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GEOMETRY AND B(1S) CORE EXCITONS OF ORTHO-CARBORANE

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ABSTRACT

The optimized C_{2v} geometry of ortho-carborane, 1,2-$C_2B_{10}H_{12}$, is determined from Hartree-Fock calculations. For this geometry, a carbon atom is substituted for a boron atom at one of the 4 inequivalent boron sites and the ground-state unrestricted Hartree-Fock eigenvalues and molecular orbitals are found. One thus obtains the valence structure of the B(1s) core-excited molecule according to the Z+1 approximation. The eigenvalue of the highest occupied molecular orbital is then subtracted from the experimental B(1s) ionization energy of the same site in ortho-carborane. This determines the excitation energy of the most tightly bound exciton for that site. Three of the sites yield nearly identical excitation energies of 191.9 eV; the fourth site yields an excitation energy of 190.9 eV.

INTRODUCTION

Recent synchrotron experiments on ortho-carborane have provided evidence for the existence of two B(1s) core excitons; that is, discrete core to valence transitions.[1] There are four inequivalent boron sites on this molecule and their B(1s) core ionization energies are resolved experimentally.[2] Thus it is of interest to attempt to understand why just two exciton peaks are observed. This can be done in the equivalent cores (or Z+1) approximation, in which the influence of the B(1s) core-excited atom on the valence electrons is approximated by that of the normal carbon atom.[3] A Z+1 Hartree-Fock calculation for a given boron site yields the energy eigenvalue of the highest occupied molecular orbital (HOMO). By Koopman's theorem[4] this is approximately equal to the energy required to remove this electron from the molecule. Thus, the difference between the experimental ionization energy for the B(1s) electron at a site and the HOMO eigenvalue from the Z+1 calculation for that site yields the core exciton excitation energy. By studying all four inequivalent sites for ortho-carborane one can predict the B(1s) exciton spectrum.

METHOD AND OPTIMIZED ORTHO-CARBORANE GEOMETRY

The Hartree-Fock calculations were carried out using the same technique and basis set applied previously to para-carborane.[5] Reference 5 contains a discussion of the methods and basis set used, and provides a comparison of the electronic valence spectrum and Raman spectrum of para-carborane with experiment. Table I summarizes the ortho- and para-carborane results. The numbering of the atoms is

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TABLE I.
Results of Restricted Hartree-Fock Calculations for ortho-carborane (C_{2v})[a] and para-carborane (D_{5d})[b]

Distances(N)				Orbital Eigenvalues (Hartree)			
$C_2B_{10}H_{12}$ (D_{5d})		$C_2B_{10}H_{12}$ (C_{2v})		$C_2B_{10}H_{12}$ (D_{5d})		$C_2B_{10}H_{12}$ (C_{2v})	
C_1-B_2	1.7297	C_1-C_2	1.6390	$3e_{1g}$	0.12206	a_2	0.11574
B_2-B_3	1.8145	C_2-B_3	1.7517	$2e_{2u}$	-0.40375	b_2	-0.41273
B_3-B_8	1.7805		1.7785	$2e_{2g}$	-0.46036	b_1	-0.42223
B_{10}-B_{11}			1.8000	$3e_{1u}$	-0.48119	a_1	-0.43093
B_{11}-B_{12}			1.7963	$2e_{1g}$	-0.48324	a_2	-0.43247
		C_2-B_7	1.7188	$4a_{1g}$	-0.49061	a_1	-0.46016
		B_3-B_7	1.8068			b_2	-0.46513
		B_7-B_{11}	1.8102			a_2	-0.47752
		B_9-B_{12}	1.8033			b_1	-0.48099
		B_8-B_{12}	1.8167			a_1	-0.50736
				$1e_{2u}$	-0.55355	b_1	-0.55525
C_1-H_1	1.0685		1.067	$2e_{1u}$	-0.55984	a_1	-0.56368
B_2-H_2	1.1744					b_1	-0.56777
B_{11}-H_{11}			1.1756			b_2	-0.56913
B_{12}-H_{12}			1.1787	$3a_{2u}$	-0.58228	a_1	-0.58634
B_3-H_3			1.1726	$2a_{2u}$	-0.66358	b_2	-0.61113
B_{10}-H_{10}			1.1782	$3a_{1g}$	-0.67680	a_1	-0.68775
				$1e_{2g}$	-0.67782	a_2	-0.69678
				$1e_{1g}$	-0.72339	b_1	-0.71032
						a_1	-0.71850
						a_1	-0.75926
				$2a_{1g}$	-0.83295	b_2	-0.78180
				$1e_{1u}$	-0.91485	b_1	-0.92266
						a_1	-0.97655
				$1a_{2u}$	-1.06089	b_2	-0.99760
				$1a_{1g}$	-1.17718	a_1	-1.22559

[a] Present work.
[b] From Reference 5.

defined in Fig. 1. In ortho-carborane atoms 1 and 2 are carbon atoms; in para-carborane atoms 1 and 12 are carbon atoms. In ortho-carborane the five sets of equivalent C_{2v} sites are (1,2), (3,6), (4,5,7,11), (8,10) and (9,12). The bond lengths in ortho-carborane were found to be from 0.01 to 0.03 N longer than those found by Ott and Gimarc[6]. The angle H_9-B_9-B_{12} is 122.7 deg, compared to 121.7 deg for the perfect icosahedron. The angle H_8-B_8-B_3 is 119.7 deg and the angle H_5-B_5-B_4 is also 119.7 deg. The angle H_1-C_1-C_2 is 116.3 deg and the angle H_3-B_3-B_8 is 132.3 deg. If X designates the center of the (4,5,7,11) plane, the angle X-B_4-H_4 is 172.0 deg, compared to 180.0 deg for the perfect icosahedron. Thus the hydrogen atoms tilt toward the carbon end of ortho-carborane. The total energy and binding energy of ortho-carborane were found to be -327.74461 and 3.1099 Hartree, compared to -327.77819 and 3.1434 Hartree for para-carborane.[5]

ORTHO-CARBORANE B(1S) CORE EXCITON SPECTRUM

Figure 1 and the preceeding discussion show that there are four inequivalent boron sites at which to make a B(1s) core hole and excite or ionize the involved electron. Since ortho-carborane is a 74 electron system, it is a good idea to use as much experimental data as possible. Fortunately the B(1s) core ionization energies have been measured.[2] This makes it possible to use the Z+1 approximation described in the introduction. With a core hole or carbon atom on sites 6,8 or 9, the system possesses a plane of symmetry. The first four calculations in Table II were carried out by first finding the molecular orbitals of the closed-shell positive ion. These were then used for the initial guess in the unrestricted Z+1 Hartree-Fock calculation for the neutral exciton state to get the ionization energy of the least-bound valence electron. The last calculation was done directly for the neutral system. The difference between the core and valence ionization energies gives the exciton excitation energy displayed in Table II.

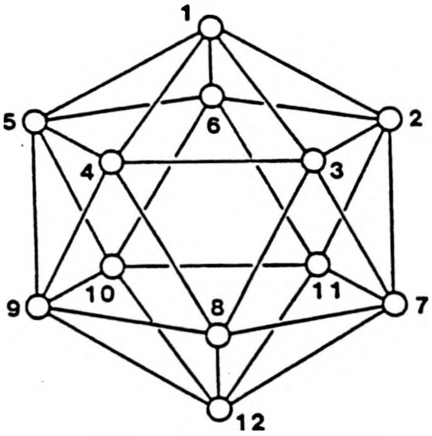

FIG. 1. Numbering of atomic positions on an icosahedron.

TABLE II.
B(1s) core exciton excitation energies for the four inequivalent sites 6, 7, 8, and 9 in ortho-carborane, 1,2-$C_2B_{10}H_{12}$.

Site[a]	B(1s) ionization energy[b] (eV)	Orbital energy of HOMO (eV)	Exciton excitation energy (eV)	Approximate relative oscillator strength[c]
6	196.3	4.3	192.0	0.36
7	195.6	3.7	191.9	0.26
8	195.0	3.1	191.9	0.29
9	194.5	3.6	190.9	0.23
9	194.5	1.2	193.3	0.03

[a] See Fig. 1 for location of numbered sites.

[b] Experiment for 1,2-$C_2B_{10}H_{12}$ from Ref. 2.

[c] Sum of squares of outer LCAO-MO p-orbital coefficients on site.

It is seen that from the four inequivalent sites just two distinct strongly allowed excitons emerge at 190.9 and 191.9 eV.

DISCUSSION

The total electron yield peaks for ortho-carborane from Ref. 1 occur at photon energies of 192.7 and 194.0 eV, about 2.0 eV higher than the values given in Table II. This result is consistent with the fact that the molecular orbital eigenvalue tends to overestimate the ionization energy. For example, a shift in this direction of about 1.4 eV was found in Ref. 5 in comparing the valence eigenvalues of para-carborane with valence photoelectron emission experiments. The experimental relative peak heights[1] are in qualitative agreement with the rough indication of the relative optical oscillator strengths given in the last column of Table II.[7] Thus the experiments of Refs. 1 and 2 appear to be rather well reconciled by the approximate theory presented here. An optically allowed B(1s) core exciton at 192.0 eV has been observed in the hexagonal BN crystal.[8] The exciton found for site 9 at 193.3 eV has a large 2s atomic population and very little p population. Comparable s-type excitons were not sought for the other sites. It would be interesting to see if these less tightly bound excitons actually exist by looking for them in electron energy loss measurements. The screening of the core hole amounts to about 0.9 electron for the allowed excitons; it is only about 0.6 electron for the s-exciton.

In application to the borane^{-2} ion in Ref. 5, the rather limited Gaussian basis set used here (3-21G in standard notation[5]) was shown to produce orbital eigenvalue shifts of about 0.12 eV compared to the better 4-31G* basis. Thus the 1 eV splitting found for the optically allowed excitons should not be reduced to zero by the use of a better basis set. The author does not know what bounds to place on the errors inherent in the Z+1 approximation.

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