The Periodicity of Morse's Function

C. H. DOUGLAS CLARK, *Department of Inorganic Chemistry, University of Leeds, England*
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The applicability of a simple modification of Morse's rule has been tested, and found generally satisfactory for simple non-hydride di-atoms and for hydrides of the KH period. Morse's function is shown to possess a periodic character, and to be capable of adjustment by the intro- duction of group numbers and period constants on the basis of the classification of di-atoms suggested by the present author. The contention that di-atoms should be regarded from the standpoint of their periodic group functions thus appears especially significant.

I. INTRODUCTORY NOTE

IN the present communication, the term "di-atom" is used in place of the conventional "diatomic molecule," for reasons which will be detailed elsewhere.

The author's proposed classification of di-atoms into periodic groups[1] has suggested a number of relations between their spectroscopic constants. In the course of this work, it was found possible to improve Morse's function (see Eq. (1) below) for simple non-hydride di-atoms.[2] The modification may also be applied to hydride di-atoms of the KK period and, with certain limitations, to more complex cases. The purpose of the present communication is to show the periodic character of the function.

The group number of a di-atom is defined by the total number of valency electrons of the constituent atoms, and denoted by n. It corresponds to the number of "shared" electrons, as distinguished from "non-bonding" electrons, the shared electrons having their atomic quantum designations more or less strongly modified when union occurs.

The classification of non-hydride di-atoms is essentially three-dimensional and consists of combining in all possible ways different pairs of non-bonding groups with different groups of shared electrons. The basis is a two-dimensional matrix of combinations between pairs of com-pleted K, L, $M \cdots$ rings on a horizontal plane, as follows:

KK	KL	KM	$\cdots$
LK	LL	LM	$\cdots$
MK	ML	MM	$\cdots$
.	.	.	
.	.	.	
.	.	.	

Vertical lines, intersecting further horizontal planes defining molecular groups and sub-groups are then erected upon each compartment of the period matrix, used as a basal plane. The details will be communicated elsewhere.

The classification of hydride di-atoms is two-dimensional, periods being denoted by KH, LH, MH $\cdots$.

Elementary di-atoms are represented by sym-bols of the type $LiLi$, NN, OO, etc.

II. MORSE'S FUNCTION

Morse[3] proposed an empirical relation between the two fundamental magnitudes ω_e, the equi-librium nuclear vibration frequency for small amplitudes, and r_e, the equilibrium nuclear separation of a di-atom, to the effect that

$$\omega_e r_e^3 = \text{a constant.} \qquad (1)$$

Whilst several authors have pointed out that Morse's rule is subject in certain cases to con-siderable errors, no one appears to have in-vestigated the matter systematically up to the present time.

A careful examination shows that the Morse expression, far from assuming a constant value, is a periodic group function of the atoms con-cerned, at any rate in the simplest cases where data are available.

[1] C. H. Douglas Clark, Proc. Leeds Phil. Soc. **2**, 502 (1934).
[2] C. H. Douglas Clark, Phil. Mag. [7] **18**, 459 (1934).
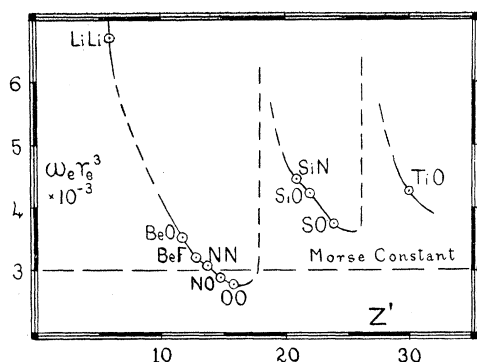[3] P. M. Morse, Phys. Rev. [2] **34**, 57 (1929).

FIG. 1. The periodicity of Morse's function in the case of simple non-hydride di-atoms containing at least one completed K ring, in their ground states.
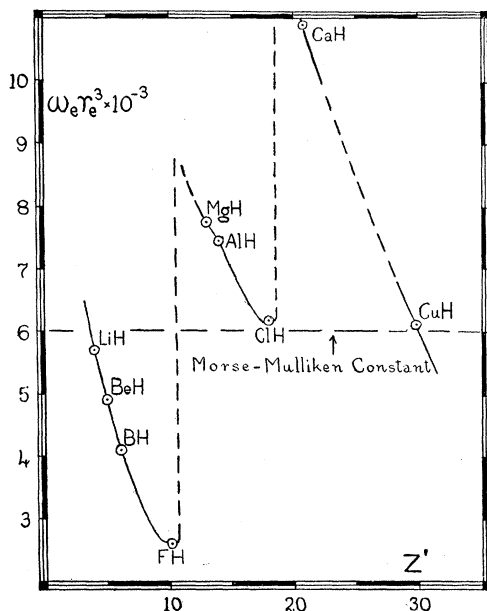

FIG. 2. The periodicity of Morse's function in the case of simple hydride di-atoms in their ground states.

The results are plotted in Fig. 1 (non-hydride di-atoms) and in Fig. 2 (hydride di-atoms) against the number of extranuclear electrons Z'. The periodic nature of the function is thus clearly demonstrated. The value of Morse's constant is taken as 3000 and 6000 for non-hydride and hydride di-atoms, respectively. The general form of the two curves is roughly the same. The apparent constancy of the function in the case of non-hydride di-atoms appears to have been due to the fact that the molecules considered were mainly those lying near the flattest portion

of the first sweep of the curve in Fig. 1. Whatever correction is appropriate for modifying Morse's expression, it appears that this periodicity must be compensated for.

The author[2, 4] has suggested a simple modification of Morse's function to the effect that

$$\omega_e r_e{}^3 \cdot n^{1/2} = K \qquad (2)$$

where K is a constant throughout any simple period of non-hydride di-atoms or di-atom ions. With the introduction of appropriate period constants determined empirically and with the group number n as defined above in all cases, very considerable improvement in the accuracy of the relation has been obtained. This is shown in Table I, for non-hydride di-atoms.

TABLE I.

Period	Period constant K	Number of electronic states considered	r_e calculated from ω_e Percentage average error	
			Morse	*Clark*
KK	9,550	29	5.2	1.3
KK^+	9,050	7	1.9	1.2
LK	12,850	7	9.2	1.3
Mean errors			5.4	1.3

The importance of a relation of the Morse type lies in the fact that it enables r_e to be calculated from ω_e in undetermined cases. These constants are required in the construction of potential energy-nuclear distance curves, by means of formulae due to Kratzer, Morse and others. The constants in these formulae are directly related to the fundamental constants of the Morse function. These curves are likely to be found of increasing practical usefulness in the interpretation of the mechanism of chemical reaction.

III. Graphical Representation of the Proposed Modification of Morse's Rule, as Applied to Simple Non-Hydride Di-Atoms

Fig. 3 shows the mean percentage errors in r_e's for different cases in the KK, KK^+ and KL molecular periods, as calculated by the method of Morse (thick lines) and of the author (barred lines). It is observed that Morse's errors tend to

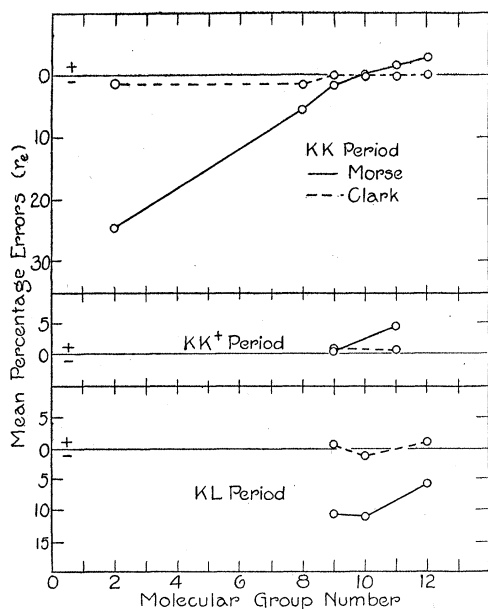[4] C. H. Douglas Clark, Nature **133**, 873 (1934).

Fig. 3. Comparison of mean percentage errors in r_e by the Morse and the modified Morse expressions in the KK, KK^+ and KL periods of non-hydride di-atoms.

Period KK mean errors:

	Group	Morse	Clark
	2	−24.7	−1.3
	8	−5.7	−1.9
	9	−1.9	0
	10	−0.2	0
	11	+1.4	−0.3
	12	+2.8	0
Period KK+:			
	9	+6.7	+0.9
	11	+4.8	+1.0
Period KL:			
	9	−10.5	+0.9
	10	−10.9	−1.3
	12	−5.8	+1.1

become increasingly positive with increasing group number in each period. In the KK period, Morse's errors become positive from a large negative error ($LiLi$). It thus happens that Morse's unmodified formula fits the facts best in the region of groups 9 to 11, where the line crosses the zero error line.

It should be borne in mind that in evaluating the cube of the equilibrium internuclear distance, any experimental error is correspondingly magnified. In comparing results obtained by the two methods, therefore, it is probably best to compare the function $r_e\omega_e^{1/3}$ with $r_e\omega_e^{1/3}n^{1/6}$. In Fig. 4, the logarithms of these functions to base 10 are plotted against molecular group numbers. The general parallelism of the two sets of curves amongst themselves is noteworthy. The Morse
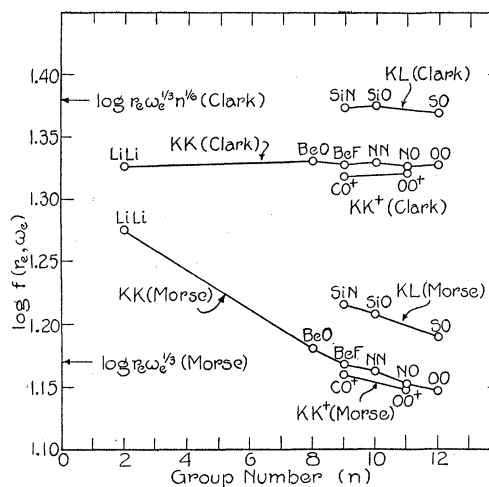

Fig. 4. Comparison of Morse and modified Morse expressions in the KK, KK^+ and KL periods of non-hydride di-atoms (ground states).

Period	Mol	$\log r_e\omega_e^{1/3}n^{1/6}$ (Clark)	$\log r_e\omega_e^{1/3}$ (Morse)
KK	LiLi	1.325	1.275
	BeO	1.331	1.181
	BeF	1.326	1.167
	NN	1.330	1.163
	NO	1.326	1.152
	OO	1.327	1.147
KK+	CO+	1.319	1.160
	OO+	1.322	1.148
KL	SiN	1.375	1.216
	SiO	1.375	1.209
	SO	1.370	1.190

functions *always fall* with increasing group number in each period. There is a *discontinuous* gap between different periods, with a small lowering for KK di-atom ions. The corrected expression gives *essential parallelism with the group axis*, as the condition for constancy requires.

Morse considered that with increasing atomic weight difference of the constituent atoms of a di-atom, an increasing correction of the type of an "asymmetry factor" $(4M_1M_2/(M_1+M_2)^2)^{1/4}$ might become necessary, where M_1, M_2 are the masses of the individual nuclei. When these masses are equal, the factor reduces to unity and therefore would not apply to the di-atom $LiLi$, where Morse's unmodified expression yields large errors in calculating internuclear distance of the order of 25 percent.[4] Hence it appears that, at any rate for the simpler cases, the correction should depend rather upon change of group number and of period, with a small correction for ionized states, as suggested by the present author.