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THE RELATIVE STRENGTHS OF IONIC, COVALENT AND MULTIPLE-BONDING IN DIATOMIC MOLECULES *

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ABSTRACT

Values of the ratio $[D_0 : e^2/r_e]$ are examined for diatomic molecules in which the bonding is essentially ionic, covalent, or multiple in character (D_0 is the dissociation energy, and e^2/r_e the coulombic energy of attraction of point-changes at the internuclear bondlength, r_e). The ratio values in single-bonded diatomic molecules range from (0.75 ± 0.17) in the essentially ionic alkali-metal halides, to (0.16 ± 0.03) in the covalent alkali-metal dimers. For multiple-bonded covalent M_2 molecules, the ratio reaches 0.74 in triple-bonded N_2 and 0.56 in sextuple-bonded Mo_2; but in many first-row transition dimetals, multiple bonding does not lead to high ratio values. Higher ratios do occur in MO molecules. In relative terms, ionic character—in particular when associated with multiple bonding—is more effective than multiplicity per se in bond-strengthening.

INTRODUCTION

The diatomic molecules formed by the alkali metals are single-bonded, ranging from ion-pairing, $\overset{+}{M}\overline{X}$, in the halides, to covalent M–M bonding in the dimetals. Single bonding is also the case in the halogens, and in the hydrides, MH, of all metals. In many other diatomic molecules, multiple bonding is to be expected; e.g. in the oxides MO in which the bonding extremes range from $M^{2+}O^{2-}$, $\overset{+}{M}\text{–}\overline{O}$, M=O, to $\overline{M} \equiv \overset{+}{O}$. Multiple bonding is the basis of strong binding in several diatomic molecules, notably in CO ($D_0 = 1072$ kJ mol^{-1}), NO$^+$ ($D_0 = 1047$ kJ mol^{-1}), and N_2 ($D_0 = 942$ kJ mol^{-1}), but it is not a guarantee of it, nor a prerequisite to it. In certain transition-metal dimers, the bonding is weak, despite high multiplicity, whereas in many metal halide single-bonded molecules the bonding is strong, even for bondlengths well in excess of 2 Å. Ion-pairing, $\overset{+}{M}\overline{X}$, is the strongest form of single bonding, and for polarized ion-pairs in contact, the attractive energy can approach (and even exceed) the coulombic potential,

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e^2/r_e, of point-changes at the equilibrium separation, r_e. The dissociation energy, D_0, to form neutral atoms is less than the ion attraction by an amount equal to the energy needed to convert the neutral atoms into charged ions, $M + X \rightarrow \overset{+}{M} + \overset{-}{X}$; nevertheless, for the more electropositive elements, M, the ion-pairing term remains dominant, and the bonding energy is high.

The average value of the ratio of $D_0(MX)$ to the coulombic potential, e^2/r_e, in the alkali-metal halides is 0.75. This is much larger than the values of this same ratio in covalent single-bonded M–M or X–X molecules, and is actually larger than the ratio value in triple-bonded N_2. The purpose in this paper is to compare values of the ratio $[D_0 : e^2/r_e]$ in diatomic MX molecules, as an assessment of the relative power of ionic and multiple bonding in different types of molecules.

ALKALI-METAL HALIDES

The binding in alkali-metal halide diatomic molecules is essentially ionic, as described by the ion-pair model of Rittner [1], for which the total binding energy (at internuclear separation r) is given by:

$$W(r) = -\frac{e^2}{r} - \frac{e^2(\alpha_1 + \alpha_2)}{r^4} - \frac{2e^2\alpha_1\alpha_2}{r^7} + Ae^{-r/\rho} - \frac{C}{r^6} \quad (1)$$

The first term is the coulombic attraction of the ions, the second and third terms arise from their mutual polarization, and $Ae^{-r/\rho}$ is the Born–Meyer potential for the repulsion of ions in contact. The last term is the Van der Waals dipole–dipole interaction energy. Rittner used values for the electronic polarizabilities of the ions, α_1 and α_2, evaluated by Pauling [2], but it has since been pointed out [3] that the polarizabilities in a molecule will differ significantly from the free-state values of Pauling. A recent re-appraisal of the original Rittner model by Shanker et al. [4] used "in-molecule" polarizabilities in place of Pauling's free-state values in eqn. (1) to predict the dipole moments, bonding energies, vibrational ($\omega_e x_e$) and rotational constants (α_e) for the alkali-metal halide diatomic molecules; the predicted values agree with experiment within an average deviation of less than 5%.

The comparison of predicted with experimental bond-dissociation energies in alkali-metal halides is made in Table 1. The experimental data are those recommended in recent critical tables compiled by Glushko and Gurvich [5] and by Huber and Herzberg [6]. The values D_0(obs), in kJ mol^{-1}, refer to the dissociation process:

$$MX(g) \rightarrow M(g) + X(g) \quad (2)$$

TABLE 1

Alkali-metal halides; D_0(obs) and D_0(calc) values

MX	D_0 (obs)	D_0 (calc)	e^2/r_e	$-W(r_e)$	$\frac{\langle D_0(\text{obs})\, r_e \rangle}{\langle e^2 \rangle}$
LiF	576	565	888	763	0.648
NaF	479	476	721	647	0.664
KF	494	489	640	582	0.772
RbF	491	488	612	565	0.802
CsF	517	505	592	555	0.872
LiCl	471	438	688	614	0.685
NaCl	408	386	588	535	0.693
KCl	422	410	521	482	0.810
RbCl	423	407	499	463	0.849
CsCl	438	421	478	449	0.916
LiBr	419	384	640	580	0.654
NaBr	363	339	555	510	0.654
KBr	378	366	492	460	0.767
RbBr	382	369	472	448	0.810
CsBr	393	380	452	432	0.869
LiI	348	311	581	536	0.599
NaI	302	277	512	476	0.589
KI	322	306	456	429	0.706
RbI	324	307	437	415	0.741
CsI	334	324	419	404	0.797
CuF	427	333	796	754	0.536
CuCl	379	264	677	663	0.560
CuBr	331	212	639	635	0.518
CuI	[285]	150	595	602	[0.48]
AgF	351	291	702	697	0.500
AgCl	311	223	609	607	0.512
AgBr	299	190	581	598	0.515
AgI	[230]	130	546	566	[0.42]

at 0 K, yielding atoms in ground states. The D_0(calc) values derive from:

$$D_0(\text{calc}) = -W(r_e) - 1/2hc\omega_e - I + E \qquad (3)$$

where I = ionization potential of M, and E = electron affinity of X. Table 1 lists values of e^2/r_e and $-W(r_e)$, and of the ratio of D_0(obs) to e^2/r_e. In all cases, this ratio is less than unity, and $e^2/r_2 > -W(r_e) > D_0$(obs). Table 1 includes results obtained from application of the modified Rittner model to the halides of Cu and Ag; as with the alkali-metal halides, $e^2/r_e > D_0$(obs), but $-W(r_e)$ is nearer to, and is sometimes larger than, e^2/r_e. (The main factor enhancing $-W(r_e)$ is the Van der Waals term, C/r_e^6, which is larger in the halides of Group 1B than in the alkali-metal halides.)

TABLE 2

Alkali-metal hydrides: D_0(obs) and D_0(calc) values

MH	D_0 (obs)	D_0 (calc)	e^2/r_e	$-W(r_e)$	$[D_0 : e^2/r_e]$
LiH	234	222	871	678	0.27
NaH	181	162	736	592	0.25
KH	178	164	620	516	0.29
RbH	176	160	587	497	0.30
CsH	175	174	557	481	0.315

ALKALI-METAL HYDRIDES

Results obtained from application of the modified ion-pair Rittner model to alkali-metal hydrides [7] are summarized in Table 2. As with alkali-metal halides, $e^2/r_e > -W(r_e) > D_0$(obs), but here $e^2/r_e \gg D_0$(obs), and the highest value of the $[D_0 : e^2/r_e]$ ratio (0.315 in CsH) is well below the lowest in Table 1.

The covalent contribution to M–H bonding in the alkali-metal hydrides is of the type *s–s*, and the ratio values lie above the norm for purely covalent *s–s* bonds (Table 3). They are augmented by the substantial ionic participation in alkali-metal hydride bonds (the measured dipole in LiH(g) is 5.88*D*, almost as large as in LiF, where $\mu = 6.28D$).

SINGLE-BONDED M_2 AND MH MOLECULES

In single-bonded covalent M_2 molecules, values of the ratio $[D_0 : e^2/r_e]$ fall well below those in alkali-metal halides. Table 3 shows this, giving ratio values in the Group I metal dimers, in halogens, and in interhalogen diatomics. The *s–s* covalent bonding in the alkali-metal dimers is less strong, relatively, than *p–p* covalent bonding in the halogens by a factor of two, except for F_2, where the bonding is exceptionally weak [8]. In contrast, the bonding in Cu_2 and Au_2 is stronger than normal for covalent *s–s*

TABLE 3

$[D_0 : e^2/r_e]$ ratios in M_2 molecules

Molecule	$D_0 : e^2/r_e$	Molecule	$D_0 : e^2/r_e$	Molecule	$D_0 : e^2/r_e$
H_2	0.231	Cu_2	0.313	FCl	0.296
Li_2	0.194	Au_2	0.395	BrCl	0.331
Na_2	0.156	F_2	0.157	ICl	0.347
K_2	0.14	Cl_2	0.342	FBr	0.311
Rb_2	0.141	Br_2	0.312	IBr	0.312
Cs_2	0.14	I_2	0.286	FI	0.382

TABLE 4

$[D_0 : e^2/r_e]$ ratios in MH molecules

LiH	BeH	BH	CH	NH	OH	FH		
0.27	0.18[5]	0.29[5]	0.27	0.26	0.29[5]	0.37		
NaH	MgH	AlH	SiH	Ph	SH	ClH		
0.25	0.16[5]	0.35	0.32	0.31	0.34	0.39		
KH	CaH					MnH	CoH	NiH
0.29	0.235					(0.30)	(0.34)	0.31[5]
CuH	ZnH	GaH	GeH	AsH	SeH	BrH		
0.28	0.09[5]	0.32[5]	0.36	0.38	0.33	0.37		
RbH	SrH							
0.30	0.24							
AgH	CdH	InH	SnH			IH		
0.26	0.08	0.32	0.34			0.34		
CsH	BaH	YbH						PtH
0.31	0.30[5]	0.27[5]						0.36[5]
AuH	HgH	TlH	PbH	BiH				
0.34	0.04[6]	0.25[5]	0.20	0.36				
BeH^+	BH^+	CH^+	NH^+	OH^+				
0.29	0.16	0.32	0.37	0.37				
MgH^+		SiH^+	PH^+	SH^+				
0.29		0.33	0.3	0.33				
ZnH^+								
0.26								
CdH^+								
0.24								
HgH^+								
0.33								

bonding, and it may be that a contribution of *d*-character is present, from some participation of d^9s^2 excited states of Cu and Au in the bonding.

Table 4 lists ratio values in MH molecules and MH^+ molecule-ions. For hydrides formed by the elements from Groups 3–7, the covalent *p*–*s* M–H bonding may be augmented by ionic contributions, either from $\overset{+}{M}\overset{-}{H}$ (when M is from Group 3 or 4) or from $\overset{-}{M}\overset{+}{H}$ (when M is from Group 7 or 6). The average value of $[D_0 : e^2/r_e]$ is 0.32, ranging from 0.20 (in PbH) to 0.39 (in HCl). For the hydrides of Group 2B, however, the ratio values are very low (average 0.07), and in Group 2A hydrides only BaH, SrH and CaH have ratio values comparable with those in alkali-metal hydrides. The high values of the ionization potentials of Zn, Cd and Hg (867–1006 kJ mol^{-1}), coupled with those for excitation to the divalent ^3P states of these atoms (360–450 kJ mol^{-1}) limit the strengthening effect from contribution of the $\overset{+}{\mathrm{M}}\overline{\mathrm{H}}$ ion-pair, and of p–s M–H covalent bonding to the weak s^2–s bonding from ground-state ^1S atoms. The lower ionization potentials in Ca, Sr, Ba (503–590 kJ mol^{-1}), and the lower excitation energies to reach the ^3P divalent states (147–181 kJ mol^{-1}) are far less prohibitive, and the $[D_0 : e^2/r_e]$ ratio values regain the normal magnitude for p–s M–H bonding.

MF AND MCl DIATOMIC MOLECULES

In MF and MCl diatomic molecules, the bonding extremes range from $\overset{+}{\mathrm{M}}\overline{\mathrm{X}}$ ion-pairing, through covalent M–X, to the back-coordinated $\overline{\mathrm{M}}=\overset{+}{\mathrm{X}}$ structure, which latter is most relevant in MX molecules from Groups 3 and 4. (The dipole moment in CF is small ($\mu = 0.65$), but oriented in the sense $\overline{\mathrm{C}}\overset{+}{\mathrm{F}}$, indicating an appreciable contribution from back-coordination in this molecule.) Ratio values for MF and MCl are listed in Tables 5 and 6; these are highest in Groups 1 and 2 (average ca. 0.7), and least in Groups 6 and 7 (average ca. 0.3), indicating that the relative binding strength is maximal when ion-pairing, $\overset{+}{\mathrm{M}}\overline{\mathrm{X}}$, is dominant. The ratio values in Groups 3 and 4 are

TABLE 5

$[D_0 : e^2/r_e]$ ratios in MF molecules

LiF	BeF	BF	CF	NF	OF	FF
0.65	0.56	0.67	0.50	0.27	0.21	0.16
NaF	MgF	AlF	SiF	PF	SF	ClF
0.66	0.57	0.80	0.63	0.50	0.39	0.30
KF	CaF	ScF				
0.77	0.74	0.77				
CuF		GaF	GeF	AsF	SeF	BrF
0.54		0.74	0.61	0.51	0.39	0.31
RbF	SrF	YF				
0.80	0.81	0.83				
AgF		InF	SnF	SbF		IF
0.50		0.73	0.66	0.59		0.37
CsF	BaF					
0.87	0.90					
		TlF	PbF			
		0.66	0.51			

TABLE 6

[$D_0 : e^2/r_e$] ratios in MCl molecules

LiCl	BeCl	BCl	CCl		OCl	FCl
0.68	0.50	0.70	0.47		0.30	0.30
NaCl	MgCl	AlCl	SiCl	PCl		ClCl
0.69	0.51	0.76	0.63	0.48		0.34
KCl	CaCl	ScCl				
0.81	0.67	0.84				
CuCl		GaCl	GeCl			BrCl
0.56		0.73	0.65			0.33
RbCl	SrCl					
0.85	0.76					
AgCl		InCl	SnCl			ICl
0.51		0.74	0.65			0.35
CsCl	BaCl					
0.92	0.87					
		TlCl	PbCl	BiCl		
		0.66	0.53	0.56		

about as high as those in Groups 1 and 2, augmented here by the back-coordinated effect.

MO DIATOMIC MOLECULES

The [$D_0 : e^2/r_e$] ratio values (Table 7) for the single-bonded MO molecules of Groups 1 and 7 range from 0.21 (in FO) to 0.49 (in CsO), the average value being 0.36. In multiple-bonded MO molecules from other groups, the average ratio value is almost twice as large, and in ThO (1.15), LaO (1.05) and CeO (1.03), the ratio values exceed unity. It is noteworthy that the ratio values for the Group 3 transition-metal oxides, ScO, YO and LaO, are much larger than those of GaO, InO and TlO. The ionization potentials of all these metals are of similar magnitude (540–630 kJ mol^{-1}), but the excitation energies needed to reach the lowest trivalent atomic state are much less for Sc, Y and La (138, 131 and 32 kJ mol^{-1}) than for Ga, In and Tl (454, 418 and 541 kJ mol^{-1}, respectively). Hence, the barriers to double-bonding, M=O, are relatively small in ScO, YO and LaO and are almost zero in the molecule-ions, $\overset{+}{\mathrm{M}}{=}\mathrm{O}$, deriving from divalent Sc$^+$, Y$^+$ and La$^+$. Comparison of ratio values in $\overset{+}{\mathrm{M}}\mathrm{O}$, MO and M_2O in Table 8 shows these differences clearly. The higher ratio values in $\mathrm{S}\overset{+}{\mathrm{c}}\mathrm{O}$ and ScO, $\overset{+}{\mathrm{Y}}\mathrm{O}$ and YO, and $\mathrm{L}\overset{+}{\mathrm{a}}\mathrm{O}$, LaO point to double bonding, and the lower ratios in Sc_2O,

TABLE 7

[$D_0 : e^2/r_e$] ratios in MO molecules

LiO	BeO	BO	CO	NO	OO	FO		
0.41	0.42	0.69	0.87	0.52	0.43	0.21		
NaO	MgO	AlO	SiO	PO	SO	ClO		
0.37	0.45	0.59	0.86	0.63	0.55	0.30		
KO	CaO	ScO	TiO	VO	CrO	MnO	FeO	
[0.45]	0.50	0.81	0.78	0.70	0.53	0.45	0.46	
CuO		GaO	GeO	AsO	SeO	BrO		
0.33		0.46	0.76	0.56	0.51	0.29		
RbO	SrO	YO	ZrO	NbO	MoO		RuO	
[0.46]	0.58	0.92	0.94	0.92	0.68		0.63	
AgO		InO	SnO	SbO	TeO	IO		
0.32		0.45	0.69	0.56	0.49	0.30		
CsO	BaO	LaO	CeO					
[0.49]	0.77	1.05	1.03					
		LuO	HfO	TaO	WO		IrO	PtO
		0.89	0.98	0.95	0.83		0.44	0.46
		TlO	PbO	BiO				
		[0.35]	0.51	0.47				
			ThO		UO	PuO		
			1.15		0.98	0.86		

Y_2O and La_2O to single bonding (with appreciable ionic character). The bondlengths reflect this, and are longer in M_2O than in the monoxides. By contrast, the ratio values in GaO, InO and TlO are smaller than in Ga_2O,

TABLE 8

[$D_0 : e^2/r_e$] ratios in $\overset{+}{M}O$, MO and M_2O molecules

Molecule	r_e	D_0 [a]	$D_0 : e^2/r_e$	Molecule	r_e	D_0 [a]	$D_0 : e^2/r_e$
$\overset{+}{Sc}O$	1.65	(700)	0.83				
ScO	1.666	677	0.81	GaO	1.725	370	0.46
Sc_2O	1.75	509	0.64	Ga_2O	1.82	440	0.58
$\overset{+}{Y}O$	1.75	734	0.93				
YO	1.788	714	0.92	InO	1.97	315	0.45
Y_2O	1.85	545	0.73	In_2O	2.0	383	0.55
$\overset{+}{La}O$	1.80	825	1.07				
LaO	1.826	797	1.05	TlO	2.10	(236)	0.35
La_2O	1.90	577	0.79	Tl_2O	2.10	287	0.43

[a] The D_0 values in M_2O are mean values, $= \Delta E^0$(atomization)/2.

In_2O and Tl_2O; double bonding is either not achieved, or only at high cost reducing the value of D_0.

M_2 DIATOMIC MOLECULES

In M_2 diatomic molecules of Groups 3–7, the bonding ranges from single-bonded M–M in the halogens to triple bonding in N_2, P_2 and other M_2 molecules from Group 5. In the transition dimetals, the range is from the single bonds in Cu_2, Ag_2 and Au_2 to the sextuple bonding of Cr_2 and Mo_2 [9]. The available $[D_0 : e^2/r_e]$ ratio values for M_2 molecules are listed in Table 9. The highest values occur in triple-bonded N_2 and P_2, and in multiple-bonded Nb_2 and Mo_2, but in no case do ratios approach close to unity, or exceed it, as in MO molecules. In the first-row transition dimetals, V_2 and Cr_2, the equilibrium bond lengths are consistent with multiple bonding, but the D_0 values are barely more than to be expected for single bonding, and the ratio values are correspondingly low. The ratio values in the second-row transition dimetals Nb_2 and Mo_2 are three times as large as for their first-row counterparts. The metallic bonding in the second and third-row transition metals (as indicated by the energies of atomization of these elements) is markedly stronger than in first-row transition metals, and the ratio values in Ta_2 and W_2 should prove to be at least as large as in Nb_2

TABLE 9

$[D_0 : e^2/r_e]$ ratios in M_2 molecules

B_2 0.33	C_2 0.54	N_2 0.74	O_2 0.43	F_2 0.17			
Al_2 0.27	Si_2 0.50	P_2 0.66	S_2 0.57	Cl_2 0.34			
	Ge_2 0.44	As_2 0.58	Se_2 0.51	Br_2 0.31			
	Sn_2 0.36	Sb_2 0.50	Te_2 0.48	I_2 0.29			
Tl_2 (0.12) [10]	Pb_2 0.18	Bi_2 0.38					
Sc_2 (0.25)	Ti_2 (0.18)	V_2 (0.23) [11]	Cr_2 0.18		Fe_2 (0.14)	Ni_2 (0.32) [12]	Cu_2 0.31
		Nb_2 (0.73)	Mo_2 0.56			Ag_2 0.29	
							Au_2 0.39

and Mo_2, and consistent with multiple bonding. The low ratio values in Ti_2, V_2, Cr_2, Fe_2, and in Pb_2 and F_2, are due to the low values of the binding energies in these molecules, which remain to be properly explained.

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