INTERRELATIONS BETWEEN EMPIRICAL FORMULAE FOR SPECTROSCOPIC CONSTANTS OF DIATOMIC MOLECULES

BORIS MUSULIN
Southern Illinois University, Carbondale

INTRODUCTION

The spectra of diatomic molecules have been studied to obtain the values of certain constants which characterize the structure of a molecule and its energy levels. The variation of potential energy, U, as a function of the internuclear distance, r, may be represented graphically by the conventional potential energy curve.

Not all spectroscopic constants are known for all molecules or even for all states of a single molecule. Various empirical relations have been proposed to predict the values of unknown constants from those known experimentally. These relations have also been used to provide insight into bonding models of molecules. Examples of these relations are found in the early work of Badger (1934) and the recent work of Smith (1956). In general, specific relations have been used to make predictions for molecules which have some common characteristics.

In this paper some of the empirical relations are examined as to their range of validity. Some standard techniques of mathematical treatment of experimental data are applied to these relations to determine whether *a priori* a certain empirical relation will be more valid than another relation. These techniques are also used to suggest two new empirical relations which should be of use in prediction of unknown spectroscopic constants.

The following notations are used to represent the various spectroscopic constants: 1) r_e, internuclear distance at the equilibrium distance; 2) D_e, dissociation energy; 3) k_e, force constant; 4) α_e, constant related to the rotational constant, B_e; 5) $\omega_e x_e$ and 6) $\omega_e y_e$, both of which are constants related to the anharmonicity (*i.e.*, the deviation from a true parabola at the equilibrium minimum).

RELATION TO ANALYTICAL EXPRESSIONS

Many investigators have sought to express the experimental potential energy curve as a mathematical equation. This has been done in both open and closed form. The closed expressions have been selected to reproduce the general shape of the curve, to obey certain limiting conditions (*cf.* Varshni, 1957), and to reproduce certain of the known spectroscopic constants. These known constants are either placed directly in the mathematical expression or used as boundary conditions to determine the values of the arbitrary constants used in the mathematical equation. In general, the more arbitrary or fixed constants which are used in the mathematical equation, the better is the "fit" to the experimental curve. In the literature, equations are found containing as few as two constants (Kratzer, 1922) and one with five constants (Hulburt and Hirschfelder, 1941).

Dunham (1932) proposed a mathematical equation in the form of a Taylor series. Although this expression has poor convergence properties, it does have the advantage of allowing flexibility in the choice of the number of constants used to "fit" the experimental curve. Dunham has also shown that the coefficients of the power series are related to the known spectroscopic constants. For example, the coefficient of the square term (the second derivative of the equation divided by two factorial) is equal to k_e.

The application of Dunham's formulae to the closed form expressions leads to analytical expressions between the known spectroscopic constants. These analytical expressions are identical in functional form to the empirical relations between spectroscopic constants proposed by various authors. However, it is not necessarily true that an equation which is a good "fit" to the experimental curve will produce a functional relation between known constants which is also good. In fact, these functional relations being derived from differentiation depend on the positioning of the constants in the analytical expression for the experimental curve. They also depend on whether arbitrary constants are used and adjusted to the boundary conditions or whether the known constants are placed in the analytical expression directly.

The analytical expression of Mecke (1927), Sutherland (1938), Varshni (1957), and Kratzer (1922) all lead to the relation

$$\frac{k_e r^2_e}{D_e} = C_2 \qquad (1)$$

where C_2 is a constant. The original expressions,

$$U = D_e \left[\frac{r - r_e}{r} \right]^2 \quad \textbf{Kratzer}$$

$$U = Ar^{n}e\text{-}ar \quad \textbf{Varshni}$$

$$U = Br^{-m} - br^{-p} \quad \textbf{Mecke-Sutherland}$$

where A, a, B, b, m, and p are arbitrary constants, are examples of a two-parameter function, a three-parameter function, and a four-parameter function, respectively. The value of C_2 should be the same for all molecules. In practice, the value of C_2 differs when individual molecules, or groups of molecules, are considered. The functional form of C_2 which relates the known constants is the same. Thus, the more flexible Mecke-Sutherland equation, which would be expected to give a more faithful representation of the experimental curve, provides the same relation between k_e, r_e, and D_e as the less flexible Kratzer equation.

COMPARATIVE TEST OF VARIOUS EMPIRICAL RELATIONS

The spectroscopic constants vary from a fivefold range (for r_e) to a thousand fold range (for α_e) for all molecules. An empirical relation that could be used to predict a spectroscopic constant would be expected to make predictions within a smaller range than the naturally occurring variation. The best relation would satisfy all possible diatomic molecules, but several useful relations have been found which satisfy certain groups of molecules.

The general procedure adopted in this work is to "fit" a particular group by finding the best arbitrary constant for that group when the relation is put into a functional form similar to equation (1). The best constant is also determined for all molecules. The average deviation from these constants is tabulated in Table 1. (A random sampling indicated that a Least Squares Deviation treatment did not change general ordering of the empirical relations with respect to deviation from a good "fit".) A sample of 21 diatomic molecules was selected. No attempt was made to select molecules which had normal behavior in their spectroscopic constants. In fact, molecules were used (N_2, CO, and NO) whose D_e is in doubt, as well as molecules which are known to have abnormal values of the spectroscopic constants (Li_2, Na_2, and K_2). The values of the spectroscopic constants used in these tests were taken from the values tabulated by Varshni (1957). The molecules were grouped according to similar chemical properties, as indicated by the Periodic Table. In each grouping of homopolar molecules, the atoms were selected from a given row or column of the Periodic Table. In each grouping of heteropolar molecules, one atom was selected from a given row or column and the other atom was the same throughout the grouping. The molecules comprising each group are listed in Table 1.

A comparison between the constancy of r_e ($r_e = C$) and $k_e r_e^2 = C_1$ is given in Table 1. The combination of two constants gives a much better "fit" within a given grouping of molecules but provides a worse "fit" when an attempt is made to

TABLE 1.—Comparison of Average Percentage Deviations.

Molecular groupings	C	C_1	C_2	C_3	$Ar_e^{-1}+B$	—L′	M′
Group VIIA-hydride............ (HF, HCl, HBr, HI)	16	1	21	13	1	9	11
Group IA-Group IA............ (Li_2, Na_2, K_2)	14	7	19	10	2	9	20
Group VA-Group VA........... (N_2, P_2)	27	16	17	36	..	5	13
Group IIB-hydride............ (ZnH, CdH, HgH)	4	4	24	21	17	17	28
Group VIIA-Group VIIA....... (Cl_2, Br_2, I_2, ICl)	8	2	14	8	7	8	10
Period 2-oxide................. (CO, NO, O_2)	3	12	17	14	10	6	7
Period 2-hydride.............. (CH, OH, HF)	8	13	11	11	11	1	1
All molecules..................	34	59	46	38	2000	28	38

use a single constant for all molecules.

The deviations from a constant of an empirical relation combining three spectroscopic constants is also given in Table 1. This is the C_2 of equation (1). The values of the deviations from C_2 are much greater within a group than are those of C_1 but somewhat better for all molecules. This better behavior when all molecules are considered is fortuitous, as can be seen by examination of the column which gives the deviations for the two parameter relation, $k_e D_e^{-1} = C_3$. In general C_3 is better than the three-parameter relation, C_2, within selected groups and also is better when all molecules are considered.

The conclusion indicated is that the spectroscopic constants may be combined in empirical relations which are reasonably accurate in predicting the values of one constant, in a given grouping of molecules. This appears to result from a fortuitous compensation in variation of the spectroscopic constants themselves. A good relation is obtained only by a judicious grouping of the original constants and does not depend on the number of constants used in the relation. In general, the opposite behavior is observed in selecting a closed relation to represent the potential energy curve.

The usual techniques of "fitting" experimental data (Scarborough, 1955: 473) to an empirical relation employ two arbitrary parameters to give a better "fit" than one arbitrary parameter and three to give a better "fit" than two, and so forth. The analytical expression of Frost and Musulin (1954a) leads to an empirical relation of the functional forms $k_e D_e^{-1} = A r_e^{-1} + B$. Previously a single constant, C_3, was used to describe the product $K_e D_e^{-1}$. This new functional form "fits" the product $k_e D_e^{-1}$ to a straight line function of r_e^{-1} by the use of two arbitrary constants, A and B. The constants A and B are determined in each grouping of molecules by the means of known experimental data. The deviations from a straight line are shown in Table 1. These deviations indicate that the adjustment of data to two arbitrary parameters does create a better "fit" to the data for molecules within a group but is much worse when one tries to fit all molecules to a single straight line.

The data indicate that it is possible to employ the usual mathematical techniques of obtaining a better "fit" to the data with an increased number of arbitrary parameters, within groupings of molecules. These data and those of the preceding columns also seem to indicate that one cannot obtain a good "fit" to both groupings of molecules and to all molecules at the same time. In fact, these results lead to a generalization of Varshni's (1957) statement that "there are no 'universal' relations connecting α_e and $\omega_e x_e$ with Δ" (the Sutherland parameter involving k_e, r_e, and D_e).

A second method of introducing a second arbitrary parameter was shown by Badger (1934) and Sutherland (1940). A term $(r\text{-}d)$ is used in their empirical relations where d is an arbitrary parameter. (There is some indication that this distance parameter may be correlated to the row of the Periodic

Table to which the constituent atoms of the diatom belong). Frost and Musulin (1954b) have also obtained relations introducing a second arbitrary parameter in this manner. Again the use of a second arbitrary parameter improves the "fit" within groupings of molecules, but this method of introducing the second parameter appears to also improve the "fit" for all molecules (Frost and Musulin, 1954b).

TWO NEW EMPIRICAL RELATIONS

Frost and Musulin (1954b) derived two new constants L and M, related to the third and fourth derivatives of the potential energy curve (and hence to α_e and $\omega_e x_e$, respectively). If one allows the second arbitrary parameter (the distance parameter) to go to zero in the expressions of L and M of Frost and Musulin (1954b), the following relations may be derived:

$$L' = \frac{\alpha_e \omega_e}{B_e^2}$$

$$M' = \frac{\omega_e x_e}{B_e}$$

where ω_e is the fundamental frequency, L' and M' are constants, and the other symbols have the significance previously given.

Since these are first order approximations, one would expect them to be less valid for all molecules. The preceding analysis would indicate that there might be an expectation that L' and M' would yield relations which would be consistent within certain groupings of molecules but not as good for all molecules. The deviations of L' and M' from constants in Table 1 do indicate that this is the case. These two new constants should prove useful in predicting values of α_e or ω_e and $\omega_e x_e$, although the relations would not be expected to hold for all molecules or for all states of a single molecule. The "fit" for all molecules is surprisingly good when compared to the other data in Table 1. M' does not appear to be as consistent as L', but this is not surprising when one considers that successive derivatives of the potential energy curve are more sensitive to errors (Frost and Musulin, 1954b).

Table 2 gives a comparison of the "fit" of L' and M' compared to L and M for the molecules given in the paper of Frost and Musulin (1954b). This table indicates that the first order approximations are not as good when considering all molecules, but in some instances the fortuitous compensations do give better "fits" within groupings of molecules.

TABLE 2.—Comparison of Average Percentage Deviations.

Molecular groupings	—L	—L′	M	M′
Group IA-Group IA	7	9	42	20
Group IIB-hydride	1	17	15	28
Group VIIA-Group VIIA	7	8	18	10
All molecules	12	31	42	39

An interesting aspect of these calculations is that the various empirical relations seem to be particularly valid, in many instances, in a given period of the Periodic Table. That relations of this type hold in periods, for polyatomic molecules, has been shown recently by Heath, *et al.* (1950).

SUMMARY

An equation giving a good representation of the potential energy curve does not necessarily provide a good relation between spectroscopic constants. In fact, it appears that a "good" relation between these constants occurs only because of the cancellation of variation in the constants. The usual mathematical methods of providing a better "fit" to a set of experimental data does lead to relations which are very useful for predicting values of unknown spectroscopic constants. This gain in usefulness is made only at the expense of losing a relation which will fit all molecules. This reasoning is used to derive two new relations useful in predicting the values of α_e or ω_e, and $\omega_e x_e$.

The use of empirical constants will continue to be useful to estimate spectroscopic constants in diatomic molecules and polyatomic molecules, but it does not seem possible to relate the varied spectroscopic behavior of many molecules or to ascertain by semi-empirical or mathematical analysis whether a given relation will be more useful than another.

ACKNOWLEDGMENT

This work was supported in part by the Graduate School of Southern Illinois University.

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Manuscript received July 1, 1959.