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Internuclear Distances in Se_2, Te_2, and HgCl by Electron Diffraction

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Electron diffraction photographs have been obtained from the gas molecules Se_2, Te_2, and HgCl. The internuclear distances found for Se_2 and Te_2 were 2.19±0.03A and 2.59±0.02A, respectively, while for HgCl a separation of 2.23±0.03A was obtained. Additional photographs were taken of $HgCl_2$ indicating an Hg-Cl distance of 2.27±0.03A near to the above value for HgCl. Comparison is made with band spectrum data on the internuclear distances for Se_2 and Te_2.

INTRODUCTION

MEASUREMENTS of the internuclear separations in diatomic selenium and tellurium have been undertaken by the electron diffraction method since band spectrum values for these distances are somewhat uncertain. In general, the rotational structure for the sulphur group molecules S_2, Se_2, and Te_2 has been difficult to analyze. In the case of S_2 the internuclear separation was obtained by the electron diffraction method[1] after several widely variant band spectrum values for this distance had been reported. Olsson[2] has given values for the rotational constants of Se_2 which involve a measurement of small combination frequency differences. Przeborski[3] has reported several possible distances for the ground state of Te_2 from band spectrum data. No information is available on the nuclear separation in HgCl although an indication of the distance to be expected can be obtained from previous electron diffraction work[4] on $HgCl_2$.

PROCEDURE AND EXPERIMENTAL ARRANGEMENT

Electron diffraction photographs were obtained by the transmission method through concentrated beams of the gas molecules. The method of analysis used, which has been previously described,[5] involved only visual measurements of the electron diffraction patterns. For the study of selenium it was necessary to raise the temperature of the vapor to at least 750°C at about 100 mm of Hg pressure in order to dissociate the higher molecular forms of selenium to Se_2.[6] Fig. 1 illustrates the quartz boiler used for this purpose. A nozzle 15 mm long having a bore 0.4 mm in diameter was heated to about 900°C to ensure the presence of a sufficient number of Se_2 molecules for diffraction. The lower part of the boiler containing the supply of material was kept at approximately 615°C for vaporizing the selenium. Three platinum radiation shields not illustrated were placed around the boiler for reduction of heat losses. The jet temperatures were measured by means of an optical pyrometer. For the case of tellurium and mercurous chloride a metal boiler as described previously[5] was used. The plate

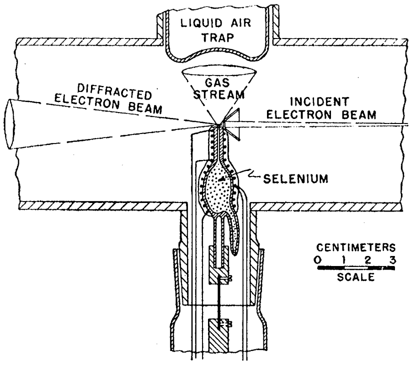

FIG. 1. Diagram of quartz boiler used in obtaining electron diffraction photographs from selenium.

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

[2] E. Olsson, Zeits. f. Physik **90**, 138 (1934); also Doctor's Thesis, Stockholm Högskola, October, 1938.

[3] A. Przeborski, Zeits. f. Physik **63**, 280 (1930); Acta phys. polon. **3**, 527 (1934), abstracted in Chemisches Zentralblatt **107**, 3640 (1936).

[4] H. Braune and S. Knoke, Zeits. f. physik. Chemie **B23**, 163 (1933); A. H. Gregg, G. C. Hampson, G. I. Jenkins, P. L. F. Jones, and L. E. Sutton, Trans. Faraday Soc. **33**, 852 (1937).

[5] L. R. Maxwell, S. B. Hendricks and V. M. Mosley, J. Chem. Phys. **3**, 699 (1935).

[6] G. Preuner and I. Brockmöller, Zeits. f. physik. Chemie **81**, 129 (1912–13).

TABLE I. *Summary of electron diffraction results obtained from* Se$_2$, Te$_2$, *and* HgCl. *Numbers in parenthesis give the number of plates measured. Variations given are the average deviations from the mean without regard for sign.*

Maximum	x	Se$_2$		Te$_2$		HgCl	
		$(1/\lambda)\sin\frac{1}{2}\theta$	l	$(1/\lambda)\sin\frac{1}{2}\theta$	l	$(1/\lambda)\sin\frac{1}{2}\theta$	l
1	—	present	—	present	—	present	—
2	13.70	0.498 (6)	2.19±0.03	0.4218 (8)	2.58±0.03	0.493 (11)	2.21±0.03
3	20.20	0.730 (6)	2.20±0.03	0.6185 (8)	2.60±0.02	0.719 (10)	2.23±0.02
4	26.50	0.963 (3)	2.19±0.01	0.8146 (8)	2.59±0.02	0.933 (4)	2.26±0.02
5	32.95	1.192 (2)	2.20±0.01	1.0176 (3)	2.58±0.01		
Average Values		2.19±0.03A		2.59±0.02A		2.23±0.03A	

distance was 10 cm and the de Broglie wavelengths ranged between 0.064 to 0.074A.

RESULTS AND DISCUSSION

Selenium[7]

Table I contains a summary of the electron diffraction results obtained from the molecules studied. Five interference maxima were obtained for Se$_2$ agreeing closely in intensity and position with the values required by a diatomic molecule.

The average value of the nuclear separation obtained from the various maxima is 2.19±0.03A. This distance can be compared with Olsson's[2] band spectrum value of 2.15A for a $^1\Sigma$ ground state which is slightly lower than the electron diffraction value but almost within the range of the average deviations obtained by the electron diffraction method. A somewhat similar situation arose for the case of S$_2$ where Olsson's band spectrum value for a $^3\Sigma$ ground state gave 1.88A while the electron diffraction value was 1.92±0.03A. He has suggested that this small difference might be due to the S$_2$ molecule having a $^1\Sigma$ state with nearly the same energy as the $^3\Sigma$ ground state but with somewhat greater nuclear separation, thus making the average electron diffraction value slightly higher than the band spectrum separation.

Magnetic measurements on selenium vapor by Bhatnagar, Lessheim, and Khanna[8] show that as the temperature is raised towards 1000°C the gas becomes paramagnetic due to the presence of Se$_2$ molecules. They concluded therefore that the ground level of Se$_2$ is a $^3\Sigma$ state. In view of these magnetic measurements Olsson has postulated that Se$_2$ also may have two low energy states, a $^1\Sigma$ and $^3\Sigma$ with a small energy difference between them. Assuming this situation for the Se$_2$ molecule the electron diffraction value may represent an average of these two levels and thus possibly give a greater internuclear distance than reported by Olsson. However, Rosen[9] has questioned the existence of a $^1\Sigma$ ground state on the basis of his absorption spectrum determinations which seem to indicate that the main system can be represented by $^3\Sigma \rightarrow {}^3\Sigma$ instead of $^1\Sigma \rightarrow {}^1\Sigma$ transition.

Photographs were also taken from the selenium vapor directly without providing any special means for dissociation. This low temperature form contained higher polymers which gave a different type of pattern both as regards intensity and position of the interference rings. Howe and Lark-Horovitz[10] have previously obtained such electron diffraction photographs and the positions of the maxima found in the present work are in essential agreement with their results. Actually, maxima were found at $(1/\lambda)\sin\frac{1}{2}\theta = 0.16$, 0.29, 0.46, 0.709, and 0.897 as compared with the values 0.157, 0.290, 0.454, and 0.698, respectively, determined by Howe and Lark-Horovitz.

Tellurium[11]

Little information is available concerning the vapor density of tellurium, so the material was heated in a simple type boiler until sufficient vapor was emitted to give electron diffraction photographs. The type of pattern formed showed clearly that the molecule was diatomic, as de-

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[7] Preliminary report, L. R. Maxwell and V. M. Mosley, Phys. Rev. **55**, 238 (1939).

[8] S. S. Bhatnagar, H. Lessheim, and M. L. Khanna, Nature **140**, 152 (1937); Proc. Ind. Acad. **A6**, 155 (1937).

[9] B. Rosen, Physica **6**, 205 (1939).

[10] J. D. Howe and K. Lark-Horovitz, Phys. Rev. **51**, 380 (1937).

[11] Preliminary report, L. R. Maxwell and V. M. Mosley, Phys. Rev. **51**, 684 (1937).

termined by the intensities and positions of the interference maxima. In Table I a summary of the results obtained gives 2.59±0.02A as the average nuclear separation for Te_2. Table II lists the internuclear distances of the sulphur-group molecules which have been measured by the electron diffraction method. Various possible band spectrum values for Te_2 obtained by Przeborski[3] are 2.87A, 2.77A, and 2.44A; none of these, however, is in agreement with the electron diffraction value.

Huggins[12] has calculated by a semi-empirical method the nuclear separation of Te_2 from the vibrational constants ω_e, $\omega_e x_e$, and a basic radius obtained from I_2. This led to $r_e = 2.61$A, which is in good agreement with the electron diffraction value. A separation of 2.55A for r_e was given by Huggins for Te_2, using an empirical formula developed by Badger; this is also near to the electron diffraction distance.

Mercurous chloride (HgCl)[7]

Considerable uncertainty has existed concerning the nature of mercurous chloride vapor. Vapor density measurements generally agree on the composition of the vapor as either HgCl or $Hg+HgCl_2$, these alternatives being indistinguishable by this method. Gucker and Munch[13] found that dry mercurous chloride vapor, when sublimed in a vacuum at 200°C on a liquid-air trap, shows no decomposition as determined by the absence of a mercury deposit. This indicates that if mercurous chloride were heated in the electron diffraction boiler it might give a vapor which has a high concentration of the single HgCl molecules. The interference pattern obtained was characteristic of a diatomic molecule and led to a nuclear separation of 2.23±0.03A as summarized in Table I. The photographs were rather poor; this is to be expected on account of the large scattering power of the mercury atom as compared to chloride. Chemical analysis[14] made of the material deposited on the liquid-air trap after the exposures had been made showed that at least 95 percent remained as the mercurous compound. Additional identification of HgCl in this deposit was made by x-ray powder photographs.[15] It is safe to conclude therefore that the material studied was the HgCl molecule. Electron diffraction results from $HgCl_2$ by Braune and Knoke[4] gave a Hg-Cl separation of 2.28A, which agrees fairly well with the present value for HgCl. However, Gregg, Hampson, Jenkins, and Jones[4] have reported a somewhat larger distance of 2.34±0.01A for the HgCl distance in $HgCl_2$. In view of the small error which these workers have reported for their distance, it appears that their Hg-Cl separation is definitely greater than the value obtained here for the mercurous compound.

TABLE II. *Internuclear distances of the sulphur-group molecules determined by the electron diffraction method. Variations given are the average deviations from the mean without regard to sign.*

Molecule	Separation (A)
S_2	1.92±0.03
Se_2	2.19 0.03
Te_2	2.59 0.02

In order to provide additional information on the possible constancy of the Hg-Cl distance, photographs were also taken of $HgCl_2$ with the same boiler and experimental set-up as used for HgCl. The $(1/\lambda)\sin\frac{1}{2}\theta$ values obtained for the 2nd, 3rd, and 4th maxima were 0.484, 0.709, and 0.922, respectively, with an average variation of about 1 percent. These data agree closely with the results of Braune and Knoke who gave the values 0.484 and 0.696 for the positions of the 2nd and 3rd maxima, but they are slightly higher than 0.474, 0.691, and 0.907, which are the respective positions given by Gregg *et al.* Since the Hg-Cl scattering term for this molecule is large compared to the Cl-Cl term, the x values for the different maxima are close to those obtained for a diatomic molecule. Thus if we take the x values used above for the diatomic molecules, i.e., 13.7, 20.2, and 26.5, we obtain Hg-Cl distances of 2.25, 2.27, and 2.29A, respectively, which give an average of 2.27±0.03A. This distance is only slightly greater than the above value for Hg-Cl in the mercurous chloride molecule.

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[12] M. L. Huggins, J. Chem. Phys. **4**, 308 (1936); J. Chem. Phys. **5**, 201 (1937).

[13] F. T. Gucker, Jr. and R. H. Munch, J. Am. Chem. Soc. **59**, 1275 (1937).

[14] The authors are indebted to Mrs. E. K. Rist of this laboratory for carrying out this analysis.

[15] The authors are indebted to Dr. Sterling B. Hendricks for taking the x-ray powder photographs of the mercurous chloride deposits.