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Theoretical study on low-lying excited states of B_3 molecule

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The electronic states of the smallest boron cluster B_3 with excitation energies up to 5 eV are systematically investigated. Geometries and spectroscopic constants for the low-lying electronic states were calculated using the multireference configuration interaction method with Davidson correction (MRCI+Q). The nondegenerate $1\,^2B_2$ and $2\,^2A_1$ states are arising from the degenerate $^2E'$ state in D_{3h} symmetry, this is also the case for $2\,^2B_2$ and $3\,^2A_1$. Furthermore, vertical excitation energies, oscillator strengths, main configurations, and transitions of the excited state of B_3 were determined. Notably, the theoretically predicted wavelengths for the $X\,^2A_1 \rightarrow 2\,^2A_1$ and $X\,^2A_1 \rightarrow 2\,^2B_2$ electronic transitions (728 nm and 457 nm, respectively) exhibit excellent agreements with experimental absorption bands observed at 736 nm and 458 nm. These theoretical findings provide critical insights into the electronic structure and geometric configuration of the B_3 cluster.

Keywords: boron trimer, MRCI+Q method, geometric structure, spectrum

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1. Introduction

As a transitional state bridging microscopic atoms/molecules and macroscopic materials, clusters composed of identical atoms have garnered significant attention for their critical roles in advancing research on semiconductors, insulators, explosives, and high-energy density materials.[1–6] Group IIIA elements are characterized by their strong binding energies, enabling them to readily form clusters with diverse structural configurations. Among these, the B_3 molecule (boron trimer) stands out in cluster chemistry due to its unconventional bonding characteristics. Boron clusters, including B_3, frequently exhibit non-classical bonding patterns, such as hybridizations of 2-center–2-electron (2c–2e) bonds and multi-center bonds (e.g., 3-center–2-electron, 3c–2e bonds), resulting in electronic structures and stabilities that markedly differ from those of conventional molecules. Investigations into B_3 and related boron clusters hold profound implications for elucidating chemical bonding principles, molecular stability mechanisms, and the design of advanced functional materials. The triangular B_3 unit is the fundamental building block in all boron-based compounds and nanostructures. The nature of chemical bonding between B_3 clusters and various atomic/molecular species has been systematically investigated through combined high-resolution photoelectron imaging spectroscopy and first-principles computational chemistry.[7–13] Furthermore, the B_3 molecule has attracted practical interest owing to its advantageous properties: low molecular mass, high enthalpy of formation, minimal toxicity, and abundant natural availability.[14,15] To fully exploit these attributes, obtaining detailed molecular parameters, such as ground-state geometries and spectroscopic constants of the low-lying electronic states, is imperative. Such data will refine our understanding of their properties, ultimately guiding the engineering of novel cluster architectures and bonding frameworks.

The previous experimental investigations on the electronic structure, optical, and magnetic properties of B_3 have advanced rapidly. Hamrick *et al.*[16,17] identified that the ground state $X\,^2A_1'$ of B_3 (corresponding to the $X\,^2A_1$ irreducible representation in the C_{2v} point group) possesses an unpaired electron and three equivalent nuclei. However, rotational level transitions were not experimentally resolved due to limitations in spectral line intensity measurements under low-temperature conditions. In 2003,[15] Wyss *et al.* measured the absorption spectra of B_3 and assigned two electronic transitions: $X\,^2A_1' \rightarrow 1\,^2E'$ at 736 nm and $X\,^2A_1' \rightarrow 2\,^2E'$ at 458 nm. Subsequent work by Cias *et al.*[18] in gas phase detected the $X\,^2A_1' \rightarrow 2\,^2E'$ transition band using pulsed cavity ring down spectroscopy, though the spectrum exhibited severe line overlap caused by interfering factors including C_2 Swan bands, neon atomic absorption lines, and isotopologue mixtures.

The extensive experimental characterization of B_3 has significantly advanced theoretical investigations.[15,19–24] Several quantum chemical approaches including unrestricted Hartree–Fock (UHF), Hartree–Fock self-consistent field (HF–

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SCF), complete active space self-consistent field (CASSCF) configuration interaction (CI), MRCI, coupled cluster singles and doubles with perturbative triples (CCSD(T)), and density functional theory (DFT) have been employed to study the electronic states of B_3. These studies have yielded critical insights into its geometries, spectroscopic constants, and potential energy surfaces. Nevertheless, the existing research predominantly focuses on the ground state and a limited number of low-lying excited states, with persistent ambiguities in spectral assignments remaining unresolved.

This work is motivated by the less extensive electronic structure information of the excited states and spectroscopy assignment of B_3. In this work, we systematically investigate the electronic structure and transition properties of B_3 using the MRCI+Q method. Geometries, spectroscopic and transition properties of low-lying states for B_3 are computed, comparisons and assignments of previous experimental spectra are presented.

2. Method

The computations are performed with the MRCI method with aid of Molpro2012.[25] Firstly, the single configuration wave function of the ground state is obtained by the Hartree–Fock self-consistent field method as the initial wave function. Then, the CASSCF method is selected to optimize the ground-state wave function in order to describe the electronstatic (near-degenerate correlation) effects fully. Finally, the MRCI+Q method is used to expand the wave function to improve the accuracy of the calculation results.

In this work, the irreducible representation of C_{2v} point group is selected. The s orbitals of three B atoms with $n = 1$ serve as the closed shell. The 9 active electrons correspond to the $2s^2 2p^1$ shells of three B atoms, the 12 active orbitals include $5a_1$, $2b_1$, $4b_2$, and $1a_2$ orbitals, corresponding to the s orbitals and p orbitals of three B atoms with $n = 2$. In order to take into account the influence of scalar relativistic effect (SR), the correlation consistent basis set with a diffusion function aug-cc-pVXZ-DK (X = T, Q, 5) is used for each B atom. Based on the MRCI method including of single electron excitation and double electron excitation, the correlation energy caused by quadruple excitation is considered via Davidson correction.[26]

The correlation consistent basis sets aug-cc-pVXZ-DK (X = T, Q, 5), which could fully consider the correlation effects between electrons and describe the radial wave function and angular wave function in detail, were used in this work.[27] Since the basis set is truncated to a certain angular momentum in the calculations of geometries and adiabatic energy, it is necessary to extrapolate the basis set to correct the error caused by neglecting the orbital basis function of higher angular momentum, as expressed below and the extrapolation successfully predicted energies or geometries of small molecules[20,27–29]

$$E_n = E_{\mathrm{CBS}} + B\,\mathrm{e}^{-(n-1)} + C\,\mathrm{e}^{-(n-1)^2}, \quad (n = 3,4,5), \qquad (1)$$

where B and C are parameters, E_3, E_4, and E_5 represent the results obtained with the aug-cc-pVTZ-DK, aug-cc-pVQZ-DK, and aug-cc-pV5Z-DK basis sets, respectively; E_{CBS} is the extrapolated result.

3. Results and discussion

In this work, firstly, the influence of different basis sets (aug-cc-pVXZ-DK (X = T, Q, 5)) on the equilibrium geometries and corresponding transition energies of the $X\,^2A_1$, $1\,^2B_1$, $1\,^4A_2$, $1\,^2B_2$, $2\,^2A_1$, $3\,^2A_1$, $2\,^2B_2$ states (in C_{2v}) of B_3 are studied within the framework of MRCI+Q theory. The results are shown in Table 1 together with available experimental and theoretical values for comparisons. As listed in Table 1, the geometrical parameters and transition energies of all the computed electronic states show convergence trends with the increasing size of basis sets. And Table 1 presents the symmetry from the D_{3h} to the C_{2v}, for example, the symmetry breaking of the $1 \sim 2^2E'$ state is driven by the Jahn–Teller effect, which is arising from the asymmetric electrons occupation in the degenerate molecular orbitals ($6a_1$ and $3b_2$ in C_{2v} point group). This symmetry-breaking phenomenon is found in two groups of electronic states, the splitting is 0.018 eV and 0.008 eV, respectively. The near-degenerate states are energetically near with 0.018 eV and 0.008 eV, the vibronic coupling effects could affect the dynamics of excited state of B_3.

Our computed bond length (R_e) of ground state $X\,^2A_1$ is 1.5626 Å at the CBS limit, which agrees well with the previous computations.[15,19,21–23,30] The latest experimentally determined bond length R_0 is 1.6038 Å,[18] this difference is due to the assumption of a negligible inertial defect in the experimental analysis, so there is a zero-point vibration in the ground state.[18] For the $1\,^2B_1$ ($^2A_2''$ in D_{3h} symmetry) state, the basis set effect for the bond lengths and the transition energy is about 0.01 Å and 0.022 eV, respectively. Our CBS estimated bond length of $1\,^2B_1$ state is ~ 0.1 Å shorter than the previous computed value at the CASSCF/cc-pVDZ level of theory, the difference is due to the dynamical correlations and basis set effect considered in this work.

For the first quartet state $1\,^4A_2$, it can be seen from Table 1 that both the bond length R_e and bond angle $\angle B-B-B$ show a slow decreasing tendency as the size of basis set increasing from aug-cc-pVTZ-DK to aug-cc-pV5Z-DK. The computed values of transition energy for the lowest quartet state $1\,^4A_2$ also converge within 0.001 eV at CBS. Our computed geometry values ($R_e = 1.5913$ Å, $\angle B-B-B = 72.58°$)

with MRCI+Q method gives smaller bond length and larger bond angle but agree reasonably with the previous theoretical values.[19,30] The symmetry of the first quartet state is distorted from D_{3h} to C_{2v} with the bond angle increasing by 12.6° compared to the ground state, reflecting the redistribution of outer shell electrons. The nondegenerate 1^2B_2 and 2^2A_1 states are arising from the degenerate $1^2E'$ state in D_{3h} symmetry, our test calculations verified it that the bond length differs little for the two states in the geometry strain of D_{3h}. While in the C_{2v} symmetry, the bond lengths of the two states 0.05 Å differ from each other at the CBS level. For the bond angles, one (1^2B_2) is larger than 60° and the other (2^2A_1) is smaller than 60°, the difference is about 8°. The next two higher states are corresponding to the previously observed state.[18] The state is denoted as the degenerate $^2E'$ state, and the molecular parameters are fitted with a fixed bond angle as 60°, our computations found that the state is split into 3^2A_1 and 2^2B_2 states. The differences of the optimized bond length and transition energy for the two states are small as ~ 0.001 Å and < 0.01 eV, respectively; while the bond angles deviate from 60° with +1.3° and −1.7° for the 3^2A_1 and 2^2B_2 states, respectively. The previous MRCI/aug-cc-pVTZ calculation on the 3^2A_1 state[15] also supports our present work as a result of good agreement for the geometry parameters.

The vertical transition energies (VTE), main configurations, and transition of 22 electronic states of B_3 at the MRCI+Q/aug–cc–pVTZ-DK level are listed in Table 2. And Table 3 lists the oscillator strengths (OS), VTEs, and transition wavelengths of low-lying 11 excited states with energy range of 0.7 eV–3.1 eV, which consists of 7 double states (1^2B_1, 2^2A_1, 1^2B_2, 1^2A_2, 2^2B_1, 3^2A_1, 2^2B_2) and 4 quadruple states (1^4A_2, 1^4B_1, 1^4A_1, 1^4B_2).

Table 1. Equilibrium geometries and transition energies of the low-lying electronic states with different basis sets.

State	Basis set	R_e (Å)	Bond angle (°)	T_0 (eV)
X^2A_1 (X^2A_1')	aug-cc-pVTZ-DK	1.5729	60.00	0
	aug-cc-pVQZ-DK	1.5652	60.00	0
	aug-cc-pV5Z-DK	1.5635	60.00	0
	CBS (TQ5)	1.5626	60.00	0
	CASSCF/cc-pVDZ[19]	1.5870	60.00	
	UHF/6-31G[30]	1.5742	60.00	
	RCCSD(T)/aug-cc-pVQZ[23]	1.5643	60.00	
	SCF/3-21G[21]	1.5530	60.00	
	B3LYP/6-311+G[22]	1.5480	60.00	
	MRCI/aug-cc-pVTZ[15]	1.5706	60.00	
	Experiment[18]	1.6038	60.00	
1^2B_1 ($^2A_2''$)	aug-cc-pVTZ-DK	1.6154	60.00	0.717
	aug-cc-pVQZ-DK	1.6074	60.00	0.735
	aug-cc-pV5Z-DK	1.6057	60.00	0.739
	CBS (TQ5)	1.6051	60.00	0.741
	CASSCF/cc-pVDZ[19]	1.6170	60.00	
1^4A_2 ($^4E''$)	aug-cc-pVTZ-DK	1.6008	72.74	1.515
	aug-cc-pVQZ-DK	1.5939	72.57	1.559
	aug-cc-pV5Z-DK	1.5923	72.56	1.569
	CBS (TQ5)	1.5913	72.58	1.574
	CASSCF/cc-pVDZ[19]	1.6070	70.40	
	UHF/6-31G[30]	1.5843	71.16	
	B3LYP/aug-cc-pVQZ[22]	1.5698	73.89	
1^2B_2 ($1^2E'$)	aug-cc-pVTZ-DK	1.5799	65.42	1.596
	aug-cc-pVQZ-DK	1.5729	65.35	1.618
	aug-cc-pV5Z-DK	1.5716	65.35	1.623
	CBS (TQ5)	1.5711	65.36	1.626
2^2A_1 ($1^2E'$)	aug-cc-pVTZ-DK	1.6397	57.11	1.615
	aug-cc-pVQZ-DK	1.6314	57.15	1.636
	aug-cc-pV5Z-DK	1.6296	57.16	1.641
	CBS (TQ5)	1.6287	57.17	1.644
3^2A_1 ($2^2E'$)	aug-cc-pVTZ-DK	1.5803	61.39	2.677
	aug-cc-pVQZ-DK	1.5738	61.31	2.679
	aug-cc-pV5Z-DK	1.5724	61.29	2.680
	CBS (TQ5)	1.5716	61.29	2.680
	MRCI/aug-cc-pVTZ[15]	1.5955	61.90	
	Experiment[18]	1.6191	60.00 (fixed)	
2^2B_2 ($2^2E'$)	aug-cc-pVTZ-DK	1.6073	58.23	2.681
	aug-cc-pVQZ-DK	1.5990	58.34	2.687
	aug-cc-pV5Z-DK	1.5973	58.36	2.688
	CBS (TQ5)	1.5965	58.37	2.688

It is found that the ground state X^2A_1 of B_3 is mainly characterized by $(1–4a_1)^2(5a_1)^1(1b_1)^2(1–2b_2)^2$ electronic configuration, and the unpaired electrons are in the sp hybrid orbital. As for the lowest quartet state 1^4A_2, the electronic configuration is $(1–4a_1)^2(5a_1)^1(1b_1)^1(1–2b_2)^2(3b_2)^1$, the unpaired electrons in the B_3 molecule undergo a transition to an out-of-plane orbital, corresponding to the $3b_2 \rightarrow 1b_1$ transition, with a dominant contribution of 87.2%. This transition results in changes of the electronic distribution, leading to an increase in the bond angle of the excited molecule. Such electronic rearrangements significantly impact the geometry and stability of the molecule, as the new orbital occupation alters the balance of forces between the boron atoms. Moreover, theoretical optical absorption transitions have been characterized in Table 3, which will contribute to the future assignment of B_3 spectra in experiments.

In the near-infrared region, the OS from ground state to the 1^2B_1 state is about 0.003, and the corresponding transition energy agree well with the previous reported by Batalov *et al.*[14] The next strong transition is the experimentally observed $X^2A_1'–^2E'$ (notation in D_{3h} symmetry), which split into two components $X^2A_1–2^2A_1$ and $X^2A_1–1^2B_2$ (notations in C_{2v} symmetry), while the OS of the $X^2A_1–2^2A_1$ is about one order of magnitude larger than that of $X^2A_1–1^2B_2$; the transition wavelength is underestimated by a few nm comparing to the experiment, and the $X^2A_1–1^2B_2$ transition may be not observed for the very small OS. The absorption of $X^2A_1–2^2B_1$ could be negligible.

The strongest band is from the $2^2B_2 \rightarrow X^2A_1$ transition with largest OS value, which is strong component of the degenerate $^2E'–X^2A_1'$ observed in the experiment,[15] and the transition wavelength is well reproduced; the weak component $3^2A_1 \rightarrow X^2A_1$ transition with small OS value could not be observed in the experiment.

Table 2. Vertical transition energies (VTE), main configurations, and main transitions of 22 electronic states of the B_3 molecule.

State	VTE (eV)	Main configuration	Main transition
X^2A_1	0	$(3a_1)^2(4a_1)^2(5a_1)^1(1b_1)^2(2b_2)^2$	
1^2B_1	0.781	$(3a_1)^2(4a_1)^2(5a_1)^2(1b_1)^1(2b_2)^2$	$1b_1 \rightarrow 5a_1$ (85.0%)
2^2A_1	1.703	$(3a_1)^2(4a_1)^2(6a_1)^1(1b_1)^2(2b_2)^2$	$5a_1 \rightarrow 6a_1$ (63.9%)
1^2B_2	1.705	$(3a_1)^2(4a_1)^2(1b_1)^2(2b_2)^2(3b_2)^1$	$5a_1 \rightarrow 3b_2$ (63.9%)
1^4A_2	2.068	$(3a_1)^2(4a_1)^2(5a_1)^1(1b_1)^1(2b_2)^2(3b_2)^1$	$1b_1 \rightarrow 3b_2$ (87.2%)
1^4B_1	2.070	$(3a_1)^2(4a_1)^2(5a_1)^1(6a_1)^1(1b_1)^1(2b_2)^2$	$1b_1 \rightarrow 6a_1$ (87.2%)
1^2A_2	2.703	$(3a_1)^2(4a_1)^2(5a_1)^1(1b_1)^1(2b_2)^2(3b_2)^1$	$1b_1 \rightarrow 3b_2$ (74.3%)
2^2B_1	2.708	$(3a_1)^2(4a_1)^2(5a_1)^1(6a_1)^1(1b_1)^1(2b_2)^2$	$1b_1 \rightarrow 6a_1$ (86.8%)
3^2A_1	2.711	$(3a_1)^2(4a_1)^1(5a_1)^2(1b_1)^2(2b_2)^2$	$4a_1 \rightarrow 5a_1$ (60.2%)
2^2B_2	2.714	$(3a_1)^2(4a_1)^2(5a_1)^2(1b_1)^2(2b_2)^1$	$2b_2 \rightarrow 5a_1$ (60.1%)
1^4A_1	3.056	$(3a_1)^2(4a_1)^2(5a_1)^1(1b_1)^2(2b_2)^1(3b_2)^1$	$2b_2 \rightarrow 3b_2$ (57.5%)
1^4B_2	3.057	$(3a_1)^2(4a_1)^1(5a_1)^1(1b_1)^2(2b_2)^2(3b_2)^1$	$4a_1 \rightarrow 3b_2$ (57.5%)
2^4A_1	3.384	$(3a_1)^2(4a_1)^1(5a_1)^1(6a_1)^1(1b_1)^2(2b_2)^2$	$4a_1 \rightarrow 6a_1$ (62.5%)
2^4B_2	3.493	$(3a_1)^2(4a_1)^2(5a_1)^1(6a_1)^1(1b_1)^2(2b_2)^1$	$2b_2 \rightarrow 6a_1$ (63.7%)
3^2B_1	3.822	$(3a_1)^2(4a_1)^2(5a_1)^1(6a_1)^1(1b_1)^1(2b_2)^2$	$1b_1 \rightarrow 6a_1$ (75.0%)
2^2A_2	3.837	$(3a_1)^2(4a_1)^2(5a_1)^1(1b_1)^1(2b_2)^2(3b_2)^1$	$1b_1 \rightarrow 3b_2$ (64.8%)
2^4A_2	3.921	$(3a_1)^2(4a_1)^2(6a_1)^1(1b_1)^1(2b_2)^2(3b_2)^1$	$5a_1$, $1b_1 \rightarrow 6a_1$, $3b_2$ (64.9%)
3^2A_2	4.592	$(3a_1)^2(4a_1)^2(6a_1)^1(1b_1)^1(2b_2)^2(3b_2)^1$	$5a_1$, $1b_1 \rightarrow 6a_1$, $3b_2$ (62.5%)
2^4B_1	4.681	$(3a_1)^2(4a_1)^1(5a_1)^2(6a_1)^1(1b_1)^1(2b_2)^2$	$4a_1$,$1b_1 \rightarrow 5a_1$,$6a_1$(57.2%)
3^4A_2	4.685	$(3a_1)^2(4a_1)^1(5a_1)^2(1b_1)^1(2b_2)^2(3b_2)^1$	$4a_1$, $1b_1 \rightarrow 5a_1$, $3b_2$ (57.0%)
3^4B_1	4.832	$(3a_1)^2(4a_1)^2(5a_1)^2(1b_1)^1(2b_2)^1(3b_2)^1$	$1b_1$, $1b_2 \rightarrow 5a_1$, $3b_2$ (60.2%)
3^4A_1	5.308	$(3a_1)^2(4a_1)^1(5a_1)^2(1b_1)^2(2b_2)^1(3b_2)^1$	$4a_1$, $2b_2 \rightarrow 5a_1$, $3b_2$ (47.0%)

Table 3. Vertical excitation energy, wavelength (in unit nm), and the corresponding oscillator strength for the B_3 molecule.

State	VTE (cm^{-1})	Wavelength (nm)	OS
1^2B_1	6299/6268[7]	1587.71	0.002853
2^2A_1	13736	728.13/736[8]	0.005742
1^2B_2	13752	727.27	0.000872
2^2B_1	21841	457.90	7.0867×10^{-11}
3^2A_1	21866	457.40/458[8]	0.0000179
2^2B_2	21890	456.89	0.01503
3^2B_1	30826	324.44	2.0639×10^{-9}

4. Conclusion

In this paper, the electronic states of B_3 are studied under the adiabatic approximation, and the electronic structure of B_3 is studied using the MRCI+Q method. The geometries of the low-lying states are obtained, some degenerate states are found split with lower symmetry, the symmetry breaking of the $1 \sim 2^2E'$ state arising from the Jahn–Teller effect, and the computed energy splitting is 0.018 eV and 0.008 eV, respectively. The molecular properties including VTE, OS, main

configurations, and transitions of the excited state of B_3 are investigated. The equilibrium geometries obtained from our calculations show excellent agreement with available experimental and theoretical data, with bond length deviations of less than 0.03 Å and bond angle differences within 2°. The corresponding transition energies agree remarkably well with spectroscopy measurements with a mean absolute error of only 0.025 eV for characterized electronic states. Based on our calculations, the previously observed spectra are assigned to the X^2A_1–2^2A_1, 2^2B_2 transitions at 728 nm and 457 nm, which are in good agreement with the observed bands (736 nm and 458 nm), though the D_{3h} high symmetry is weakly broken. The triangular B_3 unit is a fundamental bonding motif in all boron compounds and nanostructures, this study can promote the investigation the bonding between a B_3 cluster and a 3d transition metal. We expect that the present theoretical results will significantly advance experimental investigations of B_3 clusters and provide essential data for their practical applications.

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