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THE ANTISYMMETRIC STRETCHING FREQUENCY OF BO_2

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 НОГО КОЛЕБАНИЯ МОЛЕКУЛЫ BO_2

(Presented by M. Veiderma)

Boron dioxide (BO_2) has been a subject of several experimental investigations; only a few theoretical ones have been carried out [1-3]. In [2] the $C^2\Sigma_g^+$ state was calculated, the results of perturbational CI technique showing good agreement with experimental data. In [3] the results of *ab initio* SCF and CI calculations on doublet and quartet states of BO_2 have been represented, which confirm the linearity of the molecule in the ground $X^2\Sigma_g^+$ and low-lying excited states $A^2\Pi_u$, $B^2\Sigma_u^+$ and $C^2\Sigma_g^+$. The ν_1 and ν_2 fundamentals were also calculated.

Here we present the results obtained for the ν_3 fundamental frequency.

Because of selection rules, direct determination of the value of anti-symmetric stretching frequency ν_3 is quite complicated. J. W. C. Johns [4] found the value $\frac{1}{2}(2\nu_3) = 1322 \text{ cm}^{-1}$, L. V. Serebrennikov, V. A. Koryazhkin et al. [5-7] obtained the ν_3 band in the region 1840—2080 cm^{-1} , and with the help of tunable infrared diode laser spectroscopy K. Kawaguchi et al. [8] found $\nu_3 = 1278 \text{ cm}^{-1}$. As compared with analogous systems the ν_3 value in the 1300 cm^{-1} region should be considered as anomalously low, and in [8] this was assigned to a vibronic interaction between $X^2\Pi_g$ and $A^2\Pi_u$ states.

To obtain the ν_3 value, *ab initio* restricted SCF, CASSCF and CI calculations were carried out in C_s and $C_{\infty v}$ symmetries using the SPUSH program system [9]. The basis sets were the standard STO-3G set (basis I) [10] and (9s5p/4s2p) (basis II) [11]. From the reference set 200 singly and doubly excited configurations were selected [12], and the CI problem was solved with MOs from BO_2 molecule and BO_2^- and

Total energies and antisymmetric

$\Delta=R_1-R_2$ (R_1, R_2) a. u.	1	2	3	4	5
					Basis I
0.00 (2.47, 2.47)	-171.9991	-172.0564	-172.1645	-171.9561	-172.1076
0.04 (2.45, 2.49)	-172.0033	-172.0585	-172.1638	-171.9559	-172.1068
0.12 (2.41, 2.53)	-172.0103	-172.0615	-172.1638	-171.9543	-172.1016
0.20 (2.37, 2.57)	-172.0155	-172.0633	-172.1641	-171.9511	-172.0934
0.28 (2.33, 2.61)	-172.0187	-172.0636	-172.1608	-171.9462	
ν_3, cm^{-1}					
					Basis II
0.00 (2.38, 2.38)	-174.3817	-174.4196	-174.4676	-174.5137	-174.3870
0.04 (2.36, 2.40)	-174.3854	-174.4206	-174.4686	-174.5134	-174.3866
0.12 (2.32, 2.44)	-174.3911	-174.4218	-174.4691	-174.5113	-174.3838
0.20 (2.28, 2.48)	-174.3943			-174.5068	
0.28 (2.24, 2.52)	-174.3951	-174.4198	-174.4657	-174.5001	-174.3708
ν_3, cm^{-1}					
	BO ₂ , SCF C _{∞v}	BO ₂ , R.S.*	BO ₂ , CI	BO ₂ ⁻ , SCF C _{∞v}	BO ₂ , R.S.
	MO I	with MO I	with MO I	MO II	with MO II

R. S. — reference set.

BO₂⁺ ions. The ν_3 frequency was obtained by solving an ordinary vibration problem in a harmonic approximation.

As a starting point the symmetric linear configurations O—B—O at equilibrium geometries for the basis I ($R_{\text{B-O}}=2.47$ a. u.) and the basis II ($R_{\text{B-O}}=2.38$ a. u.) [3] were chosen. From these points the antisymmetric shifts of O atoms were made while $\sum R_{\text{B-O}}$ was kept constant. The results are listed in the Table.

For asymmetric configurations the SCF solutions become unstable in a case of the X²Π state of BO₂ as well as the ¹Δ state of BO₂⁺, and the total energy becomes lower than in appropriate symmetric points. Because of the multiconfigurational nature of this effect, the CI and CASSCF treatments will be considered.

When the basis I was used, SCF calculations of BO₂ in C_{∞v} symmetry and without symmetry restrictions yielded the same values of total energies but different MOs. These solutions, as mentioned above, are unstable. The CI solution with excitations on π-orbitals only in the basis I yielded also an unstable one. Only including into the reference set excitations on δ-orbitals enables to achieve stability. The CASSCF solution appears to be stable in the basis I, and yields a low

stretching frequency of BO₂

6	7	8	9	10	11
-172.1562	-171.5408	-172.0570	-172.1645	-172.1214	-172.1214
-172.1567	-171.5443	-172.0288	-172.1624	-172.1213	-172.1213
-172.1558	-171.5508	-172.0189	-172.1645	-172.1205	-172.1205
-172.1545				-172.1188	-172.1188
				-172.1159	-172.1159
				1281.4	1281.4
-174.4408	-173.8254	-174.4212	-174.4529	-174.4726	-174.4726
-174.4406	-173.8270	-174.4120	-174.4525	-174.4728	-174.4728
-174.4392	-173.8318	-174.3932	-174.4484		
	-173.8360				
-174.4333	-173.8388				
1567.1					
BO ₂ , CI	BO ₂ ⁺ , SCF	BO ₂ , R.S.	BO ₂ , CI	BO ₂ , CASSCF	BO ₂ , CASSCF
with MO II	C _{∞v} MO III	with MO III	with MO III	with MO I	with MO II

value of $\nu_3 = 1281 \text{ cm}^{-1}$ but it becomes unstable in the basis II. The CI solution with MOs from BO₂ in the basis II yields also an unstable solution.

The SCF and CI treatments with MOs from $X^1 \Sigma^-$ state of BO₂ yield stable solutions in the basis I as well as in the basis II which confirm the low ν_3 value. The CASSCF treatment with these MOs in the basis I and II yields the same total energy values as with MOs from BO₂, i. e. in the basis I it yields the stable solution, in the basis II — the unstable one. MOs from BO₂⁺ yield too large a ν_3 value.

REFERENCES

1. 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.
2. Saraswathy, V., Diamond, J. J., Segal, G. A. Theoretical calculation of the lowest electronic excited states of BO₂. — J. Phys. Chem., 1983, 87, N 5, 718—719.
3. Lomp, P.-E., Simkin, V., Stepanov, N. *Ab initio* calculations of the ground and low-lying excited states of BO₂. — ENSV TA Toim. Keemia, 1983, 32, N 4, 286—288.

4. *Johns, J. W. C.* Absorption spectrum of VO_2 . — *Can. J. Phys.*, 1961, **39**, N 12, 1738—1768.
5. *Серебрянников Л. В.* ИК-спектр поглощения молекулы VO_2 , синтезированной в матрице из аргона. — *Вестн. Моск. ун-та. Химия*, 1975, **16**, № 3, 363.
6. *Коряжкин В. А., Саламова А. А.* Частота ν_3 в основном электронном состоянии молекулы VO_2 . — *Вестн. Моск. ун-та. Химия*, 1975, **16**, № 4, 487—489.
7. *Коряжкин В. А., Матвеев В. К.* Изотопные сдвиги в электронном спектре молекулы VO_2 и колебательные постоянные основного состояния. — *Вестн. Моск. ун-та. Химия*, 1976, **17**, № 4, 490—491.
8. *Kawaguchi, K., Hirota, E., Yamada, C.* Diode laser spectroscopy of the VO_2 radical. Vibronic interaction between the $A^2\Pi_u$ and $X^2\Pi_g$ states. — *Mol. Phys.*, 1981, **44**, N 2, 509—528.
9. *Пупышев 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.
10. *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.
11. *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.
12. *Пупышев В. И., Симкин В. Я., Сафонов А. А., Дементьев А. И.* Отбор конфигураций в методе конфигурационного взаимодействия. — *Вестн. Моск. ун-та. Химия*, 1984, **25**, № 2, 161—164.

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