NOVEMBER 1, 1937 PHYSICAL REVIEW VOLUME 52

Interatomic Distances of the Alkali Halide Molecules by Electron Diffraction[1]

L. R. MAXWELL, S. B. HENDRICKS AND V. M. MOSLEY
Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D. C.

(Received August 30, 1937)

A determination of the interatomic distances of the alkali halide gas molecules has been made by the electron diffraction method. Heating the salts to a temperature of approximately 1200°C provided a molecular beam of sufficient density to give electron diffraction photographs. The nuclear distances were obtained from visual measurements of the interference maxima. Data from I_2 and Cl_2 provided a calibration of the visual measurements since the internuclear distances for these molecules are well known from band spectra. The interatomic distances for the sodium, potassium and rubidium halides were found to be about 10 percent less than the corresponding known distances in the crystal lattice. For the case of the caesium halides the distances obtained were approximately 14 percent smaller than the separations found in the crystals. Tables showing complete data on twelve molecules are given.

INTRODUCTION

PROPERTIES of the alkali halide crystals have been most amenable to study both experimentally and theoretically. However, information concerning the alkali halide molecules has been quite meager. Spectroscopic studies of the vapors have shown that the bands are diffuse and while some vibrational data can be obtained[2] the rotational structure is unknown. Electron diffraction methods can be used for the determination of internuclear distances in the molecules as they exist in the vapor. In the following work results were obtained from the chlorides, bromides, and iodides of sodium, potassium, rubidium, and caesium. The lithium halides were not studied on account of the low probability of electron scattering by lithium. Since the vapor pressures of the sodium and potassium fluorides are comparatively low no attempt was made to obtain data on any of the alkali fluorides.

ELECTRON DIFFRACTION METHOD

The intensity of electron scattering $I(s)$ from the diatomic alkali halide gas molecules[3] can be expressed as follows:

$$I(s)=k[\psi_i^2+\psi_j^2+2\psi_i\psi_j(\sin x_{ij}/x_{ij})+I_{\text{inc}}(s)], \quad (1)$$

where $\psi_i=(Z_i-F_i)/(\sin\frac{1}{2}\theta)^2$, F_i = atomic scattering factor

$$x_{ij}=l_{ij}\cdot s=4\pi l_{ij}(1/\lambda)\sin\tfrac{1}{2}\theta, \quad (2)$$

l_{ij} = nuclear separation,
k = constant.

The term $I_{\text{inc}}(s)$ represents the amount of incoherent scattering as computed by Morse.[4]

$I(s)$ shows a rapid decrease of intensity with angle without passing through maxima. However, when it is recorded on a photographic plate the diffraction pattern shows to the eye apparent maxima and minima whose positions can be measured with considerable accuracy. This affords a valuable method for determining internuclear distances by the use of Eq. (2). Having measured visually the position of the apparent experimental maxima in terms of $(1/\lambda)\sin\frac{1}{2}\theta$ it is then necessary to use the correct theoretical values of x corresponding to these maxima in order to obtain l_{ij}. A test of the proper values to use is afforded by a study of the electron diffraction pattern from those diatomic molecules whose nuclear separations are accurately known from band spectra. It has been found for Br_2[5] and Cl_2[5] that the electron diffraction results will agree closely with band spectra provided that the $x_{\max}$ values used are taken to be the same as the values of $x_{\max}$ for the $\sin x/x$ function which appears in Eq. (1). The writers[6] have also found good agreement for

---

[1] A paper on this work was read before the Society at the Washington meeting. Phys. Rev. **51**, 1000 (1937).

[2] See for instance, Sommermeyer. Zeits. f. Physik **56**, 548 (1929).

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

[4] P. M. Morse, Physik. Zeits. **33**, 443 (1932); see also L. Bewilogua, Physik. Zeits. **33**, 688 (1932).

[5] L. Pauling and L. O. Brockway, J. Chem. Phys. **2**, 867 (1934).

[6] L. R. Maxwell, V. M. Mosley and S. B. Hendricks, Phys. Rev. **50**, 41 (1936).

the case of Cl_2 where values of $x_{\max}$ for the $\sin x/x$ functions were used. For the thallium halides Grether[7] has used approximately the same $x_{\max}$ values for visual measurements with the exception of the first and second maxima. A value of 13.7 was taken for the second maximum which is about 2.5 percent less than the position of the second maximum of $\sin x/x$. In this manner Grether has obtained practically constant nuclear separations as determined by the various interference maxima.

The writers[8] have previously found the nuclear separation of the I_2 molecule to be 2.65±0.10A from densitometer records of electron diffraction photographs used in comparison with calculated intensity of scattering curves. Additional photographs are now obtained for I_2 in order to further test the accuracy of the visual measurements. The average value obtained for l_{II} was 2.66±0.01A as shown in Table I. Values of $x_{\max}$ used are those considered to be most reliable on the basis of the previous work. It is noticed that each maximum gives values for l_{II} in good agreement with both the band spectrum separation of 2.660A and the previous electron diffraction value. Grether[7] finds an internuclear distance of 2.70±0.03A for I_2 by visual measurements of electron diffraction photographs which is close to the present value.

Additional confirmation of the visual measurements for diatomic molecules can be found for the case of S_2.[6] The nuclear separation for this molecule was determined by obtaining experimental relative intensity curves which were then compared with similar calculated intensities as given by Eq. (1). The two methods in this case agreed to within the experimental error of the intensity measurements which was about 1 percent. Thus the visual method for diatomic molecules has been justified independent of spectroscopic data. For the present case of the alkali halides the visual method will be used entirely.

TABLE I. *Summary of visual measurements obtained from iodine* (I_2).

MAXIMUM	$x_{\max}$	$\frac{\sin\frac{1}{2}\theta}{\lambda}$	l_{II}
1	—	—	—
2	13.7	0.412 (5)*	2.64 ±0.02
3	20.20	0.6023 (5)	2.669±0.01
4	26.50	0.7932 (8)	2.659±0.02
5	32.95	0.9860 (5)	2.659+0.01
6	39.24	1.174 (3)	2.660+0.01
7	45.55	1.359 (1)	2.667
		Average Value	2.66 ±0.01 (A)
		Band Spectrum Value	2.660† (A)

* Numbers in parentheses give number of photographs used for measurement. Variation given represents the average deviation (without regard to sign) found between separate photographs.

† See, for instance, W. Jevons, *Report on Band Spectra of Diatomic Molecules*, p. 280.

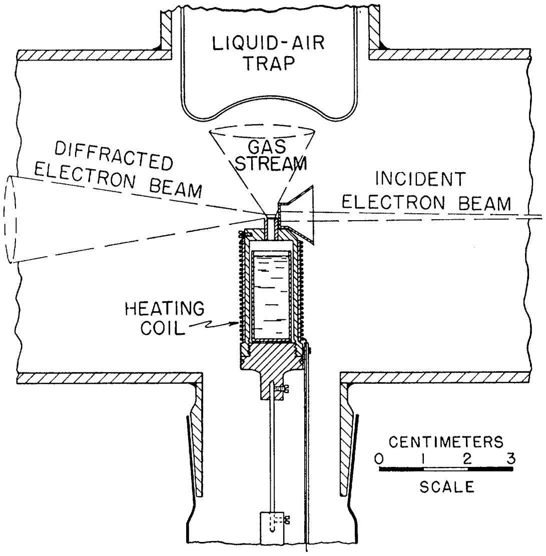

FIG. 1. Diagram showing boiler and electron diaphragm used for the alkali halides.

EXPERIMENTAL ARRANGEMENT AND PROCEDURE

The type of electron diffraction camera used has been described previously.[8] For the case of the alkali halide molecules it was necessary to heat the salts to 1100°–1300°C in order to provide sufficient gas density for diffraction photographs. The type of boiler used is shown in Fig. 1. The gas nozzle was 4 mm long with a rectangular cross section 0.1×1.0 mm in order to give greater collision volume with respect to the electron beam. The defining electron diaphragm was made an integral part of the boiler and contained a hole 0.1 mm in diameter to transmit the electrons in alignment with the gas stream. The metals used in constructing the boiler were nickel and Allegheny metal. Several platinum radiation shields not shown in Fig. 1 were used to reduce heat losses. Additional shields were mounted to reduce light

---

[7] W. Grether, Ann. d. Physik **26**, 1 (1936).

[8] S. B. Hendricks, L. R. Maxwell, V. M. Mosley and M. E. Jefferson, J. Chem. Phys. **1**, 549 (1933).

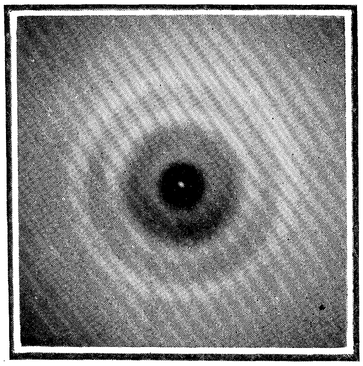

FIG. 2. Reproduction of an electron diffraction photograph obtained from RbBr.

fogging of the photographic plates. Plate distances of 10.0 and 26.0 cm were used. After each set of exposures the plate distance was measured by means of an accurately calibrated depth gauge. de Broglie wave-length readings of an electrostatic voltmeter in the region used (0.0620 to 0.0800A) were checked frequently by electron diffraction photographs from gold and sodium fluoride films.

The procedure used for taking the photographs consisted of first preheating the material in the boiler at 400°C. The salts were then raised from 400°C to 1000°C within a period of 3 minutes at which time the first electron diffraction photographs were taken. Five exposures were made during a single run while the temperature was being further increased from 1000 to 1300°C. Exposure times averaged about 25 seconds while the entire set was obtained within a period of 4 minutes. Trial photographs with the heating current off showed no change in the scattering pattern which might have been caused by magnetic fields.

PREPARATION OF COMPOUNDS

The sodium and potassium salts and the rubidium chloride used were commercial samples of C.P. purity. Other rubidium and caesium

TABLE II. *Summary of electron diffraction results obtained from the sodium halides.*

		NaCl		NaBr		NaI	
MAXIMUM	x	$\sin \frac{1}{2}\theta/\lambda$	l	$\sin \frac{1}{2}\theta/\lambda$	l	$\sin \frac{1}{2}\theta/\lambda$	l
1	—	—	—	—	—	—	—
2	13.70	0.4325 (6) ±.0052	2.520 ±.030	—	—	0.3759 (3) ±.0023	2.900 ±.018
3	20.20	0.6409 (4) ±.0023	2.507 ±.009	0.6084 (4) ±.0031	2.642 ±.013	0.5553 (2) ±.0032	2.895 ±.017
4	26.50	—	—	—	—	—	—
Average Values		2.51±0.03 (A)		2.64±0.01 (A)		2.90±0.02 (A)	

TABLE III. *Summary of electron diffraction results obtained from the potassium halides.*

		KCl		KBr		KI	
MAXIMUM	x	$\sin \frac{1}{2}\theta/\lambda$	l	$\sin \frac{1}{2}\theta/\lambda$	l	$\sin \frac{1}{2}\theta/\lambda$	l
1	—	—	—	—	—	—	—
2	13.70	0.3921 (8) ±.0030	2.780 ±.021	0.3685 (12) ±.0042	2.958 ±0.34	0.335 (14) ±.004	3.254 ±.038
3	20.20	0.5756 (6) ±.0032	2.793 ±.015	0.5489 (8) ±.0059	2.928 ±.031	0.500 (12) ±.004	3.215 ±.026
4	26.50	—	—	—	—	—	—
Average Values		2.79±0.02 (A)		2.94±0.03 (A)		3.23±0.04 (A)	

TABLE IV. *Summary of the electron diffraction results obtained from the rubidium halides.*

MAXIMUM	x	RbCl		RbBr		RbI	
		$\sin \frac{1}{2}\theta/\lambda$	l	$\sin \frac{1}{2}\theta/\lambda$	l	$\sin \frac{1}{2}\theta/\lambda$	l
1	—	—	—	—	—	—	—
2	13.70	0.3788 (7) ±.0011	2.878 ±.008	0.3538 (7) ±.0018	3.081 ±.016	0.3315 (8) ±.0018	3.288 ±.018
3	20.20	0.5536 (5) ±.0019	2.904 ±.010	0.5223 (6) ±.0027	3.078 ±.016	0.4918 (8) ±.0018	3.267 ±.012
4	26.50	—	—	0.6987 (5) ±.0059	3.018 ±.025	0.6517 (6) ±.0082	3.236 ±.041
Average Values		2.89±0.01 (A)		3.06±0.02 (A)		3.26±0.02 (A)	

TABLE V. *Summary of electron diffraction results obtained from the caesium halides.*

MAXIMUM	x	CsCl		CsBr		CsI	
		$\sin \frac{1}{2}\theta/\lambda$	l	$\sin \frac{1}{2}\theta/\lambda$	l	$\sin \frac{1}{2}\theta/\lambda$	l
1	—	—	—	—	—	—	—
2	13.70	0.3575 (16) ±.0052	3.049 ±.043	0.3459 (13) ±.0035	3.151 ±.032	0.3180 (6) ±.0030	3.428 ±.032
3	20.20	0.5224 (6) ±.0054	3.076 ±.031	0.5087 (12) ±.0042	3.160 ±.026	0.4694 (5) ±.0038	3.424 ±.027
4	26.50	—	—	0.6806 (7) ±.0078	3.098 ±.035	0.621 (2) ±.010	3.39 ±.05
Average Values		3.06±0.03 (A)		3.14±0.03 (A)		3.41±0.03 (A)	

salts were made by decomposition either of the carbonate or of the nitrate with an excess of the appropriate halogen acid. Purity of the various compounds was checked by a determination of the refractive indices. In all cases agreement existed to within 0.005 of the values reported in the literature. Other phases in each case were absent. It is estimated that the amount of impurity did not exceed 2 percent in any case.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 2 shows a reproduction of a typical electron diffraction photograph of the alkali halides which was obtained from rubidium bromide. Tables II, III, IV and V give the results obtained for the sodium, potassium, rubidium, and caesium halides. The numbers in parentheses give the number of photographs used for measurement while the variation shown represents the average deviation (without regard to sign) found between different photographs.

The positions of the apparent diffraction maxima were located by the use of ink dots 0.1 to 0.2 mm diameter placed on the glass side of the plates in alignment with the centers of the maxima. In this manner the eye can see the entire electron diffraction pattern without any obstruction while making a setting. Very reproducible ring diameter measurements were then obtained with the aid of an accurate scale and reading glass.

Each interference maximum for a diatomic molecule gives an independent measurement of the internuclear separation so that the values obtained from different maxima should all be the same. This feature is well maintained for the alkali halides as seen in the above tables. This serves to verify the initial assumption that the alkali halide molecules are diatomic. The question of association of the alkali halide molecules into double molecules has been studied by Deitz[9] from vapor pressure data. He was able to show that association does not occur which is in complete agreement with the present electron diffraction data.

Rodebush, Murray and Bixler[10] have found from measurements of dipole moments that the alkali halide molecules have large values for their electric moments. From a consideration of the nuclear separations obtained by electron diffraction it is found that the alkali halide molecules lack complete separation of charge by approximately 25 percent.

Table VI contains a comparison of interatomic distances between the crystal and the gas. It is noticed that for the sodium chloride type lattice the distances in the gas are about 10 percent less than the equivalent lattice separation. All the cases considered behave similarly with the exception of KI where the difference between the gas and crystal is less than for the other molecules. Additional data were obtained for this molecule in order to insure the correctness of the separation given. For the caesium chloride type lattice the distances within the crystal are about 14 percent greater than the corresponding distances in the gas. Deviations of this nature are expected because there is a change in coordination caused by the arrangement of 8 nearest neighbors around each ion as compared to 6 for the sodium chloride type lattice.

TABLE VI. *Comparison of interatomic distances between the crystal and the gas.*

	GAS	LATTICE*	LATTICE STRUCTURE	PERCENTAGE REDUCTION IN GOING FROM THE CRYSTAL TO THE GAS
NaCl	2.51(A)	2.814(A)	Sodium chloride type	10.8
Br	2.64	2.981	" " "	11.4
I	2.90	3.231	" " "	10.2
KCl	2.79	3.139	" " "	11.1
Br	2.94	3.293	" " "	10.7
I	3.23	3.526	" " "	8.4
RbCl	2.89	3.27	" " "	11.6
Br	3.06	3.427	" " "	10.7
I	3.26	3.663	" " "	11.0
CsCl	3.06	3.560	Caesium chloride type	14.0
Br	3.14	3.713	" " "	15.4
I	3.41	3.950	" " "	13.6

* P. P. Ewald and C. Hermann, *Strukturbericht* (1913–1928), p. 73 and p. 75.

The data on the nuclear separations given above for the gas molecules should prove useful in testing theories of ionic lattices since any successful theory should provide also a satisfactory explanation of the nuclear distance in the gas.

ERRORS

(1) de Broglie wave-lengths were determined with an error of less than one percent.

(2) Positions of each apparent maximum were measured to within about one percent for the second maximum, with decreasing error down to $\frac{1}{4}$ of one percent for the outermost maxima. The center of the scattering volume was determined to about 0.1 of one percent. The greatest error in $\sin \frac{1}{2}\theta$ for any individual maximum was not more than about one percent.

(3) Errors resulting in the choice of the $x_{\max}$ values used, as discussed above, are considered to be not greater than approximately one percent. Possible errors resulting from the different existing ψ_i values are not greater than about one percent since agreement with band spectra to within this amount has been found for Cl_2, I_2 and ICl.[5] These three molecules represent extreme cases namely, two light atoms, two heavy atoms and one heavy and one light atom, respectively. We thus conclude that one set of $x_{\max}$ values can be used for all of the alkali halide molecules.

(4) The effect of temperature on the electron diffraction measurements is usually unimportant.[6] For the case of the alkali halides no apparent diffuseness of the diffraction rings was observed which might arise from the effect of thermal vibrations of large amplitude. It is expected that the l_{ij} values should agree closely with the nuclear separations in the normal state of the molecule.

After considering all of the possible sources of error we conclude that the nuclear separations given above for the alkali halide molecules should probably be accurate to within one percent.

---

[9] V. Deitz, J. Chem. Phys. 4, 575 (1936).

[10] W. H. Rodebush, L. A. Murray, Jr. and M. E. Bixler, J. Chem. Phys. 4, 372 (1936).

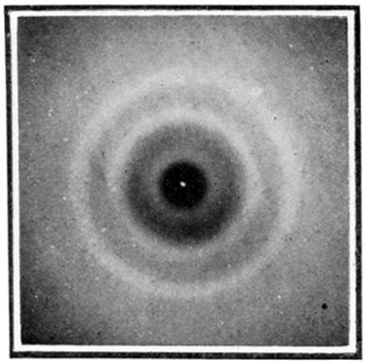

Fig. 2. Reproduction of an electron diffraction photograph obtained from RbBr.