his values for methyl amine and methyl alcohol, 6.30 and 7.65, respectively, are increased 8 percent to correct for probable effects of anharmonicity, the resulting values, 6.80 and 8.26, are in almost exact agreement with the values 6.81 and 8.24 computed from relation (IA) assuming normal single bonds.

The OH stretching constant obtained by Linnett for phenol does, however, appear to be significantly lower than that for water or for methyl alcohol. Phenol³⁰ is known to be appreciably more acidic than the aliphatic alcohols. Pauling³¹ attributes this to structures of Type II

in resonance with those of Type I.



The OH bond order predicted by relation (IA) is 5 percent lower than unity. Hence, it appears that structures of Type III are also of importance.

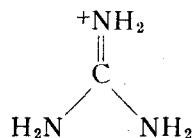
Linnett's value for the SH bond-stretching constant of thiophenol 3.8 (or for CH_3SH) after the estimated correction for anharmonicity is made becomes 4.1, the value predicted for a normal SH bond by relation (IA).

C \equiv N

The force constant of $\text{C}\equiv\text{N}$ computed from the CN vibrational frequency of NaCN ³² is 16.5, a value somewhat lower than that for the CN group of HCN. The lower force constants for the ion can be accounted for without assuming any decrease in the bond order, by decreasing the x of C by 0.3 and increasing the bond distance by 0.05A to correct for the negative charge³³ on C. The value predicted in this way from relation (IA), assuming a triple bond, is 16.2, in excellent agreement with the observed value.

Guanidonium Ion

According to Pauling³⁴ the guanidonium ion resonates equally between the equivalent structures of the type,



giving the CN bond 33 percent double bond character. Assuming $N=1.33$, and using the $k_{\text{CN}}=7.1$ computed by Kellner,³⁵ the CN distance calculated from (IA) is 1.34A. This seems to be a reasonable value. Pauling's relation³⁶ between bond distance and double bond character, assuming 33 percent double bond character, gives $d_{\text{CN}}=1.36\text{A}$.

²⁸ J. H. Hibben, reference 11, p. 466.

²⁹ J. W. Linnett, *Trans. Faraday Soc.* **91**, 223 (1945). The value given is increased by 8 percent to correct for anharmonicity.

³⁰ H. J. Lucas, *Organic Chemistry* (American Book Company, New York, 1935), p. 131.

³¹ L. Pauling, reference 13, p. 189.

³² W. Gordy and D. Williams, *J. Chem. Phys.* **3**, 664 (1935).

³³ L. Pauling, reference 13, p. 159.

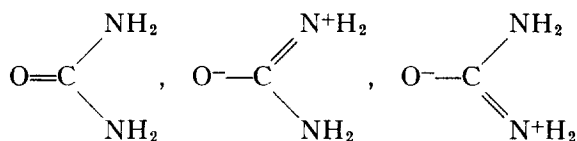
³⁴ L. Pauling, reference 13, p. 198.

³⁵ L. Kellner, *Proc. Roy. Soc.* **177**, 456 (1941).

³⁶ L. Pauling, reference 13, p. 164.

Urea

The principal structures contributing to the ground state of urea are:



Kellner³⁵ has computed from spectra $k_{\text{CO}}=9.7$ and $k_{\text{CN}}=6.6$. Using these values and the interatomic distance values $d_{\text{CO}}=1.25\text{\AA}$ and $d_{\text{CN}}=1.37\text{\AA}$, measured by Wyckoff and Corey,³⁷ the bond orders obtained from (IA) are 1.5 and 1.3 for CO and CN, respectively. Pauling³⁴ predicts 20 percent double bond character for CN and 60 percent double bond character for CO.

 B_2H_6

Because of its unusual and still somewhat uncertain structure this molecule is of great interest. Lewis³⁸ has suggested that the total of twelve valence electrons available combines into six electron pair bonds which resonate among the seven bonds to give 6/7 of a normal electron pair bond for each. Pauling³⁹ assumes that in resonance with these are several structures of the type,



containing one-electron bonds. Since a one-electron bond is approximately equivalent to one-half an electron-pair bond, each of the bonds would still average about 6/7 of a normal single bond. Taking $N=6/7$ for BH and BB and the bond distances measured by Bauer,⁴⁰ $d_{\text{BH}}=1.27\text{\AA}$, $d_{\text{BB}}=1.86\text{\AA}$, the force constants computed from relation (IA) are $k_{\text{BH}}=3.1$ and $k_{\text{BB}}=1.8$. This value of k_{BH} does not agree satisfactorily with that of 3.9 computed from the observed spectra.^{29, 41}

³⁷ R. W. G. Wyckoff and R. B. Corey, *Zeits. f. Krist.* **89**, 462 (1932).

³⁸ G. N. Lewis, *J. Chem. Phys.* **1**, 17 (1933).

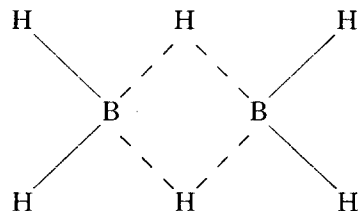
³⁹ L. Pauling, reference 13, p. 241.

⁴⁰ S. H. Bauer, *J. Am. Chem. Soc.* **59**, 1096 (1937).

⁴¹ Anderson and Burg (reference d of Table VII) tentatively assigned the widely separated frequencies 2102

The B—B vibrational band for $k_{\text{BB}}=1.8$ should occur at about 660 cm^{-1} . No very strong band is observed near this frequency in either the Raman or infra-red spectra.⁴²

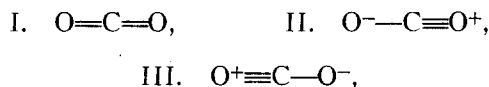
Recently Longuet-Higgins and Bell⁴³ have proposed the bridged structure



held together with hydrogen bridges, with no direct bonding between the borons and with normal single bonds between the terminal BH groups. Relation (IA) supports their interpretation. Using their value, 1.18\AA for the B—H distance, and assuming a normal single bond, $N=1$, the B—H force constant computed from (IA) agrees closely with that computed by Linnett²⁹ from the data of Stitt.⁴² See Table I.

 CO_2 , SCO , and CS_2

Normal electronic structures with double bonded links can be assigned to carbon dioxide. Nevertheless, the CO distance, 1.16\AA , is somewhat shorter than that for a double bond, and Pauling⁴⁴ has shown that the three structures,



probably contribute about equally to the ground state. Taking account of the effects of formal charges on the x value of O and of the triple bond on the x of C for the second two structures in proportion to their contribution and with N equal to the average bond character (2.00), the bond-stretching constant from (IA) is 14.4. This is in fair agreement with the observed value,⁶

cm^{-1} and 2523 cm^{-1} both to a BH stretching vibration, offering resonance splitting as a possible cause of the separation. From this questionable assignment they obtained a value of 3.0 for k_{BH} . They point out, however, that the separation of 421 cm^{-1} is abnormally large for resonance splitting.

⁴² F. Stitt, *J. Chem. Phys.* **9**, 780 (1941). See also reference d of Table VII.

⁴³ H. C. Longuet-Higgins and R. P. Bell, *J. Chem. Soc.* **250** (1943).

⁴⁴ L. Pauling, reference 13, p. 179.

15.2. A similar interpretation can be given for SCO.

The resonance energy of CS₂, only 11 kcal./mole⁴⁵ as compared with 33 kcal./mole for CO₂, indicates that structures of Types II and III are much less significant in this molecule. I have consequently regarded it as having normal double bonds. See Table I.

O₂, SO, and S₂

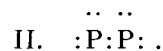
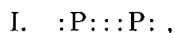
One might expect, from their covalencies, two normal electron-pair bonds in these molecules. Their ³Σ ground states,⁵ nevertheless, indicate that they have unpaired valence electrons. Pauling⁴⁶ has postulated for them a normal single bond plus two three-electron bonds. Though the two three-electron bonds in these molecules should be about equal in energy to a single bond,⁴⁶ it is not possible to regard their bond order as 2.00 in the present relation. The bond orders required to make the relation fit are 1.4, 1.7, and 1.9 for O₂, SO, and S₂, respectively. Se₂ and Te₂ behave similarly.

PN and P₂

The force constant calculated from (IA), assuming triple bonds for these molecules, is too large by 8 percent for PN and by 10 percent for P₂. It is not probable that these deviations are caused by errors in the observed *k*'s or *d*'s, which are those listed by Herzberg.⁵ They could be made to fit the relation adequately by an 8 percent reduction in the *x* value for P. However, the *x* used for P seems to be satisfactory for PH₃. There is no apparent reason why these molecules should be exceptions to the relation since the similar molecule N₂ is not an exception. PN and P₂ are usually regarded as having pure triple bonds. The tendency to form triple bonds, however, decreases rapidly with the increase in size of the atoms bonded, and tentatively I am attributing the misfit of the relation to this tendency.

The necessary reduction in bond order may be achieved in these molecules by a small contribution from structure II, containing a single

bond and incompleted octets on both atoms.



The incompletely-filled valence shells should allow the second structure to exist with the same interatomic distance as that required by I, though because of its much higher energy the contribution from II may not be very significant.

H₂O₂ and H₄N₂

In contrast to the satisfactory agreement of the similar molecules H₂S₂ and H₆C₂, both H₂O₂ and H₄N₂ appear to be exceptions to relation (IA). This behavior will be treated in a later communication.

Pyramidal AB₃ Molecules

When A is not large compared to B, these molecules are complicated by the possibility of interaction of the non-bonded atoms. The radius ratio *r*_A/*r*_B should give a relative indication of this interaction. Consequently, I have listed the molecules in Table X in the order of increasing values of *r*_A/*r*_B. From an examination of the table it is seen that the bond-stretching force constants calculated from (IA), assuming normal single bonds, agree satisfactorily with the observed values for all molecules with *r*_A/*r*_B greater than 1.5. For those with *r*_A/*r*_B between 1.2 and 1.5 the agreement is fair except for BiCl₃. The exceptional disagreement for BiCl₃ makes the observed *k* appear questionable.

No observed *k*'s are available for the iodides. Because of the large radius of iodine the radius ratio would be unfavorable to a good fit of (IA) for them.

Bond-stretching constants predicted from (IA) for SbBr₃ and BiBr₃ (radius ratios 1.24 and 1.28) are 1.71 and 1.59, respectively.

Tetrahedral AB₄ Molecules

Except when B is the small hydrogen atom, there is considerable interaction between the non-bonded corner atoms of AB₄ tetrahedral molecules. The valence force function is in general unsatisfactory for this type of molecule. For some of them Urey and Bradley⁴⁷ and

⁴⁵ L. Pauling, reference 13, p. 131.

⁴⁶ L. Pauling, reference 13, pp. 253-4.

⁴⁷ H. C. Urey and C. A. Bradley, Phys. Rev. **38**, 1969 (1931).

TABLE X. Calculated and observed bond-stretching force constants for pyramidal AB₃ type molecules.

Molecule	Bond length in Å <i>d</i> obs. ^a	Bond-stretching force constants in dynes/cm × 10 ⁻⁵ <i>k</i> obs.	<i>k</i> calc. ^b by Eq. (IA)	<i>k</i> calc. from <i>k</i> obs. % dev.	Radius ratio <i>r</i> _A / <i>r</i> _B
AsH ₃	1.56	2.81 ^c	2.84	1.1	3.32
PH ₃	1.45	3.33 ^c	3.24	2.7	2.98
NH ₃	1.014	6.86 ^c	6.81	.7	2.00
Bi(CH ₃) ₃	2.23	1.75 ^d	1.87	6.9	1.90
Sb(CH ₃) ₃	(2.13)	2.09	1.99	4.8	1.83
AsF ₃	1.72	3.92 ^e	3.79	3.4	1.75
As(CH ₃) ₃	1.98	2.44 ^d	2.34	4.1	1.63
PF ₃	1.52	4.59 ^e	4.66	1.5	1.56
BiCl ₃	2.48	1.19 ^e	1.80	(51.0)	1.48
SbCl ₃	2.37	1.78 ^e	1.91	7.3	1.43
P(CH ₃) ₃	1.87	2.14 ^d	2.60	21.5	1.43
AsCl ₃	2.16	2.03 ^e	2.30	14.8	1.27
PCl ₃	2.00	2.12 ^e	2.63	24.0	1.11
N(CH ₃) ₃	1.47	3.97 ^d	4.58	15.4	.96
PBr ₃	2.23	1.63 ^e	2.17	33.2	.96

^a The hydrides are repeated from Table I. Bond distances for other molecules are from reference *c* of Table V except those in parentheses, which are the added radii.

^b Normal single bonds are assumed.

^c See reference *c* of Table I.

^d J. E. Rosebaum, D. J. Ruben, and C. R. Sandberg, *J. Chem. Phys.* **8**, 366 (1940).

^e G. Herzberg, see reference *w* of Table VI, p. 456.

others⁴⁸ have successfully used modified valence potential functions with terms included to account for the interaction of the corner atoms.

Herzberg⁴⁹ and Silver⁵⁰ have computed bond-stretching constants for several tetrahedral type molecules assuming the simple valence force system. These values do not agree with those computed from (IA) but agree, except when A is carbon, with values computed from relation I in the form,

$$k = 3.29 \left(\frac{x_A x_B}{d^2} \right)^{\frac{1}{2}} - 0.40. \quad (\text{IF})$$

The results of this comparison are shown in Table XI. They imply that the interaction of the non-bonded atoms varies in a systematic manner for the different types listed. An equally satisfactory fit is obtained for the series CF₄, CCl₄, CBr₄, and C(CH₃)₄ if the constants *a* and *b* of relation (I) are given the values +2.94 and -1.40.

A force stretching the bond AB in these molecules would be opposed not only by the chemical binding of AB but also by components of the interaction forces of the corner atoms.

⁴⁸ N. S. N. Nath, *Ind. J. Phys.* **8**, 581 (1934). See also K. W. F. Kohlrausch, reference *r* of Table I, p. 157.

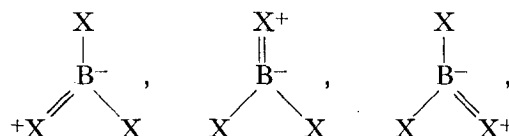
⁴⁹ G. Herzberg, reference *w* of Table VI, p. 182.

⁵⁰ S. Silver, *J. Chem. Phys.* **8**, 919 (1940).

Thus quite understandably the AB stretching constants computed from (IA), assuming only the forces of a normal single bond, are lower than those obtained from spectra using the valence force field system. An additional factor tending to make the values from (IA) (with *N*=1.00) lower than the spectral constants is the probable existence⁵¹ of some double bond character in the bond AB.

Boron Halides

The boron halides are symmetrical planar molecules with bond distances considerably shorter than those expected for normal single bonds. Pauling⁵² has predicted the three equivalent structures of type,



to be the principal ones contributing to their ground states. Neglecting all structures except the above type and counting in the ionic bond, the average bond character is 5/3. Applying relation (IA) with *N*=5/3 gives *k*=4.06, 4.77, and 8.80 for BBr₃, BCl₃, and BF₃ in this order. Assuming the valence force system, which holds reasonably well for these molecules, Herzberg⁵³ computes from their spectra 3.66, 4.63, and 8.83 for *k*_{BBr}, *k*_{BCl}, and *k*_{BF}, respectively.

SOME GENERAL DEDUCTIONS

1

If the bond order remains unchanged, a formal positive charge on one of the atoms of a bond should increase its stretching force constant, and a negative formal charge should decrease it. This follows from the fact that an increased positive charge on either atom would increase the electronegativity product and would also—unless the bond order is lowered—tend to make the bond length shorter.

The implication of the above statement is that when, as frequently happens,²⁹ a positive

⁵¹ L. Pauling, reference 13, Ch. VII.

⁵² L. Pauling, reference 13, p. 219.

⁵³ G. Gerzberg, reference *w* of Table VI, p. 178.

charge actually lowers the force constant, it also effectively reduces the bond order. That a decrease in the electron density of one of the bonded atoms would tend to reduce the bond order is not surprising. For illustrations, see the sections on $(\text{MH})^+$ and $(\text{NH}_4)^+$.

2

For bonds of different orders between the same pair of atoms the force constant k_m for any given bond order N_m is related to that k_n for some other order N_n by

$$\frac{k_m - 0.30}{k_n - 0.30} = \frac{N_m}{N_n} \left(\frac{d_n}{d_m} \right)^{\frac{1}{2}}$$

This follows obviously from relation (IA). More approximately,

$$\frac{k_m}{k_n} = \frac{N_m}{N_n} \left(\frac{d_n}{d_m} \right)^{\frac{1}{2}}$$

In the above equations d_m and d_n represent the interatomic distances for the respective bond orders, N_m and N_n .

Frequently it is desirable to know the approximate ratios of the force constants of single, double, and triple bonds between a given pair of atoms. If the interatomic distances have not been measured for the different bonds, they can be determined approximately by adding the respective single, double, or triple covalent radii given by Pauling.⁵⁴ Whenever k is known for one of the orders, the first and more accurate of the above forms can be applied. Thus the bond-stretching force constants for single, double, and triple CN bonds should have the approximate ratios, 1.00:2.37:4.10. Probably a more useful

⁵⁴ L. Pauling, reference 13, p. 154.

TABLE XI. Calculated and observed bond-stretching force constants for tetrahedral AB_4 type molecules.

Molecule	Bond length in Å d obs. ^a	Bond-stretching force constant in dynes/cm $\times 10^{-3}$		k calc. from k obs. % dev.
		k obs. ^b	Eq. (IF)	
GeBr_4	2.32	2.58	2.56	0.8
GeCl_4	2.08	3.27	3.28	.3
SiBr_4	2.19	2.92	2.94	.8
SiCl_4	2.02	3.75	3.63	3.2
$\text{Si}(\text{CH}_3)_4$	1.93	3.31	3.45	4.2
SiF_4	1.54	7.16	7.10	.8
SnBr_4	2.45	2.28	2.32	1.8
SnCl_4	2.30	2.80	2.77	1.1
TiCl_4	2.21	3.11	2.82	9.3

^a SiBr distance in SiBr_4 is assumed to be equal to that in SiBrCl_3 ; SnBr distance is determined from the Schomaker-Stevenson rule, reference 4. Other distances are from Maxwell, reference c of Table V.
^b k for $\text{Si}(\text{CH}_3)_4$ is from Silver, reference 50. k 's for the other molecules are from G. Herzberg, reference 49.

application is the prediction of bond orders from force constant ratios.

3

The concept of electronegativity, which in the past has been used principally in predicting properties associated with the partial ionic character of bonds, is of real importance in the interpretation of molecular spectra. Previous applications have been primarily concerned with the quantity, $x_A - x_B$, a fact which apparently led Wheland⁵⁵ to comment that it is only the differences between electronegativities which are significant. In the present work, wide application has been made of the electronegativity product, $x_A x_B$.

I wish to thank Vida Miller Gordy for assisting with the calculations and the preparation of the manuscript.

⁵⁵ G. W. Wheland, *The Theory of Resonance* (John Wiley & Sons, Inc., New York, 1944), p. 84.