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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 antisymmetric 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

$\Delta=R_1-R_2$ (R_1, R_2) a. u.	1	2	3	4	5
Basis I					
0.00	-171.9991	-172.0564	-172.1645	-171.9561	-172.1076
(2.47, 2.47)					
0.04	-172.0033	-172.0585	-172.1638	-171.9559	-172.1068
(2.45, 2.49)					
0.12	-172.0103	-172.0615	-172.1638	-171.9543	-172.1016
(2.41, 2.53)					
0.20	-172.0155	-172.0633	-172.1641	-171.9511	-172.0934
(2.37, 2.57)					
0.28	-172.0187	-172.0636	-172.1608	-171.9462	
(2.33, 2.61)					
ν_3, cm^{-1}					
Basis II					
0.00	-174.3817	-174.4196	-174.4676	-174.5137	-174.3870
(2.38, 2.38)					
0.04	-174.3854	-174.4206	-174.4686	-174.5134	-174.3866
(2.36, 2.40)					
0.12	-174.3911	-174.4218	-174.4691	-174.5113	-174.3838
(2.32, 2.44)					
0.20	-174.3943			-174.5068	
(2.28, 2.48)					
0.28	-174.3951	-174.4198	-174.4657	-174.5001	-174.3708
(2.24, 2.52)					
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 BO_2

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	$\text{C}_{\infty v}$ 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 BO_2 in the basis II yields also an unstable solution.

The SCF and CI treatments with MOs from $X^1\Sigma$ state of BO_2^- 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 BO_2 , i. e. in the basis I it yields the stable solution, in the basis II — the unstable one. MOs from BO_2^+ yield too large a ν_3 value.

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