

## The Structure of Caesium Enneachlordiarsenite, $\text{Cs}_3\text{As}_2\text{Cl}_9$

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## The Structure of Caesium Enneachlordiarsenite, $\text{Cs}_3\text{As}_2\text{Cl}_9$

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(Received November 28, 1934)

$\text{Cs}_3\text{As}_2\text{Cl}_9$  is shown to have a hexagonal unit of structure with  $a_0 = 7.37\text{\AA}$ ,  $c_0 = 8.91\text{\AA}$ , containing one molecule. The atomic arrangement is based upon closest-packing of caesium and chlorine, with  $D_{3d}^2 - C_{32}$  as the most probable space-group, but the amount of distortion from the closest-packed positions is not large enough to permit of the unambiguous elimination of  $D_{3d}^2 - C_{3m}$ . A structure based upon  $D_3^2$  accounts well for observed intensity data. Arsenic is shown definitely by the intensity data to have only a pseudo-coordination number of six, and the structure may

be qualitatively described as containing  $\text{AsCl}_3$  molecules embedded in an environment of caesium and chloride ions in such a way that all large atoms fit into an approximately closest-packed arrangement. This is the first structure of this type to be discovered. The ratio of  $3\text{Cl}$  per  $\text{Cs}$  is a particularly happy one for structures of this kind, and a study of this structure gives much insight into the existence and stability of the related group of compounds discussed in the Introduction.

### INTRODUCTION

A NUMBER of compounds with the type formula  $A_3B_2X_9$ , in which  $A$  may represent caesium or rubidium,  $B$  arsenic or antimony, and  $X$  chlorine, bromine, or iodine were originally prepared and described by Wheeler.<sup>1</sup> These compounds crystallize with some form of three-fold or sixfold symmetry, or in some cases with only a close approximation thereto. The crystallographic data indicate that two or more essentially distinct but probably closely related structural types are represented. Two points seem of particular interest: (1) How can we account for the existence and stability of these apparently complicated compounds, and (2) what sort of bonding and coordination properties should we ascribe to arsenic (or antimony)? In order to answer these questions, we have made an x-ray study of caesium enneachlordiarsenite,  $\text{Cs}_3\text{As}_2\text{Cl}_9$ , resulting in a determination of the atomic arrangement existing within the crystal. We have found from x-ray data that two compounds of similar formula,  $\text{Cs}_3\text{Ti}_2\text{Cl}_9$  and  $\text{Cs}_3\text{Ti}_2\text{Br}_9$ , first prepared by Pratt,<sup>2</sup> belong to quite a different structural type.<sup>3</sup>

### DETERMINATION OF THE STRUCTURE

Following the directions of Wheeler, crystals of  $\text{Cs}_3\text{As}_2\text{Cl}_9$  were prepared in the form of thin, six-sided, optically uniaxial plates somewhat less

than one mm in diameter. Laue and oscillation photographs were prepared using, respectively, general radiation from a tube with tungsten target operated at a peak voltage of about 50 kv, and  $K$ -series radiation from a tube with water-cooled molybdenum target.

Application of the Bragg formula to the observed spacings of the equatorial reflections from the basal plane appearing upon oscillation photographs gives a value for  $d_{(001)}/n_1$  of  $8.910 \pm 0.020\text{\AA}$ , spectra from a cleavage face of calcite being used as a comparison standard. Application of the Polanyi equation,  $s\lambda = I \sin \mu$ , to observed spacings of layer lines on these photographs leads to identity distances along the axes of oscillation of about  $7.4\text{\AA}$  and  $12.8\text{\AA}$  ( $=\sqrt{3} \cdot 7.4\text{\AA}$ ) accordingly as the axis of crystallographic description (using hexagonal axes) or a direction making an angle of  $30^\circ$  with it is chosen as the axis of oscillation. The data from three completely indexed Laue photographs taken with the x-ray beam inclined at various small angles to  $c$  are completely accounted for on the basis of a hexagonal unit with  $a_0 = 7.37\text{\AA}$ ,  $c_0 = 8.91\text{\AA}$ ; for no observed reflection gives a calculated value of  $n\lambda$  less than  $0.24\text{\AA}$ , the short wavelength limit of the radiation employed. On one photograph, for example, a total of about 135 spots appear with more than 40 forms reflecting in the first order; and in no case is a spot of doubtful nature observed, so that this unit may be confidently accepted as the true one. Reflections from  $(10\cdot0)$  and  $(11\cdot0)$  obtained by transmission through the very thin plate-like crystals lead to values for  $a_0$  of about  $7.4\text{\AA}$ . Inasmuch as these

<sup>1</sup> Wheeler, Am. J. Sci. **146**, 88 (1893); **146**, 269. See also Groth, *Chemische Kristallographie*, Engelmann, Leipzig, **1**, 434 (1908).

<sup>2</sup> Pratt, Am. J. Sci. **149**, 397 (1895).

<sup>3</sup> Unpublished material.

reflections were too wide for accurate measurement, we have preferred to use Wheeler's apparently reliable value of 1.209 for  $c_0/a_0$  in conjunction with our value of 8.91Å for  $c_0$ , thus leading to  $a_0 = 7.37$ Å.

With one molecule of  $\text{Cs}_3\text{As}_2\text{Cl}_9$  within the unit cell, the calculated density is 3.42 g/cc, somewhat greater than that of methylene iodide. As we had only a small amount of material, no convenient method of determining the density experimentally was available, but inasmuch as the calculated value lies within the limits to be anticipated, we conclude that we have to deal with a one-molecule unit. As we shall show, all other evidence supports this conclusion.

A Laue photograph with the x-ray beam accurately perpendicular to the basal plane shows no deviation from the threefold axis and three planes of symmetry of  $D_{3d}$ . A number of first-order reflections of the types  $\{m\cdot l\}$  with  $l$  odd and  $\{m\cdot l\}$  with  $l$  even appearing on Laue photographs together with the observation that  $\{00\cdot 1\}$  is not thirdd eliminated all space-groups with special criteria.<sup>4</sup> As  $a_0$  is found to lie along a twofold axis and  $30^\circ$  from a symmetry plane, there remain as possible space-groups  $C_{3v}$ ,  $C_3$ ,  $D_3$ ,  $D_3^2$ , and  $D_3^2$ , with no conclusive evidence at this stage to enable us to decide upon one of them. We are able, however, to proceed with a structural determination based upon convincing premises, and leading to the selection of  $D_3^2$  as the probable space-group.

The radius<sup>5</sup> of  $\text{Cl}^-$  (for coordination number six) is 1.81Å. A hexagonal unit of three layers made up of 12 spheres of this size in closest-packing would have  $a_0 = 7.24$ Å,  $c_0 = 8.86$ Å. The radius of  $\text{Cs}^+$  is 1.69Å, but little less than that of  $\text{Cl}^-$ , and our unit cell contains  $3\text{Cs}^+$  and  $9\text{Cl}^-$ . Comparing our lattice constants of  $a_0 = 7.37$ Å,  $c_0 = 8.91$ Å with those above, the conclusion seems inescapable that the structure of  $\text{Cs}_3\text{As}_2\text{Cl}_9$  is based upon a nearly closest-packed arrangement of caesium and chloride ions. Furthermore, if we make the additional and quite reasonable requirement that two caesium ions shall not be in contact with each other, it is not difficult to

see that we are led to a unique distribution (excepting small distortions) of the  $3\text{Cs}^+$  and  $9\text{Cl}^-$  within the unit cell. This ideal or undistorted arrangement is made up of three identical layers, and may be conveniently symbolized as follows: Let  $A$  represent a closest-packed layer with  $\text{Cs}^+$  at 00,  $B$  a layer with  $\text{Cs}^+$  at  $\frac{1}{3}\frac{2}{3}$ , and  $C$  a layer with  $\text{Cs}^+$  at  $\frac{2}{3}\frac{1}{3}$ . The sequence of layers along  $c$  is then  $ABCABC\cdots$ , corresponding to cubic closest-packing. (See Figs. 1-3.) The face-centered unit cube, containing 4 spheres, has  $\text{Cl}^-$  replaced by  $\text{Cs}^+$  at the corners. We note that the rhombohedral angle<sup>6</sup>  $\alpha$  for  $\text{Cs}_3\text{As}_2\text{Cl}_9$  is  $90^\circ 30'$ , which is indicative of the small amount of distortion of the structure from cubic closest-packing.

Taking layer  $A$  at  $z=0$ , we first place arsenic in  $\frac{1}{3}\frac{2}{3}\frac{2}{3}$ ,  $\frac{2}{3}\frac{1}{3}\frac{1}{3}$ , at the centers of octahedra of chlorine atoms in positions such that arsenic atoms remain far apart one from another, and also well-removed from caesium ions. The resulting arrangement is obtainable from each of the three space-groups which must be considered, in each case with highly specialized values of a number of parameters. Moreover, a comparison of calculated structure factors for this structure with observed intensities for the various orders of  $(00\cdot 1)$ ,  $(10\cdot 0)$ , and  $(11\cdot 0)$  make it appear

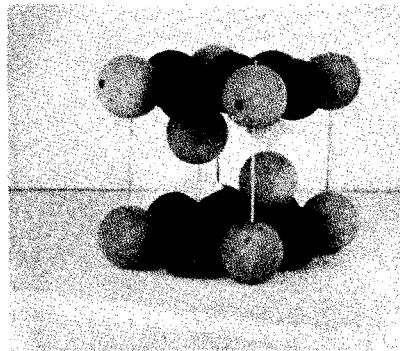


FIG. 1. Photograph of a model of the unit cell of  $\text{Cs}_3\text{As}_2\text{Cl}_9$ , with the chloride ions of layer  $A$  and all caesium ions shown as spheres in closest-packing. Positions of arsenic and of the chlorine atoms of layers  $B$  and  $C$  are indicated as the vertices of the triangular pyramids, which have the dimensions of structure 11.

<sup>4</sup> See Astbury and Yardley, *Tabulated Data for the Examination of the 230 Space-groups by Homogeneous X-Rays*, Phil. Trans. 224, 221-57 (1924).

<sup>5</sup> Linus Pauling, J. Am. Chem. Soc. 49, 765 (1927).

<sup>6</sup> The value of the crystallographic rhombohedral angle  $\alpha$  is incorrectly given by Groth, reference 1, as  $89^\circ 3'$  instead of  $90^\circ 30'$ .

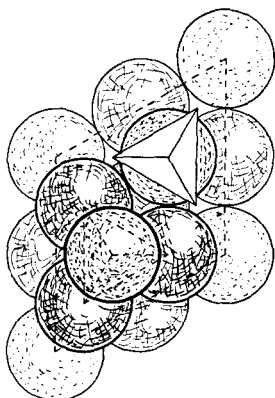


FIG. 2. Packing drawing of three layers parallel to (00·1) showing the undistorted closest-packed structure made up of spheres of the same size throughout. Caesium may be distinguished from chlorine atoms by the type of shading.

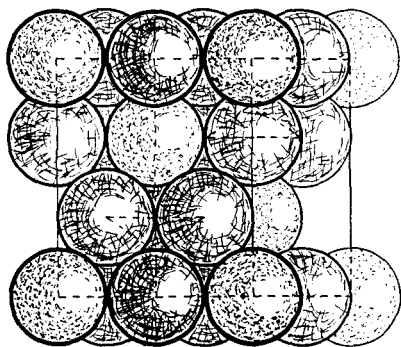


FIG. 3. Packing drawing of the unit cell normal to (10·0) with caesium and chlorine atoms shown as spheres in closest-packing. The positions of arsenic are indicated by the apices of the pyramids.

altogether likely that a suitable distortion of the ideal structure will account for all of the x-ray data.

Each chlorine of layer *A* is shared between two  $\text{AsCl}_6$  octahedra, while each chlorine of layers *B* and *C* is a part of but one such group. Regarding the structure as a purely ionic aggregate of  $\text{Cs}^+$ ,  $\text{As}^{+3}$ , and  $\text{Cl}^-$ , we see that the strength of the electrostatic valence (including the contribution of  $\text{Cs}^+$ ) reaching each  $\text{Cl}^-$  of layer *A* is  $2\frac{1}{6}$ , while to each  $\text{Cl}^-$  of layers *B* and *C* it is  $1\frac{5}{6}$ . Actually we expect the arsenic to have a strong tendency to form three normal covalent bonds with chlorine, and the ionic model shows clearly that such bonds would be formed between

arsenic and the chlorines of layers *B* and *C*; for the formation of such bonds means that arsenic layers will be found somewhat closer to layers *B* and *C* than they are to layer *A*. It appears also that the twofold axes are to be retained and that the actual structure is based upon  $D_{3d}^2$  or  $D_{3d}^3$  rather than  $C_{3v}^1$ .

With either  $D_{3d}^2$  or  $D_{3d}^3$ , caesium and arsenic are placed in the following positions: Cs in  $000$ ,  $\frac{1}{3}\frac{2}{3}u$ ,  $\frac{2}{3}\frac{1}{3}\bar{u}$ , As in  $\frac{1}{3}\frac{2}{3}v$ ,  $\frac{2}{3}\frac{1}{3}\bar{v}$ . We expect  $u \cong \frac{1}{3}$ ,  $\frac{2}{3} < v < \frac{5}{6}$ . Moreover, the complete structure factor including chlorine for (00·*l*) reflections is identical for the two space-groups, namely

$$S_{\{00,l\}} = f_{\text{Cs}}(1 + 2 \cos 2\pi lu) + 2f_{\text{As}} \cos 2\pi lv + 3f_{\text{Cl}}(1 + 2 \cos 2\pi lz),$$

in which  $z \cong \frac{1}{3}$ . We have intensity data for the first twelve orders of reflections from (00·1) with which to compare theoretical values for the proposed structure as calculated from the formula

$$I = C \frac{1 + \cos^2 2\theta}{2 \sin 2\theta} l |S|^2.$$

No corrections are included for extinction or for the decrease in intensity arising from the thermal vibrations of the atoms within the lattice. The *f*-values of Pauling and Sherman<sup>7</sup> are employed throughout this paper. The factor *l* is required since we are considering reflections at small angles from a thin plate-like but strongly absorbing crystal which was at all times completely bathed in radiation; the effective cross section of the beam was proportional then to  $\sin \theta$  and therefore to *l*. Estimating the mass absorption coefficient as about 40 for Mo  $K\alpha$ -radiation, we calculate that there would be only a quite negligible transmission except, perhaps, for the last two or three orders. Experimental intensities were estimated by visual comparison of reflections from a number of photographs with widely varying times of exposure with an intensity scale prepared for this use. The reflections become more diffuse as the order increases, and, as our considerations have to do with integrated intensities, it may be that we have somewhat underestimated the intensities of the last two or three reflections.

<sup>7</sup> Pauling and Sherman, *Zeits. f. Krist.* **81**, 1 (1932).

With the values of the parameters corresponding to closest-packing of  $\text{Cs}^+$  and  $\text{Cl}^-$ , neither caesium nor chlorine would contribute to reflections with  $l/3$  not integral. We do not find it possible to account for such reflections by considering them as due to arsenic alone, but rather that with  $0.795 < v < 0.815$  and with both  $u$  and  $z$  slightly less than  $\frac{1}{3}$ , a general agreement is obtained between calculated and observed intensities. Table I contains these data for

TABLE I. Comparison of calculated with observed intensities for  $(00\cdot l)$  reflections.

$u=0.320,$			$v=0.805,$			$z=0.325$		
$l$	Observed intensity	Calculated intensity*	$l$	Observed intensity*	Calculated intensity*	$l$	Observed intensity*	Calculated intensity*
1	8	8	7	0.5	5			
2	25	25	8	6	28			
3	150	250	9	8	93			
4	4	13	10	4	41			
5	0	1	11	0	4			
6	75	195	12	1	32			

\* Temperature factor not included.

$v=0.805$ ,  $u=0.320$ ,  $z=0.325$ , which values seem to be most satisfactory. As  $3f_{\text{Cl}}$  is nearly equal to  $f_{\text{Cs}}$ , we see that the contributions of these two kinds of atoms are nearly identical in case  $u=z$ . It seems improbable that either  $u$  or  $z$  is less than 0.315, or that both together can be appreciably less than 0.320. However, it seems most satisfactory to have both  $u$  and  $z$  somewhat less than  $\frac{1}{3}$ . Making the caesium parameter slightly less than that for chlorine appears reasonable from a consideration of dimensional relations, but is otherwise quite arbitrary.

We now proceed to compare calculated intensities for  $(h0\cdot0)$  and  $(hh\cdot0)$  reflections with the experimental data. These data are the result of transmission photographs taken through the thin plates, which, however, were of such small diameter as to be completely bathed in radiation at all times. The intensity formula employed was identical in form with that already given except for the omission of the factor  $l$ . In this case the correction for absorption increases with the order, but calculation shows that the increase is not large enough at most to be very important.

The form of the structure factor depends upon the space-group of the structure. If it be based upon  $D_{3d}^3$ , all chlorine atoms lie in planes of symmetry and the structure has but one

parameter at right angles to  $c$ ; in particular, all atoms of layer  $A$  occupy no-parameter positions, and each caesium ion is surrounded by six equidistant chloride ions. If on the other hand the true space-group be  $D_3^2$ , the planes of symmetry are no longer retained, and three of these six chlorides could be nearer than the others to each caesium ion. This second possibility seems to us the more probable, especially in view of the fact that  $\text{Rb}_3\text{As}_2\text{Cl}_9$  apparently is isomorphous with our compound, and the considerably smaller radius of 1.48A for  $\text{Rb}^+$  as compared with 1.69A for  $\text{Cs}^+$  and 1.81A for  $\text{Cl}^-$  would seem to require such a closer anion-cation approach. Six chlorine atoms would then occupy the general positions of  $D_3^2$ , and the chlorines of all layers could be rotated somewhat about the threefold axes away from the closest-packed positions for identical spheres, with probably a better distribution of structural strains than is obtainable from  $D_{3d}^3$ . We have then,

3 Cl in  $w00; 0w0; \bar{w}\bar{w}0$  with  $w=0.480$ ,

6 Cl in  $x, y, z; y-x, \bar{x}, z; \bar{y}, x-y, z;$

$y, x, \bar{z}; \bar{x}, y-x, \bar{z}; x-y, \bar{y}, \bar{z},$

with  $x \cong \frac{1}{3}$ ,  $y \cong \frac{1}{3}$ ,  $z=0.325$ . If the structure were based on  $D_{3d}^3$ ,  $x=2y$ , and  $w=\frac{1}{3}$ .

The amounts of the deviations of  $x$ ,  $y$  and  $w$  from the closest-packed positions seems to be too small to have any large effects upon the calculated intensities. In Table II we give calcu-

TABLE II. Comparison of calculated with observed intensities for  $(h0\cdot0)$  and  $(hh\cdot0)$  reflections.

Structure I:  $x=\frac{1}{3}$ ,  $y=\frac{1}{3}$ . Structure II:  $x=0.365$ ,  $y=0.200$ .

$hk\cdot0$	Observed intensity	Calculated intensity* Structure I	Structure II
11·0	40	40	40
22·0	32	45	37
33·0	4	5.4	6.5
44·0	3	10.0	6.5
55·0	0	1.4	0.8
10·0	6	6	6
20·0	1	2.4	1.2
30·0	16	36	21
40·0	0	0.8	0.3
50·0	0	0.5	0.0
60·0	8	34	14

\* Temperature factor not included.

lated intensities for structure I for which  $x=\frac{1}{3}$ ,  $y=\frac{1}{3}$ ,  $w=\frac{1}{3}$  as well as for structure II based

upon  $D_3^2$  for which  $x=0.365$ ,  $y=0.200$ ,  $w=0.480$ . The agreement is generally satisfactory in both cases, although somewhat better for the second. The data indicate that there is indeed some distortion from structure I, and that structure II is one variation which meets the intensity requirements. Table III contains some intensity

TABLE III. Comparison for structure II of calculated with observed intensities for  $(0k\cdot l)$  reflections.

$0k\cdot l$	Observed intensity	Calculated intensity*	$0k\cdot l$	Observed intensity	Calculated intensity*
01·2	3	3.0	02·2	120	140
01·2	40	47	02·2	0	0.3
01·3	0	1.5	02·3	2	2
01·3	0	0.1	02·3	1	1.2
01·4	32	80	02·4	6	12
01·4	8	20	02·4	64	125
01·5	0	0.5	02·5	24	55
01·5	2	5.5	02·5	0	1.5
01·6	6	13	02·6	4	12
01·6	2	5.5	02·6	3	10
01·7	1	5.5	02·7	0	0.3
01·7	0	0.5	02·7	12	50
01·8	3	12	02·8	12	53
01·8	2	9.2	02·8	3	17

\* Temperature factor not included.

comparisons which are representative of a more general type of reflection. The data are given only for structure II, but again the comparisons are appreciably better than for the undistorted structure. That we have arrived at essentially the correct structural type is scarcely to be doubted, but it is primarily upon the basis of dimensional and structural rather than intensity considerations that we decide that distortions from the ideal structure are to be introduced in accordance with  $D_3^2$  rather than  $D_3^3$ .

#### DISCUSSION OF THE STRUCTURE

A photograph of a model of the structure is reproduced in Fig. 1. In this model the chloride ions of layer A and all caesium ions are shown as spheres of equal size in closest-packing, while the positions of arsenic atoms and of the chlorine atoms of layers B and C are indicated as the vertices of the triangular pyramids. Figs. 2 and 3 show packing drawings of the unit cell, again with caesium and chlorine atoms indicated as spheres of equal size in true closest-packed array, and with the positions of arsenic marked by the apices of the pyramids. Study of these

drawings indicates the essential nature of the structure, and the process of going over to the parameters of structure II may then be visualized quite easily.

There are two factors which show that the plane  $z=\frac{1}{2}$  between layers B and C should be a natural cleavage plane: (1) the absence of arsenic atoms in this region, and (2) the fact that both chlorine and caesium parameters along  $c$  are slightly less than  $\frac{1}{2}$ .

Since the basal plane intensities require  $v=0.805\pm 0.010$  rather than  $\frac{1}{2}$ , we see, as is indicated in the various figures, that arsenic trichloride molecules would seem to have their identity preserved within the structure, and that the process of crystallization has consisted in embedding  $\text{AsCl}_3$  in an environment of completely ionized caesium chloride in such a manner that the large atoms or ions are in nearly closest-packing. The ratio of 3Cl per Cs, leading to the kind of layers already described, is particularly well suited to the requirements of this general type of structure. This ratio is also shown by the widely occurring perovskite or  $\text{KMgF}_3$  structure.

We believe, moreover, that the size and shape of the  $\text{AsCl}_3$  molecules are probably described well by structure II. Arsenic is expected to form three normal covalent bonds at angles somewhat greater than  $90^\circ$  but less than the tetrahedral angle.<sup>8</sup> Thus in elementary arsenic three bonds are formed at  $97^\circ$ , while electron diffraction

TABLE IV. Interatomic distances calculated from structures I and II. (The subscripts refer to the layers.)

Atom	Neighbors	Separation structure I	Separation structure II
$\text{As}_A$	$3\text{Cl}_C$	2.42A	2.25A
$\text{As}_B$	$3\text{Cl}_A$	2.75	2.76
$\text{Cs}_A$	$3\text{Cl}_A$	3.685	3.54
$\text{Cs}_A$	$3\text{Cl}_A$	3.685	3.83
$\text{Cs}_A$	$3\text{Cl}_B, 3\text{Cl}_C$	3.59	3.71
$\text{Cs}_B$	$3\text{Cl}_A$	3.55	3.56
$\text{Cs}_B$	$3\text{Cl}_C$	3.81	3.69
$\text{Cs}_B$	$3\text{Cl}_B$	3.69	3.57
$\text{Cs}_B$	$3\text{Cl}_B$	3.69	3.83
$\text{Cl}_A$	$4\text{Cl}_A$	3.685	3.70
$\text{Cl}_A$	$\text{Cl}_B, \text{Cl}_C$	3.59	3.55
$\text{Cl}_A$	$\text{Cl}_B, \text{Cl}_C$	3.59	3.55
$\text{Cl}_B$	$2\text{Cl}_B$	3.685	3.35
$\text{Cl}_B$	$2\text{Cl}_B$	3.685	4.04
$\text{Cl}_B$	$\text{Cl}_C$	3.78	3.78
$\text{Cl}_B$	$\text{Cl}_C$	3.78	4.08

<sup>8</sup> Linus Pauling, J. Am. Chem. Soc. 53, 1367 (1931).

studies<sup>9</sup> of  $\text{AsCl}_3$  lead to  $101 \pm 4^\circ$  bond angles. An As—Cl separation of  $2.18 \pm 0.03 \text{ \AA}$  is given by the electron diffraction study, while a value of  $2.20 \text{ \AA}$  is obtained from Pauling and Huggins' covalent radii.<sup>10</sup> Structure II, which has  $v \approx 0.805$ ,  $x = 0.365$ ,  $y = 0.200$ ,  $z = 0.325$ , contains  $\text{AsCl}_3$  molecules with bond angle  $95^\circ 50'$ , As—Cl =  $2.25 \text{ \AA}$ , Cl—Cl =  $3.34 \text{ \AA}$ . Table IV lists all of the pertinent interatomic distances for the two structures for which we have calculated intensities. The As—Cl separation of  $2.25 \text{ \AA}$  given by structure II is nearly that expected for a covalent bond, whereas the precise significance

of the corresponding value of  $2.42 \text{ \AA}$  given by structure I would remain doubtful. Moreover the relations of caesium with chlorine are probably more satisfactory in general for structure II than for structure I.

Possible variations in the parameter values would include having  $z$  about  $0.005$  smaller,  $v$  from  $0.005$ – $0.010$  smaller, and  $x$  and  $y$  a little nearer the closest-packed positions. Such changes would not materially alter our concept of covalent As—Cl bonds, but would lead to bond angles a little greater than  $96^\circ$ . They would result also in a somewhat smaller value than  $3.71 \text{ \AA}$  for the  $\text{Cs}_A$ —Cl<sub>B</sub> distance, which is perhaps to be anticipated.

<sup>9</sup> Brockway and Wall, *J. Am. Chem. Soc.* **56**, 2373 (1934).

<sup>10</sup> Pauling and Huggins, *Zeits. f. Krist.* **87**, 205 (1934).

## On the Two-Quantum $\Sigma$ -States of the Hydrogen Molecule

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A wave function in the form of a series with coefficients to be determined by the variational method is used to calculate the dissociation energies of the hydrogen molecule in two of its excited states:  $1s\sigma 2s\sigma {}^3\Sigma_u^+$  and  $1s\sigma 2p\sigma {}^1\Sigma_u^+$ . In the former case an 11-term wave function gives an energy less than  $0.02$  e.v. from the most probable experimental value and lying within the limits of experimental error. For the second state an energy less than  $0.08$  e.v. from

experiment is obtained by means of a function comprising 18 terms. The interelectronic distance has been introduced explicitly into the wave function and the role that it plays in reducing the energy is discussed at length. The limits of accuracy of the calculation with reference to convergence and nuclear motion are considered. Explicit wave functions are given for the two states.

### INTRODUCTION

THE treatment by wave mechanics of the electronic states of a diatomic molecule has led in general to results which are unsatisfactory from a quantitative point of view. The very simplest problems, including the excited states of the hydrogen molecule, have not been carried to the point where quantitative agreement with experiment could be obtained. The successful treatment of the normal state of the hydrogen molecule by James and Coolidge<sup>1</sup> furnishes a method whose possibilities it seems worth while to explore more thoroughly; and with this in mind a calculation has been made on several of the two quantum states of hydrogen,<sup>2</sup> and the

results for two of these states are reported in this paper.<sup>3</sup>

Previous work on these states has been based on trial wave functions that have been constructed from hydrogen atom functions<sup>4</sup> (cf. the Heitler-London method), from the wave functions for the hydrogen molecular ion,<sup>5</sup> or from a combination of the two.<sup>6</sup> In a molecule as closely

<sup>3</sup> Work has also been done on the repulsive state  $1s\sigma 2p\sigma {}^3\Sigma_u^+$  and will be published shortly in a joint paper by Drs. James and Coolidge with the writer.

<sup>4</sup> Kemble and Zener, *Phys. Rev.* **33**, 512 (1929); Zener and Guillemin, *Phys. Rev.* **34**, 999 (1929).

<sup>5</sup> E. A. Hylleraas, *Zeits. f. Physik* **71**, 739 (1931). Hylleraas fails to treat the state  $1s\sigma 2s\sigma {}^3\Sigma_u^+$ , but mentions results obtained by a rough extrapolation which appears to have little theoretical justification.

<sup>6</sup> J. K. L. MacDonald, *Proc. Roy. Soc.* **A136**, 528 (1932). MacDonald treats all of the two-quantum states for the same internuclear distance, 2 Bohr radii. Both Hylleraas and MacDonald obtain fairly good agreement with experiment on the  $\Pi$  states, but their results on the  $\Sigma$  states are unsatisfactory.

<sup>1</sup> James and Coolidge, *J. Chem. Phys.* **1**, 825 (1933).

<sup>2</sup> Two-quantum molecular states dissociate upon adiabatic separation of the nuclei into one normal atom and one atom in a two-quantum state.