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Accurate calculations on 12 Λ–S and 28 Ω states of BN^+ cation: Potential energy curves, spectroscopic parameters and spin–orbit coupling

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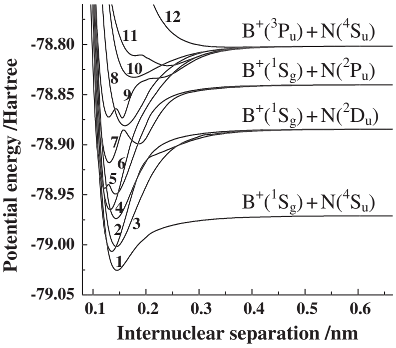
HIGHLIGHTS

- Effect of core–valence correlation and scalar relativistic corrections is included.
- Present calculations are convergent.
- PECs are extrapolated to the CBS limit.
- Spectroscopic parameters of 12 electronic states and 28 Ω states are obtained.
- Effect of SO coupling on the spectroscopic parameters is evaluated.

GRAPHICAL ABSTRACT

The PECs of 28 Ω states generated from the 12 electronic states of the BN^+ cation are studied for the first time. The $1^6\Sigma^-$, $3^2\Pi$ and $A^4\Pi$ are found to be the inverted states. Each of the $1^2\Sigma^+$, $2^2\Pi$, $3^2\Pi$ and $2^2\Sigma^-$ states possesses the double well. The PECs are calculated by the CASSCF method followed by the icMRCI approach. The core–valence correlation and scalar relativistic corrections are included. The convergence of present calculations is found with respect to the basis set and level of theory. The SO coupling effect is accounted for by the state interaction method with the Breit–Pauli Hamiltonian. The PECs are extrapolated to the CBS limit. The spectroscopic parameters are evaluated. The present spectroscopic parameters can be expected to be reliably predicted ones. The effect of SO coupling on the spectroscopic parameters is not obvious almost for all the electronic states involved here.



PECs of 12 electronic states of BN^+ cation

1-$X^4\Sigma^-$; 2-$1^2\Pi$; 3-$1^2\Sigma^-$; 4-$1^2\Delta$; 5-$1^2\Sigma^+$; 6-$A^4\Pi$; 7-$2^2\Pi$; 8-$B^4\Sigma^-$; 9-$3^2\Pi$; 10-$1^6\Pi$; 11-$2^2\Sigma^-$; 12-$1^6\Sigma^-$

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ABSTRACT

The potential energy curves (PECs) of 28 Ω states generated from the 12 states ($X^4\Sigma^-$, $1^2\Pi$, $1^2\Sigma^-$, $1^2\Delta$, $1^2\Sigma^+$, $2^2\Pi$, $A^4\Pi$, $B^4\Sigma^-$, $3^2\Pi$, $1^6\Sigma^-$, $2^2\Sigma^-$ and $1^6\Pi$) of the BN^+ cation are studied for the first time for internuclear separations from about 0.1 to 1.0 nm using an *ab initio* quantum chemical method. All the Λ–S states correlate to the first four dissociation channels. The $1^6\Sigma^-$, $3^2\Pi$ and $A^4\Pi$ states are found to be the inverted ones. The $1^2\Sigma^+$, $2^2\Pi$, $3^2\Pi$ and $2^2\Sigma^-$ states are found to possess the double well. The PECs are calculated by the complete active space self-consistent field method, which is followed by the internally contracted multireference configuration interaction approach with the Davidson correction. Core–valence correlation correction is included by a cc-pCV5Z basis set. Scalar relativistic correction is calculated by the third-order Douglas-Kroll Hamiltonian approximation at the level of a cc-pV5Z basis set. The convergent behavior of

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Spectroscopic parameter
Relativistic correction
Core–valence correlation correction

present calculations is discussed with respect to the basis set and level of theory. The spin–orbit coupling is accounted for by the state interaction approach with the Breit–Pauli Hamiltonian using the all-electron cc-pCV5Z basis set. All the PECs are extrapolated to the complete basis set limit. The spectroscopic parameters are obtained, and the vibrational properties of $1^2\Sigma^+$, $2^2\Pi$, $3^2\Pi$ and $2^2\Sigma^-$ states are evaluated. Analyses demonstrate that the spectroscopic parameters reported here can be expected to be reliably predicted ones. The conclusion is gained that the effect of spin–orbit coupling on the spectroscopic parameters are not obvious almost for all the Λ–S states involved in the present paper.

Introduction

There has been considerable interest in the spectroscopic properties of BN radical. A number of measurements and calculations have been done to obtain its spectroscopic parameters and molecular constants in the past several decades [1]. Different from the BN radical, no spectroscopic information has been reported in experiment for the BN$^+$ cation to this day, though the BN$^+$ cation was detected in 1986 by the mass spectroscopy approach. The current spectroscopic knowledge on the BN$^+$ cation as is available is all derived from the spectroscopic calculations [2–5].

Only four groups of spectroscopic calculations [2–5] can be found in the literature up to now. In 1975 Cade and Huo [2] reported the first calculations about the BN$^+$ cation. They assumed a $^2\Pi$ be the ground state of BN$^+$ in their work. Obviously, their results are too approximate to be of significance. In 1985 Karna and Grein [3] calculated the potential energy curves (PECs) of 12 low-lying valence states of BN$^+$ cation using the multireference single and double excitation-configuration interaction (MRD-CI) approach and the 5*s*3*p* contracted Gaussian basis set with polarization functions, and evaluated some spectroscopic parameters. In 1988 Karna and Grein [4] re-investigated the BN$^+$ cation using the MRD-CI method in combination with the double-zeta plus polarization basis set, obtained the PECs of several high-multiplicity states, and determined the spectroscopic parameters of $1^4\Delta$, $1^4\Sigma^+$, $2^4\Pi$ and $1^6\Pi$ states. In 1995 Mawhinney et al. [5] calculated the PECs of a number of low-lying quartet and doublet states of BN$^+$ cation by the MRD-CI approach in combination with a 6*s*5*p*3*d*1*f* basis set. The spectroscopic parameters of 13 low-lying states were derived. Summarizing these spectroscopic results [3–5], we have found that no core–valence correlation and scalar relativistic corrections were involved in previous calculations, and that no spin–orbit (SO) coupling effect were evaluated for any Ω states, though the two corrections have important influences on the spectroscopic parameters for high-quality calculations. In addition, the basis sets used in previous calculations [3–5] are small. All these factors make the spectroscopic results available in the literature cannot achieve high quality.

The aim of the present work is to extend the spectroscopic knowledge of BN$^+$ cation. Firstly, we will determine the high-quality spectroscopic properties of 12 Λ–S states resulting from the first four dissociation channels. For this reason, extensive *ab initio* calculations on the PECs will be made over a wide internuclear separation. To evaluate the spectroscopic parameters of BN$^+$ cation as accurately as possible, on the one hand, core–valence correlation and scalar relativistic corrections are taken into account since these two corrections have important effect on the accurate prediction of spectroscopic properties; on the other hand, the extrapolation to the complete basis set (CBS) limit is made so that the residual errors behind the basis sets can be eliminated. Secondly, the effect of SO coupling on the PECs will be introduced into the calculations since no PECs have been calculated for any Ω states up to now. Analyses demonstrate that the present spectroscopic results can achieve very high quality.

In the next section, we will briefly describe the theory and method used in this paper. In Results and discussion, the PECs of 12 states [$X^4\Sigma^-$ ($1^4\Sigma^-$), $1^2\Pi$, $1^2\Sigma^-$, $1^2\Delta$, $1^2\Sigma^+$, $2^2\Pi$, $A^4\Pi$ ($1^4\Pi$), $B^4\Sigma^-$ ($1^4\Sigma^-$), $3^2\Pi$, $1^6\Sigma^-$, $2^2\Sigma^-$ and $1^6\Pi$] are calculated for internuclear separations from about 0.1 to 1.0 nm. The PECs of 28 Ω states generated from these 12 Λ–S states are studied for the first time over the same internuclear separations. The PEC calculations are performed using the complete active space self-consistent field (CASSCF) method, which is followed by the internally contracted multireference CI (icMRCI) approach [6,7] with the Davidson correction (icMRCI + Q) [8,9]. The SO coupling effect is accounted for by the state interaction method with the Breit–Pauli Hamiltonian. The effect of core–valence correlation and scalar relativistic corrections on the PECs is taken into account. The PECs are extrapolated to the CBS limit. The spectroscopic parameters are calculated for all the Λ–S and Ω states involved, and compared with those available in the literature. Concluding remarks are given in Conclusion.

Theory and method

In this paper, we only investigate these Λ–S states, which dissociate into the first four dissociation channels, B$^+$(^{1}S$_g$) + N(^{4}S$_u$), B$^+$(^{1}S$_g$) + N(^{2}D$_u$), B$^+$(^{1}S$_g$) + N(^{2}P$_u$) and B$^+$(^{3}P$_u$) + N(^{4}S$_u$), of BN$^+$ cation. Therefore, we first deduce all the states generated from the four dissociation channels.

The ground and the first excited states of B$^+$ ion are the ^{3}P$_u$ and ^{1}S$_g$, and the ground, the first and the second excited states of N atom are the ^{4}S$_u$, ^{2}P$_u$ and ^{2}D$_u$, respectively. Because the BN$^+$ belongs to $C_{\infty v}$ molecular symmetry, we resolve the atomic group representations ^{3}P$_u$, ^{1}S$_g$, ^{4}S$_u$, ^{2}P$_u$ and ^{2}D$_u$ into $C_{\infty v}$ as those

$$^3\mathrm{P_u} \to {}^3\Sigma^+ \oplus {}^3\Pi, \tag{1}$$

$$^1\mathrm{S_g} \to {}^1\Sigma^+, \tag{2}$$

$$^4\mathrm{S_u} \to {}^4\Sigma^-, \tag{3}$$

$$^2\mathrm{P_u} \to {}^2\Sigma^+ \oplus {}^2\Pi, \tag{4}$$

$$^2\mathrm{D_u} \to {}^2\Sigma^- \oplus {}^2\Pi \oplus {}^2\Delta. \tag{5}$$

Therefore, the direct products of atomic group representations, ^{3}P$_u$ and ^{4}S$_u$, ^{1}S$_g$ and ^{2}P$_u$, ^{1}S$_g$ and ^{2}D$_u$, and ^{1}S$_g$ and ^{4}S$_u$, are those

$$^1\Sigma^+ \otimes {}^4\Sigma^- \to {}^4\Sigma^-. \tag{6}$$

$$^1\Sigma^+ \otimes ({}^2\Sigma^- \oplus {}^2\Pi \oplus {}^2\Delta) \to {}^2\Sigma^- \oplus {}^2\Pi \oplus {}^2\Delta, \tag{7}$$

$$^1\Sigma^+ \otimes ({}^2\Sigma^+ \oplus {}^2\Pi) \to {}^2\Sigma^+ \oplus {}^2\Pi, \tag{8}$$

$$({}^3\Sigma^+ \oplus {}^3\Pi) \otimes {}^4\Sigma^- \to {}^{2,4,6}\Sigma^- \oplus {}^{2,4,6}\Pi. \tag{9}$$

That is, the $1^4\Sigma^-$ state dissociates into the first dissociation channel, B$^+$(^{1}S$_g$) + N(^{4}S$_u$). The $1^2\Sigma^-$, $1^2\Pi$ and $1^2\Delta$ states dissociate into the second dissociation channel, B$^+$(^{1}S$_g$) + N(^{2}D$_u$). The $1^2\Sigma^+$ and $2^2\Pi$ states dissociate into the third dissociation channel, B$^+$(^{1}S$_g$) + N(^{2}P$_u$). And the $1^4\Pi$, $2^4\Sigma^-$, $3^2\Pi$, $1^6\Sigma^-$, $2^2\Sigma^-$ and $1^6\Pi$ states dissociate into the fourth dissociation channel, B$^+$(^{3}P$_u$) + N(^{4}S$_u$). As a result, altogether, there are 12 Λ–S states, which are generated from the first four dissociation channels of BN$^+$ cation. The 12 states and their dissociation channels are collected in Table 1. For convenient