

Anion photoelectron spectroscopy of BN^-

Knut R. Asmis^{a,b}, Travis R. Taylor^{a,b}, Daniel M. Neumark^{a,b,*}

^a Department of Chemistry, University of California, Berkeley, CA 94720, USA

^b Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

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Abstract

Photoelectron spectra of the BN^- anion at 266 nm and 355 nm are reported. We observe transitions to the ground and three lowest excited states of BN. The electron affinity of BN ($X^3\Pi$) is 3.160 ± 0.005 eV. Spectroscopic constants for the anion ($X^2\Sigma^+$) are $r_e = 1.284 \pm 0.005$ Å, $\omega_e = 1660 \pm 40$ cm^{-1} and $\omega_e \chi_e = 12 \pm 4$ cm^{-1} . Term energies T_0 for the excited states of BN are 0.031 ± 0.004 eV ($a^1\Sigma^+$), 0.468 ± 0.004 eV ($b^1\Pi$) and 1.221 ± 0.006 eV ($A^3\Sigma^+$). © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Boron nitride crystallizes in three allotropes, cubic-, hexagonal-, and wurtzite-BN, each having similar properties to the corresponding modifications of carbon, to which it is isoelectronic. Cubic or β -BN, which shows the most favorable combination of properties for industrial applications, e.g. high thermal conductivity, chemical inertness, excellent electrical insulation, and extreme hardness, is also of considerable interest in material science. However, it has been found to be extremely difficult to produce pure solid thin films of β -BN with the standard plasma-assisted vapor deposition techniques [1]. In order to optimize these processes it is of importance to identify the major components of the plasma and characterize their electronic structure. In this study, the first of a series of studies on boron nitride

clusters, we focus on the BN monomer and its anion BN^- .

Only a few spectroscopic studies have been performed on BN. Douglas and Herzberg originally observed the emission spectrum of BN produced in a discharge of He/ BCl_3/N_2 [2]. They reported a partial rotational analysis of a $^3\Pi - ^3\Pi$ transition and two singlet transitions. In 1970 Mosher and Frisch [3] determined that the $^3\Pi$ ($2p\sigma 2p\pi^3$) state is the electronic ground state in rare-gas matrices, in contrast to the isoelectronic C_2 , which has a $^1\Sigma_g^+$ ($2p\pi_u^4$) ground state [4]. Bredohl et al. [5,6] reinvestigated the triplet and the two singlet transitions at higher resolution, leading to improved spectroscopic constants for the triplet states, although their proposed assignments of the singlet transitions have been called into question [7–9]. The most complete work to date was reported by Lorenz et al. [9], who studied absorption and emission from BN in a neon matrix. They identified and obtained spectroscopic constants for the ground and several low-lying excited states of BN: the $X^3\Pi$, $a^1\Sigma^+$, $b^1\Pi$, $A^3\Sigma^+$, $B^3\Sigma^-$ and $D^3\Pi$

* Corresponding author. Fax: +1-510-642-6262; E-mail: dan@radon.cchem.berkeley.edu

states. This work yielded the first experimental estimate for the $a^1\Sigma_g^+$ ($2p\pi^4$) term energy ($T_e = 2\text{--}23$ meV) from analysis of the triplet and singlet manifold emission spectra. The ground and low-lying states of BN have also been investigated by high-level ab initio calculations [7,8,10–12]; the calculated energetics are by and large consistent with the work of Lorenz et al. [9].

Less is known about the anion BN^- . Reid has determined a rough estimate of the electron affinity (2.9 ± 0.3 eV) using charge inversion spectrometry [13]. Grein and coworkers [14,15] have performed extensive theoretical studies on BN^- , including calculations of the anion photoelectron spectrum. The anion is calculated to have a $X^2\Sigma^+$ ($2p\sigma 2p\pi^4$) ground state, the same molecular orbital configuration as the ground state of C_2^- .

We apply anion photoelectron spectroscopy of BN^- to examine the electronic structure of the ground and low lying excited electronic states of BN and determine selected spectroscopic constants for both the anion ground state and the low-lying electronic states of the neutral. Anion photoelectron spectroscopy is a useful tool in this study for two reasons. (1) Mass selection enables us to isolate BN^- selectively and therefore the signal carrier is unambiguously identified. (2) Due to the less stringent selection rules compared to optical spectroscopy we expect to see both triplet and singlet electronic states in the photoelectron spectrum. In particular, both the $X^3\Pi$ ($2p\sigma 2p\pi^3$) and a $^1\Sigma^+$ ($2p\pi^4$) states of BN are accessible via one-electron photodetachment from the $X^2\Sigma^+$ ground state of BN^- , enabling us to directly determine their splitting.

2. Experiment

The negative ion time-of-flight (TOF) photoelectron spectrometer used in this study has been described previously [16,17]. Boron nitride clusters are generated in a pulsed molecular beam/laser ablation source, in which a rotating and translating ‘hot-pressed’ boron nitride disc (Carborundum) is ablated using the second harmonic (532 nm) of a Nd:YAG laser. The resulting plasma is entrained in a pulse of Ar carrier gas and expanded through a clustering channel. The source conditions are chosen

to maximize formation of diatomic BN^- rather than larger species. The optimal parameters, including early firing of the ablation laser relative to the opening of the pulsed valve and high ablation laser intensity, result in vibrationally hot BN^- (see below). Ions are extracted perpendicularly to the expansion by means of a pulsed electric field into a linear reflectron time-of-flight mass spectrometer. At the spatial focus of the mass spectrometer, mass-selected ions are photodetached by a laser pulse from a Nd:YAG laser. The laser firing delay is varied until optimal temporal overlap is achieved with ions of the desired mass. The third (355 nm, 3.493 eV) and fourth harmonic (266 nm, 4.657 eV) of the Nd:YAG laser were used in the present study. The photoelectron kinetic energy (eKE) is determined by field-free time-of-flight in a 100 cm flight tube. All photoelectron spectra presented here are plotted as a function of the electron binding energy (eBE), defined as

$$\text{eBE} = h\nu - \text{eKE}, \quad (1)$$

where $h\nu$ denotes the photon energy of the detachment laser.

This apparatus also yields the angular distribution of the detached photoelectrons. The angle between the laser polarization and the direction of electron collection is varied by means of a half-wave plate. The angular distribution of the photoelectrons is given by [18]

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{tot}}(\text{eKE})}{4\pi} \left[1 + \frac{\beta(\text{eKE})}{2} (3\cos^2\theta - 1) \right], \quad (2)$$

where $\sigma_{\text{tot}}(\text{eKE})$ is the total photodetachment cross section, $\beta(\text{eKE})$ is the asymmetry parameter ($-1 \leq \beta \leq 2$) and θ measures the angle between the direction of the ejected electron and the polarization of the incident light. β is determined from

$$\beta = \frac{I_{0^\circ} - I_{90^\circ}}{1/2 I_{0^\circ} + I_{90^\circ}}, \quad (3)$$

where I_{0° and I_{90° are the relative photoelectron intensities at $\theta = 0^\circ$ and $\theta = 90^\circ$ [19]. The asymmetry parameter is not expected to change rapidly for transitions within an electronic state but can vary for transitions to different electronic states.

3. Results and analysis

The anion photoelectron spectra of BN^- measured at photon wavelengths of 355 nm and 266 nm are shown in Fig. 1. Upper and lower case letters are used to label the most intense peaks in the spectra. Asymmetry parameters β were determined for selected bands and are indicated by the solid black dots in the upper graphs of Fig. 1.

The 355 nm spectra (Fig. 1, left) show five peaks at eBEs of 2.752, 2.955, 2.991, 3.160 and 3.193 eV. The two largest peaks, at 3.160 eV (X) and 3.193 eV (a), have very different β parameters of -0.6 and 1.0 , respectively, so each appears to be the vibrational origin of a different electronic transition. Based on the previous study by Lorenz et al. [9], peaks X and a are assigned to the $\text{X}^3\Pi (v'=0) + e^- \leftarrow \text{X}^2\Sigma^+ (v=0)$ and $\text{a}^1\Sigma^+ (v'=0) + e^- \leftarrow \text{X}^2\Sigma^+ (v=0)$ photodetachment transitions. This yields 3.160 eV for the electron affinity of BN, and 0.033 eV for the splitting between the $v=0$ levels of the

$\text{X}^3\Pi$ and a $^1\Sigma^+$ states; both values are refined in the analysis presented below.

The weaker peaks at lower eBEs are attributed to hot band transitions. An assignment of the peaks at 2.991, 2.955 and 2.752 eV to the $\text{a}^1\Sigma^+ (v'=0) + e^- \leftarrow \text{X}^2\Sigma^+ (v=1)$, $\text{X}^3\Pi (v'=0) + e^- \leftarrow \text{X}^2\Sigma^+ (v=1)$ and $\text{X}^3\Pi (v'=0) + e^- \leftarrow \text{X}^2\Sigma^+ (v=2)$ transitions, respectively, is in reasonable agreement with the calculated anion vibrational frequency of 1709 cm^{-1} [14]. This assignment is also consistent with the experimental β parameters that show the peak at 2.991 eV to be from a transition to the $\text{a}^1\Sigma^+$ state and the other two from transitions to the $\text{X}^3\Pi$ state. Sequence bands originating from vibrationally excited levels of the anion are also expected to contribute. The $\text{X}^3\Pi$ state frequency is calculated to be roughly 200 cm^{-1} smaller than the anion frequency [14]. This results in a red-shift of progressively higher sequence bands, accounting for the structure observed on the low-energy tails of the peaks associated with the $\text{X}^3\Pi$ state.

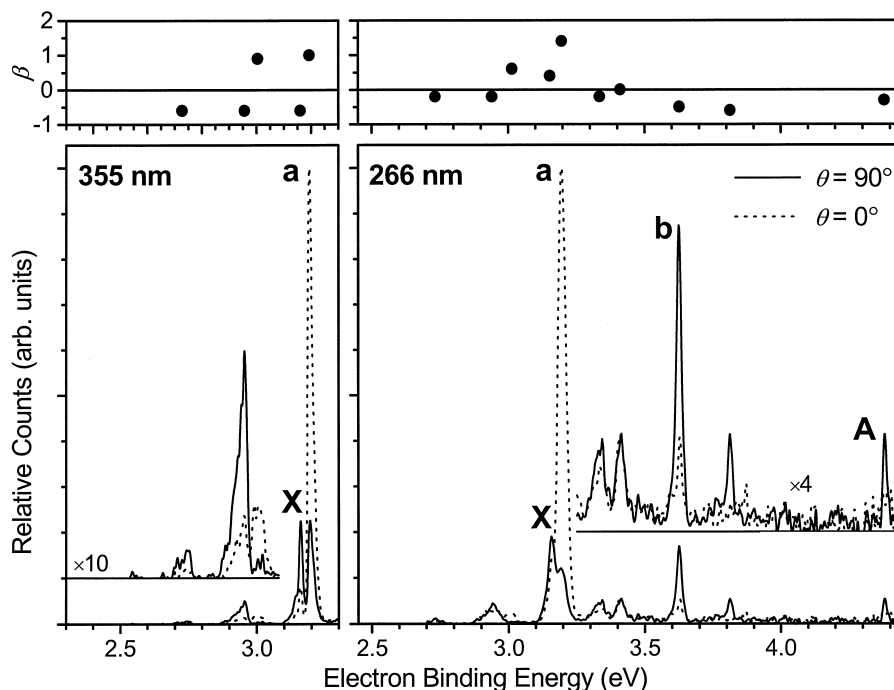


Fig. 1. Anion photoelectron spectra of BN^- recorded at photon wavelengths of 355 nm (left) and 266 nm (right). The spectra were measured at laser polarizations of $\theta = 0^\circ$ (dotted line) and $\theta = 90^\circ$ (solid line). The values of the asymmetry parameter β are indicated by the black dots above the photoelectron spectra for selected bands.

Although our assignments are consistent with the previous matrix study by Lorenz et al. [9], the photoelectron spectra present independent evidence for a $X^3\Pi$ ground state in the gas phase. Specifically, the calculation by Mawhinney et al. [14] predicts a larger change in internuclear distance for photodetachment to the $X^3\Pi$ state than the $a^1\Sigma^+$ state, so hot bands associated with the $X^3\Pi$ state should be more intense (relative to the respective 0–0 transition) than those of the $a^1\Sigma^+$ state, as is seen in our spectra. Similar reasoning was used to assign the nearly degenerate ground and first excited states of Si_2H [20].

In the 266 nm spectra (Fig. 1, right) all the peaks previously described are again observed, albeit with lower resolution, due to the higher electron kinetic energy at this wavelength. Five additional peaks are seen at eBEs of 3.343, 3.410, 3.628, 3.811 and 4.380 eV. The last three of these bands are more intense in the 90° spectrum ($\beta < 0$), while the first two are of similar intensity in both spectra ($\beta \approx 0$). These peaks can be assigned making use of the spectroscopic

constants obtained by Lorenz et al. [9]. The fundamental vibrational frequency ($\Delta G_{1/2}$) in the $X^3\Pi$ state is 0.185 eV (1494 cm^{-1}) and we thus assign the peak at 3.343 eV to the 1–0 transition, i.e. the $X^3\Pi (v' = 1) + e^- \leftarrow X^2\Sigma^+ (v = 0)$ transition. The peak at 3.628 eV (b), 0.468 eV above the ground state, is clearly the origin of another electronic state, the only candidate being the $b^1\Pi$ state, which is observed at 0.465 eV in the matrix [9]. Because both the $b^1\Pi$ and $X^3\Pi$ states result from photodetachment of an electron from a $2p\pi$ bonding orbital, transitions to the two states should have similar vibrational progressions and β values. This is what is observed and we can safely assign the peaks at 3.410, 3.628 and 3.811 eV bands to the 0–1, 0–0 and 1–0 transitions to the $b^1\Pi$ state. The slightly larger β value of the peak at 3.410 eV in comparison to the two other bands assigned to the $b^1\Pi$ state is due to a small contribution from the overlapping 1–0 transition to the $a^1\Sigma^+$ state, which should appear at 3.401 eV ($\Delta G_{1/2} = 0.208\text{ eV}$) [9]. The feature at 4.380 eV (A), corresponding to a term

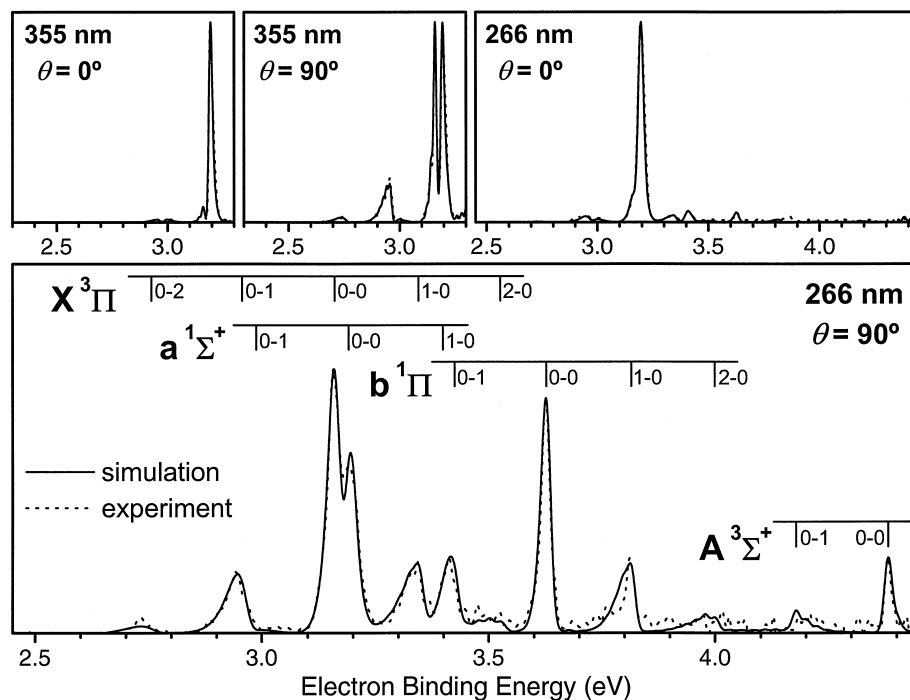


Fig. 2. Experimental (dashed) and simulated (solid) photoelectron spectra of BN^- . Peak assignments are indicated on the bottom spectrum.

Table 1
Results of the Franck–Condon analysis of the BN^- anion photoelectron spectra

State	T_{vib} (K)	EA (eV)	T_0 (eV)	ω_e (cm^{-1})	$\omega_e \chi_e$ (cm^{-1})	r_e (\AA)
$X^2\Sigma^+$	4000 ± 500	-	-	1660 ± 40	12 ± 4	1.284 ± 0.005
$X^3\Pi$	-	3.160 ± 0.005	0	(1515)	(12)	(1.325)
$a^1\Sigma^+$	-	-	0.031 ± 0.004	(1701)	(10)	1.274 ± 0.005
$b^1\Pi$	-	-	0.468 ± 0.004	(1533)	(11)	1.330 ± 0.005
$A^3\Sigma^+$	-	-	1.221 ± 0.006	(1827)	(14)	1.233^a

^aInsufficient experimental data available for a reliable error bar estimate.

Values in parentheses were taken from previous studies and not further optimized [2,9].

value $T_0 = 1.220$ eV, is assigned to the origin of the $A^3\Sigma^+$ state; this is close to the matrix value of 1.231 eV for this state [9].

To obtain more accurate spectroscopic constants, we have performed a Franck–Condon analysis of the anion photoelectron spectra of BN^- . Morse potentials, defined by a term energy T_0 , equilibrium distance r_e , vibrational frequency ω_e and anharmonicity $\omega_e \chi_e$, were employed for all electronic states. The population of the vibrational levels of the electronic ground state of the anion was assumed to be described by a Boltzmann distribution characterized by a vibrational temperature T_{vib} . Except for the relative transition intensities, identical parameters were used in the simulation of all four spectra. The vibrational constants of the neutral states were taken from the previous experimental studies [2,9]. Since a Franck–Condon analysis only allows the determination of changes in bond lengths, an experimental value is needed in order to determine absolute bond lengths. Analysis of the rotationally resolved emission spectrum of Bredohl et al. [5] yielded $r_0 = 1.329$ Å for the neutral $X^3\Pi$ state. From this value, the best estimate for r_e is 1.325 ± 0.002 Å [8,11], and this value was used to determine all other bond lengths. The simulated spectra are shown in Fig. 2 together with the experimental data; the peak assignments discussed above are also given in Fig. 2. The agreement between experiment and simulation is very good, confirming all the assignments. The simulation parameters are listed in Table 1.

4. Discussion

The electron affinity (EA) of BN is determined to be 3.160 ± 0.005 eV. This value lies within the error

bars of the only previous experimental value of 2.9 ± 0.3 eV, but is considerably more precise [13]. Our EA is also in good agreement with the multireference configuration interaction calculations of Mawhinney et al. [14] (EA = 2.84 eV), in particular if one considers their best estimate of 3.1 eV, which includes an estimate of the theoretical error. The bond dissociation energy (D_0) of BN^- ($X^2\Sigma^+$), which dissociates into B^- (3P_g) + N (4S_u), can be determined from the dissociation energy of BN ($X^3\Pi$) and the electron affinities of BN and B according to $D_0(\text{BN}^-) = D_0(\text{BN}) + \text{EA}(\text{BN}) - \text{EA}(\text{B})$. The electron affinity of atomic boron is 279.723 ± 0.025 meV [21]. The dissociation energy of BN ($X^3\Pi$) is not exactly known. Estimates based on the extrapolation of spectroscopic data yield $D_e(X^3\Pi) = 4.0 \pm 0.5$ eV [22]. The best estimate based on internally contracted multireference configuration interaction (ICMCI) calculations is $D_0(X^3\Pi) = 4.50 \pm 0.07$ eV [8]. Using the latter value and our EA of BN gives a best estimate for the dissociation energy for BN^- of $D_0(X^2\Sigma^+) = 7.38 \pm 0.08$ eV.

Our measurements represent the first experimental determination of the vibrational constants and bond length for the BN^- anion. These are $\omega_e = 1660 \pm 40$ cm^{-1} , $\omega_e \chi_e = 12 \pm 4$ cm^{-1} , and $r_e = 1.284 \pm 0.005$ Å, in good agreement with the theoretical predictions ($\omega_e = 1709$ cm^{-1} , $\omega_e \chi_e = 14.5$ cm^{-1} , and $r_e = 1.288$ Å) [14]. The optimized vibrational temperature is 4000 K, indicating formation of very hot ions and inefficient vibrational cooling in the source. However, the observed hot- and sequence-bands enable us to determine the vibrational constants of the anion with higher accuracy than if the ions were vibrationally colder. The sequence bands are also the source for minor deviations between stated peak

positions and the optimized spectroscopic constants listed in Table 1.

For the neutral we have, for the first time, experimentally identified the ground state of BN in the gas phase. Not surprisingly, the ordering of the lower lying electronic states of BN in the gas phase is found to be the same as in a rare gas matrix [9]. Our observation of the $X^3\Pi$ and a $^1\Sigma^+$ states in a single spectrum, however, yields a more direct and accurate splitting between these states, even though the energy resolution of our photoelectron spectrometer is roughly two orders of magnitude lower than that achieved in typical optical spectrometers used in emission studies. The a $^1\Sigma^+$ term energy $T_0 = 0.031 \pm 0.004$ eV lies within the error bars of the matrix experiment ($T_0 = 0.013\text{--}0.034$ eV). We find two higher-lying excited states with T_0 (b $^1\Pi$) = 0.468 ± 0.004 eV and T_0 ($A^3\Sigma^+$) = 1.221 ± 0.006 eV. For

T_0 ($A^3\Sigma^+$) a discrepancy larger than the combined error bars between the gas-phase and matrix experiment (1.231 ± 0.001 eV) is observed. This is attributed to the more diffuse nature of this electronic state and thus stronger repulsive interaction with the surrounding matrix, resulting in a blue shift of the higher term values in the matrix. The bond distances determined for the a $^1\Sigma^+$ and b $^1\Pi$ states are $r_e = 1.274 \pm 0.005$ Å and $r_e = 1.330 \pm 0.005$ Å respectively.

The term energies and bond lengths determined in the present study are listed together with the results of recent experimental and theoretical studies in Table 2. We choose to list T_e instead of T_0 values, in order to compare them to the predictions of various theoretical models, which can determine T_e with greater precision. The corrected ICMCI term energies and bond distances [8,12] agree best with

Table 2
Comparison of excited state term energies (T_e) and bond lengths (r_e) of diatomic BN

	Reference	T_e (eV)	r_e (Å)
$a^1\Sigma^+$ ($2s\sigma^2 2p\sigma^0 2p\pi^4$)			
Experiment	This work	0.019 ^a	1.274 ± 0.005
	matrix ^b	0.013 ± 0.011	-
Theory	gas phase ^c	-	1.283
	MRDCI ^d	0.03 ± 0.02^e	1.283
	QCISD(T) ^f	0.012 ^e	1.280 ^e
	ACPF ^g	0.047 ± 0.013^e	1.280 ^e
	CMRCI ^h	0.024 ± 0.013^e	1.275 ± 0.002^e
	CMRCI ⁱ	0.022 ± 0.014^e	1.277
$b^1\Pi$ ($2s\sigma^2 2p\sigma^1 2p\pi^3$)			
Experiment	This work	0.467 ^a	1.330 ± 0.005
	matrix ^b	0.464 ± 0.011	-
Theory	gas phase ^c	-	1.331
	MRDCI ^d	0.45	1.341
	CMRCI ⁱ	0.473 ^e	1.341
$A^3\Sigma^+$ ($2s\sigma^1 2p\sigma^1 2p\pi^4$)			
Experiment	This work	1.202 ^a	-
	matrix ^b	1.212 ± 0.001	-
Theory	CMRCI ⁱ	1.270	1.255

^a T_e values determined from T_0 values ($\pm 4\text{--}6$ meV) using vibrational constants listed in Table 1.

^bRef. [9].

^cRef. [6]. The data tabulated corresponds to r_0 .

^dRef. [14].

^eBest estimate.

^fRef. [11].

^gRef. [7].

^hRef. [8].

ⁱRef. [12].

our experimental values. Note, however, that the inclusion of the estimated error in all calculations is essential for achieving good agreement with experiment. The averaged coupled-pair functional (ACPF) study [7] overestimates $T_e(a^1\Sigma^+)$ considerably.

Comparing the current results to those for the isoelectronic C_2^-/C_2 system one finds expected similarities. Both the vibrational frequencies and the bond lengths of the ground state anions are intermediate between the values for the ground and first excited states of the neutral [23,24]. Just like C_2^- , BN^- is predicted to have at least one stable excited state ($A^2\Pi$) [14]. It is calculated roughly 0.8 eV above the anion ground state with a lifetime in the microsecond range. No evidence for an excited state of the anion is found in our spectra, in contrast to the anion photoelectron spectra of C_2^- [23,24], where detachment from the anion excited state is observed. We believe this is due to insufficient population of the $A^2\Pi$ excited state of BN^- , because it is predicted to lie significantly higher in energy than the $A^2\Pi_u$ state of C_2^- ($T_e = 0.494$ eV) [25].

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