GEOMETRICAL STRUCTURE OF THE MOLYBDENUM TETRABROMIDE MOLECULE IS NON-TETRAHEDRAL

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Molecular structure of molybdenum tetrabromide has been studied by electron diffractometry. The geometrical configuration of MoBr₄ has been shown to be of Cᵥ symmetry. The following values of structural parameters have been obtained: R₂(MoBr) = 233.9(6) pm, R₂(MoB) = 244.5(6) pm, \( \beta(\text{Br}_1\text{MoBr}_2) = 106(1)° \), and \( \alpha(\text{Br}_2\text{MoBr}_3) = 86(2)° \). The frequency values of the vibrational spectrum have been estimated.

Recently we have found that the geometrical configuration of the WCl₄ molecule has no tetrahedral symmetry, with the internuclear W—Cl distances differing by \( \sim 10 \text{ pm} \) [1-3]. On the basis of the established structural features of tungsten and molybdenum halides it was conjectured that the equilibrium geometrical configuration of molybdenum tetrahalides has no tetrahedral symmetry either; also, molecular constants of MoHal₄ were estimated [3-5]. However, the authors of [6] have used the results of the electron diffraction study carried out in the 1960s [7] to interpret the experimental electronic spectrum of MoBr₄ and have performed its Xα-SW calculation proceeding from the \( T_d \) symmetry. In [8] it has been shown that upon evaporation of solid MoBr₂₅ in the temperature range 770-870 K, only one molecular form, MoBr₄, passes into the gas phase. This result makes it possible to perform an electron diffraction study of MoBr₄ not complicated by the indefinite composition of the vapor.

The molybdenum bromide sample (MoBr₂₅ phase) obtained by the procedure described in [8] was evaporated from the Knudsen molybdenum effusion cell at 773 K. The procedure for measuring and processing the electron diffractograms* was similar to that used in the study of WCl₄ in [1, 2]. The electron diffractograms of MoBr₄ vapors were recorded on an ELMELG instrument under the following conditions (parameter values are given for one of the series): \( T = 773(10) \text{ K}, \lambda = 0.05409(3) \text{ Å}, L_1 = 415.7(2) \text{ mm}, k = 1.0177(8), p = 5\cdot10^{-8} \text{ Pa}, E = 110 \text{ sec}, \) and \( D \leq 0.7 \). The experimental function \( sM(\sigma) \) was determined by the procedure of division into experimental background in the range of \( s_{\text{min}} = 2.0 \text{ Å}^{-1}, s_{\text{max}} = 17.0 \text{ Å}^{-1} \) (the plot of \( sM(\sigma) \) is shown in Fig. 1). The corresponding experimental function of the type \( g(\tau) \) (see [9]) is given in Fig. 2. It is easy to see that this function is mainly composed of two structural peaks with maximum abscissae at \( \sim 239 \) and \( \sim 380 \text{ pm} \). The abscissa of the first peak is in good agreement with the internuclear distance value \( R(\text{MoBr}) \) in MoBr₄, obtained in [7]. It should be noted, however, that the ratio of maximum abscissae in Fig. 2 is much smaller than for the tetrahedral configuration. Therefore, the least-squares determination of molecular structure parameters of MoBr₄ was performed, as in the study of WCl₄ [1], in the following variants.

Variant A. The molecule has a tetrahedral configuration.

Variant B. The molecule has a distorted tetrahedral configuration (\( D_{2d} \) or \( C_{2v} \) symmetry) with equal internuclear distances \( R(\text{MoBr}) \).

Variant C. The molecule has a distorted tetrahedral configuration with unequal internuclear distances \( R(\text{Mo—Br}) \) (\( C_{2v} \) symmetry, Fig. 3).

Table 1 lists the results of our analysis. In variant A, the \( R(\text{Mo—Br}) \) to \( R(\text{Br—Br}) \) ratio, \( (1.562(4)) \), is essentially

* The authors wish to thank V. M. Pervov and S. A. Ryabov for providing the sample, and M. G. Popik for assistance in processing the electron diffractograms.
smaller than for the tetrahedral configuration (1.633). Such shortening of $R(\text{Br}-\text{Br})$ and the experimental values of mean-square amplitudes correspond to unreasonably low frequencies of the vibrational spectrum ($\nu_{\text{val}} < 200$ cm$^{-1}$; for details see [3-5]). Moreover, the agreement between the experimental and theoretical functions $s_M(s)$ in this variant is much worse than in B and C. On this basis the assumption about the tetrahedral equilibrium configuration may be refuted with confidence.

It follows from Table 1 that minimization in variants B and C leads to the same level of agreement between the theoretical and experimental functions $s_M(s)$. (As shown by the analysis of $g(r)$ and $s_M(s)_{\text{exp}}$ functions, the contribution of the internuclear distance $R(\text{Br}_1\text{Br}_4)$ into the experimental diffraction picture is negligibly small; therefore, in the least-squares analysis it was neglected.) Upon independent variation of all parameters in variant C, there appears a strong correlation (the correlation coefficients are 0.7 to 0.9) between the values of internuclear distances $R(\text{Mo}-\text{Br})$ and mean-square amplitudes $l(\text{Mo}-\text{Br})$. We note that $l(\text{Mo}-\text{Br}) = 9.8$ pm obtained in variant

![Fig. 3. Model of the MoBr$_4$ molecule.](image-url)