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THE VIBRATIONS OF PENTATONIC TETRAHEDRAL MOLECULES*

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ABSTRACT

Andrews has suggested that the restoring forces in polyatomic molecules can best be chosen as harmonic restoring forces along the directions of the chemical bonds and perpendicular to them. In order to test the suggestion, we have calculated the vibrational frequencies of tetrahedral molecules with this choice of forces. The agreement between calculated and observed values is unsatisfactory. It seems that there may be repulsive forces between the corner atoms of the type between ions of crystals or the inert gas atoms. The introduction of terms in the potential energy proportional to $1/r_j^n$, where r_j is the distance between two corner atoms, makes it possible to secure very good agreement between calculated and observed frequencies, in the case of CCl_4, $SiCl_4$, $SnCl_4$, CBr_4, and $SnBr_4$ but not such close agreement in that of $TiCl_4$. The calculated frequencies are not very sensitive to the value of n which may be anywhere from 5 to 9. The repulsive forces necessary are of the same order of magnitude as those calculated from crystal properties and the viscosities of the inert gases. In the case of the $SO_4^=$ and ClO_4^-, the inverse high power repulsive force is not sufficient, but the addition of terms, e^2/r_j, e being the electronic charge, as well as an inverse higher power term does give very good agreement between calculated and observed frequencies of these molecules.

ANDREWS[1] has made the suggestion that the most promising assumption to make in regard to the restoring forces in molecules is that these forces to a first approximation consist of harmonic forces along the directions of the chemical bonds and perpendicular to them. Kettering, Shutts and Andrews[2] have constructed ingenious molecular models on the basis of this suggestion, which duplicate many details of the vibrational frequencies of molecules. A number of years ago Bjerrum[3] considered the same choice of forces in discussing triatomic molecules of the CO_2 type, as well as the assumption of central forces, but was unable to decide definitely between them.[4] The recent theoretical investigations of Slater[5] and Pauling[6] on the nature of the chemical bond also suggest the presence of valency forces acting along and perpendicular to the chemical bond.

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[1] D. H. Andrews, Phys. Rev. **36**, 544 (1930).

[2] C. F. Kettering, L. W. Shutts, and D. H. Andrews, Phys. Rev. **36**, 531 (1930).

[3] N. Bjerrum, D. physik. Ges. Ber. **16**, 737 (1914).

[4] A study of the vibrational frequencies of the ClO_2 molecule has been made in this laboratory by Miss Helen Johnston and one of the writers (H. C. U.) which definitely favors the valence type forces.

[5] J. C. Slater, **37**, 481 (1931).

[6] L. Pauling, J.A.C.S. **53**, 1367, 3225 (1931).

Dennison[7] has solved the problem for the vibrations of the tetrahedral pentatomic molecule assuming that the forces act along the lines joining the atoms and Schaeffer[8] has given the dependence on the mass of the central atom. Trumpy[9] applied these formulae to several molecules of this type and showed that the three arbitrary constants required can be adjusted so as to give fair agreement with observation.

This type of molecule is particularly well suited to a test of the choice of restoring forces because the angles can be assumed to be known. Only two arbitrary constants are postulated and four frequencies expected, so that two can be used to calculated the constants and the calculated and observed values of the other two compared. Satisfactory agreement is not secured in this case. However, we find that the presence of repelling forces between the like atoms at the corners of the tetrahedron having the order of magnitude of known repulsive forces between inert gas atoms or ions in crystals make agreement between calculated and observed values very satisfactory for all, but one molecule, to which the calculations have been applied.

THE DYNAMICAL PROBLEM

The potential energy function which includes forces along the bonds, perpendicular to them, and along the lines joining the like atoms is,

$$\begin{aligned} V = V_0 + \sum_1^4 \frac{\partial V}{\partial r_i}\Delta r_i + \tfrac{1}{2}\sum_1^4 \frac{\partial^2 V}{\partial r_i^2}\Delta r_i^2 + \tfrac{1}{2}\sum_1^4 k_2 r_0^2 \Delta\theta_i^2 \\ + \sum_1^6 \frac{\partial V}{\partial r_j}\Delta r_j + \tfrac{1}{2}\sum_1^6 \frac{\partial^2 V}{\partial r_j^2}\Delta r_j^2, \end{aligned} \tag{1}$$

where r_i is the distance from the central atom to the ith corner atom, r_j is the distance between two corner atoms, r_0 is the equilibrium value of each r_i and $\Delta\theta_i$ is an angular displacement perpendicular to the bond direction.[10] The central force potential energy function does not include the fourth term and the valence force potential energy function does not include the second and last two terms on the right of Eq. (1). If the potential energy contributed by the interaction of the corner atoms depends on an inverse power of the distance (a usual assumption) as

$$V_j = \frac{k_3}{r_j^n}, \tag{2}$$

the last two terms may be replaced by

$$-\sum_1^6 \frac{nk_3}{a^{n+1}}\Delta r_j + \tfrac{1}{2}\sum_1^6 \frac{n(n+1)k_3}{a^{n+2}}\Delta r_j^2, \tag{3}$$

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[7] D. M. Dennison, Astrophys. J. **62**, 84 (1925).

[8] Cl. Schaeffer, Zeits. f. Physik **60**, 586 (1930).

[9] B. Trumpy, Zeits. f. Physik **66**, 790 (1930).

[10] The term containing $\Delta\theta$ is defined as the sum of four terms depending on the displacement of the bond direction from its equilibrium direction. Another way of defining this would be that this consists of the sum of six terms, $\frac{1}{2}k_2'\Sigma r_0^2\Delta\theta_j^2$, where $\Delta\theta_j$ is the change in angle between two pairs of corner atoms and the central atom. The two definitions are identical, however, for $k_2' = \frac{1}{2}k_2$ and thus only a redefinition of an empirically chosen constant is involved.

where a equals the equilibrium distance between corner atoms. If the undisplaced configuration is to be stable, the forces acting along the bonds must be balanced by forces acting between the corner atoms and this leads to a relation between $\partial V/\partial r_i$ and $\partial V/\partial r_j$, namely,

$$\frac{\partial V}{\partial r_i} = -6^{1/2}\frac{\partial V}{\partial r_j} = 6^{1/2}\frac{nk_3}{a^{n+1}}\cdot \tag{4}$$

Our potential energy function is then

$$\begin{aligned} V = V_0 + 6^{1/2}\sum_1^4 \frac{nk_3}{a^{n+1}}\Delta r_i + \tfrac{1}{2}\sum_1^4 \frac{\partial^2 V}{\partial r_i^2}\Delta r_i^2 + \tfrac{1}{2}\sum_1^4 k_2 r_0^2 \Delta\theta_i^2 \\ - \sum_1^6 \frac{nk_3}{a^{n+1}}\Delta r_j + \tfrac{1}{2}\sum_1^6 \frac{n(n+1)k_3}{a^{n+2}}\Delta r_j^2. \end{aligned} \tag{5}$$

The kinetic energy can easily be written in terms of the velocities using suitable coordinates and the problem can be solved by usual methods.[11]

The frequencies in terms of the force constants are found to be as follows,

$$\begin{aligned} \nu_1 &= \frac{1}{2\pi}\left\{\frac{k_1 + (n+1)\gamma_3}{m}\right\}^{1/2}, \\ \nu_2 &= \frac{1}{2\pi}\left\{\frac{k_2 + \dfrac{n+2}{4}\gamma_3}{m}\right\}^{1/2}, \\ \nu_{3,4} &= \frac{1}{2\pi}\left\{\left(\frac{3n+2}{2}\gamma_3 + 2k_1 + k_2\right)\frac{1}{6m} + \left(\frac{2\gamma_3 + k_1 + 2k_2}{m}\right)\frac{m}{6\mu}\right. \\ &\quad \pm\left(\left[\left(\frac{3n+2}{2}\gamma_3 + 2k_1 + k_2\right)\frac{1}{6m} - \left(\frac{2\gamma_3 + k_1 + 2k_2}{m}\right)\frac{m}{6\mu}\right]^2\right. \\ &\quad \left.\left. + \frac{2m}{9\mu}\left(\frac{\gamma_3 + k_2 - k_1}{m}\right)^2\right)^{1/2}\right\}^{1/2}, \end{aligned} \tag{6}$$

where

$$k_1 = \left(\frac{\partial^2 V}{\partial r_i^2}\right)_0, \qquad \gamma_3 = \frac{4nk_3}{a^{n+2}}, \qquad \mu = \frac{mM}{4m + M},$$

and m and M are the masses of the corner and central atoms respectively.[12]

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[11] We have found that the simplest method for securing the frequencies is that used by Lorentz, The Electron, pp. 294–297, for a similar problem. We have checked our results by setting up the determinamental equation and solving by the general method.

[12] The dependence of these formulae on γ^3 and k_1 should be derivable from the formulae of Schaeffer by using the proper values of his α and β in terms of our assumed inverse power function. This is not possible, however, unless the sign of β in all his formulae is changed or what is the same thing, unless the β is redefined with opposite sign. This error appears in Dennison's original formulae, in Schaeffer's formulae and also in Trumpy's work (see below) and in Ruark and Urey, Atoms Molecules and Quanta, McGraw-Hill, 1930, p. 441. The latter authors have also made some algebraic error in deriving formulae for ν_3 and ν_4. The error in the sign of the β does not invalidate previous numerical calculations for only the sign of an empirical constant is involved. It means that Trumpy has really assumed attracting forces instead of repelling forces between the corner atoms.

APPLICATION TO EXPERIMENTAL DATA

The experimental data consist of the Raman spectra and infrared spectra of molecules of this type. The experimental errors in these data may amount to a few wave numbers. In addition the data deal with transitions between the normal level of the molecule and levels having one of the vibrational quantum numbers equal to 1. The energy change for this transition is (in wave numbers)

$$\Delta\tilde{\nu} = \tilde{\nu}_0 - 2x\tilde{\nu}_0,$$

if the energy is of the form

$$\tilde{\nu} = \tilde{\nu}_0(v + \tfrac{1}{2}) - x\tilde{\nu}_0(v + \tfrac{1}{2})^2.$$

The quantity which we have attempted to calculate is $\tilde{\nu}_0$ and thus the theoretical formulae do not refer exactly to the observed quantities. Thus even if the theory were exact, which we do not maintain, and the experimental data very precise, which they are not, exact agreement could not be expected. Also conclusions based on agreement closer than a percent or two would be unjustified.

We first applied the formula assuming pure valency forces so that γ_3 is first assumed to be zero. The constants were calculated from the frequencies ν_1 and ν_2 and then the frequencies ν_3 and ν_4 calculated by using these constants. The results are given in Table I. The agreement between calculated and observed is not satisfactory so that the assumption of pure valency forces is not sufficient.

TABLE I

Compound	Inactive frequencies		$\tilde{\nu}_3$			$\tilde{\nu}_4$		
	$\tilde{\nu}_1$	$\tilde{\nu}_2$	Obs.	Calc.	% Diff.	Obs.	Calc.	% Diff.
(1) CCl_4	460	214	760–790	1168	+49.7	311	299	−3.8
(1) $SiCl_4$	422	149	608	724	+19.0	220	210	−4.5
(2) $TiCl_4$	386	119	491	552	+12.4	139	164	+17.9
(2) $SnCl_4$	367	104	401	437	+8.9	136	132	−2.9
(3) CBr_4	265	125	667	864.6	+14.7	183	156.2	−14.8
(2) $SnBr_4$	220	64	279	309.0	+10.7	88	87.4	−0.7
(4) $SO_4^{=}$	980	451	1113	1315	+18.1	620	579	−5.7
(5) ClO_4^{-}	935	467	1121	1241	+10.8	634	591.4	−6.7

(1) Cl. Schaeffer, Zeits. f. Physik **60**, 586 (1930).
(2) B. Trumpy, Zeits. f. Physik **66**, 790 (1930); P. Daure, Ann. de. Physique **12**, 26 (1929).
(3) A. Dadieu and K. W. F. Kohlrausch, Monat. **57**, 488 (1931).
(4) R. G. Dickinson and R. T. Dillon, Proc. Nat. Acad. Sci. **15**, 695 (1929).
(5) H. Nisi, Jap. Jour. Physik **5**, 119 (1929); R. G. Dickinson and R. T. Dillon, Proc. Nat. Acad. Sci. **15**, 695 (1929).

If γ_3 is assumed not equal to zero, we have formulae which depend on four constants which may be fixed arbitrarily and thus exact agreement between calculated and observed values should be secured. However, we are somewhat limited in our choice of the value of n. We picture the molecule $SiCl_4$ for example, to consist of the central atom and four chlorine atoms surrounded by fields of force similar to the field of force about an argon atom and in general the corner atoms to be similar in this respect to inert gas atoms generally. The general character and magnitude of the forces between atoms and ions having inert gas configurations are known from the study of crystals and the properties of the inert gases. It is found that high inverse power potential energy functions fit these data in a highly satisfactory way. We have found that a potential energy function of the form, k_3/r_j^n, with n equal to any number between about 5 and 9 would be satisfactory for the calculation of the frequencies within a few percent so that within the limits which we regard as significant as explained above any choice of n between these two would be permissible. We have found that the choice of $n=6$ or 7 gives better agreement in general than larger or smaller values.

The constants k_1, k_2 and γ_3 were determined by solving the following three linear equations in these quantities,

$$\begin{aligned} x_1 &= \tilde{\nu}_1^2 = k_1' + (n+1)\gamma_3' \\ x_2 &= \tilde{\nu}_2^2 = k_2' + \frac{n+2}{4}\gamma_3' \qquad (7) \\ x_3 &= \tilde{\nu}_3^2 + \tilde{\nu}_4^2 = \left(\frac{3n+2}{2}\gamma_3' + 2k_1' + k_2'\right)\tfrac{1}{3} + (2\gamma_3' + k_1' + 2k_2')\frac{m}{3\mu}, \end{aligned}$$

where k_1', k_2' and γ_3' are equal to k_1, k_2, and γ_3 respectively multiplied by the factor $1/4\pi^2c^2m$. The comparison with the fourth quantity $\nu_3^2-\nu_4^2$ could have been made directly, but we have chosen to calculate both ν_3 and ν_4 and compare each of these with the experimental value, since these are the observed quantities and a better judgment of the closeness of agreement can be made. Table II lists the results together with the values of k_1, k_2 and γ_3, using $n=7$.

TABLE II.

	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$			$\tilde{\nu}^4$			k_1	k_2	γ_3
			Obs.	Calc.	dev. %	Obs.	Obs.	dev. %			
CCl_4	460	214	760–790	771.2	?	311	316.6	+2.12	173,771	20,735	32,553
$SiCl_4$	422	148	608	609.5	+0.2	220	216.0	+0.82	258,321	14,818	13,387
$TiCl_4$	386	119	491	482.0	−1.83	139	166.2	+19.4	227,998	7,194	9,717
$SnCl_4$	367	104	401	403.4	+0.6	136	128.7	−5.4	230,638	9,337	5,718
CBr_4	265	123	667	666.7	+0.1	183	183.8	+0.4	139,954	17,684	23,677
$SnBr_4$	220	64	279	279.0	0.0	88	88.0	0	183,407	6,949	5,450

The agreement between calculated and observed values is as close as can be expected except in the case of $TiCl_4$. (The disagreement between the calculated and observed values of $\tilde{\nu}_4$ for $SnCl_4$ is rather great but probably not significant.) Trumpy[9] also found the poorest agreement in the case of $TiCl_4$. A comparison of our percent deviations between calculated and observed and those secured by Trumpy using the central force formulae is given in Table III. The superiority of the valence type forces is immediately evident.

In order to justify our assumption of repelling forces between the corner atoms, it is necessary to show that these forces are of the same order of magnitude as those found from the properties of crystals and the inert gases. Ex-

TABLE III. *Deviations between calculated and observed frequencies as given by Trumpy and by this paper.*

Compound	$\tilde{\nu}_1$		$\tilde{\nu}_2$		$\tilde{\nu}_3$		$\tilde{\nu}_4$	
	U. & B.	T.	U. & B.	T.	U. & B.	T.	U. & B.	T
CCl_4	0	0	0	−9.3	?	?	+2.12	−3.5
$SiCl_4$	0	0	0	−4.7	+0.2	−2.3	−1.82	+4.5
$TiCl_4$	0	0	0	−7.6	−1.83	−4.8	19.4	+13.0
$SnCl_4$	0	0	0	0	+0.6	−4.3	−5.4	−5.1
CBr_4	0	—	0	—	+0.1	—	0.4	—
$SnBr_4$	0	0	0	−4.7	0.0	−2.9	0.0	+3.4

act agreement cannot be expected because atoms, such as the chlorine atoms of CCl_4, bound by nonpolar bands to a central atom can hardly have the same potential energy relative to each other as free inert gas atoms or ions of crystals. Calculations show that agreement between calculated and observed values of $\tilde{\nu}_3$ and $\tilde{\nu}_4$ is not greatly changed by using different values of n, and also that the constants k_1 and k_2 are not greatly changed, and γ_3 changes somewhat more but remains of the same order of magnitude. In the case of $SiCl_4$ best agreement between calculated and observed is secured with $n=6$. Table IV shows the results of such calculations for $SiCl_4$.

TABLE IV.

n	$\tilde{\nu}_3$	$\tilde{\nu}_4$	k_1	k_2	γ_3
5	607.3	222.1	253,926	12,420	18,581
6	608.3	219.1	256,494	13,815	15.563
7	609.5	216.0	258,321	14,818	13,387
8	610.0	214.5	259,705	15,574	11,745
10	610.9	211.9	261,670	16,644	9,431
	608 (obs.)	220 (obs.)			

It is evident to us from these calculations and others of a similar kind that values of n from 5 to 9 are about equally satisfactory so far as this calculation is concerned and thus only order of magnitude of $\partial V/\partial r_j$ and $\partial^2 V/\partial r_j^2$ used by us and those used by others can be compared. We have calculated the values of γ_3 for CCl_4, $SiCl_4$ and $SnCl_4$ assuming $n=8$, which is the value used by Lennard-Jones and Dent[13] and calculated the value of $\partial V/\partial r_j$ from it, $\partial V/\partial r_j = -(\gamma_3 a/4)$. The values of the a's are those determined by Wierl[14] using the electron diffraction method. The values of γ_3 for CBr_4 and $SnBr_4$ have been calculated by using $n=9$, which is Lennard-Jones and Dent's value. In this case we have estimated the values of the a's from the ionic radii of Goldschmidt and Pauling,[15] reducing these values by 7 percent as was found necessary in the chlorine compounds by Wierl. The values of $-(\partial V/\partial r_j)$ so calculated are compared with Lennard-Jones and Dent's values in Table V. The two agree in order of magnitude, but our values do not follow a formula nk_3/a^{n+1} with the same k_3 for CCl_4, $SiCl_4$ and $SnCl_4$ or

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[13] J. E. Lennard-Jones and B. M. Dent, Proc. Roy. Soc. **A112,** 230 (1926).

[14] R. Wierl, Ann. d. Physik **8,** 521 (1931).

[15] L. Pauling, J.A.C.S. **49,** 765 (1927); V. M. Goldschmidt, Trans. Far. Soc. **25,** 253 (1929).

for CBr_4 and $SnBr_4$. If we take $n=6$, values for the $-(\partial V/\partial r_i)$ not greatly different for those given in Table V, are secured and they follow fairly closely a formula, nk_3/a^{n+1}.

TABLE V.

Compound	a	γ_3	$-\partial V/\partial r_i$ (dynes)	
			U. and B.	L-J. and D.
CCl_4	2.98	28530	21.25×10^{-5}	24.22×10^{-5}
$SiCl_4$	3.29	11746	9.66	9.94
$SnCl_4$	3.81	5034.9	4.80	2.65
CBr_4	3.19	18436	14.70	28.14
$SnBr_4$	4.05	4274	4.33	2.59

However it is quite evident that any discussion of the value of n, based on the frequencies of these molecules, is futile for data and calculation here given cannot give a decisive answer. We can only conclude that the assumption of valency forces and an inverse power repulsive force between the corner atoms of the correct order of magnitude is able to account for the vibrational frequencies of these molecules with the exception of $TiCl_4$. At present we cannot explain this discrepancy.

The constant, k_2, decreases regularly in the compounds CCl_4, $SiCl_4$ and $SnCl_4$, but the value for $TiCl_4$ is somewhat irregular. The constant, k_1, is smaller in the case of CCl_4 than in that of $SiCl_4$ and $SnCl_4$ and also smaller in the case of CBr_4 than in that of $SnBr_4$. This seems, at first sight, to be unlikely and not to be in agreement with an intuitive judgement based on chemical evidence.[16] By the strength of the nonpolar bond, we may refer to two properties; (1) the dissociation energy associated with the bond; and (2) the restoring force constant for small displacements from the equilibrium position, namely, $\partial^2 V/\partial r_i^2$. It is this latter idea, which appears here.

Morse[17] has shown that the following function will fit the potential energy functions of diatomic molecules with a high approximation:

$$V(r) = -2De^{-A(r-r_0')} + De^{-2A(r-r_0')}.$$

We shall take the potential energy of the tetrahedral molecule in so far as it depends on the distance, r_i, between corner and central atom as this function with r_0' as the equilibrium distance between the central and corner atoms in the absence of the repelling forces between the corner atoms. Then the potential energy is, when $r=r_0$, the equilibrium distance with the repulsive forces present

$$V = 4[-2De^{-A(r_0-r_0')} + De^{-2A(r_0-r_0')}] + 6\frac{k_3}{a^n} = -Q, \tag{8}$$

and using Eq. (4)

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[16] See Pauling's 6th property of the electron-pair band, J.A.C.S. **53,** 1369 (1931).

[17] P. M. Morse, Phys. Rev. **34,** 57 (1929).

$$\left(\frac{\partial V}{\partial r_i}\right)_{r_i=r_0} = 2DAe^{-A(r_0-r_0')} - 2DAe^{-2A(r_0-r_0')} = 6^{1/2}\frac{nk_3}{a^{n+1}}, \tag{9}$$

and

$$\left(\frac{\partial^2 V}{\partial r_i^2}\right)_{r_i=r_0} = -2DA^2e^{-A(r_0-r_0')} + 4DA^2e^{-2A(r_0-r_0')} = k_1. \tag{10}$$

It seems to us that we should expect $(\partial^2 V/\partial r_i^2)_{r=r'_0}=2DA^2$ to fit Pauling's rule rather than the quantity k_1. The quantity $2DA^2$, equal to k_1' say, can be calculated roughly in the case of CCl_4 and is larger than the k_1's for $SiCl_4$ and $SnCl_4$.

Letting $e^{-A(r_0-r_0')}=x$, Eqs. (8), (9), and (10) become

$$2x - x^2 = \frac{Q + 6\dfrac{\gamma_3 a^2}{4n}}{4D}, \quad x - x^2 = \frac{6^{1/2}}{8}\frac{\gamma_3 a}{DA}, \quad x - 2x^2 = -\frac{k_1}{2DA^2}.$$

It is possible to solve these three equations for x, D, and A in terms of Q, the heat of formation, and the constants γ_3 and k_1. When this is done, we find that $2DA^2=k_1'=385{,}000$, $r_0-r_0'=0.22$A, and $A=1.12\times10^8$. This value for k_1' is of the order of magnitude of the restoring force constants in the case of SiF in which one atom belongs in the first period of eight and the other in the second period of eight of the periodic system. Thus,

$$CCl_4, k_1' = 385{,}000, \qquad SiF, k = 491{,}400.$$

Thus k_1' is larger than the k_1 for $SiCl_4$ and for $SnCl_4$ and it seems likely that it is larger than the k_1''s of these molecules which unfortunately cannot be calculated. We expect a similar relation to hold for the k_1''s of CBr_4 and $SnBr_4$ which also cannot be calculated.

The $SO_4^=$ and ClO_4^- Ions

The assumption that there is no central force between the oxygen atoms of these ions, and the assumption that there is a high inverse power central force between them both fail to give agreement between the observed and calculated frequencies of $SO_4^=$ and ClO_4^-. This might be expected for the bonds of these ions may be partly ionic. Two possible ways of forming the $SO_4^=$ ion would be (1) from S^{6+} and $4O^=$; (2) from $S^{2+}+4O^-$. The latter according to the theories of Slater[5] and Pauling[6] should be tetrahedral. The actual ion may be a combination of both these and perhaps of other possible configurations. Therefore it occurred to us to try the addition of a term $\Sigma(e^2/r_i)$ to the potential energy as well as a high inverse power term. With this assumption very good agreement can be secured in the case of $SO_4^=$, and fair agreement in the case of ClO_4^-. The frequencies for this case are easily secured from Eqs. (6) by using two γ terms, one with $n=1$ and the other with $n=7$. The value of the $\gamma_4(=4e^2/a^3)$ was calculated using Vegard and

Maurstad's[18] values for the O – O distance in the case of $SO_4^{=}$, 1.63×10^{-8}cm, and a distance estimated from Goldschmidt and Pauling's ionic values for ClO_4^- of 1.60×10^{-8} cm. The results of these calculations are given in Table VI.

TABLE VI

Ion	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$			$\tilde{\nu}_4$			k_1	k_2	γ_3	γ_4	Number of charge oxygen
			Obs.	Calc.	% dev.	Obs.	Calc.	% dev.					
$SO_4^{=}$	980	451	1113	1127.8	+1.4	620	592.4	−4.5	634,805	115,960	33,262	0	0
$SO_4^{=}$	980	451	1113	1113.6	+0.05	620	618.9	−0.2	606,406	98,922	24,742	48,278	1
$SO_4^{=}$	980	451	1113	1079.4	−3.0	620	676.4	+9.0	521,209	47,803	−816	193,111	2
ClO_4	935	467	1121	1140.8	+1.8	631	594.4	−5.9	674,150	163,539	18,239	0	0
ClO_4^-	935	467	1121	1125.4	+0.4	631	623.3	−1.1	644,802	145,714	9,147	51,044	1
ClO_4^-	935	467	1121	1096.3	−2.2	631	672.7	+6.8	556,757	92,240	−18,131	204,176	2

The assumption that each oxygen atom of $SO_4^{=}$ and ClO_4^- carries one unit of negative charge is consistent with the observed frequencies; the calculated frequencies are not changed greatly by a considerable change in γ_4, for γ_4 must be taken equal to about 70,000 in order to get exact agreement between the calculated and observed values of $\tilde{\nu}_3$ and $\tilde{\nu}_4$ of ClO_4^-, i.e., the effective charge on an oxygen must be $\sim 1.15\ e$; however, the observed frequencies are *not* at all consistent with the assumption of either zero or two negative charges on each oxygen atom as can be seen from the table. We expected k_1, k_2 and γ_3 to be larger for ClO_4^- than for $SO_4^{=}$ because of the greater charge on the central atom, and this proves to be true for k_1 and k_2, but not for γ_3. Neither changing the value of n nor changing the value of γ_4 changes the relative values of γ_3 for the two ions appreciably. The inverse 7th power repulsion forces between the oxygens in the equilibrium position are 1.66×10^{-4} and 0.599×10^{-4} dynes in the case of $SO_4^{=}$ and ClO_4^- respectively. These forces calculated from the tables of Lennard-Jones and Dent assuming the forces are the same as those of F^- ions are 0.737×10^{-4} and 0.951×10^{-4} dynes respectively and again assuming the repulsive forces to be the same as those between $O^{=}$ ions are 3.393×10^{-4} and 4.393×10^{-4} dynes respectively. In the case of sulfate our calculated force falls between the two values calculated according to these authors as we should expect it to do considering the trends of values in their tables; however, our value for the ClO_4^- case does not follow these expectations.

A possible explanation for this difficulty, which immediately comes to mind, is our neglect of polarization forces. Such forces should be small in the case of bonds of the nonpolar type as in the chlorides and bromides considered, but, as a simple calculation shows, should be of appreciable magnitude in the case of these partially ionic bonds. The central charged atom should induce a dipole in the corner oxygens and, if these are charged, the mutual energy of these ions and dipoles should be of appreciable magnitude, thus introducing a term depending on both the r_i's and r_j's. Our agreement between calculated and observed frequencies is as good as can be expected neglecting such forces and therefore the introduction of further empirical constants could not be checked against our data. Further, an estimate of such

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[18] L. Vegard, and A. Maurstad, Zeits. f. Kristallographie **69,** 519 (1929).

a term from other data would be unreliable, for the polarizability of singly charged oxygen atoms bound by nonpolar linkages to sulphur or chlorine would be difficult to estimate.

The calculations for these ions as they stand are in accord with the assignment of single nonpolar electron-pair bonds between the sulphur and oxygens or the chlorine and oxygens in sulphate and perchlorate ions respectively as suggested by G. N. Lewis.[19]

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[19] G. N. Lewis, J.A.C.S. **38,** 762 (1916). "Valence and the Structure of Atoms and Molecules," Chem. Cat. Co., New York, 1923.