*Journal of Molecular Structure*, 68 (1980) 199—202
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

# MOLECULAR STRUCTURE OF THE BORON(III) OXIDE MOLECULE IN THE SCF APPROXIMATION

ANDREJ I. DEMENT'EV, NIKOLAJ G. RAMBIDI, VLADIMIR YA. SIMKIN and IGOR' A. TOPOL'

*Research Institute of Metrological Service, Ezdakov pr. 1, Moscow, 117 334 (U.S.S.R.)*

NIKOLAJ F. STEPANOV*

*School of Science and Engineering, Waseda University, Tokyo 160 (Japan)*

BORIS I. ZHILINSKII

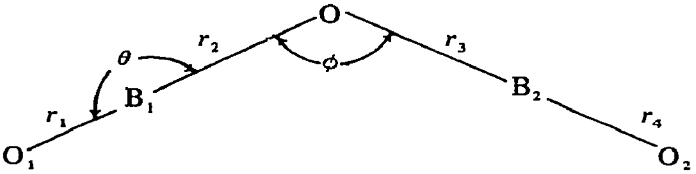
*Faculty of Chemistry, Moscow State University, Moscow 117 234 (U.S.S.R.)*

(Received 30 January 1980)

ABSTRACT

The potential surface for the boron(III) oxide ($B_2O_3$) ground state has been calculated in restricted HF approximation with a minimal STO—3G basis set. The equilibrium geometry has $C_{2v}$ symmetry; the corresponding structural parameters are as follows: $r(O_1—B_1) = 1.241$ Å; $r(B_1—O) = 1.341$ Å; $\angle B_1OB_2 = 142°$ and $\angle O_1B_1O = 177°$. Calculations were also carried out using the SCF—X$\alpha$ approach for two configurations of $B_2O_3$ with $C_{2v}$ and $D_{\infty h}$ symmetry.

The spectra and molecular structure of the $B_2O_3$ molecule have been studied in a series of experimental and theoretical investigations [1—14]. Gas electron diffraction data [1—14] support a V-shaped structure of $C_{2v}$ symmetry



with $r(B_1—O_2) \equiv r_1 = r_4 = 1.219 \pm 0.007$ Å, $r(B_1—O) \equiv r_2 = r_3 = 1.323 \pm 0.008$ Å and $\phi = \angle B_1OB_2 = 137.5 \pm 6.3°$, $\theta = \angle O_1B_1O = 180°$ [4]. The other models (the same configuration with equal distances $r(B_1—O_1)$ and $r(B_1—O)$ and a T-shaped configuration) gave slightly larger values for the $R$-factor. In a recent simultaneous treatment of electron diffraction and spectroscopic data, Gershikov and Spiridonov [5] obtained approximately the same values for the geometry parameters with angle $\theta$ a little less (ca. 10°) than 180°.

---

*Author to whom all correspondence should be addressed. Permanent address: Department of Physical Chemistry, Faculty of Chemistry, Moscow State University, Moscow 117 234, U.S.S.R.

In IR spectra of the $B_2O_3$ molecule and its isotopomers ($^{10}B$ and $^{18}O$) in Ar matrices [10—12], two intensive bands were observed at 2061 and 489 $cm^{-1}$ (for $^{11}B_2{}^{16}O_3$) together with three less definitely assigned bands of medium intensity at 518, 462 and 73 $cm^{-1}$. In the Raman spectra only one intense band at 1062 $cm^{-1}$ was found as well as a very broad fluorescence band in the region of 2000 $cm^{-1}$. The positions of the most intense bands (2061, 1062 and 489 $cm^{-1}$) are also close to vibrational bands of the $BO_2$ radical and $BO_2$ fragment in alkali metaborate molecules: the symmetric stretching mode $\nu_1$ at 1030—1095 $cm^{-1}$, the bending vibration $\nu_2$ at 450—600 $cm^{-1}$ and the antisymmetric stretching mode $\nu_3$ at 1930—1960 $cm^{-1}$. For $C_{2v}$ structure all fundamentals are allowed in the Raman spectrum and all but one ($A_2$) in the IR spectrum.

Theoretical investigations support the V-shaped $C_{2v}$ structure in the MO—SCF [13] and valence INDO [14] approximations. However, in both these calculations the geometry was not optimized completely. The equilibrium value of $\phi$ obtained in the INDO approximation was close to 102°.

To better understand the structure of $B_2O_3$, why its vibrational spectra are so poor and why different selection rules are satisfied (as in spectra of linear molecules) we calculated a large number of points on the potential surface of the ground state of this molecule.

## COMPUTATIONAL DETAILS

The calculations were carried out in a restricted Hartree—Fock approximation with a minimal STO—3G basis set and in the muffin-tin SCF—X$\alpha$ approximation with and without polarization $d$-functions. Preliminary calculations on the plane T-shaped and bipyramidal $D_{3h}$ configurations gave energy values which were 0.2—0.5 a.u. higher than the nearby minimum values, so that configurations of these types were omitted from the following considerations. In the RHF approximation the lowest energy values were obtained for partially distorted V-shaped configurations. In the vicinity of the equilibrium position the geometry was optimized using the internal symmetry coordinates which represent displacements $q_i$ of nuclei from some reference positions supposed to be close to the equilibrium position. The optimization was only done for the plane configurations.

## RESULTS AND DISCUSSION

The minimal energy value (—270.33218 a.u.) refers to the following geometry: $r_1 = r_4 = 1.241$ Å, $r_2 = r_3 = 1.341$ Å, $\phi = 142°$, $\theta = 177°$. However, the optimized energy value for the linear $D_{\infty h}$ configuration exceeds the minimal value by only 0.00223 a.u. $\simeq$ 489 $cm^{-1}$. The bond distances for the $D_{\infty h}$ configuration are very similar to those of the bent configuration: $r_1 = 1.241$ and $r_2 = 1.333$ Å. The bottom of the potential surface near the equilibrium position is rather shallow so that nuclei can move more or less freely around their equilibrium sites. This suggests large-amplitude vibrations ought to be inherent to the molecule. In such vibrations the internuclear distances $r_i (i = 1, 2, 3, 4)$ remain almost unchanged and they can be counted as coordinates of rigid motions for the $B_2O_3$ molecule as a semi-rigid bender.

When a simplified basis set (minimal STO—1G) is used the equilibrium value of angle $\phi$ diminishes for the V-shaped configuration until ca. 103°. Hence the INDO results can be juxtaposed to this very crude approximation.

Since the equilibrium configuration energy for $B_2O_3$ is very close to the energy of a linear configuration and since in the course of the low-frequency vibrations the molecule is passing through the linear configuration (in the classical sense), then the selection rules must be approximately the same as those for linear molecules. The consequences of this statement are clear. For a linear configuration there are two $\Sigma_g^+$ modes for which fundamentals are allowed in Raman transitions. One of them is linked to the vibrations of terminal BO fragments ($B_1$—$O_1$ and $B_2$—$O_2$). Its frequency must be approximately equal to 2000 $cm^{-1}$, hence it cannot be observed in a Raman spectrum because of the above-mentioned intensive fluorescence in this region. Another mode of this type corresponds to the symmetric mode $\nu_1$ of the $B_2O$ fragment (ca. 1000 $cm^{-1}$). The transitions related to these modes are almost forbidden in IR spectra for a slightly bent configuration.

There are also two $\Sigma_u^+$ modes, which can be juxtaposed to the antisymmetric $\nu_3$ mode of $BO_2$ (ca. 2000 $cm^{-1}$) and to the mode of the same $\nu_3$ type for the $A_2O$ molecule with rigid BO groups as A. The fundamentals of this type of symmetry are allowed in the IR spectrum. Among the two $\Pi_u$ modes, one should correspond to a low-frequency bending motion of the $B_1$—$O_1$ and $B_2$—$O_2$ wings around the central oxygen atom and the second to the bending motions of the $BO_2$ and $B_2O$ fragments, so that the proper frequency can be estimated as ca. 500 $cm^{-1}$. The corresponding transitions are allowed in the IR spectrum. The $\Pi_g$ mode answers to a comparatively low frequency of rotational motion of two $B_i$—$O_i$ groups around their centres of masses. The corresponding transition is allowed in the Raman spectrum but would not be very intense.

Hence, the results obtained and the considerations given above provide a clear qualitative background for the simultaneous interpretation of gas electron diffraction and spectroscopic data.

In conclusion we shall briefly indicate some results of the SCF—X$\alpha$ calculations. These calculations were carried out for two geometries, the experimental V-shaped one with $\phi = 137.5°$ and the linear one, optimized in RHF calculations; for both geometries two basis sets were used, $\{s, p\}$ and $\{s, p, d\}$. The vertical transition energy is almost the same for both basis sets: the lowest excited state $^3B_2$ is higher than the ground state by 6.7—7.3 eV for a $C_{2v}$ configuration and by 6.9—7.2 eV for a linear configuration. The first ionization potential is 12.1—12.5 eV (from the $2b_2$ orbital). The Mulliken gross atomic charges are as follows (in *spd*-basis): $q(O) = -0.43$, $q(B_1) = q(B_2) = 0.65$, and $q(O_1) = q(O_2) = -0.44$.

## ACKNOWLEDGEMENTS

The authors express their gratitude to Prof. A. A. Mal'tsev (Moscow State University) and to Prof. R. Itoh (Waseda University, Tokyo) for very fruitful discussions; they are also grateful to Prof. A. A. Mal'tsev and Prof. V. P. Spiridonov for provision of data prior to publication.

## REFERENCES

1 P. A. Akishin and V. P. Spiridonov, Dokl. Akad. Nauk SSR, 131 (1960) 557.
2 Yu. S. Ezhov, S. M. Tolmachev, V. P. Spiridonov and N. G. Rambidi, Teplofiz. Vys. Temp., 6 (1968) 67.
3 Yu. S. Ezhov, S. M. Tolmachev and N. G. Rambidi, Zh. Strukt. Khim., 11 (1970) 527.
4 V. P. Spiridonov and E. Z. Zasorin, in J. W. Hastie (Ed.), Characterization of High-Temperature Vapors and Gases, NBS Spec. Publ. No. 561, Vol. 1, 1979, pp. 711—755.
5 A. G. Gershikov and V. P. Spiridonov, private communication.
6 D. White, P. N. Walsh and D. E. Mann, J. Chem. Phys., 28 (1958) 508.
7 D. White, D. E. Mann, P. N. Walsh and A. Sommer, J. Chem. Phys., 32 (1960) 481.
8 W. Weltner and J. R. W. Warn, J. Chem. Phys., 37 (1962) 292.
9 A. Sommer, D. White, M. J. Linevsky and D. E. Mann, J. Chem. Phys., 38 (1963) 87.
10 L. V. Serebrennikov and A. A. Mal'tsev, Vest. Mosk. Univ., Khim., 16 (1975) 250.
11 L. V. Serebrennikov, S. B. Osin, Yu. N. Sekachev and A. A. Mal'tsev, Materialy Vsesoyuznoj Konferentsii "KRS — 78", 2nd, Moscow, 1978, p. 243.
12 L. V. Serebrennikov, Yu. N. Sekachev and A. A. Mal'tsev, High Temperature Science, to be published (1981).
13 J. F. Chiang and D. R. Whitman, Theor. Chim. Acta, 17 (1970) 155.
14 M. A. Ali and A. Shaikh, J. Mol. Struct., 13 (1972) 179.