Intramolecular Force Field of Some Tetrahedral Thio and Seleno Anions *

Nitish K. Sanyal and Parvez Ahmad

Department of Physics, University of Gorakhpur,
Gorakhpur 273001, India

(Z. Naturforsch. **29 a**, 826–828 [1974]; received December 18, 1973)

The orbital valence force field (OVFF) and the Urey-Bradley force field (UBFF) have been employed to evaluate the force constants of thio and seleno anions of VA, VB, VIB and VIIB group atoms of the periodic table. These constants were utilized to examine the relative strength of chemical bonds in isoelectronic sequences. Further, for these anions, the variation of the ratio L_{12}/L_{21} with the mass coupling term $(T = G_{12}/\sqrt{|G|})$ has been studied. This appears to be an excellent support to the extended L-matrix approximation **.

Recently, Müller et al.[1, 2] have reported the infrared and Raman spectra of tetrathio and tetraseleno anions of Vanadium, Niobium and Tantalum and the tetrathio anion of Phosphorus. They have studied the force constants of the above anions[1] along with those of MoS_4^{2-}, WS_4^{2-}, ReS_4^-, $MoSe_4^{2-}$ and WSe_4^{2-} on the basis of tetrahedral symmetry employing the L-matrix approximation[3], the P.E.D. method[4] and Fadini's approximation[5]. In the present communication, OVFF[6–8] and UBFF[9] have been applied to describe the nature of the force field. The variation of the ratio L_{12}/L_{21} with the mass coupling term[10] $(T = G_{12}/\sqrt{|G|})$ has also been examined.

Table 1. Vibrational frequencies[1, 2] (in cm^{-1}) for some tetrahedral thio and seleno anions.

Ion	$\nu_1(a_1)$	$\nu_2(e)$	$\nu_3(f_2)$	$\nu_4(f_2)$
PS_4^{3-}	421	201	547	266
VS_4^{3-}	375	178	460	178
NbS_4^{3-}	408	163	421	163
TaS_4^{3-}	424	170	399	170
MoS_4^{2-} (Cs–Salt)	460	195	480	195
WS_4^{2-} (Cs–Salt)	485	185	465	185
ReS_4^-	501	200	486	200
VSe_4^{3-}	232	121	365	121
$NeSe_4^{3-}$	239	100	316	100
$TaSe_4^{3-}$	249	103	277	103
$MoSe_2^{2-}$ (NH_4–Salt)	255	120	340	120
WSe_4^{2-} (Cs–Salt)	281	107	309	107

The fundamental vibrations of $XY_4(T_d)$ type systems are distributed as $a_1 + e + 2f_2$. Wilson's[11] FG matrix method has been used to evaluate the force constants. The expressions for the F and G matrices were taken from Krebs and Müller[6].

Table 2. OVFF and the UBFF constants (in mdyn/Å) for some tetrahedral thio and seleno anions.

Ions	$k_1(K)$	$k_\alpha'(3H)$	$A(F/2)$	$B/R(F')$
PS_4^{3-}	1.832	0.475	0.168	−0.018
	(2.03)*	(0.45)*	(0.16)*	(−0.02)*
VS_4^{3-}	2.011	0.537	0.081	−0.099
	(2.020)	(0.471)	(0.079)	(0.032)
NbS_4^{3-}	2.064	0.271	0.135	−0.039
	(2.089)	(0.246)	(0.132)	(0.007)
TaS_4^{3-}	2.108	0.235	0.161	−0.011
	(2.142)	(0.216)	(0.157)	(−0.017)
MoS_4^{2-}	2.713	0.464	0.160	−0.067
	(2.750)	(0.420)	(0.155)	(0.010)
WS_4^{2-}	2.931	0.282	0.189	0.013
	(2.975)	(0.258)	(0.184)	(−0.019)
ReS_4^-	3.232	0.405	0.189	−0.027
	(3.294)	(0.372)	(0.181)	(−0.021)
VSe_4^{3-}	1.819	0.675	0.076	−0.146
	(1.856)	(0.579)	(0.081)	(0.064)
$NbSe_4^{3-}$	2.068	0.399	0.074	−0.081
	(2.065)	(0.348)	(0.074)	(0.032)
$TaSe_4^{3-}$	2.051	0.333	0.104	−0.048
	(2.104)	(0.315)	(0.098)	(0.016)
$MoSe_4^{2-}$	2.402	0.639	0.078	−0.124
	(2.373)	(0.546)	(0.082)	(0.039)
WSe_4^{2-}	2.616	0.324	0.132	−0.055
	(2.638)	(0.291)	(0.130)	(0.016)

* Reference[2].

(The values in parentheses indicate the UBFF constants K, $3H$, $F/2$ and F'.)

It is evident from Table 2 that the OVFF constants k_1, k_α' and A are comparable with the corresponding UBFF constants K, $3H$, and $F/2$. It is worth noting that for the same metal, the metal-sulphur bond is stronger than the metal-selenium bond. This conclusion, supported also by the electronegativity differences, shows that as the mass of the peripheral atom increases, the force constant decreases and the bond gets weakened. The variation of the stretching force constant (k_1) in thio anions of different metals indicates that as the mass of the central atom increases the relative strength of the chemical bonds increases. This is also true in the case of seleno anions of different metals. In the isoelectronic groups viz. NbS_4^{3-}, MoS_4^{2-}, TaS_4^{3-}, WS_4^{2-}, ReS_4^-, $NbSe_4^{3-}$, $MoSe_4^{2-}$, and $TaSe_4^{3-}$, WSe_4^{2-}, it is observed that the stretching force constant increases with the increase of the oxidation state. It is, therefore, inferred that the relative

---

Reprint requests to Dr. N. K. Sanyal, Department of Physics, University of Gorakhpur, *Gorakhpur 273001*, India.

* Part of the work has been presented at the 43rd Session of the National Academy of Sciences, held at Jodhpur, India, in October 1973.

** Z. Naturforsch. **27 a**, 129 [1972].

strength of chemical bonds increases with the decrease of the formal charge. The interaction constant, A, shows the same trend and supports the above conclusion which indicates that the interaction constant is greater for smaller non-bonded distances. The angle bending force constant k_a' decreases with increasing mass of the central atom in the same group only. The present calculation leads to a negative value of B/R for all the ions. It follows that the OVFF model, making use of a single interaction term in B/R, cannot represent satisfactorily the interaction between non-bonded atom pairs. Several other investigators [6, 7, 12, 13] have also reported the negative B/R in the case of ions. Another set of OVFF constants has also been computed assuming the relation $A = 6.5\ (B/R)$, but the constants obtained do not lead the satisfactory reproduction of the observed frequencies. This part is not reported here. Krebs and Müller [6] also found the failure of the relation $A = 6.5\ (B/R)$ in some ions and concluded that the application of a Lennard-Jones potential resulting in the assumption $A = 6.5\ (B/R)$ is not reasonable in the case of ions.

Recently Müller et al. [10] have studied the variation of the ratio L_{12}/L_{21} with the mass coupling term $(T = G_{12}/\sqrt{|G|})$ for molecules of the type $XY_4(T_d)$, $XY_3(D_{3h})$ and $XY_2(C_{2v})$. They formulated an empirical constraint for the calculation of force constants (extended L-matrix approximation). From their empirical study, they concluded that an average value of the factor $L_{12}/L_{21} = -0.075$ may be taken as an empirical constraint in fixing the force constants of the second order vibrational eigenvalue problem in $XY_4(T_d)$ type systems. They found that the values of the force constants determined from this empirical approach are in good agreement with the exact force field data. We, therefore, examined the dependence of the ratio L_{12}/L_{21}

Table 3. Elements of L-matrix * (a. m. u.)$^{-1/2}$ for some tetrahedral thio and and seleno anions.

S. No.		L_{11}	L_{12}	L_{21}	L_{22}	L_{12}/L_{21}	Method
1	PS_4^{3-}	0.271	0.027	−0.362	0.454	−0.074	Fad.
		0.271	0.027	−0.351	0.342	−0.077	OVFF
		0.271	0.024	−0.359	0.479	−0.067	UBFF
2	VS_4^{3-}	0.238	0.020	−0.247	0.326	−0.081	Fad.
		0.239	0.015	−0.211	−0.129	−0.071	OVFF
		0.239	0.015	−0.223	0.068	−0.067	UBFF
3	NbS_4^{3-}	0.213	0.011	−0.151	0.312	−0.073	Fad.
		0.213	0.016	−0.108	−0.349	−0.148	OVFF
		0.213	0.013	−0.114	−0.346	−0.114	UBFF
4	TaS_4^{3-}	0.196	0.009	−0.089	0.290	−0.101	Fad.
		0.195	0.010	−0.043	−0.610	−0.233	OVFF
		0.196	0.010	−0.049	−0.506	−0.204	UBFF
5	MoS_4^{2-}	0.212	0.018	−0.148	0.197	−0.119	Fad.
		0.212	0.015	−0.108	−0.318	−0.139	OVFF
		0.212	0.014	−0.117	−0.219	−0.119	UBFF
6	WS_4^{2-}	0.196	0.013	−0.085	0.165	−0.150	Fad.
		0.195	0.018	−0.047	−0.298	−0.382	OVFF
		0.195	0.015	−0.052	−0.293	−0.288	UBFF
7	ReS_4^{-}	0.196	0.007	−0.087	0.252	−0.080	Fad.
		0.195	0.012	−0.049	−0.297	−0.241	OVFF
		0.195	0.012	−0.055	−0.299	−0.215	UBFF
8	VSe_4^{3-}	0.196	0.015	−0.283	0.223	−0.053	Fad.
		0.197	0.013	−0.265	−0.006	−0.049	OVFF
		0.197	0.013	−0.274	0.123	−0.047	UBFF
9	$NbSe_4^{3-}$	0.164	0.005	−0.181	0.223	−0.028	Fad.
		0.164	0.014	−0.170	−0.062	−0.082	OVFF
		0.164	0.014	−0.175	0.002	−0.080	UBFF
10	$TaSe_4^{3-}$	0.141	0.009	−0.118	0.202	−0.076	Fad.
		0.141	0.008	−0.095	−0.188	−0.084	OVFF
		0.141	0.008	−0.098	−0.190	−0.082	UBFF
11	$MoSe_4^{2-}$	0.163	0.012	−0.187	0.214	−0.064	Fad.
		0.163	0.011	−0.168	−0.033	−0.065	OVFF
		0.163	0.014	−0.176	0.062	−0.079	UBFF
12	WSe_4^{2-}	0.141	0.008	−0.115	0.203	−0.070	Fad.
		0.141	0.008	−0.090	−0.214	−0.089	OVFF
		0.141	0.006	−0.094	−0.215	−0.064	UBFF

* Calculated by equations given in Reference 3.

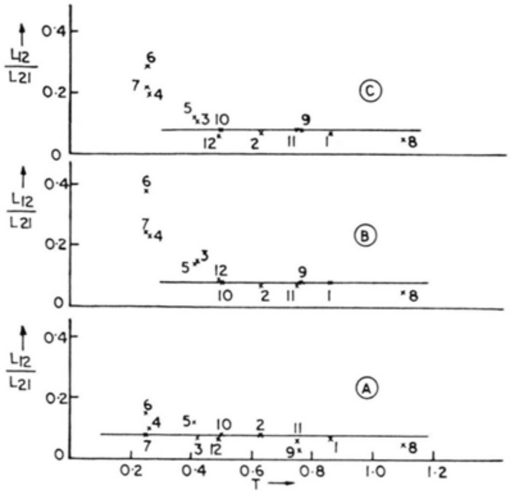

FIG. VARIATION OF $\frac{L12}{L21}$ VS. MASS COUPLING TERM $(T = \frac{G12}{\sqrt{|G|}})$

Ⓐ $\frac{L12}{L21}$ BY FADINI'S FORCE FIELD CONTANTS.

Ⓑ $\frac{L12}{L21}$ BY O.V.F.F. CONTANTS.

Ⓒ $\frac{L12}{L21}$ BY U.B.F.F. CONTANTS.

Fig. 1.

on the mass coupling term, T, in the present case of thio and seleno anions using the force constants calculated by Fadini's method[1, 5], OVFF constants and UBFF constants. It is found from Fig. 1 that the force field data from Fadini's method give an average value of the constraint $L_{12}/L_{21} = -0.08$, which is in good agreement with the value proposed by Müller et al.[10]. The OVFF and UBFF constants also give the same average value of the constraint L_{12}/L_{21} for ions of higher mass coupling terms. However, in the case of ions having lower mass coupling terms, the ratios L_{12}/L_{21} are found to be greater due to the higher F_{12} values from OVFF and UBFF constants. Hence it may be concluded that Fadini's approximation is closer to an exact force field.

The authors are thankful to Sri L. Dixit for help and valuable discussions. Financial assistance provided by the University Grants Commission, New Delhi, to one of us (PA) in the form of a fellowship is thankfully acknowledged.

[1] A. Müller, K. H. Schmidt, K. H. Tytko, J. Bouwma, and F. Jellinek, Spectrochim. Acta **28 A**, 381 [1972].

[2] A. Müller, N. Mohan, P. Cristophliemk, I. Tossidis, and M. Drager, Spectrochim. Acta **29 A**, 1345 [1973].

[3] C. J. Peacock and A. Müller, J. Mol. Spectrosc. **26**, 454 [1968].

[4] H. J. Becher and K. Ballein, Z. Phys. Chem. N. F. **54**, 302 [1967].

[5] A. Fadini, Z. Naturforsch. **21 a**, 426 [1966].

[6] B. Krebs and A. Müller, J. Mol. Spectrosc. **22**, 290 [1967].

[7] N. K. Sanyal, A. N. Pandey, and H. S. Singh, J. Mol. Spectrosc. **30**, 144 [1969].

[8] B. P. Singh, J. Mol. Spectrosc. **33**, 169 [1970].

[9] A. Müller and B. Krebs, J. Mol. Spectrosc. **24**, 180 [1967].

[10] A. Müller, N. Mohan, and U. Heidborn, Z. Naturforsch. **27 a**, 129 [1972].

[11] E. B. Wilson, D. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill Book Co., New York 1955.

[12] A. N. Pandey, D. K. Sharma, and H. P. Mital, Z. Naturforsch. **27 a**, 1211 [1972].

[13] B. B. Srivastav, A. K. Dublish, A. N. Pandey, and A. K. Mithal, Z. Naturforsch. **27 a**, 1213 [1972].