Intramolecular Force Field of some Tetrahedral Molecules and Ions

B. B. SRIVASTAVA and A. K. DUBLISH
Department of Physics, Institute of Advanced Studies, Meerut University, Meerut, India
and A. N. PANDEY and A. K. MITHAL
Department of Physics, Meerut College, Meerut, India

(Z. Naturforsch. **27 a**, 1213—1216 [1972]; received 15 June 1972)

The orbital valence force field (OVFF), and the Urey-Bradley force field (UBFF) have been employed to calculate the force constants for six molecules and ions ($AlCl_4^-$, $AlBr_4^-$, AlI_4^-, TiI_4, $Os^{16}O_4$, and $Os^{18}O_4$). The results have been discussed in the light of the relative stability of the bonds. The applicability of the Lennard-Jones potential is also examined. The kinetic constants have been computed and the results have been correlated with the corresponding force constants.

Introduction

In recent years, considerable efforts have been made to understand the nature of the intramolecular forces by employing different force field models. Among the different models, the general valence force field (GVFF), the Urey-Bradley force field (UBFF) [1], and the orbital valence force field (OVFF) [2–7] have been extensively used in the case of the tetrahedral XY_4 type molecular system. With the aid of laser and far-infrared devices in vibrational spectroscopy complete vibrational analyses of the fundamental frequencies of some of the tetrahedral molecules and ions are now available in the literature [8–10] with a fair degree of accuracy ($AlCl_4^-$, $AlBr_4^-$, AlI_4^-, TiI_4, OsO_4^{16}, and OsO_4^{18}). Therefore, it was thought worthwhile to study the nature of interatomic forces by using the orbital valence force field on the one hand and the Urey-Bradley force field on the other. Since the force constants are a convenient measure of the strength of a chemical bond, such a study is useful in understanding the relative stiffness of the chemical bonds as well as the nature of the non-bonded interaction. Although some of the force fields in the case of $AlCl_4^-$ [4] and OsO_4 [5–11] have been used by previous workers also, the frequency data used by them have not been as accurate as those known at present. Furthermore, the kinetic constants have also been computed and the results have been correlated with the corresponding force constants.

Method of Computation

Molecules and ions of the type XY_4 belong to the point group T_d, and the fundamental vibrations are distributed as $a_1 + e + 2f_2$. The force constants have been evaluated by solving the secular equation [12] $|GF - E\lambda| = 0$ in the usual manner. The expressions for F and G matrices are taken from MÜLLER and KREBS [1] and KREBS and MÜLLER [2]. In applying the orbital valence force field two sets of force constants were calculated. The first set of force constants was calculated with the help of four equations [2] using four fundamental frequencies while the second set of force constants was calculated by approximating the interaction between non-bonded atoms pair by a Lennard-Jones potential.

According to WILSON [12], the general expression for the kinetic energy associated with molecular vibration is

$$2T = \dot{S}^T G^{-1} \dot{S}$$

where S^T is the transpose of S, both being matrices composed of time derivatives of internal coordinates and G^{-1} is the inverse kinetic energy matrix.

The kinetic energy expression can also be put into the form

$$2T = \sum_{i,j} K_{ij} \dot{r}_i \dot{r}_j .$$

where $\dot{r}_i$ and $\dot{r}_j$ stand for the time derivatives of the internal coordinates and K_{ij} are certain reduced masses [13] representing the vibrational inertial coefficients. Therefore, from the knowledge of the G^{-1} matrix, the above coefficients can be conveniently calculated. In the present work this procedure has been adopted for calculating these coefficients. The G matrix is the same as employed in the computation of the force constants. These coefficients are

Reprint requests to B. B. SRIVASTAVA, Department of Physics, Meerut College, *Meerut (U.P.)*, Indien.

known as "Kinetic Constants" and are of significant importance in molecular dynamical problems as pointed out by THIRUGNANASAMBANDAM [14].

Results and Discussion

All the four orbital valence force constants: k_1, the bond stretching force constant; k_α', the angle bending constant; and A and B/R, the interaction constants between non-bonded atom pairs, as well as the corresponding Urey-Bradley force constants K, H, F and F' are summarized in Table 1. The force constants exactly reproduce the observed frequencies and hence the latter are not shown explicitly. It is apparent from Table 1 that the calculated OVFF constants k_1, k_α' and A compare well with the UBFF constants, K, $3H$ and $F/2$.

In order to discuss the relative stability of the bonds in different species, the most valuable information is contained in the bond stretching force constant. It can be seen from Table 1 that in the case of haloanions of aluminium the stretching force constant decreases with increase of the atomic weight of the ligand, which shows the stiffening of the bond in the order $Al-Cl > Al-Br > Al-I$. This is consistent with the decrease in electronegativity from Cl to Br and then from Br to I. In this series it is found that the value of the non-bonded repulsion is in decreasing order. A similar variation has also been reported in case of other haloanions of III A group elements by SINGH [4].

It is seen from Table 1 that for titanium tetraiodide the value of the non-bonded repulsion force constant from the OVFF model is less than that from the UBFF model, while for osmium tetraoxide its value from the OVFF model is greater than that from the UBFF model. The possibility that the OVFF model may overestimate the repulsion force constant, as in OsO_4 here, has been pointed out by ANDREWS and BARROW [15] and LINNETT and HEATH [16]. The OVFF constants of OsO_4 have also been used to calculate the fundamental frequencies of isotopic $Os^{18}O_4$. The calculated frequencies are $\nu_1 = 918.3$, $\nu_2 = 325.4$, $\nu_3 = 926$ and $\nu_4 = 328.8$ (in cm^{-1}). It is seen from Table 2 that these calculated values are in fairly good agreement with the observed values of these frequencies.

For studying the nature of the forces between non-bonded atom pairs, the interaction has been approximated by a Lennard-Jones potential ($A = 6.5\ B/R$) in the OVFF model. In the UBFF model for tetrahedral molecules the assumption $F' = -0.1\ F$ has been criticised by DUNCAN [17]. Therefore, this assumption has not been used in the present work. The new set of force constants obtained after incorporating the Lennard-Jones potential approximation is also included in Table 1. For examining the applicability of the Lennard-Jones potential, these constants in turn were employed to calculate the vibrational frequencies. The observed and calculated frequencies are compared in Table 2. It is seen that for $AlBr_4^-$ and AlI_4^- the average percentage

Table 1. The OVFF constants, the UBFF constants and the OVFF constants using the Lennard-Jones potential $A = 6.5\ B/R$ (Mdyne/Å).

Molecule/Ion	Field	k_1, K	k_α', $3H$	A, $F/2$	$\frac{B}{R}$, $-F'$
$AlCl_4^-$	OVFF	1.6597	0.0334	0.1142	0.0440
	UBFF	1.6651	0.0335	0.1135	0.0452
	$A = 6.5\ B/R$	1.7562	0.0858	0.1021	0.0157
$AlBr_4^-$	OVFF	1.3849	0.0793	0.0839	0.0176
	UBFF	1.3806	0.0688	0.0845	0.0271
	$A = 6.5\ B/R$	1.4037	0.0891	0.0816	0.0126
AlI_4^-	OVFF	0.9898	0.0214	0.0755	0.0221
	UBFF	0.9867	0.0177	0.0759	0.0250
	$A = 6.5\ B/R$	1.0330	0.0435	0.0701	0.0108
TiI_4	OVFF	1.6386	0.1280	0.0404	−0.0144
	UBFF	1.6297	0.1100	0.0416	0.0013
	$A = 6.5\ B/R$	1.5570	0.0854	0.0506	0.0078
$Os^{16}O_4$	OVFF	7.6891	0.8420	0.1569	−0.0331
	UBFF	7.8556	0.7838	0.1361	0.0667
	$A = 6.5\ B/R$	7.5811	0.7557	0.1704	0.0262
$Os^{18}O_4$	OVFF	7.6975	0.8438	0.1564	−0.0335
	UBFF	7.8581	0.7837	0.1363	0.0668
	$A = 6.5\ B/R$	7.5857	0.7562	0.1704	0.0262

Table 2. Comparison of observed frequencies (cm^{-1}) with those calculated using OVFF (A=6.5 B/R) constants.

Molecule/Ion	Field	ν_1	ν_2	ν_3	ν_4	Average percentage error ν_1 and ν_3	ν_2 and ν_4	all freq.
$AlCl_4^-$	Observed	351	121	496	186			
	$A = 6.5\ B/R$	351	121	502	172	0.7	4.5	2.6
$AlBr_4^-$	Observed	209	75	409	114			
	$A = 6.5\ B/R$	209	75	420	111	1.8	1.6	1.7
AlI_4^-	Observed	146	51	336	82			
	$A = 6.5\ B/R$	146	51	337	78	0.2	3.0	1.6
TiI_4	Observed	162	51	324	67			
	$A = 6.5\ B/R$	162	51	322	77	0.4	8.5	4.4
$Os^{16}O_4$	Observed	974.3	345.2	976.9	345			
	$A = 6.5\ B/R$	974.3	345.2	968.0	369	0.5	3.5	2.0
$Os^{18}O_4$	Observed	918.5	325.4	926.6	328.3			
	$A = 6.5\ B/R$	918.5	325.4	918.2	352.1	0.5	3.6	2.0

Table 3. Kinetic constants (10^{-23} g).

Molecule/Ion	K_r	K_{rr}	$-K_{r\alpha} = K_{r'\alpha}$	$-K_{\alpha\alpha}$	K_α	$-K_{\alpha'\alpha}$	$\sum K$	$4\mu_y \sum K$
$AlCl_4^-$	4.6503	0.4121	0.5829	0.4906	1.1380	0.1568	21.8983	14.8798
$AlBr_4^-$	10.2095	1.0196	1.4420	1.1057	2.3835	0.1721	48.9948	14.7705
AlI_4^-	16.0696	1.6673	2.3580	1.7560	3.6892	0.1772	77.6170	14.7340
TiI_4	16.2579	1.6046	2.2692	1.7560	3.8148	0.3028	77.8681	14.7816
$Os^{16}O_4$	2.4894	0.0557	0.0788	0.2214	0.7741	0.3313	10.4034	15.6643
$Os^{18}O_4$	2.7843	0.0684	0.0968	0.2491	0.8597	0.3614	11.6846	15.6338

error over all frequencies is 1.65 and therefore, this approximation is fairly adequate to take into account the interaction between non-bonded atom pairs while in other cases, it is not a reasonable approximation. From this it can be concluded that in systems where the approximation is valid the dispersion forces are responsible for the interaction between non-bonded atom pairs whereas in cases where it is not applicable, Coulomb forces besides dispersion forces should also be taken into account, as suggested by KREBS and MÜLLER [2].

The results of the kinetic constants calculations are presented in Table 3. Here the constants are: K_r, the stretching kinetic constant; K_α, the bending kinetic constant and K_{rr}, $K_{\alpha\alpha}$, $K_{\alpha\alpha'}$, the interaction kinetic constants. In tetrahedral molecular systems the algebraic sum of the bondangle interaction kinetic constants and of the bending and angle-angle interaction kinetic constants separately vanishes. There remain the bond stretching and bond-bond interaction kinetic constants which contribute to the sum $\Sigma K = 4K_r + 8K_{rr}$. On comparison of the bond stretching force constants and kinetic stretching constants from Tables 1 and 3 it can be seen that in the case of the haloanions of aluminium the trend of variation is quite opposite. From this it is inferred that the stretching kinetic constant mainly depends on the atomic weight of the ligand. An interesting feature is shown by ΣK which is approximately equal for the same ligand as for AlI_4^- and TiI_4. The value of the configuration constant [14] $4\mu_y \Sigma K$ for the present system lies between 14.73 and 15.66.

Acknowledgement

The authors wish to thank Prof. Dr. A. MÜLLER, University of Dortmund, West Germany, for constant encouragement. They are also thankful to Professor S. P. KHARE, Institute of Advanced Studies, Meerut University, Meerut, India, for providing the necessary facilities in the Institute.

[1] A. MÜLLER and B. KREBS, J. Mol. Spectroscopy **24**, 180 [1967].
[2] B. KREBS and A. MÜLLER, J. Mol. Spectroscopy **22**, 290 [1967].
[3] N. K. SANYAL, A. N. PANDEY, and H. S. SINGH, J. Mol. Spectroscopy **30**, 114 [1969].
[4] B. P. SINGH, J. Mol. Spectroscopy **33**, 169 [1970].
[5] M. PRASAD and A. N. PANDEY, Aust. J. Chem. **23**, 2011 [1970].

[6] N. K. SANYAL, H. S. SINGH, A. N. PANDEY and B. P. SINGH, Ind. J. Pure and Appl. Phys. **8**, 72 [1970].
[7] D. V. R. A. RAO and D. K. RAI, Ind. J. Pure and Appl. Phys. **7**, 277 [1969].
[8] G. M. BEGUN, C. R. BOSTON, G. TORSI, and G. MAMANTOV, Inorg. Chem. **10**, 886 [1971].
[9] R. J. H. CLARK and C. J. WILLIS, J. Chem. Soc. A, 838 [1971].
[10] R. S. MCDOWELL and M. GOLDBLATT, Inorg. Chem. **10**, 625 [1971].
[11] R. S. RAM and S. N. THAKUR, Ind. J. Pure and Appl. Phys. **9**, 34 [1971].
[12] E. B. WILSON, JR., J. C. DECIUS, and D. C. CROSS, Molecular Vibrations, Mc Graw-Hill, New York 1955.
[13] P. THIRUGNANASAMBANDAM, Proceedings of the Seminar on Raman and Infrared Spectroscopy, University of Kerala (India) 174 [1964].
[14] P. THIRUGNANASAMBANDAM and G. J. SRINIVASAN, J. Chem. Phys. **50**, 2467 [1969].
[15] E. W. ANDREWS and R. F. BARROW, Proc. Phys. Soc. London **64 A**, 481 [1951].
[16] J. W. LINNETT and D. F. HEATH, Trans. Faraday Soc. **48**, 592 [1952].
[17] J. L. DUNCAN, J. Mol. Spectroscopy **18**, 62 [1965].

Die Bestimmung der Terme äquivalenter Elektronen bei LS-Kopplung

HEINZ KLEINDIENST
Institut für Physikalische Chemie der Universität Düsseldorf

(Z. Naturforsch. **27 a**, 1216—1221 [1972]; eingegangen am 22. April 1972)

Determination of Terms for LS-coupled Equivalent Electrons

In this paper a simple method for the determination of all antisymmetric terms allowed according to Pauli principle is presented. Using group theory it allows to evaluate the terms for all electronic configurations of the type l^r with $l \leqq 3$.

1. Die Schrödinger-Gleichung

Bei Vernachlässigung der Kernbewegung lautet die zeitunabhängige Schrödinger-Gleichung für ein Atom mit N Elektronen

$$H\,\Psi = E\,\Psi \tag{1}$$

mit

$$H = -\frac{\hbar^2}{2\,m}\sum_{k=1}^{N}\Delta_k - \sum_{k=1}^{N}\frac{Z\,e^2}{r_k} + \frac{1}{2}\sum_{\substack{i,k\\ i\neq k}}^{N}\frac{e^2}{r_{ik}}\ *.$$

Die Lösungen (Spin-Bahn-Funktionen) von (1) ergeben sich im Falle von LS-Kopplung als Produkte aus einem ortsabhängigen und einem spinabhängigen Teil zu

$$\Psi(r,\sigma) = \psi(r)\,\chi(\sigma),$$

wobei r für die Gesamtheit der Ortsvariablen und σ für die der Spinvariablen steht. Da H die Spinvariablen nicht enthält, sind durch Gl. (1) nur die Ortsfunktionen $\psi(r)$ bestimmt. Die Spinfunktionen $\chi(\sigma)$ ergeben sich durch die Folgerungen aus dem Stern-Gerlach-Versuch (s. Abschnitt 3).

Sonderdruckanforderungen an Dr. HEINZ KLEINDIENST, Institut für Physikalische Chemie der Universität Düsseldorf, *D-4000 Düsseldorf*, Gelände d. Fa. Henkel, Gebäude Z 10, Bonner Straße.

Zur Klassifizierung der Eigenfunktionen von H werden sowohl die Symmetrieeigenschaften der Bahn- wie die der Spinfunktionen benötigt, denn nach dem Pauli-Prinzip sind nur solche Lösungen zulässig, die bei gleichzeitiger Vertauschung von Orts- und Spinvariablen zweier Teilchen antisymmetrisch sind. Die gruppentheoretische Charakterisierung der Eigenfunktionen von H erfolgt nun in der Weise, daß man zunächst die Untersuchungen für die Orts- bzw. Spinfunktionen getrennt durchführt und nachträglich das Pauli-Prinzip berücksichtigt.

2. Symmetrieeigenschaften der Ortsfunktionen

Zur Klassifizierung der spinfreien Eigenfunktionen von H dienen die IR's (irreduzible Darstellungen) der Symmetriegruppe

$$G_H = O_3{}^+ \times S_N$$

des Operators H. Dabei bedeuten $O_3{}^+$ die dreidimensionale Drehgruppe, S_N die Permutationsgruppe von N Elementen und $O_3{}^+ \times S_N$ das direkte Produkt aus beiden.

* Bezüglich der Bezeichnungen vgl. [1]; bezüglich der Festlegung des Definitionsbereiches D_H von H siehe [2].