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Abstract

Full Text

Physical Chemistry

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Electron-Diffraction Study of the Structure of Beryllium Halide Molecules

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The present communication is devoted to a study of the structure of the molecules of vapor-phase beryllium halides—fluoride, chloride, bromide, and iodide—for which data on their geometrical parameters are absent from the literature. The preparations used in the work were prepared as follows: BeF_2—by thermal decomposition of ammonium fluoroberyllate; $BeCl_2$—by the action of chlorine on metallic beryllium on heating; $BeBr_2$—by the action of dry bromine on powdered beryllium in absolute ether, followed by precipitation of the salt with absolute benzene; BeJ_2—by the action of hydroiodic acid on powdered beryllium on heating. Purification of the preparations was carried out by recrystallization from solvents and by sublimation in vacuum*.

Fig. 1. Curves of radial distribution for beryllium halide molecules

The apparatus and procedure used to obtain the electron diffraction patterns have been described previously (^{1}). Owing to the high hygroscopicity of the beryllium halides, their loading into the evaporator ampoule was carried out in a dry chamber. Before the electron diffraction patterns were recorded, all substances were thoroughly degassed in high vacuum directly in the electron-diffraction apparatus. The electron diffraction patterns were recorded on diapositive and ion-optical (NIKFI, type MK) photographic plates, with exposures from 2 to 30 sec.

For all vapor-phase beryllium halides, 8-10 series of electron diffraction patterns were obtained (3 photographs per series) at electron wavelengths from 0.0403 to 0.0627 Å. The electron diffraction patterns obtained had the following intensity distribution: the even (2nd, 4th, 6th, 8th, and 10th) maxima were intense; the odd (3rd, 5th, 7th, and 9th) had lower intensity than the even ones; the intensity of the even and, correspondingly, odd maxima decreased uniformly with increasing scattering angle; moreover, the relative intensity of the odd maxima increased on going from beryllium fluoride to the iodide; the minima

Fig. 2. Theoretical (valence angle 180°) and experimental intensity curves for beryllium halide molecules

Figure 2: Fig. 2. Theoretical (valence angle 180°) and experimental intensity curves for beryllium halide molecules

preceding the even maxima were deep, and those preceding the odd maxima were shallow (see the experimental curves in Fig. 2).

The interpretation of the electron diffraction patterns was carried out by the radial-distribution method in the Walter-Beach variant (^{2}) and then by the method of successive approximations (^{3}). The radial distribution curves $r^2D(r)$ for the molecules of all the beryllium halides studied (Fig. 1) have two

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well-defined peaks, which are naturally interpreted as the distances $r(\mathrm{Be-X})$ and $r(\mathrm{X-X})$, with the following values:

$$\begin{array}{rll}
\mathrm{BeF_2}: & r(\mathrm{Be-F}) = 1.43, & r(\mathrm{F-F}) = 2.80\ \text{Å}; \\
\mathrm{BeCl_2}: & r(\mathrm{Be-Cl}) = 1.77, & r(\mathrm{Cl-Cl}) = 3.51\ \text{Å}; \\
\mathrm{BeBr_2}: & r(\mathrm{Be-Br}) = 1.90, & r(\mathrm{Br-Br}) = 3.84\ \text{Å}; \\
\mathrm{BeJ_2}: & r(\mathrm{Be-J}) = 2.12, & r(\mathrm{J-J}) = 4.22\ \text{Å}.
\end{array}$$

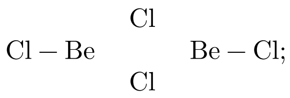
There were no other peaks on the radial-distribution curves that could have been regarded as structural. Thus, the data obtained by the radial-distribution method unambiguously indicate that the electron diffraction patterns of beryllium halide vapors correspond to linear triatomic molecules $\mathrm{BeX_2}$.

Fig. 2. Theoretical (valence angle 180°) and experimental intensity curves for beryllium halide molecules

Figure 2 presents theoretical curves of the intensity of scattered electrons, constructed for linear $\mathrm{BeX_2}$ molecules, which reproduce well all the characteristic features of the electron diffraction patterns of beryllium halide vapors. The results of the calculation by the method of successive approximations are given in Tables 1-4.

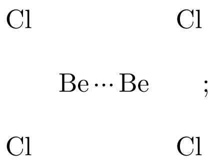
In our previous papers ($^{4-9}$) it was noted that a characteristic feature of the electron diffraction patterns of vaporous halides of zinc, cadmium, magnesium, calcium, strontium, and barium is the asymmetry of the contour of the diffraction rings, weakly expressed for fluorides and increasing on passing to chlorides, bromides, and iodides (in individual cases turning into intensity steps on the outer side of the rings), in connection with which the accuracy in determining the valence angle from the $I(s)$ curves increases from fluorides to iodides (we note that in most cases the question of the valence angle in fluorides could be resolved only by making use of radial-distribution data). Since for all beryllium halides the charge of the halogen atoms exceeds the charge of the metal atom, the electron diffraction patterns of the vapors show an alternation of intense (even) and weak (odd) maxima, whose contour changes only slightly when the valence angle is varied; moreover, the $I(s)$ curve of $\mathrm{BeF_2}$ is most sensitive to variation of the valence angle $\mathrm{X-Be-X}$, and the $I(s)$ curve of $\mathrm{BeJ_2}$ is least sensitive. Since in the literature (^{10}) there was an indication of the presence in the vapors of beryllium halides of dimeric molecules $\mathrm{Be_2X_4}$, we tested, using beryllium chloride as an example, a number of $\mathrm{Be_2X_4}$ models:

1) model of the type (X = Cl)



$$\begin{array}{ccc} & \mathrm{Cl} & \\ \mathrm{Cl-Be} & & \mathrm{Be-Cl}; \\ & \mathrm{Cl} & \end{array}$$

2) model of the type (X = Cl)



$$\begin{array}{ccc} \mathrm{Cl} & & \mathrm{Cl} \\ & \mathrm{Be\cdots Be} & ; \\ \mathrm{Cl} & & \mathrm{Cl} \end{array}$$

3) an octahedral model, in which four chlorine atoms form a square, and two beryllium atoms are located on both sides of the plane of the square at equal distances from it. It turned out that the theoretical

Table 1

Molecule $\mathrm{BeF_2}$; $r_{\text{theor}} = 1.40$ Å

Max.	Min.	Intensity	s_{theor}	s_{exp}	$\frac{s_{\text{theor}}}{s_{\text{exp}}}$	r_{exp}, Å
1		+10	2.44	2.81	(0.868)	(1.22)
	2	−14	3.68	3.94	(0.934)	(1.31)
2		+20	5.17	5.03	1.028	1.44
	3	−4	6.55	6.23	(1.051)	(1.47)
3		+2	6.92	7.27	(0.952)	(1.33)
	4	−8	8.22	8.45	0.973	1.36
4		+12	9.69	9.55	1.015	1.42
	5	−2	11.03	10.72	1.029	1.44
5		+1	11.42	11.79	0.969	1.36
	6	−5	12.71	12.91	0.985	1.38
6		+6	14.18	13.99	1.014	1.42
Average value					1.002	1.40

Max.	Min.	Intensity	s_{theor}	s_{exp}	$\frac{s_{\text{theor}}}{s_{\text{exp}}}$	r_{exp}, Å
Mean deviation					$±$0.022	$±$0.03

Table 2

Molecule $BeCl_2$; $r_{\text{theor}} = 1.76$ Å

Max.	Min.	Intensity	s_{theor}	s_{exp}	$\frac{s_{\text{theor}}}{s_{\text{exp}}}$	r_{exp}, Å
1		+10	2.10	2.48	(0.847)	(1.49)
	2	−15	3.00	3.32	0.904	1.59
2		+20	4.08	4.13	0.988	1.74
	3	−6	5.02	5.18	0.969	1.71
3		+2	5.67	5.98	(0.948)	(1.67)
	4	−12	6.60	6.92	(0.954)	(1.68)
4		+10	7.65	7.69	0.995	1.75
	5	−3	8.61	8.57	1.005	1.77
5		+1	9.24	9.46	0.977	1.72
	6	−5	10.17	10.16	1.001	1.76
6		+4	11.23	11.04	1.017	1.79
	7	−2	12.17	12.09	1.007	1.77
7		+1	12.83	13.02	0.985	1.73
	8	−4	13.73	13.89	0.988	1.74
8		+3	14.80	14.80	1.000	1.76
	9	−1	15.73	15.68	1.003	1.77
9		+1	16.42	16.56	0.992	1.75
	10	−2	17.32	17.39	0.996	1.75
10		+1.5	18.37	18.24	1.007	1.77
Average value					0.995	1.75
Mean deviation					$±$0.010	$±$0.02

curves $I(s)$ corresponding to models 1–3 bear no resemblance to the experimentally found intensity distribution in the diffraction pattern of beryllium chloride.

On the other hand, diatomic molecules of the BeX type, if present in the vapors of the substances studied, would give an intensity distribution (a simple damped sinusoid) sharply different from the experimentally obtained pattern. From this one may conclude that, under the conditions of the electron-diffraction experiment, in the vapors of beryllium halides dimeric (Be_2X_4) and diatomic (BeX) molecules either are entirely ab-

Table 3

Molecule $BeBr_2$; $r_{\text{theor}} = 1.90$ Å

Max.	Min.	Intensity	s_{theor}	s_{exp}	$\frac{s_{\text{theor}}}{s_{\text{exp}}}$	r_{exp}, Å
1		+15	2.00	2.02	0.990	1.88
	2	−20	2.83	2.97	0.953	(1.81)
2		+20	3.77	3.77	1.000	1.90
	3	−7	4.59	4.61	0.996	1.89
3		+8	5.33	5.39	0.989	1.88
	4	−12	6.15	6.22	0.989	1.88
4		+10	7.06	7.00	1.009	1.92
	5	−5	7.90	7.88	1.003	1.91
5		+4	8.63	8.66	0.997	1.89
	6	−8	9.45	9.50	0.995	1.89
6		+5	10.36	10.25	1.011	1.92
	7	−3	11.21	11.10	1.011	1.92
7		+2	11.93	11.87	1.006	1.91
	8	−4	12.77	12.64	1.010	1.92
8		+3	13.66	13.46	1.015	1.93
	9	−2	14.50	14.23	1.019	1.94
9		+1	15.23	15.03	1.013	1.92
	10	−3	16.05	15.84	1.013	1.92
10		+1.5	16.98	16.72	1.016	1.93
Average value					1.005	1.91
Mean deviation					$±$0.009	$±$0.02

Table 4

Molecule BeJ_2; $r_{\text{theor}} = 2.10$ Å

Max.	Min.	Intensity	s_{theor}	s_{exp}	$\frac{s_{\text{theor}}}{s_{\text{exp}}}$	r_{exp}, Å
1		+15	1.83	1.81	1.011	2.12
	2	−20	2.57	2.67	(0.963)	(2.02)
2		+20	3.37	3.40	0.991	2.08
	3	−6	4.13	4.18	0.988	2.07
3		+6	4.83	4.90	0.986	2.07
	4	−10	5.57	5.66	0.984	2.07
4		+10	6.37	6.36	1.002	2.10
	5	−3	7.13	7.12	1.001	2.10
5		+3	7.83	7.83	1.000	2.10

Max.	Min.	Intensity	s_{theor}	s_{exp}	$\frac{s_{\text{theor}}}{s_{\text{exp}}}$	r_{exp}, Å
	6	−5	8.57	8.55	1.002	2.10
6		+5	9.37	9.25	1.013	2.13
	7	−1	10.13	10.05	1.008	2.12
7		+1	10.83	10.79	1.004	2.11
	8	−2	11.57	11.50	1.006	2.11
8		+2	12.37	12.22	1.012	2.13
Average value					1.000	2.10
Mean deviation					$±$0.008	$±$0.02

are absent, or else are present in concentrations lying beyond the sensitivity limits of the electron-diffraction method. This is confirmed by approximate calculations carried out by Brewer (^{11}), according to which, for example, for BeF_2 50% dissociation does not occur up to 3000°K, and for $BeCl_2$, up to 2000°K.

Thus, both methods used for interpreting the electron-diffraction patterns of the vapors (radial distribution and successive approximations) give mutually consistent results for the configuration (linear structure) and geometrical parameters of the molecules of the vapor-like beryllium halides (see Table 5), obtained for the first time in our work.

Table 5

Geometrical parameters of linear molecules of beryllium halides

Compounds	Distance Be–X, Å
BeF_2	1.40 ± 0.03
$BeCl_2$	1.75 ± 0.02
$BeBr_2$	1.91 ± 0.02
BeJ_2	2.10 ± 0.02*

* In paper (^{14}), in Table 1, a misprint was made in the value of the Be–J distance.

It is interesting to note that the interatomic distances in the molecules BeF and BeCl (1.36 and 1.70, respectively), determined spectroscopically (^{12}), are close to the interatomic distances in the molecules BeF_2 and $BeCl_2$ (see Table 5), differing from the latter by 0.04–0.05 Å. There are no spectroscopic data for the molecules BeBr and BeJ, but if it is assumed that the interatomic distances in these molecules are also smaller than the corresponding distances in $BeBr_2$ and BeJ_2 by approximately 0.05 Å, then we obtain values, respectively, of 1.86 and

2.05 Å, which differ markedly from the values (Be—Br) = 2.05 Å and (Be—J) = 2.33 Å obtained in Margreave' s work (13) on the basis of an electrostatic model; apparently, this estimate must be regarded as very rough.

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named after M. V. Lomonosov

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