

A Relation Between Internuclear Distances and Bond Force Constants

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It has been found that for diatomic molecules the relation between the bond force constant, k_0 , and the internuclear distance, r_e , is quite accurately given by the expression $k_0(r_e - d_{ij})^3 = 1.86 \times 10^5$, where d_{ij} is a constant depending only on the rows in the periodic table in which the two elements comprising the molecule are located. The expression holds not only for the normal state but for all excited states with a few possible exceptions. Some uses of the relation are discussed and an extension to polyatomic molecules is suggested.

THREE criteria have recently been much employed in estimating the strength and character of chemical bonds, namely, the energy of dissociation, the internuclear distance, and the so-called "force constant" of the bond, that is, the force per unit displacement which would have to be applied for infinitesimal stretching or compression of the bond. This last quantity, which in further discussion we shall call simply k_0 , is in the case of diatomic molecules easily calculated from the frequency of vibration for infinitesimal amplitudes, $\omega_e c$ (which is the quantity appearing in the expression for the vibrational energy $E_{vib} = hc \{ \omega_e (v + \frac{1}{2}) - \omega_e x (v + \frac{1}{2})^2 \}$) by the relation $\omega_e c = (1/2\pi)(k_0/\mu)^{\frac{1}{2}}$.

Now since the energy of dissociation is frequently unobtainable with any accuracy the other two criteria must be employed, and it occurred to the author to find what relation might exist between them. That there is a relationship between ω_e and r_e for the various states of a given molecule has been pointed out by Mecke,¹ and Morse² has attempted to find a general relation whereby r_e could be approximately calculated from ω_e for any molecule. His expression $\omega_e r_e^3 = 3000$ is, however, known not to be very reliable except for a certain limited class of molecules.

In a search for a more exact expression the author treated graphically a large number of data for diatomic molecules, and in plotting k_0

against r_e soon found that within given classes of molecules a very definite relation does exist between these quantities. It was found further that if $(1/k_0)^{\frac{1}{3}}$ is plotted against r_e for all available data, for both normal and excited states, the points so obtained separate into groups, each of which falls practically on a straight line, as may be seen in Fig. 1. The points for the various states of the hydrogen molecule fall on or near the first line, those for the hydrides of the elements in the first row of the periodic system on a second, and those for diatomic molecules comprising elements each of which is found in the first row of the periodic system on still another. Evidently the class or group to which a molecule belongs depends only on the rows in the periodic system in which the elements composing it appear.

In some of the groups the data are rather meager but it appears that the best straight lines drawn through the respective groups lie practically parallel. Consequently the relation between r_e and k_0 may be represented analytically by the expression:

$$k_0(r_e - d_{ij})^3 = 1.86 \times 10^5,$$

where k_0 is given in dynes per cm, r_e in Angstrom units, and d_{ij} is a constant characteristic of all diatomic molecules made up of one element in the i th row and one in the j th row of the periodic system. Values for the constant d_{ij} are given in Table I.

Unfortunately data are as yet rather scanty for molecules made up of elements low down in

¹ R. Mecke, *Zeits. f. Physik* **32**, 823 (1925).

² P. M. Morse, *Phys. Rev.* **34**, 57 (1929).

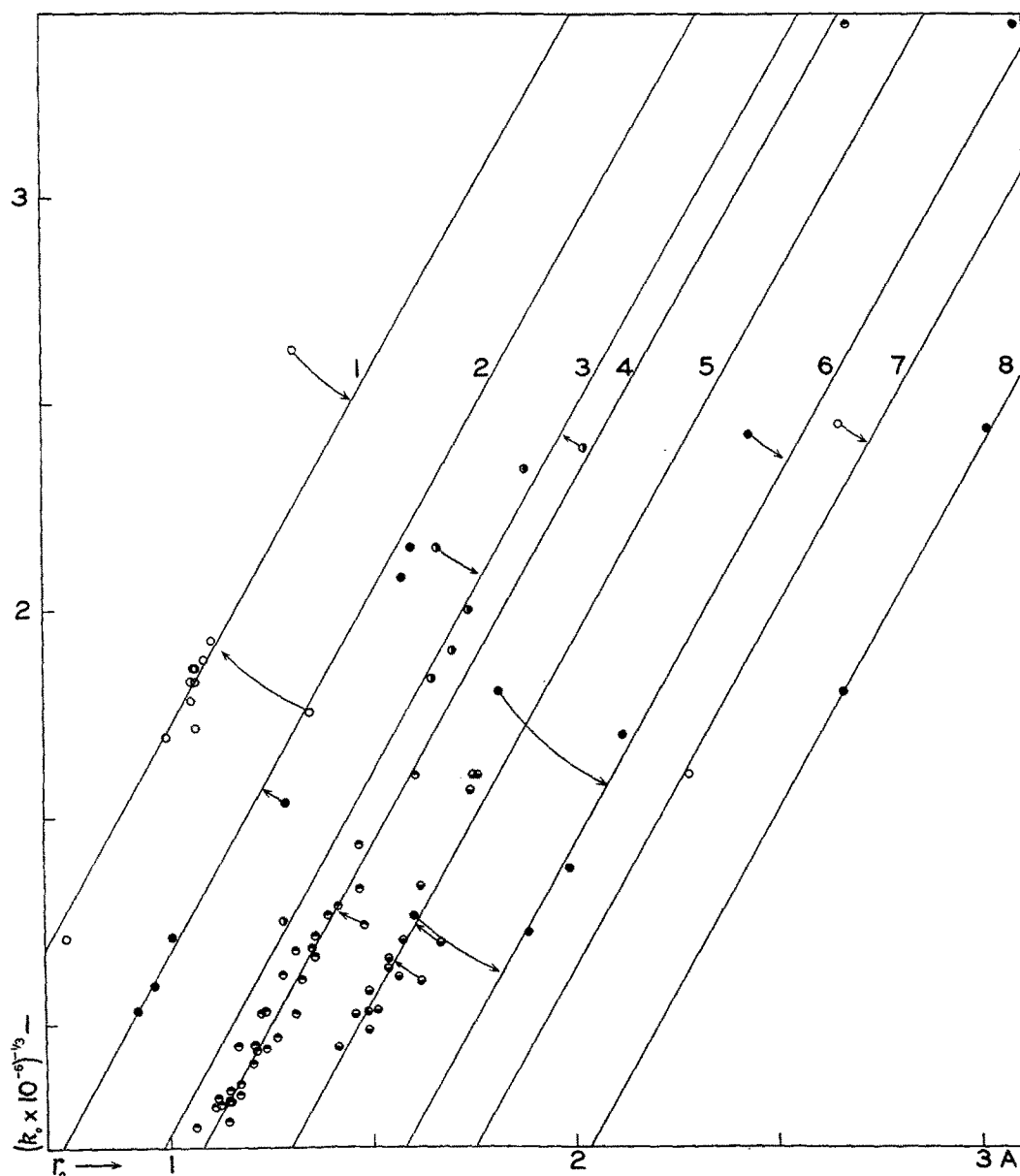


FIG. 1. A plot of the reciprocal of the cube root of the bond force constant against the internuclear distance for normal and excited states of the following molecules:

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|--|---|
| Line 1. Hydrogen | Line 5. PN, SiO, CS, SO, SiN, PO, AlO |
| Line 2. LiH, BeH ⁺ , OH, FH | Line 6. Na ₂ , P ₂ , S ₂ , Cl ₂ |
| Line 3. NaH, MgH, MgH ⁺ , ClH, AlH | Line 7. Br ₂ |
| Line 4. Li ₂ , C ₂ , N ₂ , O ₂ , F ₂ , BeF, BeO, BO, CO, CN, NO | Line 8. I ₂ |

the periodic system, and five of the constants given were determined from data from only one molecule for each. In these cases the greatest weight was given to the normal states in estimating the constants, and it is believed that they are sufficiently accurate to be of considerable use

in making predictions regarding other molecules. It will be interesting to note the behavior of elements lying in the transition portions of the long periods, when data become available, since the d_{ij} 's appear to depend on the completeness of the inner shells of the respective atoms, and

TABLE I.

Type of Molecule		Examples	$d_{ij}(A)$
Atom i	Atom j		
H	H	H ₂	0.025
H	Element in row 1	HF, LiH, BeH ⁺	0.335
H	Element in row 2	HCl, NaH, MgH	0.585
H	Element in row 3	HBr, KH	0.650
Element in row 1	Element in row 1	N ₂ , O ₂ , NO, CO	0.680
Element in row 1	Element in row 2	CS, PN, SiO	0.900
O	Ti	TiO	0.985
O	Pb	PbO	1.125
Element in row 2	Element in row 2	Cl ₂ , P ₂ , Na ₂	1.180
Cl	I	ICl	1.280
Br	Br	Br ₂	1.350
I	I	I ₂	1.635

not much on the outer shells. The d_{ij} 's might be called the *distances of nearest approach* of the two nuclei, and can nearly, though not quite, be taken as the sum of two radii which could be ascribed to the respective atoms. This fact, however, may be of assistance in obtaining by interpolation, constants for types of molecules for which no data exist.

It did not seem possible to indicate in the figure the molecules to which the various points belong, and a few data have not been included either to avoid confusion where the regions of different groups nearly coincided, or on account of practical limitations of size. It may suffice to say that all data which appear to make any pretensions to accuracy have been treated (with possible accidental exceptions), and to discuss the deviations in some detail, as is done in Table II, where the large deviations are specifically noted.

In group 1,1 (line 4), which includes the greater part of the really reliable data, the fit of the relation with the data is extremely satisfactory in all cases, including two excited states of the

lithium molecule which fall without the limits of the diagram. Some few points in other groups which fall outside the diagram (e.g., an excited state of the sodium molecule and excited states of the alkali metal hydrides) fit somewhat less well, and in the HBr group, not shown on the plot, the deviations are considerable though not extreme. The most unsatisfactory fit is in the case of the sulfur molecule, but if the data are reliable in this case the internuclear distance is certainly so abnormally small as to be worthy of further investigation. The deviations do not appear to be systematic though there is a slight indication that k_0 may fall off more rapidly at large distances than given by the relation, so that at present it should be used with caution in regions not covered by the plot.

In the preparation of the plot some apparently large deviations were discovered to result from obvious numerical errors in the literature (for example, the internuclear distance of chlorine given by Elliot³), and it may not be unduly optimistic to suppose that some of the remaining

³ A. Elliot, Proc. Roy. Soc. **A127**, 638 (1930).

TABLE II. Deviations in r_e calculated by the relation from the experimental value.

Group	Line in figure	Number of points with an absolute deviation (A units)			Large	Total number of points
		<0.025	0.025-0.050	0.05-0.15		
0,0	1	8	1	1	2($A_0=90,204$ 99,269)	12
0,1	2	3	2	1(BeH ⁺)	0	6
0,2	3	4	1	2(AlH, MgH ⁺)	0	7
1,1	4	21	12	1(F ₂ ')	0	34
1,2	5	8	5	3(AlO, MgF)	0	16
2,2	6	3	0	2(Na ₂ '', Cl ₂ ')	2(S ₂)	7

ones may be due to less apparent errors in band analysis.

Some brief comments on possible uses of the relation between r_e and k_0 may not be out of place. The most common use may be the calculation of moments of inertia or internuclear distances of molecules in case only a vibrational analysis of the bands has been made; an example is the case of antimony where the relation yields $r_e = 2.52\text{A}$, which the author believes is much more nearly correct than the value 2.21A obtained by Genard⁴ from the relation of Morse.

In some cases of stellar spectra, for example, where the emitter of certain bands has not been identified it may be helpful in indicating in what part of the periodic system the atoms comprising the molecule in question are located. But perhaps the most interesting possible use is in the construction of potential functions for, and in the interpretation of the spectra of polyatomic molecules. It is not certain how well the relation will be found to hold for polyatomic molecules, since because of the difficulties involved in the extrapolation to infinitesimal vibrations there is only one case so far where an accurate value for k_0 is known. This is for CO_2 ⁵ where the relation does indeed fit almost exactly. In other cases, where approximate values for the k_0 's and the internuclear distances are known, the deviations appear to be not very large.

⁴ J. Genard, Phys. Rev. **44**, 468 (1933).

⁵ A. Adel and D. M. Dennison, Phys. Rev. **44**, 99 (1933).

Two cases may be cited in which the relation will be of use even if it is only rather approximate. Sutherland⁶ has recently given an interpretation of the infrared spectrum of N_2O_4 on the assumption that the molecule is plane and symmetrical, with two NO_2 groups loosely held together by a weak N—N bond. In the interpretation of certain bands which are supposed to be due to bending vibrations it is necessary to know the N—N separation. It seems improbable that this distance can be secured from electron diffraction experiments, or indeed in any other direct way, but it is possible from the spectrum to estimate roughly the stretching constant for the bond in question. From this quantity, 1.5×10^5 dynes per cm, we may estimate the internuclear distance to be around 1.75A , which leads to a ratio between two of the bending frequencies which seems to fit with experiment much better than that taken by Sutherland on the basis of an improbably small distance.

In certain other cases of molecules where both bending and elongation force constants are important in some vibrations, the interpretation of the spectra would be considerably facilitated by an approximate value of the latter which could be estimated if internuclear separations have been determined from electron diffraction experiments.

⁶ G. B. B. M. Sutherland, Proc. Roy. Soc. **A141**, 342 (1933).