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# High-lying Rydberg states of vinyl bromide studied by two-photon resonant ionization spectroscopy

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**Abstract**

High-lying Rydberg states of vinyl bromide at 70 000–79 500 $\mathrm{cm}^{-1}$ have been investigated using 2 + 1 resonance-enhanced multiphoton ionization (REMPI) spectroscopy. Seven Rydberg series, including one s, three p, two d, and one f, have been identified from fitting the term values of observed electronic states to Rydberg formula rendering the ionization energy of $79194 \pm 17$ $\mathrm{cm}^{-1}$ ($9.819 \pm 0.002$ eV). All of the seven series converge to the same ionization-energy limit, corresponding to the ground state of vinyl bromide cation. The adiabatic ionization energy of vinyl bromide determined from this study is in excellent agreement with the values reported recently by other methods.

## 1. Introduction

Spectroscopic investigations of the excited electronic states and potential energy surfaces of polyatomic molecules are of fundamental importance to study molecular photochemical reactions. The spectroscopic [1–12] and dissociation dynamical [13–18] studies of vinyl bromide ($C_2H_3Br$, abbreviated as VB hereafter) have been extensively studied in the past decades. Following our previous investigations of vinyl chloride ($C_2H_3Cl$) ranging from its first excited electronic state to the first ionization energy (IE) [19–21], we are now extending the spectroscopic study to VB, an analogue to vinyl chloride with a halogen substitution.

In an early spectroscopic study, Chadwick et al. [1] used photoelectron spectroscopy (PES) to obtain the spectra of VB, 1,2-dibromoethylene, and 2-bromopropene, from which the interaction between lone-pair electrons located at the Br atom and π-bonding electrons was studied. Mines and Thompson [2] also applied PES in the range of 6–21 eV to determine the IEs of vinyl halides and allyl halides. Schander and Russell [3] reported the vacuum ultraviolet (VUV) absorption spectrum of VB at 110–210 nm, and identified two Rydberg series, $\pi \rightarrow n\mathrm{s}$ and $\pi \rightarrow n\mathrm{p}$, convergent to the first IE of 79 860 $\mathrm{cm}^{-1}$. In the same work, they also assigned three Rydberg series, $n \rightarrow n\mathrm{s}$, $n \rightarrow n\mathrm{p}$, and $n \rightarrow n\mathrm{d}$, with the same convergence limit to the second IE of 87 880 $\mathrm{cm}^{-1}$. Later, Sze et al. [4] obtained valence-shell electron energy lost (VSEEL) spectra of monohaloethylenes, in which s, p, and d Rydberg states were tentative assigned.

Recently, Hoxha et al. [5,6] applied synchrotron radiation to observe the VUV absorption spectrum of VB, and identified three Rydberg series, $2a'' \rightarrow n\mathrm{s}$, $2a'' \rightarrow n\mathrm{p}$, and $2a'' \rightarrow n\mathrm{d}$, convergent to the first IE of 9.804 eV. Spectroscopic analysis for the transitions with excitation energies at 5.0–12.0 eV revealed that the electronic transitions involve the excitations of valence to virtual valence states and Rydberg series. Lee and Kim [7] reported a very accurate IE = $9.8171 \pm 0.0006$ eV ($79180 \pm 5$ $\mathrm{cm}^{-1}$) of VB by one-photon VUV mass

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analysis threshold ionization (MATI) spectroscopy, and assigned most of the observed vibronic transitions to the cationic ground state based on calculated vibrational frequencies and Franck–Condon factors. Qian et al. [8] employed high-resolution pulsed field ionization-photoelectron (PFI-PE) and threshold photoelectron (TPE) spectroscopies to measure the first IE of 9.8200 ± 0.0015 eV (79 204 ± 12 $\text{cm}^{-1}$) and second IE of 10.9156 ± 0.0010 eV (88 040 ± 8 $\text{cm}^{-1}$) in VB. In the same study, members of four Rydberg series ($7a' \rightarrow n$s, $7a' \rightarrow n$d, and two $7a' \rightarrow n$p) convergent to the second IE were observed. Other spectroscopic studies of VB also include the measurements of vibrational and rotational features in the infrared and microwave spectral regions [9–11].

In the present work, we have focused on the study of the high-lying Rydberg states of VB at 70 000–79 500 $\text{cm}^{-1}$ by 2 + 1 REMPI spectroscopy. From the observed 2 + 1 REMPI spectrum of VB, we have been able to identify seven Rydberg series, and to determine the first IE to be 79 194 ± 17 $\text{cm}^{-1}$, in excellent agreement with the recently reported values of 79 180 ± 5 $\text{cm}^{-1}$ by MATI spectroscopy [7] and 79 204 ± 12 $\text{cm}^{-1}$ by PFI-PE spectroscopy [8].

## 2. Experimental

The experimental details for obtaining 2 + 1 REMPI molecular spectra in our laboratory have been described in several earlier publications [22–25]. Briefly, VB (Aldrich, 98%) of 60 Torr partial pressure was seeded in 2 atm helium to form a mixture, which was then expanded into a vacuum chamber through a pulsed valve. A focused laser beam was led to cross the molecular beam and to ionize VB. The VB ions, repelled by an electric field, moved across a field-free time-of-flight (TOF) mass spectrometer and were finally detected by a microsphere plate. An optogalvanic hollow-cathode lamp filled with Ne was employed simultaneously in the spectral scan to calibrate the laser frequency.

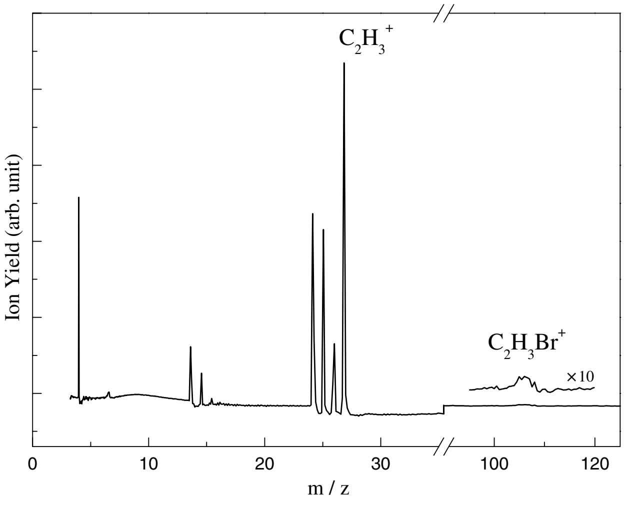

Fig. 1. Time-of-flight mass spectrum of vinyl bromide excited at 292.5 nm by two-photon resonant ionization.

A typical TOF mass spectrum of VB via 2 + 1 REMPI is shown in Fig. 1. Based on a similar experience in our previous study of vinyl chloride [19,20], the signal of $m/z = 27$ ($C_2H_3^+$), the strongest one in the observation (Fig. 1), was monitored as a function of laser frequency due to the weak parent ion ($C_2H_3Br^+$) signal. Care was taken to ensure that the 2 + 1 REMPI spectra are identical by monitoring either the fragmentary $C_2H_3^+$ or the parent ion $C_2H_3Br^+$.

## 3. Results and discussion

The 2 + 1 REMPI spectrum of VB at 70 000–79 500 $\text{cm}^{-1}$ is shown in the lower trace of Fig. 2. The sharp edge at ~78 750 $\text{cm}^{-1}$ marks the onset of ionization continuum of VB. The adiabatic IE = 79 180 $\text{cm}^{-1}$ of VB determined by MATI spectroscopy [7] is marked by an arrow. The upper trace in Fig. 2 from 70 000 to 78 750 $\text{cm}^{-1}$ has been magnified five times with respect to the lower one for clearer visualization of the spectral features. The well-resolved peaks with their transition frequencies and relative intensities are tabulated in Table 1.

In identifying the Rydberg series of VB, we have taken the previous REMPI spectroscopic analysis of vinyl chloride for comparison [19–21]. The Br atom could cause large quantum defects owing to its effective hindrance to Rydberg electrons when they travel close to the molecular core of VB. More congested spectral features might also be expected because of a possibly higher density of quantum states due to the heavier Br atom. Observed transitions from the 2 + 1 REMPI spectrum are analyzed using the Rydberg formula [26]

$$v = \mathrm{IE} - R/(n - \delta^2),$$

where $v$ is transition frequency, IE is ionization energy, $R = 109736.7526$ $\text{cm}^{-1}$ is the Rydberg constant taking the mass of VB into account, $n$ is a principal quantum number, and $\delta$ is the corresponding quantum defect. The value of $n$–$\delta$ can also be denoted as an effective quantum number of $n^*$, which represents quite distinctively for different Rydberg orbitals.

In the present study, we have been able to identify seven Rydberg series of VB (Table 1) from the observed REMPI spectrum as due to the promotion of a π-electron to the s, p, d, and f Rydberg states. A series of transitions with regular and strong peak intensities have been fitted into the Rydberg formula. Fig. 3 shows the best fit of this series to the Rydberg formula rendering IE = 79 195 ± 14 $\text{cm}^{-1}$. This series has been assigned as

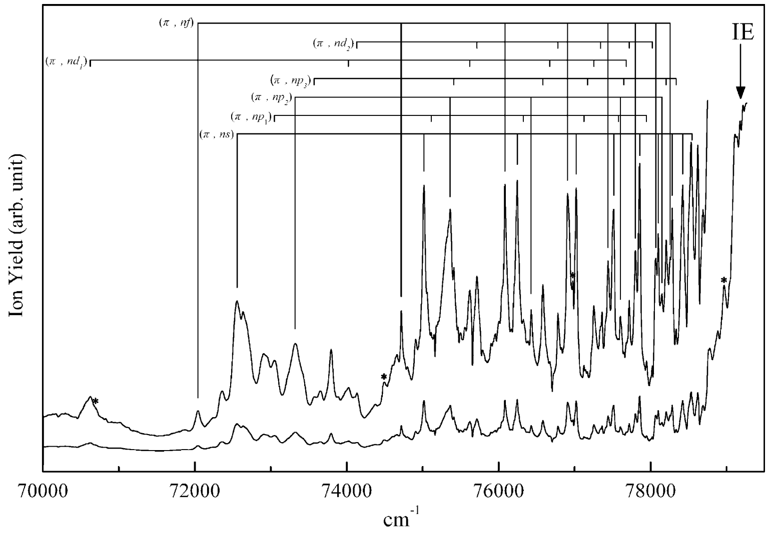

Fig. 2. 2 + 1 REMPI spectra and spectroscopic labelings for the transitions as due to the promotion of a π-electron to the s, p, d, and f Rydberg series of vinyl bromide at 70000–79500 cm$^{-1}$. The upper trace has been magnified five times with respect to the lower one.

Table 1
Peak positions ($\nu$), effective quantum numbers ($n^*$), ionization energies (IE) for the identified Rydberg series of vinyl bromide at 70000–79500 cm$^{-1}$[a]

| | (π,*n*s) | | (π,*n*p$_1$) | | (π,*n*p$_2$) | | (π,*n*p$_3$) | | (π,*n*d$_1$) | | (π,*n*d$_2$) | | (π,*n*f) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $n^*$ | $\nu$ | $n^*$ | $\nu$ | $n^*$ | $\nu$ | $n^*$ | $\nu$ | $n^*$ | $\nu$ | $n^*$ | $\nu$ | $n^*$ | $\nu$ |
| | 2.124 | 54757[b] | | | | | 2.523 | 61830[c] | | | 2.852 | 65581[d] | | |
| | 2.090 | 54735[e] | | | | | 2.469 | 61862[f] | | | | | | |
| | 3.102 | 67670[b] | | | | | 3.438 | 69791[c] | 3.582 | 70624(m) | 3.934 | 71985[d] | 3.917 | 72041(m) |
| | 3.017 | 67801[e] | | | | | 3.438 | 70577[f] | | | | | | |
| | 4.065 | 72555(s) | 4.223 | 73051(m) | 4.327 | 73321(s) | 4.417 | 73572(m) | 4.614 | 74023(m) | 4.651 | 74134(m) | 4.953 | 74718(s) |
| | 4.093 | 72525[b] | | | | | 4.434 | 73493[c] | | | 4.839 | 74388[d] | | |
| | 4.040 | 73137[e] | | | | | 4.434 | 74278[f] | | | | | | |
| | 5.126 | 75018(s) | 5.178 | 75112(w) | 5.360 | 75362(s) | 5.384 | 75410(s) | 5.555 | 75621(s) | 5.605 | 75715(s) | 5.941 | 76083(s) |
| | 5.096 | 74848[b] | | | | | 5.330 | 75211[c] | | | 5.825 | 75840[d] | | |
| | 5.052 | 75560[e] | | | | | 5.392 | 76086[f] | | | | | | |
| | 6.100 | 76246(s) | 6.173 | 76325(w) | 6.312 | 76428(s) | 6.479 | 76582(s) | 6.617 | 76671(w) | 6.723 | 76780(s) | 6.932 | 76908(s) |
| | 6.148 | 76171[b] | | | | | 6.572 | 76534[c] | | | 6.931 | 76784[d] | | |
| | 6.053 | 76865[e] | | | | | 6.425 | 77202[f] | | | | | | |
| | 7.106 | 77022(s) | 7.226 | 77123(w) | | | 7.360 | 77170(w) | 7.552 | 77253(s) | 7.667 | 77341(m) | 7.912 | 77439(s) |
| | | | | | | | 7.452 | 77099[c] | | | 7.882 | 77308[d] | | |
| | | | | | | | 7.481 | 77899[f] | | | | | | |
| | 8.080 | 77514(s) | 8.210 | 77577(w) | 8.334 | 77602(m) | 8.420 | 77648(w) | 8.565 | 77681(w) | 8.588 | 77720(s) | 8.879 | 77800(s) |
| | 9.056 | 77857(s) | 9.329 | 77944(w) | | | | | | | 9.619 | 78022(w) | 9.876 | 78067(s) |
| | 10.015 | 78101(s) | | | 10.302 | 78148(m) | 10.523 | 78205(s) | | | | | 10.839 | 78258(s) |
| | 10.975 | 78284(s) | | | | | 11.303 | 78337(m) | | | | | | |
| | 11.923 | 78423(s) | | | | | | | | | | | | |
| | 12.973 | 78543(s) | | | | | | | | | | | | |
| IE | 79195 ± 14 | | 79205 ± 27 | | 79182 ± 19 | | 79196 ± 20 | | 79177 ± 25 | | 79208 ± 27 | | 79192 ± 13 | |

[a] $\nu$ and IE are in cm$^{-1}$. Average FWHM is ~30 cm$^{-1}$ for the observed transitions in this work. Relative intensities are indicated in parentheses with s (strong), m (medium), and w (weak).

[b] Rydberg series of 2a″ → *n*s taken from [6] with average FWHM ~100 cm$^{-1}$.

[c] Rydberg series of 2a″ → *n*p taken from [6].

[d] Rydberg series of 2a″ → *n*d taken from [6].

[e] Transition of π → *n*s taken from [3] with average FWHM ~250 m$^{-1}$.

[f] Transition of π → *n*p taken from [3].

(π, *n*s) based on the identified π → *n*s [3] and 2a″ → *n*s [6] in two earlier studies, which have also been listed in Table 1 for comparison.

For other Rydberg series of VB, there were several reports in previous studies. Schander and Russell [3] assigned π → *n*s and π → *n*p transitions convergent to the first IE with $\delta$ values of 2.97 and 2.57, respectively. In the same study, they also assigned n → *n*s ($\delta$ = 2.96), n → *n*p ($\delta$ = 2.55), and n → *n*d ($\delta$ = 2.11) series converging to the second IE. In addition, their Rydberg-formula

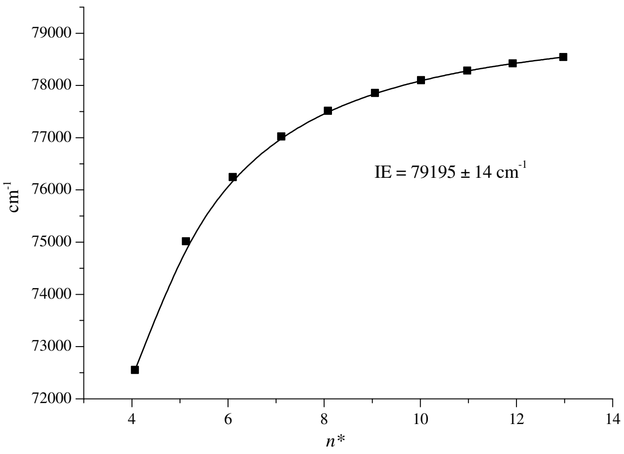

Fig. 3. The best fitting curve of the (π, *n*s) Rydberg series of vinyl bromide.

fittings for the transitions of bromomethanes and dibromoethylenes render the $\delta$ values between 2.0 and 3.0 for s and p Rydberg series [3,27,28]. Sze et al. [4] obtained the VSEEL spectrum of VB, in which Rydberg states of 5–10s (5–11s), 5–8p (5–7p), and 4d (4–6d) convergent to the first (second) IE were tentatively assigned. Based on their assignment, we have tried to fit their observed transitions to Rydberg formula and obtained the $\delta$ values of ~2.9 (~3.2), ~2.5 (~2.5), and ~1.4 (~1.1), respectively, for s, p, and d Rydberg orbitals convergent to the first (second) IE. Recently, Qian et al. [8] employed high-resolution PFI-PE and TPE spectroscopies to measure the first and second IE's of VB, and to identify one $7a' \rightarrow n$s ($\delta = 1.075$), two $7a' \rightarrow n$p ($\delta = 0.465$ and 0.816), and one $7a' \rightarrow n$d ($\delta = 0.235$) Rydberg series converging to the second IE. It is noted that their determined $\delta$ values for the Rydberg series of VB differ significantly from those reported earlier [3,4].

In the past, $\delta$ values were often used to identify the types of Rydberg states. For instance, typical $\delta$ values accompanying with the Rydberg series of a hydrocarbon molecule are ~1, ~0.5, ~0.3, and ⩽0.1 for s, p, d, and f orbitals, respectively [26,28]. To date, definite $\delta$ values for the Rydberg series of VB, however, are still lacking. Inconsistency in the $\delta$ values of VB from different reports [3,4,8] is evidenced as discussed above. While the determination of $\delta$ values requires a definitive assignment for the $n$ quanta, an effective quantum number $n^*$, on the other hand, can be obtained quite straightforwardly from a Rydberg-formula fitting. In general, definite identifications of $n$ and $\delta$ in a Rydberg series can be facilitated with an unambiguous assignment starting from the low-lying members in the Rydberg series, either from spectroscopic assignment or with the aid of theoretical calculations, e.g. our previous study of vinyl chloride [19–21].

Since the information about the lowest-lying member in each Rydberg series of VB is so far scarce, we will only determine the corresponding $n^*$ values for the observed Rydberg states in this study. The type of Rydberg series, nevertheless, can still be figured out from the decimal of $n^*$. For instance, when the Rydberg states have the decimals of $n^*$ to be ~0.1, 0.2–0.5, 0.5–0.8, and ~0.9, they correspond, respectively, to s, p, d, and f Rydberg series [6]. In the following analyses for the p, d, and f series of VB, the decimal of $n^*$ will be used as a guideline for spectral assignments.

Three Rydberg series from our REMPI observation have been assigned to $\pi \rightarrow n$p transitions, denoted as $(\pi, n\mathrm{p}_1)$, $(\pi, n\mathrm{p}_2)$, and $(\pi, n\mathrm{p}_3)$, with IE = 79 205 ± 27, 79 182 ± 19, and 79 196 ± 20 $\mathrm{cm}^{-1}$, respectively. The observed transitions for the $(\pi, n\mathrm{p}_1)$ series are either congested with other bands and located at peak shoulders or showing up with weak intensities. Transitions in the $(\pi, n\mathrm{p}_2)$ series, on the other hand, are of medium to strong spectral intensities as shown in Fig. 2, although peaks corresponding to $n^* \sim 7.3$ and 9.3 were not observed. Peaks belonging to the $(\pi, n\mathrm{p}_3)$ series are relatively weak at $n^* = 7.360$ and 8.420, but have medium to strong intensities elsewhere. Except the $(\pi, n\mathrm{p}_3)$ series, which has been reported before [3,6], both $(\pi, n\mathrm{p}_1)$ and $(\pi, n\mathrm{p}_2)$ are identified for the first time.

As listed in Table 1, Rydberg series with IE = 79 177 ± 25 and 79 208 ± 27 $\mathrm{cm}^{-1}$ are, respectively, assigned to $(\pi, n\mathrm{d}_1)$ and $(\pi, n\mathrm{d}_2)$. The $(\pi, n\mathrm{d}_2)$ series has also been reported before by Hoxha et al. [6] and is listed in Table 1 for comparison. Comparing to the strong (π, *n*s) series, transitions in the (π, *n*d) series appear fewer in number. Peak intensities in the two (π, *n*d) series are widely distributed from strong to weak, and fluctuate along the series.

In the $\pi \rightarrow n$f transitions of VB, a long series with sharp peaks and strong spectral intensities has been observed to converge to 79 192 ± 13 $\mathrm{cm}^{-1}$. This series is a newly discovered one, whose peak positions appear near the (π, *n*s) series. Two factors have brought us to assign this series as (π, *n*f). First, based on the decimal of $n^*$ close to 1, it is legitimate to assign the concerned series as (π, *n*f). Second, in view of the transitions to *f* Rydberg states of vinyl chloride [18,19], ethylene [29], and chloroethylenes [30], narrow lineshapes with strong peak intensities are common features in all of these observations. Moreover, because the relatively higher-lying f orbitals could have less perturbations from valence states, the long (π, *n*f) series can be expected to provide more accurate IE values. Indeed, IE = 79 192 ± 13 $\mathrm{cm}^{-1}$ resulting from the Rydberg-formula fit of the (π, *n*f) series is very close to IE = 79 195 ± 14 $\mathrm{cm}^{-1}$ obtained from another long (π, *n*s) series and both consist with the recently reported values by MATI [7] and PFI-PE [8] spectroscopies.

Due to the better spectral resolution of laser-assisted REMPI technique and the narrower population distribution of jet-cooled molecules in the present work, detailed features in the congested spectrum of VB can be discerned. The much better spectral resolution in this work (FWHM ~30 $cm^{-1}$ for the observed REMPI peaks), comparing to those in some earlier observations (FWHM's of ~250 and ~100 $cm^{-1}$ in the VUV absorption spectra by Schander and Russell [3] and Hoxha et al. [6], respectively), has allowed us to identify four new Rydberg series, ($\pi$,$n$p$_1$), ($\pi$,$n$p$_2$), ($\pi$,$n$d$_1$), and ($\pi$,$n$f). In an early study of $\pi \rightarrow n$s and $\pi \rightarrow n$p by Schander and Russell [3], the series converge to IE = 79 860 $cm^{-1}$ which is ~700 $cm^{-1}$ away from the accurate values determined recently [7,8]. Nevertheless, based on similar transition frequencies, these two series of $\pi \rightarrow n$s and $\pi \rightarrow n$p [3] should correspond, respectively, to ($\pi$,$n$s) and ($\pi$,$n$p$_3$) of this work. In the study by Hoxha et al. [6], three series of VB, 2a″ → $n$s, 2a″ → $n$p, and 2a″ → $n$d, were identified. In their assignment, IE = 9.804 eV determined from their PES data (~120 $cm^{-1}$ away from the recently measured IEs [7,8]) was used in the Rydberg-formula fit of their observed transitions. The 2a″ → $n$s, 2a″ → $n$p, and 2a″ → $n$d series [6] should also correspond, respectively, to the ($\pi$,$n$s), ($\pi$,$n$p$_3$), and ($\pi$,$n$d$_2$) series of this work.

Most of the features observed in our 2 + 1 REMPI spectrum have been assigned to the Rydberg states converging to the first IE. However, some unassigned transitions are still remained in Fig. 2. These unassigned transitions might belong to either some other unidentified Rydberg series convergent to the first IE or the Rydberg series with convergence limit to the second or higher IE. For example, several peaks marked with asterisks in our 2 + 1 REMPI spectrum (Fig. 2) are found close/coincident with the transitions convergent to the second IE observed by Hoxha et al. [6], e.g. the REMPI peak at 70 708 $cm^{-1}$ possibly corresponding to the assigned 7a′ → 5p$_\perp$ transition at 70 824 $cm^{-1}$ in [6], and peaks at 74 500, 76 980, and 78 971 $cm^{-1}$ to the 7a′ → 5d, 7a′ → 6s, and 7a′ → 6p$_\perp$ transitions, respectively. In our measurements, we have not been able to obtain the transitions higher than the first IE, which however are crucial for the assignment of such Rydberg series convergent to the second or higher IE. In summary, the seven identified Rydberg series observed in this study fit very well to the Rydberg formula. We have taken the average IE value of the seven series to be 79 194 ± 17 $cm^{-1}$ (9.819 ± 0.002 eV) as the adiabatic IE, which is in excellent agreement with the values obtained previously from various methods [1,2,4,5,7,8,12].

## 4. Conclusion

Using 2 + 1 REMPI spectroscopy, we have observed seven Rydberg series of VB at 70 000–79 500 $cm^{-1}$, which have been assigned as due to the promotion of a $\pi$-electron to the s, p, d, and f Rydberg orbitals. Among the seven Rydberg series, four of them are analyzed for the first time. The adiabatic IE of VB determined to be 79 194 ± 17 $cm^{-1}$ (9.819 ± 0.002 eV) is in excellent agreement with the recently reported values by MATI and PFI-PE spectroscopies.

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