Journal of Quantitative Spectroscopy & Radiative Transfer 148 (2014) 13–17

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy & Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Journal of
Quantitative
Spectroscopy &
Radiative
Transfer

Extended analysis of the $B^2\Sigma^+$–$X^2\Sigma^+$ and $A^2\Pi$–$X^2\Sigma^+$ systems of ZrN

Soumen Bhattacharyya [a], Sheo Mukund [a,b],
Suresh Yarlagadda [b], S.G. Nakhate [a,b,*]

[a] Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[b] Homi Bhabha National Institute, Bhabha Atomic Research Centre, Mumbai 400 085, India

ARTICLE INFO

Article history:
Received 10 February 2014
Received in revised form
14 June 2014
Accepted 16 June 2014
Available online 23 June 2014

Keywords:
ZrN
Electronic spectra
Jet-cooled molecular beam
LIF spectroscopy
Rotational
Vibrational constants

ABSTRACT

Rotationally resolved spectra of (1,0), (1,1), (2,0), (2,1) and (2,3) bands of $B^2\Sigma^+$–$X^2\Sigma^+$ and (3,3) band of $A^2\Pi$–$X^2\Sigma^+$ systems have been measured in a laser-induced fluorescence spectra of jet cooled ZrN molecule. Rotational analysis have been extended to include the levels $v=3$ of $X^2\Sigma^+$, $v=1,2$ of $B^2\Sigma^+$ and $v=3$ of $A^2\Pi$ states. The vibrational constants of the $X^2\Sigma^+$ state have been determined. Perturbations were observed in all the rotational branches of the B–X system and $A^2\Pi_{1/2f}$–$X^2\Sigma^+$ subband.

1. Introduction

Using conventional emission spectroscopy, Bates and Dunn [1] first recorded the spectra of ZrN molecule, the (0,0) band of $B^2\Sigma^+$–$X^2\Sigma^+$ system in violet and (0,0), (1,1), and (2,2) bands of $A^2\Pi$–$X^2\Sigma^+$ system in yellow spectral range. They determined the molecular constants for $v=0$ of $X^2\Sigma^+$ and $B^2\Sigma^+$ and $v=0$–2 of $A^2\Pi$ states. In the yellow system, they reported severe perturbations in $A^2\Pi_{3/2}$–$X^2\Sigma^+$ subband and their spectral analysis in the violet system was hampered by limited observations, especially absence of low-J rotational lines. Bates and Gruen [2] confirmed the $X^2\Sigma^+$ as the ground state of ZrN by matrix isolation spectroscopy. Later, Cheung and co-workers revisited the yellow and violet band systems of ZrN [3–9] using laser-induced fluorescence (LIF) spectroscopy. They studied the previously observed (0,0), (1,1), and (2,2) bands [4,5,7] of $A^2\Pi$–$X^2\Sigma^+$ system for the various isotopomer of ZrN and determined the magnetic hyperfine structure of the $X^2\Sigma^+$ state of ^{91}ZrN [3,9]. Recently, Moskvitina and Kuzyako [10] investigated A–X system. More recently, Farhat et al. [11] computed the potential energy curves for 21 low-lying electronic states of the ZrN molecule.

The motivation for this work was to extend the analysis of the $B^2\Sigma^+$–$X^2\Sigma^+$ and $A^2\Pi$–$X^2\Sigma^+$ systems to higher vibrational levels. Because this molecule is of astrophysical interest, it is important to gather as much spectroscopic information as possible for a meaningful search of its existence in the stellar atmosphere.

2. Experiment

The ZrN molecules were produced in a pulsed free-jet apparatus, which was discussed in detail in our previous publication [12]. In brief, a rotating and translating zirconium metal rod was ablated with the third harmonic beam

---

[*] Corresponding author at: Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India.
Tel.: +91 22 25592362; fax: +91 22 25505151.
E-mail address: nakhate@barc.gov.in (S.G. Nakhate).

http://dx.doi.org/10.1016/j.jqsrt.2014.06.009
0022-4073/

(354.7 nm, ~10–15 mJ/pulse) of a Nd:YAG laser (Quanta System, SYL 203) focused to an ~1 mm^2 spot. The laser produced Zr metal plasma reacted with 2% ammonia seeded in helium gas emerging from a pulse valve under a backing pressure of 275 kPa. The products of the reaction were expanded into vacuum, cooling the internal degrees of freedom of the molecules and were probed at right angle to the supersonic expansion axis about 50 mm downstream the nozzle by a XeCl excimer (Coherent, CompexPro 201) pumped pulse dye laser (Coherent, ScanmatePro). The resulting laser-induced fluorescence was imaged on an entrance slit of a monochromator (Spex, 270M) equipped with a Peltier cooled photomultiplier tube (Hamamatsu, R943-02). An output signal from the photomultiplier was amplified by a 1 GHz bandwidth amplifier (Femto Messtechnik, DUPVA-1-60), integrated by a gated integrator (Stanford Research System, SR250), and stored on a computer. Excitation spectra were obtained by scanning the pulsed dye laser and recording the laser-induced fluorescence through the monochromator set at fixed wavelength corresponding to the strongest fluorescence terminating either to a ground or an excited state. Here monochromator was used as a broad band filter by setting width of the entrance and exit slits to 2.24 mm. The excitation spectra were obtained with a typical resolution of 0.08 cm^{-1}. Transition wavenumbers were calibrated by using laser wavelength calibration facility of the dye laser utilizing neon optogalvanic spectral lines as well as by known atomic lines of Zr I [13] appeared in the spectra with an absolute precision of ~0.1 cm^{-1}. The dispersed fluorescence (DF) spectra were recorded by scanning the monochromator. Lifetimes of the excited electronic states were recorded by acquiring the fluorescence decay curve on a 200 MHz digital storage oscilloscope (Tektronics, TDS 2024) having sampling rate of 2 Giga-samples/s and rise time < 2 ns. The decay curve was averaged for 128 shots in order to obtain a good signal to noise ratio.

3. Data analysis and results

3.1. $B^2\Sigma^+$–$X^2\Sigma^+$ system

Naturally abundant ammonia and zirconium was used in this study. Naturally abundant Zr has five isotopes, ^{90}Zr (51.45%), ^{91}Zr (11.23%), ^{92}Zr (17.11%), ^{94}Zr (17.40%) and ^{96}Zr (2.80%). The spectral resolution employed in the present study does not permit to observe isolated rotational branches for each ZrN isotopic molecule. However, simulating *B*–*X* (0,0) band with the data from Ref. [8] with a resolution ~0.1 cm^{-1}, we could infer that the peaks corresponding to P_1 and P_2 branches of the main isotope ^{90}ZrN gets only slightly blended by P_2 of other two ^{92}ZrN and ^{94}ZrN isotopes. The rotational branches of ^{91}ZrN and ^{96}ZrN are expected to be weak because of their lower natural abundance. This simulated spectra of ZrN isotopic molecule in a given rotation *N* is in line with our experimental observations and in this work we report the spectral analysis of ^{90}Zr^{14}N molecule. First, Bates and Dunn [1] and later Chen et al. [8] observed and analyzed *B*–*X* (0,0) band. Bates and Dunn reported that their analysis was hampered by the absence of low-*J* rotational lines and perturbations maximized at $N=44$ caused by an interacting excited vibrational level of $A^2\Pi$ substate. Chen et al. determined the rotational constants for three isotopic molecules ^{90}ZrN, ^{92}ZrN and ^{94}ZrN. They found that all the rotational branches were perturbed and made efforts to identify the perturbing state and concluded that further high-resolution studies were necessary for establishing the identity of the perturbing state unambiguously. They searched for the (1,0) band of this transition but did not find it and concluded a very unfavorable Franck–Condon factor as the reason. However, we observed (1,0), (1,1), (2,0), (2,1), (2,3) bands with considerable intensity and a weak (3,4) band. All the bands other than (3,4) were analyzed by simulating the spectra with the Pgopher program [14]. The rotational constants for $\nu'=1$, 2 of *B* state were determined by fitting to the effective Hamiltonian for $^2\Sigma^+$ state given in the Pgopher program [14]. In the (1,0) band, clear rotational lines of *N* up to 16 in the *P* and *N* up to 14 in the *R* branch were observed, where it forms band head in *R*. Similarly, in the (2,0) band, *P* branch lines could be followed up to $N=25$ and *R* branch forms band head at $N=12$. After turning, *R* branch rotational lines merged with lower *J* members and could not be clearly identified because of limited resolution. Even though, *P* branch lines could be observed for a few more *N* in the (1,0) band, they could not be identified for certainty with lower state combination differences because of band head formations in *R*. In the (1,0) band, a small local rotational perturbation was observed at $J'=13.5$ of F_1 component. The (2,0) band was found to be perturbed at $15.5 \le J \le 21.5$ in P_1- and at $12.5 \le J \le 17.5$ in P_2-branch.The rotational constants were determined for both bands by fitting the above mentioned lines of *P* and *R* branches and are listed in Table 1. The constants in Table 1 were derived by fitting 60 lines ($J=1.5$ to 16.5 in P_1, $J=1.5$ to 15.5 in P_2, $J=0.5$ to 14.5 in $R_1$and $J=0.5$ to 13.5 R_2) in (1,0) and 59 lines ($J=1.5$ to 14.5; 22.5–24.5 in P_1, $J=1.5$ to 11.5; 18.5–25.5 in P_2, $J=0.5$ to 11.5 in R_1 and $J=0.5$ to 9.5 in R_2) in the (2,0) band. The output from Pgopher program including lower state combination difference fit is given in the Supplementary information. The molecular constants for the $\nu''=0$ level of $X^2\Sigma^+$ state were fixed in the fit to the more accurate values from Cheung et al. [7]. The centrifugal distortion constant D_ν could not determined in the present work because of its small magnitude and observations limited to low rotational levels populated in the jet-cooled source. The spin-splitting in the *P* branches were not found to increase linearly with *N* because of rotational perturbations and thus γ_ν for the $B^2\Sigma^+$ state could only be estimated and not accurately determined.

The presence of severe perturbation in the rotational spectra of (0,0) band was reported by earlier workers [1,8]. Bates and Dunn [1] reported perturbations only at the excited levels of F_2 component at high *N*, maximum at $N=44$. They suggested an excited vibrational state of $A^2\Pi$ as the perturbing state. Later Chen et al. [8] reported perturbations at both the F_1 and F_2 component at different *J* values. From the shift of perturbations occurring at different *J* values for different isotopes in F_1, while at the same *J* for F_2, they concluded that at least two perturbing states were involved and suggested $A^2\Pi$ or $^4\Sigma^-$ as possible perturbing state. In a recent ab initio calculation, Farhat