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A Redetermination of the Carbon–Oxygen Distance in Calcite and the Nitrogen–Oxygen Distance in Sodium Nitrate

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For the case of carbon–carbon interaction in molecules an empirical function has been found[1] which relates the observed interatomic distances to the type of bond formed. The same function, with a suitable translation and change of scale, has been used to predict distances between other atoms, notably carbon–oxygen and nitrogen–oxygen distances. A large discrepancy occurs for the carbonate ion between the predicted distance, 1.32 Å., and the distance reported for calcite.[2] This disagreement and the desirability of testing the assumptions involved in the use of the function have led to a reinvestigation of the parameters in calcite and sodium nitrate.

Crystals of calcite and sodium nitrate were ground on (111) and (211) faces[3] and Laue photographs obtained of each substance in two orientations, one with the primary beam perpendicular to the cleavage plane, the other with the X-rays parallel with the three-fold axis. On each set of photographs pairs of reflections were found having nearly the same values of sin Θ and of $n\lambda$. The relative intensities of each pair were estimated visually by comparing photographs having different known exposures. The more important reflections were photometered on an alpha-ray integrating microphotometer.[4]

Theoretical structure factors, F_{hkl}, were based on the Pauling and Sherman[5] tables of atomic scattering factors. Since the comparisons involve the ratio of intensities of reflections having approximately the same wave length and scattering angle, no other terms need be included in the calculations. The ratio of the intensities reflected from two planes, (hkl) and $(h'k'l')$, was then assumed to be equal to the ratio of the squares of the corresponding structure factors

$$I_{hkl}/I_{h'k'l'} = F^2_{hkl}/F^2_{h'k'l'}$$

The possibility that the intensities might be proportional to the first power of the structure factors was also considered.[6] When calculations are made on this basis, the individual intensity ratios of Tables I and II lead to a very wide range of parameter values, whereas the spread is small when the squares of the structure factors are used. This indicates strongly that for the separate crystal sections used in this investigation the intensities are closely proportional to F^2.

In Tables I and II there are given the results of the microphotometric measurements for calcite and sodium nitrate, respectively. In all cases but one, two carbon prints were measured for

TABLE I

PARAMETER DETERMINATION FOR CALCITE USING MICROPHOTOMETER VALUES OF INTENSITIES

Reflecting planes	Interplanar distance	Wave length	I/I'		Parameter	
$1\bar{7}2$	1.032	0.37	2.46	2.30	0.2624	0.2633
905	1:040	.36				
5.12.7	1.031	.37	1.95		.2614	
$4\bar{5}3$	1.031	.36				
921	0.530	.32	1.63	1.79	.2630	.2656
$37\bar{2}$	.535	.32				
$7\bar{1}6$	.530	.32	1.75	1.71	.2650	.2642
$37\bar{2}$	.535	.31				
$37\bar{2}$	.535	.32	1.16	1.02	.2631	.2670
$17\bar{2}$	.534	.31				
720	.628	.35	12.11	13.18	.2628	.2637
$45\bar{2}$	.635	.36				
$\bar{1}27$	.591	.36	4.25	4.13	.2640	.2646
$74\bar{1}$	.580	.36				

Weighted average value of the parameter, 0.2635 ± 0.0011.

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(1) Pauling, Brockway and Beach, THIS JOURNAL, **57**, 2705 (1935).

(2) Wyckoff, *Am. J. Sci.*, **50**, 317 (1920).

(3) The indices employed in this paper refer to the smallest rhombohedral units of structure. The lattice constants for calcite are $a_0 = 6.36$Å., $\alpha = 46°6'$; those for sodium nitrate are $a_0 = 6.32$ Å., $\alpha = 47°15'$. The space group of both substances is $D^6_{3d} - R\bar{3}c$, with atoms in the positions

Ca or Na: $^1/_4\ ^1/_4\ ^1/_4;\ ^3/_4\ ^3/_4\ ^3/_4$
C or N: $0\ 0\ 0;\ ^1/_2\ ^1/_2\ ^1/_2$
O: $u\ \bar{u}\ 0;\ \bar{u}\ 0\ u;\ 0\ u\ \bar{u};\ ^1/_2 - u,\ ^1/_2 + u,\ ^1/_2;$
$^1/_2 + u,\ ^1/_2,\ ^1/_2 - u;\ \ ^1/_2,\ ^1/_2 - u,\ ^1/_2 + u.$

(4) The application of the alpha-ray integrating microphotometer to the determination of X-ray intensities was first reported by Astbury, *Proc. Roy. Soc.*, **123**, 575 (1929). The microphotometer measures the intensity of alpha-rays passing through a carbon print of an X-ray negative. The necessary conditions for obtaining integrating properties are that a linear relation exist between the X-ray intensity of a given reflection and the corresponding alpha-ray intensity, taken as the rate of discharge of an electroscope; and that zero X-ray intensity correspond to zero alpha-ray intensity. These conditions are easily met by adjusting the constants of the apparatus.

(5) Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).

(6) This phenomenon has been observed in the case of calcite by P. E. Tahvonen, *Societas Scientiarum Fennica, Commentationes Physico-Mathematicae*, VIII, 6 (1935), and other investigators.

TABLE II

PARAMETER DETERMINATION FOR SODIUM NITRATE USING MICROPHOTOMETER VALUES OF INTENSITIES

Reflecting planes	Interplanar distance	Wave length	I/I'		Parameter	
207	0.670	0.45	2.10	2.11	0.2400	0.2400
$\bar{1}36$	.695	.46				
$\bar{2}34$	.800	.44	2.17	2.14	.2385	.2390
$\bar{1}25$	.825	.44				
$\bar{1}50$	.790	.39	1.84	2.00	.2398	.2392
$\bar{2}34$	.800	.38				

Weighted average value of the parameter, 0.2394 ± 0.0005.

TABLE III

PARAMETER DETERMINATION FOR CALCITE USING VISUAL ESTIMATES OF INTENSITIES

Reflecting planes	Interplanar distance	Wave length	I/I'	Parameter
$1\bar{1}4$	0.970	36	2.5	0.260
$42\bar{1}$	.960	37		
723	.807	34	6.5	.261
241	.798	33		
12.7.7	.534	36	2.5	.262
$\bar{3}64$	.529	36		
$5\bar{2}3$	.690	43	2.0	.265
945	.635	44		
$\bar{3}43$	.650	32	7.0	.261
$6\bar{1}4$	.640	33		
$\bar{3}56$	.492	30	2.0	.262
10.1.3	.484	30		
$\bar{2}37$	.535	30	1.5	.257
$\bar{2}71$	.534	29		

Weighted average value of the parameter, 0.261 ± 0.002.

TABLE IV

PARAMETER DETERMINATION FOR SODIUM NITRATE USING VISUAL ESTIMATES OF INTENSITIES

Reflecting planes	Interplanar distance	Wave length	I/I'	Parameter
$\bar{1}14$	0.995	0.41	1.33	0.235
$2\bar{1}4$	.985	.41		
$\bar{1}50$	.790	.40	1.90	.240
106	.760	.40		
$5\bar{1}4$	.750	.40	1.75	.239
106	.760	.40		
$\bar{5}01$	.790	.47	1.60	.240
163	.810	.47		

Weighted average value of the parameter, 0.239 ± 0.002.

each pair of reflections, giving the intensity ratios I/I' in the fourth columns.

In Figs. 1 and 2, corresponding to Tables I and II, the intensity ratios of pairs of reflections are plotted as ordinates with the parameters as abscissas. The final parameter values in the fifth columns of the tables were read directly from these graphs.

Each parameter value was multiplied by the slope of the corresponding intensity curve as a weight factor in obtaining the average values, for it is clear that, other effects being equal, the reliability of a single result is proportional to this slope. The limits of error are taken as the average deviations.

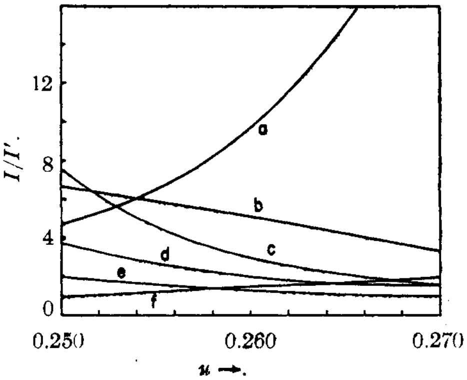

Fig. 1.—$a = I_{720}/I_{45\bar{2}}$; $b = I_{\bar{1}27}/I_{74\bar{1}}$; $c = I_{1\bar{7}2}/I_{906}$; $d = I_{5.12.7}/I_{4\bar{6}3}$; $e = I_{37\bar{2}}/I_{17\bar{2}}$; $f = I_{7\bar{1}6}/I_{37\bar{2}}$; and $I_{921}/I_{37\bar{2}}$.

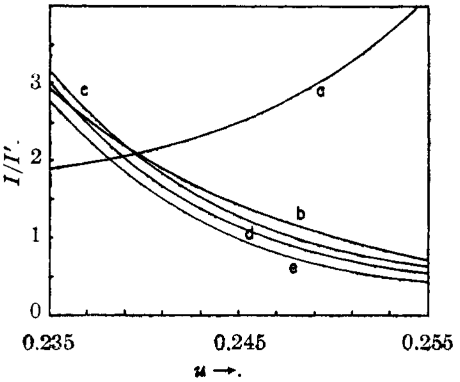

Fig. 2.—$a = I_{207}/I_{\bar{1}36}$; $b = I_{\bar{2}34}/I_{\bar{1}25}$; $c = I_{\bar{1}50}/I_{106}$; $d = I_{\bar{1}50}/I_{\bar{2}34}$; $e = I_{5\bar{1}4}/I_{106}$.

The parameter values found for calcite and sodium nitrate, 0.2635 and 0.2394, respectively, are not in disagreement with the results of Wyckoff's[2,7] experiments which allow a range of 0.24 to 0.26 with the probable value 0.25 in each case.

The observation of a weak reflection $(31\bar{1})$ on several photographs of both substances in the present investigation suggests that the parameters cannot be exactly 0.25. This reflection has zero amplitude for $u = 0.25$ inasmuch as the structure factor has the form $f_0 \sin 2u(h-k) + \sin 2u(k-l) + \sin 2u(l-h)$ for planes the sum of whose indices is odd. Other planes of this type are too weak to reflect and do not appear on the

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(7) Wyckoff, *Phys. Rev.*, **16**, 149 (1920).

photographs. Failure to observe $(31\bar{1})$ on Wyckoff's photographs is due to the excessive fogging of the negatives by the incident radiation in the region around the central image.

The values found for the C–O and N–O distances are 1.313 and 1.210 Å. On comparing these with the values 1.32 and 1.26 Å., respectively, predicted by Pauling, Brockway and Beach,[1] we see that the disagreement which had existed in the case of the carbonate ion has been removed, but that a difference of 0.05 Å. is found for the nitrate ion.[8] It seems probable that this difference shown by the nitrate ion is to be attributed to a previously unrecognized phenomenon, namely, the effect of resultant charge of an atom on its covalent radius. From the electronic-structural point of view we interpret the decrease in the sequence of values 0.77, 0.70, 0.66, 0.64 Å. for the single-bond covalent radius of carbon, nitrogen, oxygen, fluorine, respectively, as due to an increase in effective nuclear charge of the atoms, which can be estimated with the use of screening constants to amount to about 0.6 unit from one atom to the next.[9] In the case of a bond between two atoms with formal charges of opposite sign, the interatomic distances would be given approximately by the sum of the radii for neutral atoms, since the increase in radius of the negatively charged atom would be approximately compensated for by the decrease in radius of the positively charged atom. In the nitrate ion a nitrogen atom with formal charge +1 is connected by single bonds to oxygen atoms with formal charge −1 and by a double bond to a neutral oxygen atom. For the single bond we accordingly expect approximately the normal single-bond distance, but for the double bond we expect a distance shorter than the normal value, corresponding to an increase for nitrogen of about one unit in effective nuclear charge. This would lead to a value for the double-bond radius between those of oxygen and fluorine, that is, about 0.05 Å. less than the normal double-bond radius of nitrogen. Resonance between this double bond and the single bonds would lead to an expected nitrogen to oxygen distance in the nitrate ion 0.05 Å. less than that predicted by Pauling, Brockway and Beach, and in exact agreement with the new experimental value. This agreement between the experimental value and the value predicted by the above straightforward argument provides strong evidence for the correctness of the postulated dependence of the covalent radius on effective nuclear charge. The phenomenon should be observed in many other substances, such as, for example, the tetramethylammonium ion; experiments to test these predictions are planned.

The author wishes here to express his thanks to Professor Linus Pauling for suggesting this research, for his continued help and interest throughout the course of the investigation, and for a major contribution to the discussion at the end of this paper, and to Dr. J. H. Sturdivant for kind advice and direction in the preparation of the Laue photographs and in the use of the alpha-ray microphotometer.

Summary

A reinvestigation of the parameters of calcite and sodium nitrate has been carried out using data obtained from Laue photographs. The parameters found are 0.2635 for calcite and 0.2394 for sodium nitrate. These values lead to the interatomic distances 1.313 Å. for the carbon–oxygen bond and 1.210 Å. for the nitrogen–oxygen bond. A comparison with the distances predicted by Pauling, Brockway, and Beach[1] is made, and agreement found for the carbonate ion. The short nitrogen–oxygen distance is discussed in relation to the effect of resultant charge of an atom on its covalent radius.

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[8] The revision of the table of covalent radii and of the resonance curve reported by Pauling and Brockway, THIS JOURNAL, **59**, 1223 (1937), leads to no change in the predicted distances.

[9] See Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).