[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 651]

The Electron Diffraction Investigation of Aluminum Chloride, Bromide, and Iodide

BY K. J. PALMER AND NORMAN ELLIOTT

The unusual physical and chemical properties of aluminum chloride, bromide, and iodide lend considerable interest to the electron diffraction investigation of these compounds in the gas phase. Vapor density measurements have shown that in the gaseous state below approximately 400° the substances exist as the dimeric molecules Al_2Cl_6, Al_2Br_6, and Al_2I_6.

The same configuration is suggested for these molecules by considerations based on the extreme ionic and the extreme covalent points of view. The radius ratio of the ions Al^{3+} and Cl^- is 0.40 (ratio of univalent radii[1]), which corresponds to tetrahedral coördination. This can be achieved for a molecule Al_2X_5 by the sharing of an edge between two tetrahedra, as shown in Fig. 1. From the covalent point of view this configuration would be expected as the result of the tendency of the aluminum atoms to complete their octet valence shells, the electronic structure of the molecule being

The suggestion of this as a possible structure for the aluminum halides was made by Fajans.[2]

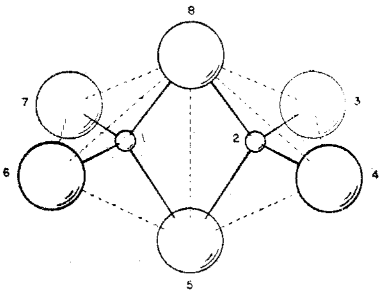

Fig. 1.—The spatial configuration of the dimeric molecule Al_2X_6. Positions 1 and 2 correspond to the aluminum atoms; the remaining positions are occupied by halogen atoms.

We have carried out the study of these substances by the electron diffraction method, and have verified the double-tetrahedral configuration of Fig. 1, with some deformation of the tetrahedra, as described below.

Experimental

The electron diffraction photographs were obtained and interpreted in the usual way.[3] The wave length of the electrons was 0.0613 Å. and the camera distance 10.85 cm. for the chloride and bromide and 20.16 cm. for the iodide.

The strong tendency of the aluminum halides to hydrolyze made it necessary to transfer the samples to the high temperature nozzle inside a moisture proof box. The nozzle[4] could then be sealed and inserted into the electron diffraction apparatus, the sample not being allowed to come into contact with moist air. This procedure proved to be satisfactory, as was verified by inspection of the nozzle after the exposures were made. In no case was there any sign of decomposition.

Merck C. P. aluminum chloride was used without further purification. The aluminum bromide was made by the method of Richards and Krepelka.[5] The aluminum iodide was prepared by heating iodine with excess aluminum in an evacuated glass tube held in a vertical position. The temperature was maintained at 300° for six hours, in which time the color due to the iodine vapor had disappeared completely. The aluminum iodide which collected in the lower part of the tube along with the excess aluminum was separated from the latter by distilling it to the upper part of the tube and then sealing the tube off at the center. The product appeared in the form of colorless highly refractive crystals. There was no evidence of any iodine vapor being present either during or after the distillation. These crystals were used without further purification.

Aluminum Chloride.—The photographs of aluminum chloride show nine maxima. The averaged values of s_0, I (the visually estimated intensities), and C (equal to $Is_0^2e^{-as_0^2}$) are given in Table I. The qualitative appearance of the photographs is well represented by curve F of Fig. 3

---

(1) Linus Pauling, THIS JOURNAL, **49**, 765 (1927).

(2) K. Fajans, *Z. Elektrochemie*, **34**, 502 (1928).

(3) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(4) L. O. Brockway and K. J. Palmer, THIS JOURNAL, **59**, 2181 (1937).

(5) T. W. Richards and H. Krepelka, *ibid.*, **42**, 2221 (1920).

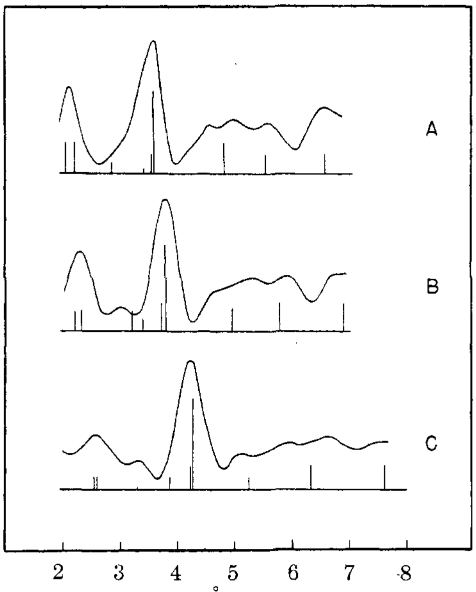

Fig. 2.—Radial distribution curves for (A) aluminum chloride, (B) aluminum bromide and (C) aluminum iodide.

which was calculated for the finally accepted model. The radial distribution curve,[6] curve A of Fig. 2, calculated using the values of C (Table I) in place of I, shows principal peaks at 3.56 and 2.11 Å. These values are interpreted as the Cl–Cl and the short Al–Cl distances, respectively. The ratio of these, 1.69, is close to that (1.633) for a regular tetrahedral arrangement of chlorine atoms about the aluminum atoms. Strong support for this structure is provided by the simplified theoretical intensity curve calculated for the regular tetrahedral model (curve A of Fig. 3), which shows good, although not complete, agreement with the characteristics of the photographs.

In order to find a model in which the ratio of Cl–Cl to Al–Cl is 1.69, all of the edges of the two tetrahedra except the shared edge were assumed to have the value 3.56 Å., and the eight smallest Al–Cl distances the value 2.11 Å. The shared edge would then have the value 2.58 Å. Although this distance is much less than the distance of closest approach (2.86 Å.) observed for two non-bonded chlorine atoms, a theoretical intensity curve was calculated for this model (curve B, Fig. 3), which again is in good but not complete agreement with the photographs. Curves C and

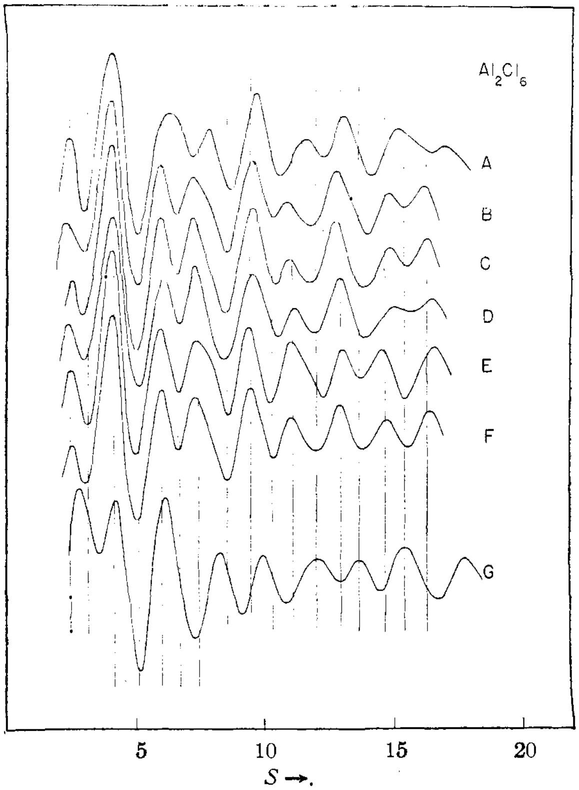

Fig. 3.—Theoretical intensity curves for aluminum chloride.

D, Fig. 3, were calculated for models in which the shared edge has the value 2.75 and 2.85 Å., respectively. The other ten edges have the values 3.56 Å. in model C and 3.54 Å. in model D and the smallest Al–Cl distances the values 2.12 and 2.11 Å., respectively. These curves do not agree with the photographs quite so well as does curve B.

A very large decrease in the value of the shared edge is necessary in order to obtain the ratio 1.69 when at the same time one keeps the other edges of the tetrahedron about equal to 3.56 Å. and the short Al–Cl distances all equal to 2.11 Å. Thus it is evident that the models so far assumed have been oversimplified, and that the stable configuration, although approximating two regular tetrahedra sharing an edge, is in reality considerably distorted. In order to obtain an insight into the type of distortion to be expected the following calculation was made.

The molecule is assumed to be completely ionic, and to be represented by the potential function

$$V = -\sum_{ij} \frac{e_i e_j}{r_{ij}} + \sum_{ij} \frac{B_{ij} e_i e_j}{r_{ij}^n}$$

in which r_{ij} is the distance between the ith and jth atoms, B_{ij} is the Born coefficient, n is a con-

---

(6) L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935). The use of the values of C in place of I has been suggested by V. Schomaker and C. Degard. They will publish an account of their investigation soon in THIS JOURNAL.

stant, taken to have the value 9 for this calculation, and e_i, e_j are the charges on the ith and jth atoms, taken equal to -1 and $+3$ for chlorine and aluminum, respectively. It was further assumed that the ratio of the B's is given by the expression

$$\frac{B_{\mathrm{Al-Cl}}}{B_{\mathrm{Cl-Cl}}} = \frac{(R_{\mathrm{Al}} + R_{\mathrm{Cl}})^8}{(2R)_{\mathrm{Cl}}^{\,8}}$$

where R_{Al} and R_{Cl} are the ionic radii of aluminum and chlorine, respectively. The absolute magnitudes of the B's were obtained by setting $\partial V/\partial r = 0$ and using r_{ij}'s corresponding to two regular tetrahedra with all short Al–Cl distances equal to 2.11 Å. The values so obtained are $B_{\mathrm{Al-Cl}} = 48.15$ and $B_{\mathrm{Cl-Cl}} = 1755$. These values were retained throughout the calculation.

A method of successive approximations was used to carry out the calculation. Each of the four independent parameters necessary to specify the structure was successively varied, the process being repeated once. The final values of the parameters so obtained indicate the type of distortion to be expected in such a structure. With a charge of $+3$ assumed to reside on each of the two aluminum atoms the repulsion between them is very strong, and the most notable changes in going from two regular tetrahedra to the final equilibrium configuration are the decrease in the length of the shared edge and the increase in the Al–Al distance. This latter effect changes the values of the short Al–Cl distances by a large amount. The final values of the interatomic distances calculated in this way are $\mathrm{Al_1{-}Al_2} = 3.60$, $\mathrm{Al_2{-}Cl_3} = 1.99$, $\mathrm{Al_2{-}Cl_8} = 2.31$, $\mathrm{Al_2{-}Cl_6} = 4.89$, $\mathrm{Cl_3{-}Cl_4} = 3.49$, $\mathrm{Cl_3{-}Cl_8} = 3.57$, $\mathrm{Cl_5{-}Cl_8} = 2.90$, $\mathrm{Cl_3{-}Cl_7} = 5.52$, $\mathrm{Cl_3{-}Cl_6} = 6.52$ Å. The subscripts on the atomic symbols refer to the position of the atoms as given in Fig. 1. The average of the four $\mathrm{Al_2{-}Cl_3}$ distances, equal to 1.99 Å., and the four $\mathrm{Al_2{-}Cl_8}$ distances, equal to 2.31 Å., (refer to Fig. 1) is 2.15 Å., in fair agreement with the radial distribution peak at 2.11 Å. However, if this were the correct model, the two shortest $\mathrm{Al_2{-}Cl}$ distances probably would appear as separate peaks in the radial distribution curve. Moreover, the intensity curve calculated for this model (curve E, Fig. 3) does not agree qualitatively with the photographs; the sixth maximum is too high and the eighth and ninth minima are not of equal depth.

Seven additional intensity curves were calculated for models in which the four parameters were varied. The model finally selected gives an intensity curve (curve F, Fig. 3) which reproduces the qualitative features of the photographs in every respect. The values of the interatomic distances for this model are listed in Table II. Table I gives the values of s and s_0 and their ratio, s/s_0, for model F.

TABLE I

ELECTRON DIFFRACTION DATA FOR ALUMINUM CHLORIDE

Max.	Min.	I	C	s_0	s^a	s/s_0
1		5	2	2.24	2.35	(1.049)
	2			3.08	2.91	(0.946)
2		10	14	4.08	3.93	(.963)
	3			4.96	4.91	(.989)
3		5	12	5.86	5.86	1.000
	4			6.61	6.51	0.985
4		3	10	7.43	7.18	.967
	5			8.33	8.40	1.008
5		4	16	9.23	9.32	1.009
	6			10.11	10.20	1.009
6		1	4	10.98	10.90	0.993
	7			11.90	11.91	1.000
7		3	12	12.71	12.77	1.005
	8			13.42	13.71	1.022
8		1	3	14.47	14.60	1.009
	9			15.22	15.41	1.013
9		2	5	16.07	16.30	1.014
				Average		1.003
				Average deviation		0.010

[a] Calculated for model F.

TABLE II

INTERATOMIC DISTANCES IN ALUMINUM CHLORIDE

	Distance, Å.	Number of times distance occurs in molecule
$\mathrm{Al_2{-}Cl_3}$	2.06 ± 0.04	4
$\mathrm{Al_2{-}Cl_8}$	2.21 ± .04	4
$\mathrm{Cl_5{-}Cl_8}$	2.83 ± .10	1
$\mathrm{Cl_3{-}Cl_4}$	3.53 ± .04	2
$\mathrm{Cl_3{-}Cl_8}$	3.56 ± .02	8
$\mathrm{Al_1{-}Al_2}$	3.41 ± .20	1
$\mathrm{Cl_3{-}Cl_7}$	5.49 ± .05	2
$\mathrm{Cl_3{-}Cl_6}$	6.52 ± .05	2
$\mathrm{Al_2{-}Cl_6}$	4.77 ± .15	4

Aluminum Bromide.—The photographs of aluminum bromide show seven well-defined rings and have the same qualitative features as those for aluminum chloride. The radial distribution curve has two well-defined peaks at 2.28 and 3.77 Å. The ratio of 3.77 to 2.28 is 1.65, indicating that the tetrahedra in this molecule probably are not distorted to so great an extent as for the chloride. Curve A of Fig. 4 was calculated for two regular tetrahedra sharing an edge. The curve is in good but not complete qualitative agreement with the photographs. Curves B and C of

Fig. 4 were calculated for models having the same type of distortion as that found for the chloride, but smaller in magnitude. The two models are essentially the same except for the length of the shared edge. In model B this edge was assumed to be 3.36 Å. and in model C 3.20 Å. The Al_2–Br_3 and Al_2–Br_8 distances were taken equal to 2.21 and 2.33 Å., respectively, in model C, and 2.21 and 2.35 Å. in model B.

The qualitative agreement of curve C with the photographs is better than that of curve B in that the fifth maximum in the former is slightly more intense than the fourth, in agreement with the appearance of the photographs. The differences in these two curves are, however, very slight in spite of the fact that the Br_5–Br_8 distance has been changed by 0.16 Å. The insensitiveness of the intensity curves to variations in this parameter makes it necessary to assign to it a large probable error. In Table III there are listed the values of I, C, s_0, s (for model C), and the ratio of s/s_0, and in Table IV there are given the values of the interatomic distances for the molecule and their estimated probable errors.

TABLE III

ELECTRON DIFFRACTION DATA FOR ALUMINUM BROMIDE

Max.	Min.	I	C	s_0	s^a	s/s_0
1		5	2	2.11	2.11	1.000
	2			2.85	2.87	1.007
2		10	11	3.78	3.72	0.998
	3			4.68	4.61	.999
3		6	11	5.48	5.60	1.022
	4			6.28	6.22	0.990
4		4	9	7.02	6.88	.980
	5			7.85	7.88	1.004
5		5	13	8.73	8.78	1.006
	6			9.59	9.68	1.009
6		1	2	10.38	10.35	0.997
	7			11.19	11.17	.998
7		2	3	11.84	12.08	1.023
				Average		1.003
				Average deviation		0.009

[a] Calculated for model C.

TABLE IV

INTERATOMIC DISTANCES IN ALUMINUM BROMIDE

	Distance, Å.	Number
Al_2–Br_3	2.21 ± 0.04	4
Al_2–Br_8	2.33 ± .04	4
Br_5–Br_8	3.20 ± .10	1
Br_3–Br_4	3.72 ± .03	2
Br_3–Br_8	3.78 ± .03	8
Al_1–Al_2	3.39 ± .10	1
Br_3–Br_7	5.76 ± .10	2
Br_3–Br_6	6.86 ± .10	2
Al–Br	4.93 ± .10	4

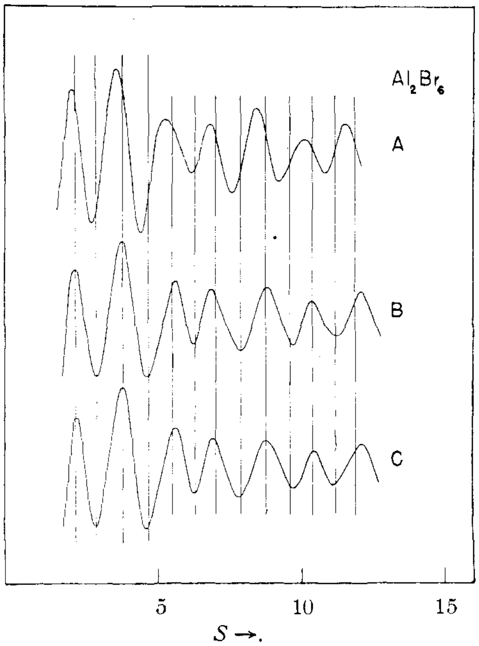

Fig. 4.—Theoretical intensity curves for aluminum bromide.

Aluminum Iodide.—The photographs of aluminum iodide, taken with a camera distance of 20.16 cm., show seven well-defined maxima, the general appearance of the photographs being closely similar to that for the chloride and bromide. This similarity is strong evidence for the assumption that the structures of the three molecules are similar in configuration.

The radical distribution curve (curve C, Fig. 2), shows principal peaks at 2.58 and 4.23 Å. The ratio of the latter to the former distance is 1.64, indicating that the structure is very nearly that of two regular iodine tetrahedra sharing an edge.

The ratio of the scattering due to the iodine atoms to that due to the aluminum atoms is very large in aluminum iodide; this makes the determination of the positions of the aluminum atoms with any degree of accuracy impossible. The intensity curves shown in Fig. 5 were calculated for models approximating those described for aluminum bromide. Curve A is for undistorted tetrahedra, and curves B and C for tetrahedra whose shared edge has the value 4.00 and 3.85 Å., respectively, and for which the Al_2–I_3 and Al_2–I_8 distances have the values 2.58 and 2.54 Å., respectively. Curve A does not agree with the photographs in that the relative intensities of the maxima are unsatisfactory. Curve C gives a somewhat better representation of the appearance of the photographs than curve B, but the differences in these two curves, namely, the variation of the intensities of the third, fourth, and fifth maxima, are so small that, as in the case of the bromide, it is impossible to determine the length of the shared edge with much accuracy.

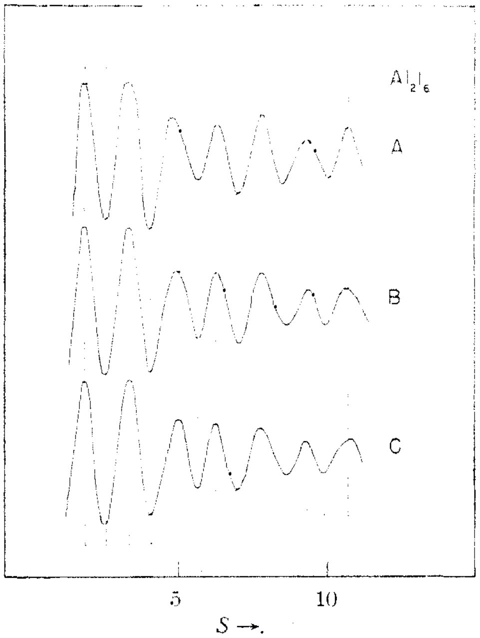

Fig. 5.—Theoretical intensity curves for aluminum iodide.

The values of the interatomic distances with their estimated probable errors are given in Table VI. The quantitative comparison of the s values obtained from curve C with the observed s_0 values is given in Table V.

TABLE V

ELECTRON DIFFRACTION DATA FOR ALUMINUM IODIDE

Max.	Min.	I	C	s_0	s^a	s/s_0
1		9	3	1.88	1.87	0.995
	2			2.51	2.52	1.004
2		10	9	3.32	3.33	1.003
	3			4.14	4.08	0.986
3		7	10	4.85	4.99	1.029
	4			5.56	5.65	1.016
4		6	9	6.29	6.26	0.995
	5			7.03	7.00	.996
5		5	10	7.80	7.75	.994
	6			8.62	8.67	1.006
6		2	3	9.27	9.29	1.002
	7			9.95	9.89	0.994
7		1	1	10.67	10.70	1.003
				Average		1.002
				Average deviation		0.008

[a] Calculated for model C.

TABLE VI

INTERATOMIC DISTANCES IN ALUMINUM IODIDE

	Distance, Å.	Number
$Al_2–I_3$	2.53 ± 0.04	4
$Al_2–I_5$	2.58 ± .04	4
$I_5–I_8$	2.90 ± .15	1
$I_3–I_4$	4.20 ± .03	2
$I_3–I_5$	4.24 ± .02	8
$Al_1–Al_2$	3.24 ± .15	1
$I_3–I_7$	6.24 ± .15	2
$I_3–I_6$	7.54 ± .10	2
$Al_2–I_6$	5.22 ± .15	4

Discussion

The only report on the structures of aluminum chloride, bromide, or iodide previous to the present one is that of Ketelaar[7] on the structure of aluminum chloride crystals. He found that the chlorine atoms are in hexagonal closest packing, this arrangement being compatible with that found for the gas molecule in this investigation. However, he chose to place two aluminum atoms inside an octahedron of chlorine atoms, and only 0.56 Å. apart, rather than one each inside of two tetrahedra sharing an edge, both of these possibilities being provided by the hexagonal closest packed arrangement. The extent to which the X-ray data can be accounted for by this latter configuration is being investigated by one of us. Curve G, Fig. 2, is the simplified theoretical intensity curve calculated for the "octahedral" model of Ketelaar; it is apparent from a comparison with curve F that this model cannot represent the structure of the gas molecule.

The large difference in electronegativity between aluminum and the halogen atoms leads one to expect that the Al–X bond will be largely ionic, and this is confirmed by the observed contraction of the shared edge. The percentage decrease in length of the shared edge is found to be largest in the chloride and least in the iodide, which is in accordance with expectation.

The sums of the tetrahedral radius of aluminum and the normal radii for the halogen atoms are 2.25, 2.40, and 2.59 Å. for the chloride, bromide, and iodide, respectively. These values are to be compared with the observed values, 2.06, 2.21, and 2.53 Å., which are the $Al_2–X_3$ distances, and 2.21, 2.33, and 2.58 Å., which are the $Al_2–X_8$ distances, for the chloride, bromide, and iodide, respectively. The observed shortening in the case of the $Al_2–X_3$ distances is probably due to the excited structures in which an X_3 halogen atom

---

[7] J. A. A. Ketelaar, *Z. Krist.*, **90**, 237 (1935).

swings in a pair of electrons and forms a double bond with the aluminum atom. This type of resonance is not expected to occur to the same degree for halogen atoms forming two bonds, which accounts for the fact that the observed Al_2–X_8 distances are nearly equal to the sum of the appropriate radii.

It is interesting to note that the observed values of the Al_2–X_3 distances show a greater tendency for the chlorine and bromine atoms to form double bonds than of iodine atoms; this is compatible with the results of other investigations.

We wish to express our thanks to Professor Linus Pauling for his aid and helpful criticism during the course of this investigation.

Summary

It is shown that in the gaseous state the dimeric molecules of aluminum chloride, bromide, and iodide consist of two tetrahedra sharing an edge with six halogen atoms at the corners, each tetrahedron containing one aluminum atom. The final values of the interatomic distances are as follows

The subscripts on the atomic symbols refer to their positions in the molecule as given in Fig. 1.

	Al_2Cl_6	Al_2Br_6	Al_2I_6
Al_1–Al_2	3.41 ± 0.20 Å.	3.39 ± 0.10 Å.	3.24 ± 0.15 Å.
Al_2–X_3	2.06 ± .04	2.21 ± .04	2.53 ± .04
Al_2–X_8	2.21 ± .04	2.33 ± .04	2.58 ± .04
Al_2–X_6	4.77 ± .15	4.93 ± .10	5.22 ± .15
X_3–X_4	3.53 ± .04	3.72 ± .03	4.20 ± .03
X_3–X_8	3.56 ± .02	3.78 ± .03	4.24 ± .02
X_5–X_8	2.83 ± .10	3.20 ± .10	2.90 ± .15
X_3–X_7	5.49 ± .05	5.76 ± .10	6.24 ± .15
X_3–X_6	6.52 ± .05	6.86 ± .10	7.54 ± .10

PASADENA, CALIF. RECEIVED MAY 31, 1938

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORY OF BROWN UNIVERSITY]

Photochemical Studies. XXVI. A Further Study of the Fluorescence of Acetone Vapor and its Relationship to the Photochemical Decomposition

BY MAX S. MATHESON AND W. ALBERT NOYES, JR.

The fluorescence of acetone vapor was reported by Damon and Daniels,[1] who stated that it is greenish and is changed to blue by the presence of small amounts of oxygen. The oxygen disappears during illumination and this fact has been used as a means of determining small amounts of this substance.[2]

Two regions, one extending from 4100 to 4820 Å. (maximum 4580 Å.) and the other from 4990 to the limit of plate sensitivity (5210 Å.), were found by Damon and Daniels.[1] Norrish, Crone and Saltmarsh[3] report three bands of fluorescent emission (all diffuse) with maxima at 5117, 5572 and 6095 Å. More recently Padmanabhan[4] has found that the bands are not devoid of structure but consist of diffuse bands superimposed upon a continuous spectrum. Ten bands, two considered to be doubtful, were reported.

Herzberg[5] first found a discrete structure in the near ultraviolet absorption of acetone vapor and this has been confirmed by other workers.[3,6] The detailed analysis of these bands and their interpretation is still lacking, but the existence of such a structure is in conformity with the fact that fluorescence is observed. However, structure is difficult to observe in many polyatomic molecules even though fluorescence is found. Such seems to be the case with ethyl methyl ketone[7] and diethyl ketone.[8]

All authors who have studied the quantum yield of acetone decomposition in the near ultraviolet at room temperature agree that it is low.[9] The explanation of this fact is not complete. Damon and Daniels[1] state that the fluorescence is too weak to be the primary cause of this effect. However Fisk and Noyes[10] studied the fluorescence excited by the 3130 Å. line of mercury and found (with the very low intensities used) a Stern–Volmer mechanism to be obeyed. At moderate pressures it was found that the number of quanta absorbed was roughly equal to the sum

---

(1) Damon and Daniels, THIS JOURNAL, **55**, 2363 (1933).

(2) Damon, *Ind. Eng. Chem., Anal. Ed.*, **7**, 133 (1935); Fugassi, THIS JOURNAL, **59**, 2092 (1937); Fugassi and Daniels, *ibid.*, **60**, 771 (1938).

(3) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

(4) Padmanabhan, *Proc. Ind. Acad. Sci.*, **5A**, 594 (1937).

(5) For mention see Scheibe, Povenz and Linström, *Z. physik. Chem.*, **20B**, 292 (1933).

(6) Noyes, Duncan and Manning, *J. Chem. Phys.*, **2**, 717 (1934); Noyes, *Trans. Faraday Soc.*, **33**, 1495 (1937).

(7) Duncan, Ells and Noyes, THIS JOURNAL, **58**, 1454 (1936).

(8) J. W. Zabor, M.S. Thesis, Brown University, 1938.

(9) See refs. 1 and 3, Leermakers, THIS JOURNAL, **56**, 1900 (1934).

(10) Fisk and Noyes, *J. Chem. Phys.*, **2**, 654 (1934).