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ORBITAL VALENCY FORCE FIELD FOR TRIGONAL PLANAR AND TRIATOMIC LINEAR MOLECULES AND IONS

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A new method for the calculation of cartesian symmetry coordinates, recently proposed by Gburski, is applied to planar XY_3 and linear XY_2 type systems. The orbital valency force constants K, F, F' and D have been evaluated for twenty six planar XY_3 and fifty four linear XY_2 type molecules and ions using reliable vibrational wave numbers. The results are discussed in the light of available information, and much emphasis is given to elucidating the nature of the chemical bond and the structure of both types of systems. $F' = -0.1\,F$, the common empirical assumption in OVFF, is tested for XY_3 type systems.

1. *Introduction*

Tyson et al. [1] have recently expressed the orbital valency force field (DVFF) of XY_n type molecules in cartesian coordinates and pointed out that the use of cartesian coordinates makes the computational procedure extremely simple. Following their method Kim et al. [2] and Gburski [3] successfully studied the OVFF constants of $XY_4(T_d)$ and, $XY_3(D_{3h})$ and $XY_2(D_{\infty h})$ type molecules respectively and suggested its application to some more molecules of the XY_n type. Therefore, it is aim of this paper to apply OVFF model to compute the force constants for $XY_3(D_{3h})$ and $XY_2(D_{\infty h})$ type molecules and ions. The results are used to discuss the rigidity of the chemical bonds and structure of the systems. The validity of the common empirical assumption $F' = 0.1\,F$ is tested for the system under present study.

2. *Molecular models and selection rules*

The symmetrical planar XY_3 and linear XY_2 type molecules and ions belong to D_{3h} and $D_{\infty h}$ point groups, respectively. The normal modes of vibration in both molecular models are classified as:

$$\Gamma_{\text{vib}}(D_{3h}) = A_1' + A_2'' + 2E',$$

$$\Gamma_{\text{vib}}(D_{\infty h}) = \Sigma_g^+ + \Pi_u + \Sigma_u^+.$$

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Here in the case of the $XY_3(D_{3h})$ type system the mode A_1' is Raman active and A_2'' infrared active while the modes E' are active in both. Whereas for the $XY_2(D_{\infty h})$ type system, the gerade mode is Raman active and ungerade modes are infrared active.

3. Theoretical basis and method of computation

The general potential energy function can be expressed in terms of $3N$ cartesian displacement coordinates in matrix notation as

$$2V = x'Ax, \tag{1}$$

where A is the potential energy matrix and x' the transpose of x which is the Cartesian displacement coordinate in the column matrix.

The secular equation in the Cartesian coordinates can be written as

$$|M^{-1}A - I| = 0, \tag{2}$$

where M is the diagonal $3N \times 3N$ matrix of atomic masses and I a unit matrix.

Factorizing the matrices A and M^{-1} with the help of symmetry coordinates one obtains separate secular equations for the various symmetry species. On solving te factorized secular equations, we obtained the following relations:

For $XY_3(D_{3h})$

$$\lambda_1(A_1') = (K+3F)/m_y, \tag{3}$$

$$\lambda_2(A_2'') = (D-3F')(m_x+3m_y)/m_x m_y, \tag{4}$$

$$\lambda_3(E')+\lambda_4(E') = [m_x(K+3F+D)+(m_x+3m_y)(K+\Delta-3F')]/2m_x m_y, \tag{5}$$

$$\lambda_3(E')\lambda_4(E') = (m_x+3m_y)[(K+3F+D)(K+D-3F')-(K+3F'-D)^2]/4m_x m_y^2. \tag{6}$$

For $XY_2(D_{\infty h})$

$$\lambda_1(\Sigma_g^+) = (K+2F)/m_y, \tag{7}$$

$$\lambda_2(\Pi_u) = (D-2F')(m_x+2m_y)/m_x m_y, \tag{8}$$

$$\lambda_3(\Sigma_u^+) = K(m_x+2m_y)/m_x m_y. \tag{9}$$

In the above equations m_x and m_y stand for the atomic masses of the central and ligand atoms, respectively. λ_i is the vibrational parameter. K, D, F and F' represent bond stretching, angle bending and non-bonded interaction force constants respectively.

Eqs. (3) to (9) have been used to compute the force constants. The fundamental vibrational wave numbers utilized in the present evaluation are collected in Tables I and III for XY_3 and XY_2 type molecules and ions, respectively.

TABLE I

Vibrational wavenumbers (in cm^{-1}) for trigonal planar molecules and ions

Mol/Ion	$\nu_1(A'_1)$	$\nu_2(A''_2)$	$\nu_3(E')$	$\nu_4(E')$	Ref.
$^{11}BF_3^a$	880	656	1433	477	[6]
$^{11}BF_3^b$	878	632	1405	477	[6]
$^{10}BF_3^a$	880	688	1488	477	[6]
$^{10}BF_3^b$	878	665	1476	477	[6]
$^{11}BCl_3$	471	460	956	243	[6]
$^{10}BCl_3$	471	480	995	244	[6]
$^{11}BBr_3$	378	374	802	151	[6]
$^{10}BBr_3$	378	392	845	150	[6]
$^{11}BI_3$	190	336	740	100	[6]
$^{10}BI_3$	190	352	724	100	[6]
CO_3^{2-}	1063	880	1415	680	[7]
CS_3^{2-}	510	516	920	314	[8]
CSe_3^{2-}	290	426	802	185	[8]
NO_3^-	1050	830	1390	720	[7]
SO_3	1068	496	1391	529	[7]
MoO_3	800	390	830	340	[9]
WO_3	780	298	791	314	[9]
$ZnCl_3^-$	280	151	306	127	[4]
$ZnBr_3^-$	183	98	232	84	[4]
ZnI_3^-	140	82	192	59	[4]
$CdCl_3^-$	265	98	287	90	[4]
$CdBr_3^-$	168	73	184	58	[4]
CdI_3^-	124	56	161	51	[4]
$HgCl_3^-$	296	89	290	65	[4]
$HgBr_3^-$	188	61	200	45	[4]
HgI_3^-	134	52	156	39	[4]

[a] Liquid. [b] Solid.

4. *Results and discussion*

The results of the present calculations are summarized in Table II for trigonal planar XY_3 type systems and in Table III for linear XY_2 type systems. In order to test the common empirical assumption between non-bond atom-pairs interactions F and F', we have also calculated the ratio F'/F for XY_3 type systems, which are included in Table II.

It is apparent from Table II that the assumption $F' = -0.1\,F$ is not good for XY_3 type systems. A similar conclusion has also been drawn by Gburski [3] for boron trihalides. We have compared the OVFF constants K and F, in Table II, with the corresponding UBFF constants. It is seen from the table that force constants are well comparable. It is noted from Table II that for BCl_3, BI_3, MoO_3 and trihalides of the metals of the II B group the bending force constant, D, comes out to be negative. It is difficult to explain whether the negative values of D represent failure of the model or whether they are physically meaningful is not clear. In the case where they carry physical significance, a distortion

TABLE II

OVFF constants (in 10^2 Nm^{-1}) for trigonal planar molecules and ions

Mol/Ion	K	F	D	F'	F'/F
$^{11}BF_3^a$	5.932	0.912	0.935	0.052	0.057
$^{11}BF_3^b$	5.712	0.972	0.900	0.059	0.060
$^{10}BF_3^a$	5.950	0.906	0.875	0.028	0.030
$^{10}BF_3^b$	5.875	0.916	0.970	0.077	0.084
	6.044^c	0.926			
$^{11}BCl_3$	2.972	0.553	−0.093	−0.168	−0.306
$^{10}BCl_3$	2.967	0.555	−0.088	−0.167	−0.301
	3.021^c	0.543			
$^{11}BBr_3$	2.299	0.446	−0.128	−0.054	−0.120
$^{10}BBr_3$	2.339	0.433	0.130	−0.053	−0.123
	2.302^c	0.454			
$^{11}BI_3$	2.024	0.225	0.234	−0.001	−0.004
$^{10}BI_3$	1.741	0.315	−0.038	−0.092	−0.288
	1.772^c	0.299			
CO_3^{2-}	5.473	1.726	1.168	−0.098	−0.056
	5.439^c	1.736			
CS_3^{2-}	2.802	0.704	0.520	−0.013	−0.018
	2.683^c	0.807			
CSe_3^{2-}	2.408	0.514	0.775	0.123	0.245
	2.441^c				
SO_3	9.958	0.264	3.816	0.962	3.639
	10.016^c	0.243			
MoO_3	5.168	0.288	−0.054	−0.336	−1.168
WO_3	5.073	0.220	0.685	0.007	0.031
$ZnCl_3^-$	1.023	0.205	−0.216	−0.132	−0.647
$ZnBr_3^-$	0.840	0.245	−0.217	−0.105	−0.427
ZnI_3^-	0.658	0.269	−0.424	−0.166	−0.617
$CdCl_3^-$	1.145	0.170	−0.117	−0.073	−0.068
	1.126^d	0.114			
$CdBr_3^-$	0.734	0.199	−0.372	−0.150	−0.074
	0.740^d	0.196			
CdI_3^-	0.689	0.153	−0.143	−0.065	−0.042
	0.698^d	0.150			
$HgCl_3^-$	1.403	0.142	−0.452	−0.187	−1.312
$HgBr_3^-$	1.170	0.164	−0.451	−0.177	−1.075
HgI_3^-	0.914	0.143	−0.328	−0.132	−0.929

[a] Liquid. [b] Solid. [c] Values of the corresponding rows are from Peacock et al., *Mol. Struct.* **2**, 163 (1968). [d] Values of the corresponding rows are from Sanyal, Singh, *Indian J. Pure Appl. Phys.* **9**, 758 (1971).

TABLE III

Vibrational wavenumbers (in cm^{-1}) and OVFF constants (in $10^2\ Nm^{-1}$) for linear symmetrical molecules and ions

Mol/Ion	$\nu_1(\Sigma_g^+)$	$\nu_2(\Pi_u)$	$\nu_3(\Sigma_u^+)$	K	F	$D-2F'$	Ref.
BeF_2	680	345	1555	5.188	0.006	0.255	[6]
$BeCl_2$	390	250	1135	3.034	0.071	0.147	[6]
$BeBr_2$	—	220	1010	2.563	—	0.122	[6]
BeI_2	—	—	873	1.954	—	—	[6]
MgF_2	550	249	841.8	3.095	0.145	0.271	[10]
$MgCl_2$	326.5	93	600.8	1.925	0.150	0.046	[10]
$MgBr_2$	197.9	81.5	497.1	1.536	0.154	0.035	[10]
MgI_2	147.6	55.8	444.9	1.294	0.168	0.020	[10]
CrF_2	—	155.4	654.5	2.771	—	0.156	[11]
MnF_2	—	124.8	700.1	3.243	—	0.103	[11]
$MnCl_2$	—	83	477	2.074	—	0.062	[11]
FeF_2	—	141	731.3	3.563	—	0.132	[11]
$FeCl_2$	—	88	492	2.227	—	0.071	[11]
$CoCl_2$	—	95	493	2.304	—	0.085	[11]
$CoBr_2$	—	—	396	1.989	—	—	[11]
$NiCl_2$	341	85	521	2.568	—	—	[11]
$NiBr_2$	—	69	415	2.178	—	0.060	[11]
$CuCl_2$	—	—	492	2.390	—	—	[11]
$ZnCl_2$	304	118	343	1.179	0.376	0.139	[4]
$CuCl_2^-$	300	109	405	1.619	0.130	0.117	[12]
$CuBr_2^-$	193	81	322	1.338	0.182	0.088	[12]
CuI_2^-	148	65	279	1.165	0.236	0.063	[12]
$AgCl_2^-$	268	88	333	1.397	0.051	0.097	[12]
$AgBr_2^-$	170	61	253	1.214	0.073	0.070	[12]
AgI_2^-	132	149	215	1.031	0.136	0.053	[12]
$AuCl_2^-$	329	116	350	1.881	0.190	0.207	[13]
$AuBr_2^-$	209	77	254	1.677	0.190	0.154	[13]
AuI_2^-	158	63	210	1.440	0.213	0.130	[13]
$ZnCl_2$	361	295	516	2.668	0.027	0.872	[4]
$ZnBr_2$	230	225	400	2.186	0.152	0.692	[4]
ZnI_2	168	—	340	1.770	0.170	—	[4]
$CdCl_2$	—	—	409	2.142	—	—	[4]
$CdBr_2$	—	—	315	1.929	—	—	[4]
CdI_2	—	—	265	1.611	—	—	[4]
$HgCl_2$	258	70	413	2.632	0.022	0.076	[4]
$HgBr_2$	218	41	293	2.249	0.006	0.044	[4]
HgI_2	155	33	237	1.854	−0.028	0.036	[4]
TiO_2	874	305	1129	7.203	0.001	0.526	[14]
ZrO_2	865	271	1003	7.020	0.163	0.512	[14]
HfO_2	860	244	935	6.988	0.008	0.476	[14]
VO_2	882	291	1135	7.458	−0.627	0.490	[14]
NbO_2	870	262	1009	7.138	0.002	0.481	[14]
TaO_2	864	244	935	7.002	0.017	0.477	[14]
MoO_2	776	232	895	5.662	0.007	0.380	[9]

TABLE III (continued)

Mol/Ion	$\nu_1(\Sigma_g^+)$	$\nu_2(\Pi_u)$	$\nu_3(\Sigma_u^+)$	K	F	$D-2F'$	Ref.
WO_2	770	216	835	5.598	0.004	0.374	[9]
CO_2	1343	667	2349	14.194	1.403	1.144	[6]
CS_2	656.5	397	1510	6.794	0.673	0.470	[6]
CSe_2	364	313	1303	5.582	0.290	0.322	[6]
SiO_2	885	378	1295	7.389	0.003	0.629	[14]
NO_2^+	1400	538	2375	16.187	1.144	0.830	[6]
UO_2^{2+}	856	—	931	7.202	−0.147	—	[15]
NpO_2^{2+}	844	—	934	7.245	−0.265	—	[15]
PuO_2^{2+}	818	—	930	7.200	−0.447	—	[15]
AmO_2^{2+}	749	—	914	6.958	−0.835	—	[15]

[a] Vibrational wavenumbers in solution.

in the valence bond structure of the system from planarity occurs, but the non-bonded repulsion being strong enough keeps it planar. In agreement with this the repulsion constant F (in 10^2 Nm^{-1}) has relatively large positive values than the bending constant D for BCl_3, BI_3 and MoO_3 and therefore in these cases planarity is maintained. But in the case of trihalides of the metals of the IIB group, in general, $D > F$ in magnitude (Table II) which implies that in these cases planarity is disturbed. Waters et al. [4] have also concluded from the study of the vibrational spectra of these halide complexes in solution that the planarity is disturbed in these systems on account of solvent–solute interactions. From the variation of the stretching force constant K, among trihalides it is inferred that the flexibility of the chemical bonds is in the order $M-I > M-Br > M-Cl > M-F$. It is noted from Table II that the non-bonded repulsion constant F follows the same trend as the stretching force constant K for the compounds of the elements of IIIA and IVA groups. In the case of other compounds it shows a trend opposite to that of the stretching force constant. A minor change in the stretching force constant with the physical state is also obvious from Table II for boron trifluoride.

The effect of increasing atomic mass of the ligand atom on the stretching force constant, K, for linear XY_2 type systems (keeping the central atom constant) is apparent from Table Table III. It decreases with the increase in the atomic mass of the ligand. It is in keeping with the expected increase in bond length. From this trend it is inferred that the flexibility of the chemical bonds is in the order $M-I > M-Br > M-Cl > M-F$ and $M-Sc > M-S > M-O$. The increase in the electronegativity of the ligand atom from I to F and Sc to O supports this trend. It is also noted that for divalent halides of transition metals the non-bonded repulsion constant F follows the trend opposite to that of the stretching force constant with an increase in the mass of the ligand.

It is of interest to study the trend in the stretching force constant with respect to the number of d-electrons for the divalent first row transition metals chloride. For this purpose we have plotted the force constant K versus the number of d-electrons in Fig. 1. The feature of this diagram is that the variation of K with the number of d-electrons is not smooth,

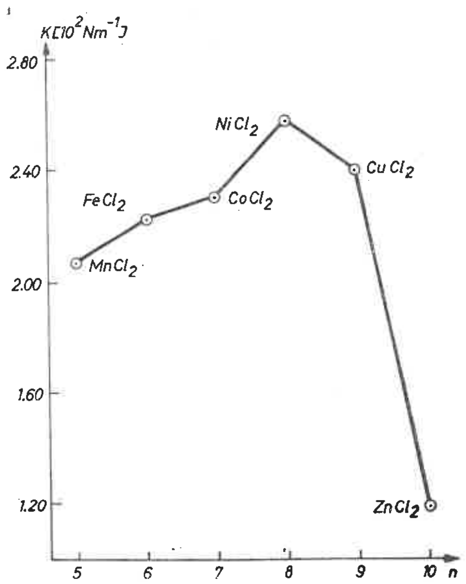

Fig. 1. OVFF stretching force constant K vs number of non-bonding d-electrons

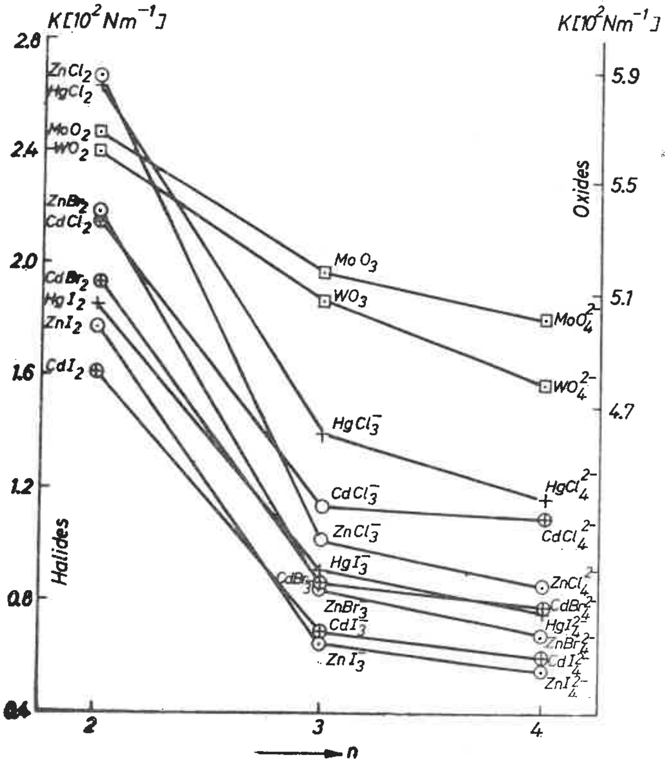

Fig. 2. GVFF stretching force constant K vs coordination number n

but it resembles the plot of lattice energies against the number of *d*-electrons. Thus the trend in K with the number of *d*-electrons is justified. The variation in the radii of divalent iron-group ions and crystal field parameters [5] (stabilization energies) supports the above trend. The strength of the chemical bonds also varies in a similar way.

Figure 2 shows the variation of the stretching force constant with the coordination numbers ranging from 2 to 4 for the halides and oxides of transition metals. It is apparent from this figure that K decreases with the increase in coordination numbers. This leads us to conclude that the rigidity of the chemical bonds decreases with the increase in coordination number. This is in agreement with the slight increase in bond length with the increase in coordination number. As in the case of metal oxide bond lengths (in pm) are WO_2(1.78), WO_3(1.81), WO_4^-(1.82), MoO_2(1.73), MoO_4^-(1.80).

5. *Conclusions*

The following conclusions are drawn from the present study:

1. The common empirical assumption $F' = -0.1\,F$ is not applicable for trigonal planar XY_3 type systems.

2. The distortion in planarity is understood in the case of trihalides of the metals of the zinc group.

3. The rigidity of the chemical bonds is in the order $M-\mathrm{F} > M-\mathrm{Cl} > M-\mathrm{Br} > M-\mathrm{I}$ and $M-\mathrm{O} > M-\mathrm{S} > M-\mathrm{Sc}$.

4. A dependence of the stretching force constant, K, versus the number of *d*-electrons exists for the dichlorides of iron-group elements.

5. The relative rigidity of the chemical bonds (in the same oxidation state of the central atom) is in the order $MX_2 > MX_3^- > MX_4^2$.

Editorial note. This article was proofread by the editors only, not by the authors.

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