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**AB INITIO CALCULATIONS OF THE GROUND AND LOW-LYING
 EXCITED STATES OF BO₂**

P.-E. LOMP, V. SIMKIN, N. STEPANOV. BO₂ MOLEKULI MITTEEMPIIRILISED PÕHIOLEKU
 JA ERGASTATUD OLEKUTE ARVUTUSED

П.-Э. ЛОМП, В. СИМКИН, Н. СТЕПАНОВ. НЕЭМПИРИЧЕСКИЕ РАСЧЕТЫ ОСНОВНОГО И
 НИЗКОЛЕЖАЩИХ ВОЗБУЖДЕННЫХ СОСТОЯНИЙ МОЛЕКУЛЫ ВО₂

(Presented by M. Veiderma)

Many theoretical and experimental studies of the energy levels of linear or near-linear triatomic molecules in open-shell electronic states have been reported in recent years. BO₂, similarly to isoelectronic CO₂⁺, has been the subject of several investigations.

Detailed study of the BO₂ absorption spectrum was carried out by Johns [1]. According to his results, BO₂ is linear in the ground X²Π_g and two lowest excited states, A²Π_u and B²Σ_u⁺. The laser-excited fluorescence spectrum investigations [2, 3] confirmed the previous results. But some papers [4-6] predict BO₂ to be bent.

Only few *ab initio* calculations of the electronic states of BO₂ [7-9] have been reported. In [7, 8] only the ground X²Π_g state was considered. In [9] the C²Σ_g⁺ state was predicted, and the perturbational CI technique gave excellent agreement with experimental data. No previous theoretical or experimental studies of the quartet states of BO₂ have been published. In our communication we present the calculation results, obtained for some fragments of potential surfaces of doublet and quartet states for linear (D_{∞h}) or bent (C_{2v}) molecule.

Potential energy was calculated by the standard LCAO-MO-SCF method using the SPUSH [10] system of programs. The basis sets for B and O atoms consisted of the standard STO-3G sets (basis I) with exponents from [11] or of the standard Huzinaga basis set 9s5p with Dunning's 4s2p contraction (basis II) [12].

The leading configurations for ²A₁, ²A₂, ²B₁, ²B₂, ⁴A₁, ⁴A₂, ⁴B₁ and ⁴B₂ states were chosen from the proper CI solution. For doublet states, CI calculations were carried out with MO's obtained for the ⁴A₁ state of BO₂⁻ and the ²B₂ state of BO₂ in a frame of the restricted SCF procedure. For quartet states, MO's were taken from SCF calculations on ⁴A₂ and ⁴B₂ ones. The leading configurations were, in all the cases, the fundamental ones of the paper [9], similar to those of CO₂⁺ [13].

The SCF calculations were carried out in C_{2v} and D_{∞h} symmetries. The internuclear distance R_{B-O} varied between 2.20 and 2.80 a. u., and bond angle between 180 and 100°. For all doublet states as well as for the ⁴A₁ and ⁴A₂ states, the total energy minimum corresponds to linear geometry. The ⁴B₁ and ⁴B₂ states are bent.

Differences in the total energy values, calculated at different symmetry restrictions, C_s, C_{2v}, D_{∞h}, originate from the different schemes of

Hartree—Fock calculations, used for these symmetries and from the symmetry-breaking effects. They are a subject of the next publication.

Equilibrium parameters have been calculated by quadratic approximation of fragments of potential surfaces. The results of geometry optimization, appropriate total energies, excitation and dissociation energies are listed in Table 1.

Table 1

Equilibrium parameters of BO_2

	State			
	$X^2\Pi_g$	$A^2\Pi_u$	$B^2\Sigma_u^+$	$C^2\Sigma_g^+$
$R_{\text{B-O}}$, Å				
SCF basis I	1.342	1.396	—	—
basis II	1.258	1.302	1.289	1.268
CI [°]	—	—	—	1.246
Experimental [1]	1.265	1.302	1.273	—
Total energy (a. u.)				
SCF basis I	-171.996	-171.824	—	—
basis II	-174.360	-174.246	-174.229	-174.193
CI [°]	-174.597*	-174.498**	-174.486*	-174.457
T_0 , eV				
SCF basis II		3.115	3.554	4.546
CI [°]		2.446	2.998	3.785
Experimental [1]		2.329	3.039	—
D_e , eV				
SCF basis II	2.085	1.158	0.719	—

* Calculated at $R_{\text{B-O}}=1.265$ Å.

** Calculated at $R_{\text{B-O}}=1.302$ Å.

The equilibrium distances $R_{\text{B-O}}$, calculated in basis I, are slightly longer than the experimental ones, but the agreement of basis II and experimental results is excellent.

The fundamental frequencies ν_1 and ν_2 were calculated by solving the ordinary vibration problem in a harmonic approximation; their values are listed in Table 2.

Table 2

Vibration frequencies of BO_2 , cm^{-1}

State	Vibration	SCF basis		Experimental value [1]
		I	II	
$X^2\Pi_g$	ν_1	1079	1099	1070
	ν_2	464	—	464
$A^2\Pi_u$	ν_1	1123	982	994
	ν_2	541	—	502
$B^2\Sigma_u^+$	ν_1	—	906	—
$C^2\Sigma_g^+$	ν_1	—	1149	—

Conclusions. SCF calculations confirm the BO_2 molecule to be linear in the ground $X^2\Pi_g$ and low-lying excited states $A^2\Pi_u$, $B^2\Sigma_u^+$ and $C^2\Sigma_g^+$.

REFERENCES

1. *Johns, J. W. C.* Absorption spectrum of BO_2 . — *Can. J. Phys.*, 1961, **39**, N 12, 1738—1768.
2. *Russell, D. K., Kroll, M., Dows, D. A., Beaudet, R. A.* Excited fluorescence spectra of BO_2 . — *Chem. Phys. Lett.*, 1973, **20**, N 1, 153—155.
3. *Russell, D. K., Kroll, M., Beaudet, R. A.* Analysis of the laser-excited fluorescence spectra of BO_2 . — *J. Chem. Phys.*, 1977, **66**, N 5, 1999—2008.
4. *Серебрянников Л. В.* ИК-спектр поглощения молекулы BO_2 , синтезированной в матрице из аргона. — *Вестн. Моск. ун-та. Химия*, 1975, **16**, № 4, 363.
5. *Коряжкин В. А., Саламова А. А.* Частота ν_3 в основном электронном состоянии молекулы BO_2 . — *Вестн. Моск. ун-та. Химия*, 1975, **16**, № 4, 487—489.
6. *Коряжкин В. А., Матвеев В. К.* Изотопные сдвиги в электронном спектре молекулы BO_2 и колебательные постоянные основного состояния. — *Вестн. Моск. ун-та. Химия*, 1976, **17**, № 4, 490—491.
7. *Jug, K., Nanda, D. N.* SINDO 1. III. Application to ground states of molecules containing fluorine, boron, beryllium and lithium atoms. — *Theor. Chim. Acta (Berlin)*, 1980, **57**, N 2, 131—144.
8. *Зайцевская Р. В.* Неэмпирические расчеты молекул BH_2 , BO_2 и B_2O . Дипломная работа. Хим. фак. Моск. ун-та. М., 1980, 49.
9. *Saraswathy, V., Diamond, J. J., Segal, G. A.* Theoretical calculation of the lowest electronic excited states of BO_2 . — *J. Phys. Chem.*, 1983, **87**, N 5, 718—719.
10. *Путьшев В. И., Симкин В. Я., Сафонов А. А., Хрустов В. Ф., Дементьев А. И., Степанов Н. Ф.* Комплекс программ для неэмпирических расчетов молекул. — *Вестн. Моск. ун-та. Химия*, 1983, **24**, № 1, 38—39.
11. *Clementi, E., Roetti, E.* Roothaan—Hartree—Fock atomic wave functions. Basis functions and their coefficients for ground and certain excited states of neutral and ionized atoms. — *Atom. Data and Nucl. Data Tables*, 1974, **14**, N 3, 177—478.
12. *Dunning, T. H.* Gaussian basis functions for use in molecular calculations. I. Contraction of $(9s5p)$ atomic basis sets for the first row atoms. — *J. Chem. Phys.*, 1970, **53**, N 7, 2823—2833.
13. *Praet, M. Th., Lorquet, J. C., Raseev, G.* Unimolecular reaction paths of electronically excited species. IV. The $C^2\Sigma_g^+$ state of CO_2^+ . — *J. Chem. Phys.*, 1982, **77**, N 9, 4611—4618.

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