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The Polarizabilities of Ions from Spectra

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The polarizabilities of the gaseous alkali ions, and several other ions of rare gas structure, have been calculated by the Born-Heisenberg method from the corresponding spectra. Correction has been made for the effect due to "penetration" and for higher order distortion of the ion. The quantum mechanical derivation of the method has been given. The values of the polarizabilities of the alkali ions so obtained are found to be somewhat lower than those previously assumed. The polarizabilities of the gaseous negative ions must be correspondingly higher. The decrease in polarizability of the negative ion and increase of the positive ion on inclusion in a crystal is in agreement with known frequency shifts.

INTRODUCTION

THE sum of the polarizabilities of a negative and a positive ion in a crystal or in solution may be obtained by measurements of the dispersion. These sums indicate that the polarizability of a given ion is by no means independent of the state of the ion. It is different in solution and in crystal, and varies with the crystal. Fajans and Joos[1] have calculated values of the polarizabilities of the ions in the gaseous state, using reasonable but by no means certain assumptions. Pauling[2] by a semi-theoretical, semi-empirical method has calculated the polarizabilities of gaseous ions using the known polarizabilities of the corresponding rare gas and the assumed value of the negative ion. Since just the negative ions show polarizabilities extremely susceptible to the state, there is considerable doubt concerning their polarizabilities in the gaseous phase, and Pauling's method cannot be considered unimpeachable.

The only method of obtaining directly the polarizability in the gaseous state which may be called experimental, is that of Born and Heisenberg,[3] which uses the values of spectral terms. The actual calculations made by them (1924) are, however, by means of the Bohr model of the atom, which introduces considerable error. Great improvements have also been made since in the values and assignment of, spectral terms. Although the method is frequently referred to in the literature[4] it appears that no comprehensive attempt has been made to recalculate polarizabilities by this method using the quantum mechanics. Further, no quantum mechanical derivation of the fundamental equation of this method, Eq. (1) of this paper, appears to have been published. Whitelaw and Van Vleck[5] have reported the conditions under which the proof can be made, but their complete work has not been published. It has been thought desirable to make the proof and calculate some polarizabilities by this method. Throughout, the term values given in the new book by Bacher and Goudsmit[6] have been used.

METHOD

The principle of the Born and Heisenberg method is simple. Consider the energy of a spectral term with high quantum numbers n and l, of an alkali metal. The state of the valence electron may, to the zeroth approximation, be considered to be given by a hydrogen-like function which is assumed not to have appreciable amplitude inside of the ionic kernel. That is, the electron is assumed to be nonpenetrating. The poten-

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[1] K. Fajans and G. Joos, Zeits. f. Physik **23**, 1 (1924).

[2] L. Pauling, Proc. Roy. Soc. **A114**, 181 (1927).

[3] M. Born and W. Heisenberg, Zeits. f. Physik **23**, 407 (1924).

[4] An excellent discussion is given by J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities*, page 215.

[5] N. G. Whitelaw and J. H. Van Vleck, Phys. Rev. **41**, 389, Abstract of Report to the New Haven meeting (1932).

[6] R. F. Bacher and S. Goudsmit, *Atomic Energy States*, McGraw-Hill, New York (1932).

tial on the electron is that due to the singly charged undeformed ionic kernel, plus a dipole perturbation potential due to the deformed ion, polarized under the influence of the valence electron. The zeroth order electrostatic potential of the undeformed ion would account for exactly the energy of a hydrogen state with the same quantum numbers. The perturbation method allows us to calculate the decrease of energy due to the polarization of the ion,

$$-\Delta E=\tfrac{1}{2}\alpha e^2(\overline{r^{-4}}). \qquad (1)$$

In this equation $\overline{r^{-4}}$ is the average value of r^{-4} for the hydrogen state, that is,

$$\overline{r^{-4}}=\frac{\int r^{-2}|R_{n,\,l}(r)|^2dr}{\int r^2|R_{n,\,l}(r)|^2dr} \qquad (2)$$

if $R_{n,\,l}(r)$ is the (unnormalized) radial hydrogen function with the quantum numbers n, l, of the term in question. By use of experimental deviations of term energies from those of hydrogen terms the polarizability α of the ion may be calculated. This is, of course, the polarizability of the ion under the influence of a field with the frequency of the atomic term in question. In all cases treated in this paper the frequency is so far below the resonance line of the ion that this correction is less than one percent.

The justification and details of the calculation will be given under the heading "Calculations." By this method the calculated polarizabilities for any single ion are found to vary considerably with the term used. In general the calculated polarizability is found to increase with the total quantum number n in a series of constant l, and to have lower values if a series of higher l is used in the calculation.

However, the values of α so calculated from the P and D terms of Li I, Be II, B III and C IV; the D and F terms of Na I, Mg II and Al III; and the F and G terms of K I, Rb I, Cs I, Ca II, Sr II, are sufficiently close to the probable values of α for the corresponding ions, and show a sufficient regularity in the trend to give hope that by considering second order effects reliable values may be obtained. Two corrections have then been made, a correction for the perturbation energy due to higher order distortion of the ion, and a correction due to penetration.

The effect on the energy due to higher than dipole distortion of the ion can be shown to be due to a constant of the ion which may be termed its "quadrupolarizability," the ratio of which to the "dipolarizability" can be estimated.

A further perturbation which is present even were the ion undistorted may be termed the penetration perturbation. If $Z(r)$, the effective nuclear charge at the radius r from the center of the ion, be defined as the net charge, in units of the charge on an electron e, lying within the radius r, then a perturbation potential at r exists $U_{\text{pen}}(r)$ defined by the equation

$$\frac{dU}{dr}=\frac{e^2(Z(r)-Z_\infty)}{r^2}.$$

Although $Z(r)$ has been calculated for many ions to obtain form factors which determine x-ray reflection intensities, values for only a few ions have been published. The values for Na^+, Cl^-, He and Rb^+ are found in an article by Hartree,[7] for Li^+, in an article by Hargreaves,[8] and a curve from which the values for K^+ may be obtained in an article by James and Brindley.[9] Some other curves of electron density obtained from experimental data have been published[10] but are of little value for the range of large radii which are here important. The authors are indebted to Professor J. C. Slater for a copy of a table of $Z(r)$ values for Cs^+, obtained by him from Hartree.

Graphical integration of the perturbation potential times ψ^2, which gives the perturbation energy, indicates that the perturbation at large radii alone is important ($r>1.5$ in units of $a_0=0.5285\times10^{-8}$ cm). For this portion of the ion an empirical analytical expression for $Z(r)$ may be obtained, the constants of which can be extrapolated for other ions.

The calculations are given in more detail under that heading. In Table I the results of the calcu-

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[7] D. R. Hartree, Proc. Camb. Phil. Soc. **24**, 89 (1927).

[8] J. Hargreaves, Proc. Camb. Phil. Soc. **25**, 75 (1928).

[9] R. W. James and G. W. Brindley, Proc. Roy. Soc. **A121**, 155 (1928).

[10] R. J. Havighurst, Phys. Rev, **29**. 1 (1927).

TABLE I.

Element, spectrum, and charge	Term	Term value T cm^{-1}	$T/Z^2-R/n^2$ $=\Delta T_{\mathrm{exp}}/Z^2$ cm^{-1}	$\Delta T_{\mathrm{pen}}/Z^2$ cm^{-1}	$\Delta T_\alpha/Z^2$ cm^{-1}	$\alpha_0\times 10^{24}$ cm^3	C_q	$\alpha\times 10^{24}$ cm^3
Li	$2P$	28 582.5	1150.3	187.0	963.3	0.0310	?	
Sp. Li I	$3P$	12 560.4	368.4	73.2	295.2	0.0289	?	
$Z=1$	$4P$	7 018.2	160.1	32.2	127.9	0.0284	?	
	$3D$	12 203.1	11.1	0.5	10.6	0.0258	1.05	0.0246
	$4D$	6 863.5	5.4	0.2	5.2	0.0273	1.06	0.0258
	$5D$	4 389.6	0.5	0.0	0.5	0.005	1.07	
Be^{++}	$2P$	114 959.6	1302.4	279.0	1023.4	0.00825	?	
Sp. Be II	$3P$	50 384.4	402.4	73.0	329.4	0.00805	?	
$Z=2$	$4P$	28 122	172	33	139	0.00785	?	
	$3D$	48 828.5	14.8	1.0	13.8	0.00841	1.11	0.00756
	$4D$	27 459.5	6.7	0.9	5.8	0.00746	1.14	0.00656
	$5D$	17 570.4	3.4	0.5	2.9	0.00696	1.15	0.00605
B^{+++}	$2P$	257 555.5	1170	190	980	0.00340	?	
Sp. B III	$3P$	112 976.8	356	62	294	0.00320	?	
$Z=3$	$4P$	63 100.1	153	27	126	0.00312	?	
	$3D$	109 861.0	14.4	1.1	13.3	0.00361	1.16	0.00311
	$4D$	61 794.7	7.75	0.67	0.67	0.00405	1.20	0.00338
	$5D$	39 541.8	4.27	0.32	3.95	0.00421	1.21	0.00348
	$4F$	61 731.9	.87	0.00	0.87	0.0035	1.01	0.0035
C^{++++}	$2P$	435 637.9	919	153	766	0.00154	?	
Sp. C IV	$3P$	200 110.4	314	48	266	0.00162	?	
$Z=4$	$4P$	111 858.7	133	22	111	0.00155	?	
	$3D$	195 292	13.2	1.1	12.1	0.00185	1.20	0.00154
	$4D$	109 837.6	6.6	0.6	6.0	0.00193	1.25	0.00154
	$5D$	70 286.5	3.6	0.3	3.3	0.00198	1.26	0.00157
	$4F$	109 743.7	0.7	0.0	0.7	0.00157	1.02	0.00154
Na^+	$3D$	12 276.18	83.45	8.13	75.32	0.184	1.11	0.165
Sp. Na I	$4D$	6 900.35	41.94	4.66	37.28	0.192	1.13	0.170
$Z=1$	$5D$	4 412.47	23.09	2.82	20.27	0.194	1.14	0.170
	$4F$	6 860.37	1.96	0.02	1.95	0.070	1.01	0.069
	$5F$	4 390.37	0.99	0.01	0.98	0.062	1.01	0.061
Mg^{++}	$3D$	49 777.0	251.5	31.5	220.0	0.134	1.27	0.105
Sp. Mg II	$4D$	27 955.3	130.4	18.0	112.4	0.144	1.34	0.107
$Z=2$	$5D$	17 846.3	72.2	11.2	61.0	0.146	1.36	0.107
	$4F$	27 467.4	8.43	0.17	8.26	0.074	1.03	0.072
	$5F$	17 577.2	4.92	0.14	4.78	0.076	1.03	0.074
	$6F$	12 204.8	3.02	0.12	2.90	0.074	1.03	0.072
Al^{+++}	$3D$	113 497.9	418	46.5	371.5	0.100	1.47	0.069
Sp. Al III	$4F$	61 841.7	12.89	0.39	12.50	0.050	1.05	0.047
$Z=3$	$5F$	39 578.6	8.24	0.31	7.93	0.056	1.06	0.053
	$6F$	27 484.5	5.64	0.23	5.41	0.061	1.06	0.058
	$5G$	39 526.2	2.41	0.01	2.40	0.070	1.00	0.070
K^+	$4F$	6 878.5	20.0	0.14	19.9	0.715	1.03	0.694
Sp. K I	$5F$	4 404.2	14.8	0.1	14.7	0.925	1.04	0.890
$Z=1$	$6F$	3 056.5	8.3	0.1	8.2	0.840	1.04	0.807
Ca^{++}	$4F$	27 694.0	65.0	1.5	63.5	0.571	1.06	0.540
Sp. Ca II	$5F$	17 714.1	39.1	1.2	37.9	0.600	1.08	0.555
$Z=2$	$6F$	12 290.0	24.3	0.9	23.4	0.600	1.09	0.550
	$6G$	12 211.0	4.54	0.0	4.54	0.46	1.01	0.46
Rb^+	$4F$	6 987.6	39.0	1.0	38.0	1.37	1.05	1.30
Sp. Rb I	$5F$	4 418.2	28.7	0.8	27.9	1.77	1.06	1.66
$Z=1$	$6F$	3 068.0	19.7	0.6	19.1	1.95	1.07	1.83
Sr^{++}	$4F$	27 960.4	131.5	8.6	122.9	1.10	1.15	0.96
Sp. Sr II	$5F$	17 896	84	7.0	77	1.22	1.19	1.02
$Z=2$	$6F$	12 412	55	5	50	1.28	1.21	1.06
Cs^+	$4F$	6 932.80	74.27	2.73	71.54	2.58	1.07	2.38
Sp. Cs I	$5F$	4 433.00	43.55	2.26	41.29	2.61	1.09	2.39
$Z=1$	$6F$	3 074.77	26.54	1.58	24.96	2.56	1.10	2.33
	$5G$	4 393.5	4.05	0.01	4.06	1.1	1.02	1.1
	$6G$	3 057.0	8.77	0.01	8.76	3.6	1.02	3.5

lation are given. The method is to subtract the experimental term value T divided by Z^2 from the hydrogenic value, R/n_0^2. This difference is given in column 4. The part of this, $\Delta T_{\text{pen}}/Z^2$, calculated as due to penetration, tabulated in column 5, is subtracted, leaving $\Delta T_\alpha/Z^2$ (column 6). This $\Delta T_\alpha/Z^2$ is the term defect, divided by the ionic charge squared, due to distortion of the ion. From this α_0, the polarizability, is calculated, (column 7) without consideration of the effect due to the quadropolarizability. The effect of the higher distortion is then taken into account by dividing by a factor C_q, the expression for which is given in Eq. (14) and which is tabulated in column 8. In column 9 the final value of the polarizability α is given.

CALCULATIONS

(a). The deformation effect

The complete zeroth order function Ψ_k of the atom, neglecting interaction between the ionic kernel and the valence electron is written as a product of the ionic function $\psi_m{}^i$ with the quantum numbers m, and a hydrogen-like function $\psi_p{}^v$ for the valence electron. p is an abbreviation for the quantum numbers n, l, and the orientation quantum number m_l. We wish to calculate the perturbation of a state $k=0(m=0,\ p=p_0)$.

$$\Psi_k=\psi_m{}^i\psi_p{}^v,\quad \Psi_0=\psi_0{}^i\psi_{p_0}{}^v,\quad \overset{0}{E}_k=\overset{0}{E}_m{}^i+\overset{0}{E}_p{}^v. \tag{3}$$

The perturbation potential H due to the distortion of the kernel may be written

$$H=H^a+H^b \qquad \text{with} \qquad H^a=-e^2\frac{\mathbf{R}\cdot\mathbf{r}}{r^3},\qquad H^b=-\frac{1}{2}e^2\frac{1}{r^3}\left[3\left(\frac{\mathbf{R}\cdot\mathbf{r}}{r}\right)^2-R^2\right], \tag{4}$$

$$\mathbf{R}=\textstyle\sum_i\mathbf{r}_i,\qquad R=|\mathbf{R}|$$

in which $\mathbf{r}$ and $\mathbf{R}$ designate the vector radii of the valence electron and the ion, respectively. Correctly $\mathbf{R}$ is a sum over the vector radii $\mathbf{r}_i$ of all of the electrons i in the kernel. r and R are the respective magnitudes. H^a is the dipole, H^b the quadrupole distortion.

If we define H_{0k} by the equations,

$$H_{0k}=H_{0k}{}^a+H_{0k}{}^b,\qquad H_{0k}{}^a=\int\Psi_0H^a\Psi_kd\tau,\qquad H_{0k}{}^b=\int\Psi_0H^b\Psi_kd\tau, \tag{5}$$

all products $H_{0k}{}^a\times H_{k0}{}^b$ as well as the first order energy H_{00} are zero because of the form of H. Further, the degeneracy in the orientation quantum number m_l of the hydrogen state is not lifted by the perturbation, and the states of different l are the correct zeroth order approximations to the problem. Applying the conventional method of the perturbation theory, one obtains

$$\Delta E_0=\Delta E_0{}^{(2)}=\textstyle\sum_{mp}\left[|(H^a{}_{0p_0,\ mp}|^2+|H^b{}_{0p_0,\ mp}|^2)/(\overset{0}{E}_0-\overset{0}{E}_m{}^i-\overset{0}{E}_p{}^v)\right]. \tag{6}$$

The energy term $\overset{0}{E}_p{}^v$ which is small compared to $\overset{0}{E}_0-\overset{0}{E}_m{}^i$ is neglected. (The term $m=0$ does not occur in this sum.) The sums over p are then evaluated by observing that

$$\begin{aligned}\textstyle\sum_p|H^a{}_{0p_0,\ mp}|^2+|H^b{}_{0p_0,\ mp}|^2&=-e^4\textstyle\sum_p\left|\left\{\mathbf{R}_{0m}\cdot\left(\frac{\mathbf{r}}{r^3}\right)\right\}_{p_0,\ p}\right|^2+\frac{1}{4}\left|\left\{\frac{1}{r^3}\left[3\left(\frac{\mathbf{R}\cdot\mathbf{r}}{r}\right)^2_{0m}-R_{0m}\right]\right\}_{p_0,\ p}\right|^2\\&=-e^4\left\{\left(\mathbf{R}_{0m}\cdot\frac{\mathbf{r}}{r^3}\right)^2+\frac{1}{4r^6}\left[3\left(\frac{\mathbf{R}\cdot\mathbf{r}}{r}\right)^2_{0m}-R_{0m}{}^2\right]^2\right\}_{p_0p_0}=-\frac{e^4}{3}\left[|R_{0m}|^2(r^{-4})_{p_0p_0}+\frac{3}{5}|R_{0m}{}^2|^2(r^{-6})_{p_0p_0}\right].\end{aligned} \tag{7}$$

The complete expressions for the change of energy due to deformation becomes

$$-\Delta E=(e^4/3)\{(r^{-4})_{p_0p_0}\sum_m[|R_{0m}|^2/(\overset{0}{E}_0-\overset{0}{E}_m)]+\tfrac{3}{5}(r^{-6})_{p_0p_0}\sum_m[|R_{0m}{}^2|^2/(\overset{0}{E}_0-\overset{0}{E}_m)]\}. \quad (8)$$

The polarizability α of the ion is given by

$$\alpha=\tfrac{2}{3}e^2\sum_m[|R_{0m}|^2/(\overset{0}{E}_0-\overset{0}{E}_m)]. \quad (9)$$

It is now desirable to obtain an approximate value for the second sum in Eq. (8) in terms of the polarizability. A customary approximation is to assume that all the significant terms in Eq. (9) occur at approximately the same energy, obtaining,

$$\sum_m[|R_{0m}|^2/(\overset{0}{E}_0-\overset{0}{E}_m)]\cong R_{00}{}^2/E_\alpha, \quad (10)$$

in which E_α is some average energy, approximately the ionization energy. A similar approximation leads to the equation,

$$\sum_m[|R_{0m}{}^2|^2/(\overset{0}{E}_0-\overset{0}{E}_m)]\cong\frac{R_{00}{}^4}{E_q}\cong\frac{(R_{00}{}^2)^2}{NE_\alpha}\cong\frac{R_{00}{}^2}{N}\sum_m[|R_{0m}|^2/(\overset{0}{E}_0-\overset{0}{E}_m)], \quad (11)$$

in which N is the number of outer electrons. The approximation (11) has been obtained in the following manner, both $R_{00}{}^2$ and $R_{00}{}^4$ are the sums of the average of these functions of r for the individual electrons i of the ion in its normal state. That is,

$$R_{00}{}^2=\sum_i(r_{00}{}^2)_i, \qquad R_{00}{}^4=\sum_i(r_{00}{}^4)_i. \quad (12)$$

There are N outer electrons of the ion whose individual $r_{00}{}^2$ and $r_{00}{}^4$ will be about equal, and these functions of all other (inner) electrons will be negligible. $r_{00}{}^4$ will be about equal to, and somewhat larger than, the square of $r_{00}{}^2$, making $R_{00}{}^4\cong(R_{00}{}^2)^2/N$. Further the average energy E_q will be somewhat larger than E_α. Numerically the values $N=8$ (and 2 for Li^+) have been chosen in making the arithmetical calculations.

Substituting (9) and (11) in (8) one obtains for the change in energy,

$$-\Delta E=\frac{1}{2}\,\alpha e^2(r^{-4})_{p_0p_0}\left[1+\frac{3}{5}\frac{R_{00}{}^2}{N}\frac{(r^{-6})_{p_0p_0}}{(r^{-4})_{p_0p_0}}\right]. \quad (13)$$

The unperturbed energy is that of a hydrogen like state, $-\overset{0}{E}=Rhc/n_0{}^2$, and the term value T is the negative of the energy divided by hc. One may then write the equation for α,

$$\alpha=\frac{2(R/n_0{}^2-T_{p_0})hc}{e^2(r^{-4})_{p_0p_0}[1+3R_{00}{}^2(r^{-6})_{p_0p_0}/5N(r^{-4})_{p_0p_0}]}=B_{p_0}Z_\infty{}^{-4}C_q{}^{-1}[R/n_0{}^2-T_{p_0}], \quad (14)$$

$$B_{p_0}Z_\infty{}^{-4}=\frac{2hc}{e^2}(r^{-4})_{p_0p_0}{}^{-1}, \qquad C_q=[1+3R_{00}{}^2(r^{-6})_{p_0p_0}/5N(r^{-4})_{p_0p_0}].$$

The values of $(r^{-4})_{p_0p_0}$ and of $(r^{-6})_{p_0p_0}$ may be easily evaluated knowing the hydrogen radial functions. Waller[11] has given an expression for $(r^{-4})_{p_0p_0}$. $R_{00}{}^2$ is connected with the specific magnetic susceptibility χ by the equation

$$R_{00}{}^2=(6m_0c^2/Ne^2)\chi. \quad (15)$$

The values of χ used are the experimental values tabulated by Pauling,[12] except for the first row of the periodic system, for which Pauling's theoretical values are used. The bracket in the denominator of Eq. (15), which is abbreviated as C_q, the correction for higher distortions is tabulated in Table I, column 8. $(r^{-6})_{p_0p_0}$ is divergent for P states and the correction cannot be made. This merely means that the P orbits

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[11] I. Waller, Zeits. f. Physik **38**, 635 (1926).

[12] L. Pauling, Phys. Rev. **34**, 954 (1929).

penetrate the ion too strongly for this method of approximation.

(b). The penetration effect

Instead of using the difference between the experimental term value T and the hydrogen-like term value in the numerator of Eq. (15) the change in T, ΔT_{pen}, due to penetration has been subtracted. This effect is due to the deviation in the true potential from the assumed zeroth approximation due to the *undistorted* ionic kernel and may be handled independently of the distortion effects.

If $Z(r)$ is the effective nuclear charge as a function of r and Z_∞ the charge on the ion, the perturbation potential may be written.

$$\begin{aligned} dU/dr &= e^2(Z(r)-Z_\infty)/r^2, \\ -U &= e^2\left[\frac{Z(r)-Z_\infty}{r} - \int_r^\infty \frac{1}{r}\frac{dZ(r)}{dr}dr\right]. \end{aligned} \tag{16}$$

The first order effect on the term value alone is considered.

$$\Delta T = -\frac{\Delta E}{hc} = -\frac{e^2}{hc}\int \bar{\psi}_{p_0}{}^v U \psi_{p_0}{}^v d\tau, \tag{17}$$

$Z(r)-Z_\infty$ is assumed to have the analytical form $\beta b r^2 e^{-\beta r}$, in which case $U(r)$ will have the form $U(r) = -(e^2 b/a_0)e^{-\beta r}$, when r is measured in units of a_0, the radius of the first Bohr orbit of hydrogen, ($a_0 = 0.5285 \times 10^{-8}$ cm.). This empirical equation for $Z(r)$ can be made to fit all the given tables of $Z(r)$ for large values of r by the proper choice of the constants b and β. Since the whole effect is at large r values it is unimportant that the equation is absolutely false for small r. No tables were at hand for the multiply charged ions. It was assumed that the equation $\beta = 2Z_e/n$ was approximately true with n the total quantum number of the outer electrons of the ion, and Z_e the effective charge on the electrons. Z_e was then assumed to increase by one as the charge on the ion increased by one, for the same configuration. In Table II are given the assumed values of b and β for the various ions. A few graphical integrations showed that the total penetration effect occurred in the region where the assumed form of the function $Z(r)$ was in agreement with the tabulated values.

TABLE II. *Empirical constants of the penetration potential.*

Ion	Li^+	Be^{++}	B^{+++}	C^{++++}	Na^+	Mg^{++}	Al^{+++}	K^+	Ca^{++}	Rb^+	Sr^{++}	Cs^+
b	9.5	9.5	9.5	9.5	33	33	33	34	34	35	35	36
β	5.43	7.43	9.43	11.43	4.05	5.05	6.05	3.09	3.76	2.42	2.92	2.11

RESULTS

In Table III are given the most probable values of α, as deduced only from the internal evidence of this calculation. Values previously published in the literature are included for comparison. The values for the rare gases are experimental, and quite accurate. They are copied from Pauling's tables.

Some considerations lead to misgivings about the accuracy of the values here computed. The consistently lower values of α obtained from a higher series in comparison with a lower series, F compared with D in sodium for instance, indicates some sort of systematic error. This may be a gross underestimation of the quadrupolariza-

TABLE III. *Polarizabilities of the gaseous ions.* ($\alpha \times 10^{24}$ in cm^3.)

Ion	This paper	Pauling	Fajans and Joos	Born and Heisenberg ($k = l + \frac{1}{2}$)
He		0.204		
Li^+	0.025	0.0295	0.079	0.075
Be^{++}	0.007	0.0080	0.039	
B^{+++}	0.0033	0.00303		
C^{++++}	0.0015	0.00135		
Ne		0.396		
Na^+	0.17	0.182	0.197	0.21
Mg^{++}	0.10	0.092	0.110	0.12
Al^{+++}	0.53	0.054		0.065
Ar		1.645		
K^+	0.80	0.844	0.879	0.87
Ca^{++}	0.54	0.474	0.447	
Kr		2.49		
Rb^+	1.5 (?)	1.42	1.485	1.81
Sr^{++}	1.0	0.87	0.883	1.42
Xe		4.05		
Cs^+	2.35	2.45	2.577	2.79

bility correction, which is not unlikely since our approximation gives a lower limit to this correction, or a gross underestimation of the penetration effect which is less likely. Any such explanation would tend to give more weight to the values obtained from the higher series, indeed the true value would then be slightly less than that of the higher series, which seems unreasonable in the case of sodium at least.

For some ions an error may be introduced by a false estimation of the series limit. That is, although the differences in term values are well known, the absolute values are uncertain. That such uncertainties exist is apparent. Bacher and Goudsmit and the *International Critical Tables* differ by 2.6 cm^{-1} in the case of K I, and 98 cm^{-1} in Sr II. However the term values of Na I are probably known with great accuracy.

The results of this paper agree quite well with the calculations of Pauling. It is particularly to be noted that the agreement for the ions of the elements of the first row of the Periodic Table lends great support to Pauling's method, which for these ions is purely theoretical and assumes no empirical constants.

For most of the singly charged positive ions, (alkalis), the polarizabilities appear to be slightly lower than Pauling's values, and considerably lower than those of Fajans and Joos. Pauling has obtained the values which he gives by assuming a linear extrapolation of a screening constant, calculated from the polarizabilities of the corresponding rare gas atom and negative halide ion. If the deviation above noted is real, it would lead to the conclusion that the polarizabilities of the gaseous negative ions are greater, and indeed considerably greater, than those assumed by Pauling. This means that the gaseous negative ions have considerably higher polarizabilities than the same ions in crystals, and the gaseous positive ions somewhat lower α's than in the crystals.

If the approximation of Eq. (10) is used, leading to

$$\alpha \overset{\frown}{=} \tfrac{2}{3}e^2(R_{00}{}^2/E_\alpha), \tag{18}$$

it might be assumed that $R_{00}{}^2$ is approximately independent of the state of any given ion and that the polarizability α varies inversely with the "main frequency." The absorption frequencies of negative ions in a crystal are more than double the probable absorption frequencies (near the electron affinity), in the gaseous state. The absorption frequencies of the positive ions, on the other hand, are probably lowered by inclusion in a crystal. It seems then, qualitatively, probable that the polarizabilities of positive ions are increased somewhat in passing from the gaseous into the crystalline (or aqueous) state, while those of the negative ions are enormously (twofold?) decreased by the same change of state.

For convenience the values of $B_{n_0l_0}$ of Eq. (14) are included in Table IV for different terms.

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TABLE IV.

Term	$2P$	$3P$	$4P$	$3D$	$4D$	$5D$	$4F$	$5F$	$6F$	$5G$	$6G$	$6H$
$B_{n_0l_0}\times 10^4$	0.322	0.978	2.228	24.4	51.5	96.0	360	634	1025	2640	4080	12850