



MRCI study of the spectroscopic parameters and transition properties of the 36 low-lying electronic states of the B₂ molecule



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ARTICLE INFO

Article history:

Received 22 March 2017

Received in revised form 29 May 2017

Accepted 31 May 2017

Available online 1 June 2017

Keywords:

Potential energy curve
Spectroscopic parameter
Transition dipole moment
Electric dipole transition
Avoided crossing
Vibrational state

ABSTRACT

This paper studied the spectroscopic and transition properties of 36 low-lying states, which came from the first two dissociation limits of B₂ molecule. The potential energy curves were calculated with the complete active space self-consistent field (CASSCF) method, which was followed by the internally contracted multireference configuration interaction (icMRCI) plus Davidson modification (icMRCI + Q) approach. Of these 36 states, the 2⁵Σ_u⁻, 1³Σ_u⁺, 2⁵Π_u, and 1⁵Δ_u states were repulsive; the B³Δ_u, E³Σ_u⁺, f¹Σ_u⁻, g¹Π_g, 2³Π_u, 3³Σ_g⁻, 3³Π_u, 1⁵Π_g, and 3³Σ_u⁺ states had double wells; the B³Δ_u, E³Σ_u⁺, G³Σ_u⁺, f¹Σ_u⁻, g¹Π_g, 3³Σ_g⁻, 2³Π_u, 3³Π_u, 1⁵Π_g, 2⁵Π_g, 2⁵Σ_g⁻, and 3³Σ_u⁺ states had one barrier; the 2⁵Σ_g⁻ state and the second wells of B³Δ_u, E³Σ_u⁺, 1⁵Π_g, f¹Σ_u⁻, g¹Π_g, and 2³Π_u states were weakly bound; and the 2⁵Σ_g⁻ state had no vibrational levels. The avoided crossings existed between the B³Δ_u and 2³Δ_u states, the E³Σ_u⁺ and G³Σ_u⁺ states, the G³Σ_u⁺ and 3³Σ_u⁺ states, the 3³Σ_u⁺ and 4³Σ_u⁺ states, the 2³Π_u and 3³Π_u states, the g¹Π_g and 2¹Π_g states, the 2³Σ_g⁻ and 3³Σ_g⁻ states, the 1⁵Π_g and 2⁵Π_g states, the 2⁵Π_g and 3⁵Π_g states, the 2⁵Σ_g⁻ and 3⁵Σ_g⁻ states, as well as the F³Π_g and 3³Π_g states. Core-valence correlation and scalar relativistic corrections were taken into account. The extrapolation to the complete basis set limit was done. The spectroscopic parameters and vibrational properties were obtained. The transition dipole moments were calculated. Franck-Condon factors of some transitions were evaluated. The spin-orbit coupling (SOC) effect on the spectroscopic parameters and vibrational properties is tiny and sometimes even can be negligible. The results determined in this paper can provide some powerful guidelines to observe these states, in particular the states which have not been studied in the experiment.

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1. Introduction

Boron clusters and boron-rich materials have a number of important technological applications such as in explosives, refractory materials, stable chemical insulators, high-temperature semiconductor devices, high modulus boron fiber composites, and thermoelectric power conversion [1–4]. There has also been considerable research in the use of boron-rich materials as high energy density fuels [4]. In addition, calculations have shown that atomic and diatomic boron additives could provide significant increases in specific impulse for cryogenic propellant systems [5]. The low atomic weight, high heat of combustion, and increased specific impulse of boron make atomic boron, boron clusters, and boron-containing molecules attractive propellant additive candidates. In particular, in the potential cryogenic propellant applications, B₂ is expected to be a major by-product of boron atom deposition into solid hydrogen [4]. Spectroscopic knowledge of B₂ molecule is needed in the studies of these applications. For this reason, many experimental

[4–12] and theoretical [2,3,13–29] studies of this molecule have been done in the past several decades.

Experimentally, Douglas and Herzberg [6] in 1940 reported the electronic spectrum of X³Σ_g⁻-2³Σ_u⁻ transitions for the first time and made the partial rotational analysis of three ¹¹B₂ bands (0-0, 1-0 and 1-1) as well as two ¹⁰B¹¹B bands (0-0 and 1-0). Verhaegen and Drowart [7] in 1962 determined D₀ of X³Σ_g⁻ state to be approximately 2.8403 ± 0.2385 eV. Graham and Weltner [8] in 1976 observed the X³Σ_g⁻-2³Σ_u⁻ transitions and confirmed that the ground state was the X³Σ_g⁻. Huber and Herzberg [30] in 1979 summarized some accurate spectroscopic parameters and molecular constants as of that time. Bredohl et al. [9] in 1982 re-studied the emission spectrum and analyzed 6 bands of ¹¹B₂ (0-0, 1-1, 1-0, 2-1, 3-2, and 0-1) as well as four bands of ¹⁰B¹¹B (0-0, 1-0, 2-1, and 3-2). Chase et al. [10] in 1985 obtained the ground-state D₀ as 2.9488 ± 0.5989 eV. Using the rotational analysis of the 0-12, 0-13, 0-14, and 0-15 bands of the X³Σ_g⁻-2³Σ_u⁻ transition, Bredohl et al. [11] in 1987 made a better description of the ¹¹B₂ ground state. Brazier and Carrick [12] in 1992 observed several new electronic transitions. Two years later, they [4] characterized the F³Π_g-A³Π_u system for the first time. DeRose et al. [5] in 1995 observed the emission spectra of 1¹Σ_u⁺-c¹Σ_g⁺ transition for the first time and presented the spectra of 0-

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0, 1-1, 2-2, 3-3, and 4-4 bands together with their rotational analyses. With these spectra observed, some spectroscopic parameters and molecular constants were evaluated for the 8 states, $X^3\Sigma_g^-$, $A^3\Pi_u$, $b^1\Delta_g$, $c^1\Sigma_g^+$, $D^3\Pi_g$, $F^3\Pi_g$, $2^3\Sigma_u^-$, and $2^3\Pi_u$.

Theoretically, Padgett and Griffing [13] in 1959 calculated the potential energy curves (PECs) of the 16 states using the linear combination of atomic orbitals (LCAO) molecular orbital (MO) theory. Bender and Davidson [14] in 1967 studied the PECs of 21 states by the configuration interaction (CI) approach. However, they [13,14] thought that the ground state was the $1^3\Sigma_u^-$. Dupuis and Liu [15] in 1978 made the accurate CI calculations for the 3 states and determined the ground state to be the $1^3\Sigma_g^-$. Bruna and Wright [16–19] in 1989 and 1990, respectively, computed the PECs of many states by the multireference (single and) double CI (MRD-CI) methods. Langhoff and Bauschlicher [3] in 1991 studied the PECs of 27 states using the multireference CI (MRCI) method. Hachey et al. [20] in 1992 investigated the PECs of 55 low-lying states by the CI method. Yan et al. [21] in 1993 calculated the PECs of 11 low-lying states by the self-consistent field (SCF) and second-order CI (SOC) approaches. And Manaa and Yarkony [22] in 1994 determined the PECs and the spin-orbit coupling (SOC) splitting interactions of 4 states. With these PECs, they [2,13–22] evaluated some spectroscopic parameters of this molecule. However, obvious differences of spectroscopic parameters can be seen between theory and experiment.

Subsequently, Yang et al. [2] in 2001 used the quadratic CI calculation to determine the ground-state PEC. Müller et al. [23] in 2001 studied the PECs of 25 low-lying states using several *ab initio* methods. Hald and Jørgensen [24] in 2001 used the standard coupled cluster hierarchy to determine the PECs of several states. Tzeli and Mavridis [25] in 2005 employed the MRCI and coupled cluster (CC) methods to compute the PECs of 5 low-lying states. Nguyen et al. [26] in 2009 used the coupled-cluster method with all singles and doubles and noniterative inclusion of triples [CCSD(T)] approach with the aug-cc-pVnZ ($n = D, T, Q, 5$) basis sets to determine the geometries of 3 states, and extrapolated the results to the complete basis set (CBS) limit. Bezugly et al. [27] in 2010 made the MRCI calculations of ground-state PEC. Miliordos and Mavridis [28] made the MRCI calculations of PECs for the 3 low-lying states. And Bytautas et al. [29] in 2012 calculated the PECs of 6 low-lying states. With the PECs obtained by these calculations [2,23–29], some spectroscopic and transition properties of this molecule were evaluated. However, few results can achieve high quality.

Recently, we calculated the PECs of 36 states of B_2 molecule and evaluated their spectroscopic parameters and transition properties. Our results had the following remarkable features. (1) A number of avoided crossings were found. These avoided crossings existed between the $B^3\Delta_u$ and $2^3\Delta_u$ states, the $E^3\Sigma_u^+$ and $G^3\Sigma_u^+$ states, the $G^3\Sigma_u^+$ and $3^3\Sigma_u^+$ states, the $3^3\Sigma_u^+$ and $4^3\Sigma_u^+$ states, the $2^3\Pi_u$ and $3^3\Pi_u$ states, the $g^1\Pi_g$ and $2^1\Pi_g$ states, the $2^3\Sigma_g^-$ and $3^3\Sigma_g^-$ states, the $1^5\Pi_g$ and $2^5\Pi_g$ states, the $2^5\Pi_g$ and $3^5\Pi_g$ states, the $2^5\Sigma_g^-$ and $3^5\Sigma_g^-$ states, as well as the $F^3\Pi_g$ and $3^3\Pi_g$ states. However, few avoided crossings were reported in previous work. (2) The 9 states ($B^3\Delta_u$, $E^3\Sigma_u^+$, $f^1\Sigma_u^-$, $g^1\Pi_g$, $2^3\Pi_u$, $3^3\Sigma_g^-$, $3^3\Pi_u$, $1^5\Pi_g$, and $3^3\Sigma_u^+$) had double wells. Except for the first well, however, only one theoretical work [3] reported the second well of $3^3\Sigma_g^-$ state. (3) Franck-Condon (FC) factors of electronic transitions showed that almost all the bound states except for the second wells of $B^3\Delta_u$, $E^3\Sigma_u^+$, $f^1\Sigma_u^-$, $g^1\Pi_g$, $2^3\Pi_u$, and $1^5\Pi_g$ states were not difficult to observe by a proper spectroscopic approach. (4) The $2^5\Sigma_u^-$, $1^5\Sigma_u^+$, $2^5\Pi_u$, and $1^5\Delta_u$ states were repulsive. The $2^5\Sigma_g^-$ state was weakly bound and had no vibrational levels. These repulsive and weakly-bound states were not reported in previous work. These features make us believe that it deserves to report the spectroscopic and transition properties of these states in this paper.

In the next section, we will briefly introduce the methodology employed. In Section 3, the PECs of 36 states are reported. The spectroscopic parameters and transition properties were predicted. The transition dipole moments (TDMs) were determined. The FC factors of some electronic transitions were calculated. The SOC effect on the

spectroscopic parameters and vibrational properties of $X^3\Sigma_g^-$, $A^3\Pi_u$, and $F^3\Pi_g$ states was evaluated. In Section 4, some conclusions are drawn. The spectroscopic parameters and transition properties obtained here can be expected to be reliably predicted ones.

2. Theory and Method

The ground and first excited states of B atom are 2^2P_u and 4^2P_g , respectively. Therefore, the first two dissociation limits of B_2 molecule are only the $B(2^2P_u) + B(2^2P_u)$ and $B(2^2P_u) + B(4^2P_g)$. Using the molecular group theory, we deduced the 36 states, which were generated from the first two dissociation limits. These states together with the dissociation limits are collected in Table 1. For reasons of comparison, we also collect the experimental [31] and other theoretical energy separation [20] in Table 1. It should be noted that the relative energy of 4^2P_g state to the ground state is calculated by averaging the energy levels of $4^2P_{1/2}$, $4^2P_{3/2}$ and $4^2P_{5/2}$ states [31], since no experimental energy level of 4^2P_g state can be available in the literature.

The PECs were calculated with the complete active space self-consistent field (CASSCF) method followed by the internally contracted multireference configuration interaction (icMRCI) plus Davidson modification (icMRCI + Q) approach [32,33] for internuclear separations from approximately 0.08 to 1.06 nm. Here, the CASSCF was used as the reference wavefunction for the icMRCI calculations. The basis sets used were the aug-cc-pV5Z and aug-cc-pV6Z [34,35]. The calculations were done with the MOLPRO 2010.1 program package [36] in the D_{2h} point group. The point spacing interval used was 0.02 nm for each state. To accurately determine each PEC, the point spacing interval used was 0.002 nm for internuclear separations from approximately 0.12 to 0.50 nm because the equilibrium separations were fallen into this range for all the bound states involved. Here, the smaller step was adopted near the equilibrium position of each state so that the properties of each PEC could be displayed more clearly.

The MOs used for the icMRCI calculations came from the CASSCF results. The state-averaged technique was used in the CASSCF calculations. Each state had the same weight factor of 0.0277778. We put the 8 outermost MOs ($2a_g$, $1b_{3u}$, $1b_{2u}$, $2b_{1u}$, $1b_{2g}$, and $1b_{3g}$) into the active space, corresponding to the $2\sigma_g$, $3\sigma_g$, $2\sigma_u$, $3\sigma_u$, $1\pi_u$, and $1\pi_g$ MOs in the B_2 molecule. No additional MOs were added to the active space. The 6 valence electrons were distributed into the 8 valence MOs. As a result, this active space was referred to as CAS (6, 8). We put the rest 4 inner electrons into the 2 lowest MOs ($1a_g$ and $1b_{1u}$). For the aug-cc-pV6Z basis set, the total number of external orbitals was 244, corresponding to $43a_g$, $30b_{3u}$, $30b_{2u}$, $19b_{1g}$, $43b_{1u}$, $30b_{2g}$, $30b_{3g}$, and $19a_u$. In summary, we altogether used the 10 MOs ($3a_g$, $1b_{3u}$, $1b_{2u}$, $3b_{1u}$, $1b_{2g}$, and $1b_{3g}$) to calculate the PECs of all the 36 states.

Scalar relativistic correction was computed with the cc-pV5Z-DK basis set [37]. Its contribution to the total energy was denoted as DK. Core-valence correlation correction was calculated with the cc-pCV5Z basis set [38]. Its contribution to the total energy was denoted as CV. The SOC effect was determined by the state interaction method with the Breit-Pauli operator [39] at the level of icMRCI theory with the all-electron cc-pCV5Z basis set. The all-electron cc-pCV5Z basis set with and without Breit-Pauli operator was used to calculate the contribution to the potential energy by the SOC effect. The difference between the two energies was the SOC splitting energy and was denoted as SOC. The extrapolation to the CBS limit was made with the aug-cc-pV5Z and aug-cc-pV6Z basis sets. The energy obtained by the extrapolation was denoted as 56. The extrapolation scheme [40] was as follows,

$$\Delta E_X^{ref} = E_\infty^{ref} + A^{ref} X^{-\alpha}, \quad (1)$$

$$\Delta E_X^{corr} = E_\infty^{corr} + A^{corr} X^{-\beta}. \quad (2)$$

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