

## ESTIMATION OF MOLECULAR CONSTANTS

### 2.1 INTRODUCTION: -

Numerous attempts have been made to correlate different molecular constants by empirical or semiempirical relations. The vibrational constant is one such important molecular constant and several relations have been suggested for its calculation<sup>1-8</sup>. Tandon et al<sup>9</sup> proposed a relation which gives about the dependence of the rotational constant on the electronegativity of the metal. He tested the applicability of the relation in the case of over one hundred diatomic halides. The relations suggested by various authors<sup>10-14</sup> indicate that the vibrational constant has inverse relationship with the reduced mass. Sharma and Hussain<sup>15</sup> proposed a relation for the evaluation of bond length inclusion of electronegativities. Tantti<sup>16</sup> has evaluated fundamental vibration energies in alkali halide molecules. Some attempts have been made to study the hybrid potential functions from Morse<sup>1</sup>, Rydberg<sup>17</sup> and Kratzer<sup>18</sup>. Iyer and Sharma<sup>19</sup> suggested the potential function which is a linear combination of Morse and Rydberg. Behere and others<sup>20</sup> derived a function which is a linear combination of Morse, Rydberg and Kratzer potential functions. Tulsigeri<sup>21</sup> has made a comparative study of Rydberg - Kratzer potential with different other potential functions through  $\alpha_e$  comparison. On the basis of least

percentage of deviation, Tulsigeri<sup>11</sup> stated that R-K potential function is found to be applicable to hydrides of alkaline earths and homonuclear diatomic molecules. All the hybrid potential functions suggested in literature are used for calculation of  $\alpha_e$  and  $w_e x_e$  using Varshni Criteria<sup>12</sup>. After critical examination it is concluded that the linear combinations of potentials to approximate a diatomic potential, it is seen that such linear combinations are worse as the number of individual potentials in the linear combination is increased. The average errors in  $\alpha_e$  and  $w_e x_e$  are not less than 20%.

For the purpose of the study of molecular spectra in astrophysical work, Pekeris<sup>10</sup> thought that it is necessary to examine the effect of the rotational motion on the vibrational levels of a diatomic molecule in which the internuclear potential is of the Morse form. The importance of rotational modification of the vibrational wave functions and the resulting possibilities of transition is of special interest in astrophysics since at the high temperatures involved the recorded band - head maximum intensities occur at high J - values. The importance of the rotational vibrational constant  $\alpha_e$  in the spectroscopy of diatomic molecules has been studied by many workers<sup>1, 11, 13, 15</sup>. The role of the Pekeris relation in the construction of potential energy

curves has been described by Murthy and Murthy<sup>25</sup>, however, its use yields poor estimates for  $\alpha_e$  in diatomic hydrides. As such, Reddy et al<sup>26</sup> determined a generalised relation for calculating the rotational - vibrational constant ( $\alpha_e$ ) for diatomic hydride molecules. An empirical relation between force constant and electronegativities of a diatomic molecule has been proposed by Gordy<sup>27</sup>.

In the studies of Molecular orbital theory, the bond orders which is defined as the amount of charge located on a bond is of great importance in the evaluation of various molecular parameters eg. dipolemoment and oscillator strength. This quantity also gives an insight into the understanding of chemical properties associated with the bond. The procedure used for the evaluation of bond order involved the linear combination of atomic orbitals on the two atoms joined by the bond with suitable coefficients. This, makes the computation of total bond order a tedious job. However, Parr and Borkman<sup>28-31</sup> and Politzer<sup>32-34</sup> suggested simple formulae for the calculation of bond order.

## 2.2. Dependence relations

Sharma and Hussain<sup>15</sup> have proposed a relation for bond length of diatomic hydride molecules, which has the form

$$w_e r_e^3 (X_A X_B)^{0.4} = K_s \quad \text{-----> (1)}$$

Where  $w_e$  is the vibrational frequency,  $X_A$ ,  $X_B$  are

the electronegativities of constituent atoms of a molecule,  $r_e$  is the bond length and  $K_s$  is a constant for a molecular period. The values of  $K_s$  are evaluated for each molecular period and it is taken as a constant. The accuracy of the results mainly depend on  $K_s$  for which good experimental constants are to be considered. Keeping  $K_s$  as a constant for each molecular period, the rest of the parameters are estimated. Reddy et al<sup>35</sup> have proposed a relation for the calculation of bond order (q), the relation is as follows

$$q = 1.5783 \times 10^{-3} \left( \frac{w_e^2 r_e^{1/2}}{B_e} \right) \text{-----} (2)$$

Here  $B_e$  is the rotational constant. The other symbols have their usual significance.

According to Herzberg<sup>14</sup>

$$r_e = \frac{4.1061}{\sqrt{\mu B_e}} \text{ in } (A^\circ) \text{-----} (3)$$

where  $\mu$  is the reduced mass.

Substituting equations (3) and (2) in equation (1) the following relation is obtained

$$q = 3.8438 \times 10^{-4} \left[ \frac{K_s w_e \mu}{(\chi_A \chi_B)^{0.4}} \right]^{1/3} \text{-----} (4)$$

The suggested relation for the computation of vibrational - rotational constant ( $\alpha_e$ ) of hydride molecules is as

follows.

$$\alpha_e = \frac{415.37 (X_A, X_B)^{0.4} (w_e x_e^{1/2} - B_e^{1/2})}{\mu^{1.5} K_s} \quad \text{-----} \rightarrow (5)$$

In equation 5,  $w_e x_e$  is the anharmonic constant. The necessary experimental spectroscopic constants and electronegativity values are taken from Huber and Herzberg<sup>36</sup> and Pauling<sup>37</sup>.

### 2.3. Results and Discussion

Utilising equation (1), the bond lengths for various diatomic hydrides molecules are evaluated and are presented in table.1. These values are in good agreement with the literature values.  $K_s$  values are also listed in the same table. The author's main aim is to use Sharma and Hussain relation (equation (1)) for the evaluation of bond order ( $q$ ) and vibrational - rotational constants ( $\alpha_e$ ) of diatomic molecules. The advantage of the equation (4) is that one can evaluate bond orders by knowing vibrational frequency ( $w_e$ ) only. Since reduced mass ( $\mu$ ) and electronegativity values ( $X_A, X_B$ ) are readily available values. The relations proposed by Parr and Borkman<sup>31</sup> and Reddy et al<sup>35</sup> requires three molecular constants ( $w_e, B_e$  and  $r_e$ ) for the evaluation of bond orders. Bond orders are calculated for various diatomic hydride molecules using equation (4) and are presented in Table.2. For the purpose of comparison,  $q$  values are

TABLE - 1  
 COMPARISON OF BOND LENGTHS ( $r_e$ ) OF DIATOMIC HYDRIDE  
 MOLECULES.

Molecule	$K_s$	$r_e(\text{A}^\circ)$ (Cal)	$r_e(\text{A}^\circ)$ (exptl.)
LiH	7694.55	1.5957	1.5957
BeH		1.3307	1.3426
BH		1.2228	1.2324
CH		1.1146	1.1199
OH		1.0389	1.0362
HF		0.9746	0.9696
NaH	12321.21	2.0122	1.8874
MgH		1.7856	1.7297
AlH		1.6664	1.6478
SiH		1.5248	1.5201
PH		1.4223	1.4223
SH		1.3277	1.3409
HCl		1.2542	1.2745
KH	13650.21	2.2425	2.2425
CaH		1.9843	2.0025
GaH		1.7368	1.6630
GeH		1.6453	1.5880
AsH		1.5340	(1.5344)
SeH		1.4387	(1.4750)
HBr		1.3638	1.4144
RbH		15290.80	2.3670
SrH	2.1120		2.1456
InH	1.8397		1.8380
CsH	16752.49	2.5259	2.4938
BaH		2.2317	2.2317
TlH		1.9191	1.8702
PbH		1.8462	1.8388
BiH		1.8057	1.8050

TABLE - 2  
 COMPARISON OF BOND ORDERS ( $q$ ) OF VARIOUS DIATOMIC HYDRIDE  
 MOLECULE.

Molecule	$K_e$	$q$ (present method)	$q/(0.5r_e)^2$	$q$ Ref.35	$q$ Ref.35
LiH	7684.55	1.044	1.640	1.019	1.02
BH		1.182	2.113	1.196	0.89
CH		1.246	3.976	1.255	1.25
NH		1.295	4.825	1.290	1.29
BeH		1.158	2.569	1.173	1.17
OH		1.346	5.726	1.335	1.33
HF		1.385	6.593	1.366	1.36
NaH		1.264	1.419	1.148	1.14
MgH		1.348	1.803	1.286	1.28
AlH		1.371	2.020	1.348	1.34
SiH		1.457	2.523	1.451	1.46
PH	12321.21	1.523	3.012	1.523	1.54
SH		1.576	3.506	1.611	--
HCl		1.598	3.935	1.637	1.63
KH	13650.21	1.258	1.001	1.258	1.25
CaH		1.383	1.379	1.402	1.39
GaH		1.407	2.035	1.318	--
GeH		1.469	2.331	1.406	--
AsH		1.551	2.635	1.552	--
SeH		1.558	2.920	1.649	--
HBr		1.618	3.235	1.709	1.70
RbH	15290.80	1.309	0.934	1.309	1.30
SrH		1.420	1.234	1.454	1.45
InH		1.378	1.631	1.413	--
CsH		1.375	0.884	1.349	1.34
BaH	16752.49	1.497	1.203	1.497	1.49
TlH		1.424	1.628	1.369	--
PbH		1.510	1.786	1.501	--
BiH		1.528	1.876	1.530	--

also estimated using equation (2) of Reddy et al<sup>35</sup> and Parr and Borkman<sup>31</sup> and are included in the same table. The results are in good agreement with the literature values<sup>31</sup>. The results in table 2 shows that OH, HF, AlH, GaH, RbH, CsH and SiH, SrH and BaH have same 'q' values 1.3 and 1.45 respectively. It has no meaning in having the same bond order for different molecules. To understand the special characteristic features of bond order, the author equation (2) is employed and evaluated the bond orders for ionised and non-ionised molecules also. The relevent results are presented in table 3. It is interesting to note here also that BeH<sup>+</sup>, CH, CdH, OH<sup>+</sup> and ZnH are of having the same bond order of 1.2.

This odd behaviour is already observed by many workers<sup>35, 38, 40</sup>. This discrepancy may be removed by considering Politzer's<sup>33, 34</sup> view. According to him, the correct definition for bond order is  $q/(0.5 r_e)^2$  but not simple q. These values are also presented in the same table. The present study strongly supports Politzer's view.

Szoke pointed out that the molecular ions are formed by removal of a bonding or antibonding electron. If a bonding electron is removed, the bond order decreases by 0.5. In the opposite case, it increases by same value. This is based on the



Table 3. Bond orders of diatomic ionized and non-ionized molecules

Molecules	q	$q/(0.5 r_e)^2$
$^{27}\text{Al}^1\text{H}$	1.348	1.985
$^{75}\text{As}^{16}\text{O}$	2.793	4.238
$^{75}\text{As}^{16}\text{O}^+$	2.991	4.866
$^{75}\text{As}^{32}\text{S}^+$	2.961	2.910
$^{75}\text{As}^{32}\text{S}^+$	3.179	3.362
Be Ar <sup>+</sup>	1.158	1.065
$^9\text{Be}^1\text{H}$	1.173	2.602
$^9\text{Be}^2\text{H}^+$	1.222	2.838
$^9\text{Be}^2\text{H}$	1.173	2.605
$^9\text{Be}^2\text{H}^+$	1.220	2.838
$^{12}\text{C}_2$	2.418	6.264
$^{12}\text{C}_2^+$	1.886	4.457
$^{12}\text{C}_2^-$	2.395	5.956
$^{114}\text{Cd}^1\text{H}$	1.220	1.539

Contd.

Table 3 (continued)

Molecules	q	$q/(0.5 r_e)^2$
$^{114}\text{Cd}^1\text{H}^+$	1.466	2.109
$^{114}\text{Cd}^2\text{H}^+$	1.465	2.115
$^{12}\text{C}^1\text{H}$	1.255	4.002
$^{35}\text{Cl}_2$	2.521	2.551
$^{12}\text{C}^{14}\text{N}$	2.564	7.468
$^{12}\text{C}^{14}\text{N}^+$	2.523	7.335
$^{12}\text{C}^{16}\text{O}$	2.617	8.222
$^{19}\text{F}_2$	1.822	3.655
$^{19}\text{F}_2^+$	1.933	4.424
$^1\text{H}_2$	0.766	5.574
$^1\text{H}^{81}\text{Br}$	1.709	3.416
$^1\text{H}^{81}\text{Br}^+$	1.632	3.111
$^1\text{H}^{35}\text{Cl}$	1.637	4.030
$^2\text{H}^{35}\text{Cl}^+$	1.534	3.550
$^1\text{H}^{19}\text{F}$	1.366	6.500
$^1\text{H}^{19}\text{F}^+$	1.164	4.645

Contd.

Table 3 (continued)

Molecules	q	$q/(0.5 r_e)^2$
$^{24}\text{Mg}^1\text{H}$	1.285	1.717
$^{24}\text{Mg}^2\text{H}$	1.284	1.717
$^{24}\text{Mg}^2\text{H}^+$	1.364	1.999
$^{14}\text{N}_2$	2.759	9.159
$^{14}\text{N}^{16}\text{O}$	2.493	7.530
$^{14}\text{N}^{16}\text{O}^+$	2.737	9.682
$^{16}\text{O}_2$	2.279	6.252
$^{16}\text{O}^1\text{H}$	1.336	5.682
$^{16}\text{O}^1\text{H}^+$	1.216	4.594
$^{16}\text{O}^2\text{H}$	1.334	5.678
$^{16}\text{O}^2\text{H}$	1.218	4.607
$^{31}\text{P}_2$	3.077	3.433
$^{31}\text{P}_2^+$	2.845	2.885
$^{31}\text{P}^{19}\text{F}$	2.238	3.542

Contd.

Table 3 (continued)

Molecules	$q$	$q/(0.5 r_e)^2$
$^{31}\text{P}^{19}\text{F}^+$	2.553	4.536
$^{28}\text{Si}^1\text{H}$	1.451	2.511
$^{28}\text{Si}^1\text{H}^+$	1.508	2.666
$^{64}\text{Zn}^1\text{H}$	1.239	1.948
$^{64}\text{Zn}^1\text{H}^+$	1.367	2.382

separated atomic orbital configuration. The present results reveal that there can be decrease or increase in the bond order for ionised molecules. Parr and Borkman<sup>31</sup> pointed out that bond order values for positively charged species are generally lower than the parent neutral compounds. It is not true in all cases. In the case of AsO, AsS, CdH, ZnH, NO, SiH, MgH and its ionised molecules, it is different eg.  $q(\text{NO}) = 2.49$ ,  $q(\text{NO}^+) = 2.73$ ,  $q(\text{LiH}) = 1.22$ ,  $q(\text{CdH}^+) = 1.46$  etc. A keen observation of the results reveals that there is a correlation between the bond order and the molecular parameters. If the vibrational frequency for the ionized molecule is high its bond order is also high compared to its non-ionized molecule. Similarly, if the internuclear distance for the ionized molecule is high, its bond order is low. Compared to its non-ionized molecule. From this study it is concluded that there must be, a definite relation between bond order, vibrational frequency and internuclear distance.

Utilising equation (5), the vibrational - rotational constants ( $\alpha_e$ ) are estimated and are presented in table 4. For the purpose of comparison,  $\alpha_e$  values are also evaluated using Pekeris relation<sup>12</sup>. The chief merit of equation (5) is that only knowledge of  $w_e$ ,  $x_e$  and  $B_e$  is enough to evaluate  $\alpha_e$ , where as in Pekeris relation an addition of  $w_e$  is also needed. An average percentage deviation obtained for the present and Pekeris

TABLE - 4  
 COMPARISON OF VIBRATIONAL-ROTATIONAL CONSTANTS ( $e_{\nu}$ ) VALUES OF  
 VARIOUS DIATOMIC HYDRIDE MOLECULES.

Molecule	$K_{\nu}$	$\alpha C_e$ ( $\text{cm}^{-1}$ )			
		Cal	Pekeris	Exptl	
LiH	7684.55	0.1835	0.1824	0.2132	
BeH		0.2789	0.2714	0.3030	
BH		0.3852	0.3762	0.4170	
CH		0.4841	0.4772	0.5340	
VH		0.5900	0.5944	0.6490	
OH		0.6325	0.6421	0.7242	
HF		0.6631	0.6819	0.7980	
MgH	12321.21	0.1659	0.1824	0.1859	
SiH		0.1926	0.1944	0.2190	
PH		0.2373	0.2372	0.2514	
SH		0.3160	0.3003	(0.2700)	
HCl		0.2913	0.2775	0.3072	
KH	13650.21	0.0745	0.744	0.0817	
CaH		0.0811	0.0941	0.0970	
GeH		0.1824	0.1991	0.1916	
HBr		0.2374	0.2128	0.2333	
RbH		15290.80	0.683	0.0683	0.0720
SrH			0.0811	0.0773	0.0814
InH			0.1349	0.1282	0.1428
CsH	0.0564		0.0586	0.0579	
BaH	16752.49	0.0629	0.0629	0.0660	
PbH		0.1355	0.1371	0.1440	
BiH		0.1440	0.1433	0.1480	

Average % of deviation

relations are 6.63 and 7.31 respectively. Our values are in good agreement with experimental values. Hence, it is concluded that equation (5) can be used for the evaluation of  $\alpha_e$ .

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