

Studies on the P-Branch Emission Spectral Lines in the $d^1\Sigma^+ - b^1\Sigma^+$ Electronic State Transition of NbN Molecule

Qi Wang,¹ Qunchao Fan,^{2,*} Weiguo Sun,^{2,3,†} and Hao Feng²

¹*School of Material Science and Engineering and Research Center for Advanced Computation, Xihua University, Chengdu, Sichuan 610039, People's Republic of China*

²*School of Physics and Chemistry and Research center for Advanced Computation, Xihua University, Chengdu, Sichuan 610039, People's Republic of China*

³*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, Sichuan 610065, People's Republic of China*

(Received May 8, 2011; Revised September 23, 2011)

Using a new analytical formula which was proposed for calculating the P -branch transitional spectra of a diatomic molecule in Sun's previous work, the correct values of the unknown emission spectral lines up to $J = 80$, which may not be available experimentally for the (0, 0), (2, 2) bands in the $d^1\Sigma^+ - b^1\Sigma^+$ electronic state transition of the NbN molecule, are obtained in this work. This study provides a correct method and important physical information for those who are working on the NbN molecular structure.

PACS numbers: 33.15.Mt, 34.50.Ez, 33.20.Wr

I. INTRODUCTION

The transition spectral lines, particularly the high-lying data, are very important for researching molecular structures and molecular properties [1–5]. In recent years, there are many experimental techniques used to study the molecular transition spectra, such as laser induced fluorescence (LIF) [6], Fourier transform spectrometer (FTS) [7, 8], and optical heterodyne and magnetic rotation enhanced velocity modulation spectroscopy (OH-MR-VMS) [9]. Although a large number of spectral lines and/or rovibrational energies are observed by using the above modern experimental methods for a given band of some molecular electronic states [6–9], there are many cases where the spectral data are not available for high-lying rotational states. Some progress has been made in theoretical studies [10–14], but studies which can accurately predict the high-lying transition spectral lines are few.

The intensity of the spectra is also a very important physical quantity. The transition probabilities and the source temperature can be determined by measurements of the absolute intensity or relative intensity of the spectra, and the absolute intensity of the spectra can be obtained quantum mechanically or experimentally [15]. As long as the wave function (ψ) is good enough, the transition probability of a spectral line can be calculated

*Electronic address: fanqunchao@sina.com

†Electronic address: swg@mail.xhu.edu.cn

theoretically, which gives the theoretical value of the intensity of the spectra. It is necessary to have an absolute calibration for measuring the absolute intensity of emission spectra experimentally. Usually, a standard light source for a known light intensity will be compared with test ones for measuring. At the same time, the resolution of the spectrometer, the reflection and absorption of the instruments caused by energy loss, the absolute sensitivity of the detector, and other relevant parameters should be corrected experimentally.

The NbN molecule belongs to the typical B-1 compounds, with a crystal structure of sodium chloride, its molecular properties and structure have been extensively studied using various experimental techniques [16–24]. The electronic spectra of NbN were first observed by Dunn and Rao in 1969 [16]. They observed a ${}^3\Phi - {}^3\Delta$ electronic state transition in the visible region and initially named it as $A^3\Phi - X^3\Delta$. This transition was later investigated by the Féménias group [17] and by the Azuma *et al.* group [18, 19]. In their works the laser excitation spectra of the $C^3\Pi - X^3\Delta$, $e^1\Pi - X^3\Delta_2$, and $f^1\Phi - a^1\Delta$ transitions were recorded, and the $X^3\Delta_2 - X^3\Delta_1$ and $X^3\Delta_3 - X^3\Delta_2$ intervals of 400.5 ± 0.1 and 490.5 ± 0.1 cm^{-1} were determined for the $X^3\Delta$ state of the NbN molecule. Although some other theoretical methods were presented to further study emission spectral lines for some transitional electronic states of the NbN molecule in recent years [20–24], accurate high-lying values are still few for each transition band.

In this paper, the P -branch emission spectral lines of the (0, 0), (2, 2) bands in the $d^1\Sigma^+ - b^1\Sigma^+$ electronic state transition for the NbN molecule are studied by using an analytical formula which was suggested in Sun's previous work [25]. The specific derivation of the analytical formula is described in Section II. The calculated results for the NbN molecule are discussed in Section III. Section IV summarizes this study.

II. THEORY AND METHOD

For a molecular electronic state, when an electron transits from a higher energy state ($'$) to a lower energy state ($''$), the first state-state energy difference can be expressed as [5]

$$\nu = \nu_e + \nu_v + \nu_r = (T'_e - T''_e) + (G' - G'') + (F' - F''). \quad (1)$$

The base line $\nu_0 = \nu_e + \nu_v = \left\{ (T'_e - T''_e) + (G' - G'') \right\}$ is a constant, starting from the classic expression [5]

$$\begin{aligned} \nu &= \nu_0 + F'(J') - F''(J'') \\ &= \nu_0 + B_{v'}J'(J'+1) - D_{v'}J'^2(J'+1)^2 + H_{v'}J'^3(J'+1)^3 + \dots \\ &\quad - [B_{v''}J''(J''+1) - D_{v''}J''^2(J''+1)^2 + H_{v''}J''^3(J''+1)^3 + \dots], \end{aligned} \quad (2)$$

where the rotational constants related to vibration can be expressed as [26]

$$B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) + \gamma_e \left(v + \frac{1}{2} \right)^2 - \sum_{i=3}^7 \eta_{ei} \left(v + \frac{1}{2} \right)^i, \quad (3)$$

$$D_v = \tilde{D}_e + \beta_e \left(v + \frac{1}{2} \right) - \sum_{k=2}^7 \delta_{ek} \left(v + \frac{1}{2} \right)^k, \quad (4)$$

$$H_v = h_e + \sum_{k=1}^7 h_{ek} \left(v + \frac{1}{2} \right)^k. \quad (5)$$

This paper mainly studies the spectral mechanisms of the *P*-branch, namely the spectral choice satisfies $\Delta J = -1$. It is known that for a majority of diatomic molecules, in cm^{-1} , the rotational constant B_v is usually on the order of 10^{-1} to 10, D_v is about 10^{-5} , and H_v is as small as 10^{-10} experimentally or theoretically. Therefore, one may neglect the H_v term and all other higher terms smaller than 10^{-10} in Eq. (2), so it can be given by

$$\nu = \nu_0 + J [B_{v'} (J - 1) - B_{v''} (J + 1)] - J^2 [D_{v'} (J - 1)^2 - D_{v''} (J + 1)^2]. \quad (6)$$

The following derivations are based on Eq. (6) and multiple energy (spectral line) differences. The first spectral line difference (but the second energy difference) between two rotational states J_1 and J_2 is

$$\begin{aligned} \nu_{J_2} - \nu_{J_1} = & J_2 (J_2 - 1) B_{v'} - J_2 (J_2 + 1) B_{v''} - J_2^2 (J_2 - 1)^2 D_{v'} \\ & + J_2^2 (J_2 + 1)^2 D_{v''} - [J_1 (J_1 - 1) B_{v'} - J_1 (J_1 + 1) B_{v''} \\ & - J_1^2 (J_1 - 1)^2 D_{v'} + J_1^2 (J_1 + 1)^2 D_{v''}]. \end{aligned} \quad (7)$$

Eq. (7) is valid for rotational states J_3, J_4 , namely

$$\begin{aligned} \nu_{J_4} - \nu_{J_3} = & J_4 (J_4 - 1) B_{v'} - J_4 (J_4 + 1) B_{v''} - J_4^2 (J_4 - 1)^2 D_{v'} \\ & + J_4^2 (J_4 + 1)^2 D_{v''} - [J_3 (J_3 - 1) B_{v'} - J_3 (J_3 + 1) B_{v''} \\ & - J_3^2 (J_3 - 1)^2 D_{v'} + J_3^2 (J_3 + 1)^2 D_{v''}]. \end{aligned} \quad (8)$$

By subtracting Eq. (7) from Eq. (8), one has the second spectral line difference. The rotational constant $D_{v''}$ may be given by

$$\begin{aligned} D_{v''} = & \frac{(\nu_{J_4} - \nu_{J_3} - \nu_{J_2} + \nu_{J_1})}{P_4(J_1, J_2, J_3, J_4)} - B_{v'} \frac{P_1(J_1, J_2, J_3, J_4)}{P_4(J_1, J_2, J_3, J_4)} + B_{v''} \frac{P_2(J_1, J_2, J_3, J_4)}{P_4(J_1, J_2, J_3, J_4)} \\ & + D_{v'} \frac{P_3(J_1, J_2, J_3, J_4)}{P_4(J_1, J_2, J_3, J_4)}. \end{aligned} \quad (9)$$

Eq. (9) is also correct for arbitrary rotational states $J_5 - J_8$:

$$\begin{aligned} D_{v''} = & \frac{(\nu_{J_8} - \nu_{J_7} - \nu_{J_6} + \nu_{J_5})}{P_4(J_5, J_6, J_7, J_8)} - B_{v'} \frac{P_1(J_5, J_6, J_7, J_8)}{P_4(J_5, J_6, J_7, J_8)} + B_{v''} \frac{P_2(J_5, J_6, J_7, J_8)}{P_4(J_5, J_6, J_7, J_8)} \\ & + D_{v'} \frac{P_3(J_5, J_6, J_7, J_8)}{P_4(J_5, J_6, J_7, J_8)}. \end{aligned} \quad (10)$$

Eq. (9) and Eq. (10) are equal, we can get the expression for $D_{v'}$:

$$D_{v'} = (\nu_{J_8} - \nu_{J_7} - \nu_{J_6} + \nu_{J_5}) S_1 - (\nu_{J_4} - \nu_{J_3} - \nu_{J_2} + \nu_{J_1}) S_2 + B_{v'} S_3 - B_{v''} S_4. \quad (11)$$

Eq. (11) also applies to the rotational states $J_9 - J_{16}$:

$$D_{v'} = (\nu_{J_{16}} - \nu_{J_{15}} - \nu_{J_{14}} + \nu_{J_{13}}) S_5 - (\nu_{J_{12}} - \nu_{J_{11}} - \nu_{J_{10}} + \nu_{J_9}) S_6 + B_{v'} S_7 - B_{v''} S_8. \quad (12)$$

Similarly, Eq. (11) equals Eq. (12); after being reorganized, $\nu_{J_{16}}$ can be expressed in the following form [25]:

$$\begin{aligned} \nu_{J_{16}} = & (\nu_{J_{15}} + \nu_{J_{14}} - \nu_{J_{13}}) + (\nu_{J_8} - \nu_{J_7} - \nu_{J_6} + \nu_{J_5}) \frac{S_1}{S_5} \\ & - (\nu_{J_4} - \nu_{J_3} - \nu_{J_2} + \nu_{J_1}) \frac{S_2}{S_5} + (\nu_{J_{12}} - \nu_{J_{11}} - \nu_{J_{10}} + \nu_{J_9}) \frac{S_6}{S_5} \\ & + B_{v'} \left(\frac{S_3}{S_5} - \frac{S_7}{S_5} \right) - B_{v''} \left(\frac{S_4}{S_5} - \frac{S_8}{S_5} \right), \end{aligned} \quad (13)$$

where $\nu_{J_{16}}$ is the value of the unknown P -branch transition line and $(\nu_{J_1} \cdots \nu_{J_{15}})$ are the spectral lines selected from a group of known experimental transition lines for a given transition band of a diatomic system. $(B_{v'}, B_{v''})$ are the rotational constants, respectively, for the vibrational states v' and v'' . (S_1, S_2, S_3, S_4) are functions of the rotational quantum numbers $(J_1 \cdots J_8)$, and (S_5, S_6, S_7, S_8) are those of $(J_9 \cdots J_{16})$ through the P_k functions [25]

$$S_1 = \frac{P_4(J_1, J_2, J_3, J_4)}{P_3(J_1, J_2, J_3, J_4) P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4) P_3(J_5, J_6, J_7, J_8)},$$

$$S_2 = \frac{P_4(J_5, J_6, J_7, J_8)}{P_3(J_1, J_2, J_3, J_4) P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4) P_3(J_5, J_6, J_7, J_8)},$$

$$S_3 = \frac{P_1(J_1, J_2, J_3, J_4) P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4) P_1(J_5, J_6, J_7, J_8)}{P_3(J_1, J_2, J_3, J_4) P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4) P_3(J_5, J_6, J_7, J_8)},$$

$$S_4 = \frac{P_2(J_1, J_2, J_3, J_4) P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4) P_2(J_5, J_6, J_7, J_8)}{P_3(J_1, J_2, J_3, J_4) P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4) P_3(J_5, J_6, J_7, J_8)},$$

$$S_5 = \frac{P_4(J_9, J_{10}, J_{11}, J_{12})}{\begin{pmatrix} P_3(J_9, J_{10}, J_{11}, J_{12}) P_4(J_{13}, J_{14}, J_{15}, J_{16}) \\ - P_4(J_9, J_{10}, J_{11}, J_{12}) P_3(J_{13}, J_{14}, J_{15}, J_{16}) \end{pmatrix}},$$

$$S_6 = \frac{P_4(J_{13}, J_{14}, J_{15}, J_{16})}{\begin{pmatrix} P_3(J_9, J_{10}, J_{11}, J_{12}) P_4(J_{13}, J_{14}, J_{15}, J_{16}) \\ - P_4(J_9, J_{10}, J_{11}, J_{12}) P_3(J_{13}, J_{14}, J_{15}, J_{16}) \end{pmatrix}},$$

$$S_7 = \frac{\begin{pmatrix} P_1(J_9, J_{10}, J_{11}, J_{12}) P_4(J_{13}, J_{14}, J_{15}, J_{16}) \\ - P_4(J_9, J_{10}, J_{11}, J_{12}) P_1(J_{13}, J_{14}, J_{15}, J_{16}) \end{pmatrix}}{\begin{pmatrix} P_3(J_9, J_{10}, J_{11}, J_{12}) P_4(J_{13}, J_{14}, J_{15}, J_{16}) \\ - P_3(J_{13}, J_{14}, J_{15}, J_{16}) P_4(J_9, J_{10}, J_{11}, J_{12}) \end{pmatrix}},$$

$$S_8 = \frac{\begin{pmatrix} P_2(J_9, J_{10}, J_{11}, J_{12}) P_4(J_{13}, J_{14}, J_{15}, J_{16}) \\ - P_4(J_9, J_{10}, J_{11}, J_{12}) P_2(J_{13}, J_{14}, J_{15}, J_{16}) \end{pmatrix}}{\begin{pmatrix} P_3(J_9, J_{10}, J_{11}, J_{12}) P_4(J_{13}, J_{14}, J_{15}, J_{16}) \\ - P_3(J_{13}, J_{14}, J_{15}, J_{16}) P_4(J_9, J_{10}, J_{11}, J_{12}) \end{pmatrix}},$$

$$P_1(J_1, J_2, J_3, J_4) = J_4(J_4 - 1) - J_3(J_3 - 1) - J_2(J_2 - 1) + J_1(J_1 - 1),$$

$$P_2(J_1, J_2, J_3, J_4) = J_4(J_4 + 1) - J_3(J_3 + 1) - J_2(J_2 + 1) + J_1(J_1 + 1),$$

$$P_3(J_1, J_2, J_3, J_4) = J_4^2(J_4 - 1)^2 - J_3^2(J_3 - 1)^2 - J_2^2(J_2 - 1)^2 + J_1^2(J_1 - 1)^2,$$

$$P_4(J_1, J_2, J_3, J_4) = J_4^2(J_4 + 1)^2 - J_3^2(J_3 + 1)^2 - J_2^2(J_2 + 1)^2 + J_1^2(J_1 + 1)^2.$$

It is shown from Eq. (13) that using 15 known experimental transition lines ($\nu_{J_1} \cdots \nu_{J_{15}}$) and the known rotational constants ($B_{v'}, B_{v''}$), the correct value of the unknown transition line $\nu_{J_{16}}$ of a P -branch transition band (v', v'') for a given rotational state J_{16} of a diatomic molecule can be predicted. It is known, from the definitions of the S_i and the P_k functions, that a rotational quantum state J which defines the P'_k s might not be used if the $P_k = 0$ when calculating $\nu_{J_{16}}$ using Eq. (13).

If one can get a subgroup of M known accurate emission spectral lines for a given transition band, one may choose 15 emission spectral lines out of the M one at a time, and have $N = C_M^{15}$ selections. Then solving N times Eq. (13), since the error (and hence the physical accuracy) included in each of the M measured data is different, the physical information embedded in each of the N selections will be different.

There must be a set of emission spectral lines which should best meet the following physical criteria [25].

$$|\nu_{J,\text{expt}} - \nu_{J,\text{cal}}| \rightarrow 0, \quad (14)$$

$$|\Delta_{J,\text{expt}} - \Delta_{J,\text{cal}}| \rightarrow 0, \quad \Delta_J = \nu_{J-1} - \nu_J, \quad (15)$$

$$|\Delta_{J,\text{expt}} / \nu_{J-1,\text{expt}}| - |\Delta_{J,\text{cal}} / \nu_{J-1,\text{cal}}| \rightarrow 0. \quad (16)$$

Such a set is the best representation of the profound physics embedded in all the known experimental lines of this diatomic system, where Δ_J is the spectral line difference. In the above derivation, no mathematical approximations and physical models are used except that, in the rotational transition spectral expansion, all higher order terms of the rotational constants with the order of 10^{-10} and smaller are neglected. Eq. (13) does not contain any unknown parameters; it is an effective parameter-free expression. Thus, the accuracy of the 15 known experimental data themselves almost uniquely determines the accuracy and the physics of the predicted unknown rovibrational spectral lines. Namely, the smaller the error of the experimental lines, the better the accuracy and the physics of the predicted ones.

III. APPLICATION AND DISCUSSION

This paper studies the P -branch emission spectral lines of the (0, 0), (2, 2) bands in the $d^1\Sigma^+ - b^1\Sigma^+$ electronic state transition system of the NbN molecule by using Eq. (13). Table I not only lists the values of B_v , but also the 15 lines of the 40 experimental data that best satisfy the physical criteria in Eqs. (14)–(16) which correspond to the rotational quantum number ($J_1 \cdots J_{15}$) are also listed. We can see from Table I, on application of Eq. (13), the selecting of the emission spectral lines is random, and the selecting of the rotational quantum number is so that the final theoretical calculation result can best fulfill the physical criteria in Eqs. (14)–(16). And some spectral data which contain important transition information can even be selected more than once. For example, the emission spectral line of which the rotational quantum number is $J = 34$ for the (0, 0) band in the $d^1\Sigma^+ - b^1\Sigma^+$ electronic state transition has been selected twice.

Table II lists the known accurate experimental emission spectral lines of the P -branch, values of the unknown emission spectral lines up to $J = 80.5$ are predicted using the new formula, the data comparison of related items, such as the spectral difference (expt.–cal.) between the experimental and theoretical data, the experimental spectral difference $\Delta_{J,\text{expt}}$, the calculated spectral difference $\Delta_{J,\text{cal}}$, the experimental spectral ratio $\text{Rate}_{J,\text{expt}}$, and the calculated spectral ratio $\text{Rate}_{J,\text{cal}}$, respectively. The 15 known experimental emission spectral lines which are used by the new formula are marked in bold face, they correspond to the 15 rotational quantum numbers in Table I respectively. All quantities except Rate_J are in cm^{-1} .

TABLE I: The rotational constants B_v (cm^{-1}) and rotational quantum numbers are selected for calculating P -branch emission spectral lines of the (0, 0), (2, 2) bands in the $d^1\Sigma^+ - b^1\Sigma^+$ transition of NbN molecule.

	(0, 0) Band	(2, 2) Band
B_v [24]	0.5040215 ($v = 0$)	0.4990410 ($v = 2$)
	0.4994432 ($v = 0$)	0.4938840 ($v = 2$)
J_1	9	5
J_2	3	6
J_3	13	9
J_4	14	11
J_5	21	15
J_6	24	16
J_7	23	29
J_8	25	25
J_9	26	26
J_{10}	27	27
J_{11}	32	17
J_{12}	28	28
J_{13}	33	32
J_{14}	34	39
J_{15}	34	21

TABLE II: Experimental and theoretical P -branch emission spectra and related data of the (0, 0), (2, 2) bands in the $d^1\Sigma^+ - b^1\Sigma^{++}$ transition electronic state of the NbN molecule. (All quantities except Rate_J are in cm^{-1})

J	(0, 0) Band						
	$\nu_{J,\text{expt}}$ [24]	$\nu_{J,\text{cal}}$	expt.-cal.	$\Delta_{J,\text{expt}}$ *	$\Delta_{J,\text{cal}}$	$\text{Rate}_{J,\text{expt}}$ #	$\text{Rate}_{J,\text{cal}}$
0							
1		8044.4603					
2		8043.4706			0.9897		1.2303E-04

Continued...

J	(0, 0) Band						
	$\nu_{J,\text{expt}}$ [24]	$\nu_{J,\text{cal}}$	expt. - cal.	$\Delta_{J,\text{expt}}^*$	$\Delta_{J,\text{cal}}$	Rate $_{J,\text{expt}}^{\#}$	Rate $_{J,\text{cal}}$
3	8042.4940	8042.4901	0.0039		0.9805		1.2190E-04
4	8041.5150	8041.5187	-0.0037	0.9790	0.9713	1.2173E-04	1.2077E-04
5	8040.5540	8040.5566	-0.0026	0.9610	0.9621	1.1950E-04	1.1965E-04
6	8039.6070	8039.6037	0.0033	0.9470	0.9529	1.1778E-04	1.1851E-04
7	8038.6590	8038.6601	-0.0011	0.9480	0.9437	1.1792E-04	1.1738E-04
8	8037.7240	8037.7257	-0.0017	0.9350	0.9344	1.1631E-04	1.1624E-04
9	8036.8020	8036.8006	0.0014	0.9220	0.9251	1.1471E-04	1.1510E-04
10	8035.8880	8035.8847	0.0033	0.9140	0.9158	1.1373E-04	1.1395E-04
11	8034.9770	8034.9782	-0.0012	0.9110	0.9065	1.1337E-04	1.1281E-04
12	8034.0810	8034.0810	0.0000	0.8960	0.8972	1.1151E-04	1.1166E-04
13	8033.1930	8033.1932	0.0002	0.8880	0.8878	1.1053E-04	1.1051E-04
14	8032.3150	8032.3147	0.0003	0.8780	0.8785	1.0930E-04	1.0935E-04
15	8031.4460	8031.4457	0.0003	0.8690	0.8691	1.0819E-04	1.0820E-04
16	8030.5860	8030.5860	0.0000	0.8600	0.8597	1.0708E-04	1.0704E-04
17	8029.7360	8029.7358	0.0002	0.8500	0.8502	1.0585E-04	1.0587E-04
18	8028.8980	8028.8950	0.0030	0.8380	0.8408	1.0436E-04	1.0471E-04
19	8028.0630	8028.0638	-0.0008	0.8350	0.8313	1.0400E-04	1.0354E-04
20	8027.2400	8027.2420	-0.0020	0.8230	0.8218	1.0252E-04	1.0236E-04
21	8026.4300	8026.4297	0.0003	0.8100	0.8122	1.0091E-04	1.0119E-04
22	8025.6260	8025.6270	-0.0010	0.8040	0.8027	1.0017E-04	1.0001E-04
23	8024.8310	8024.8339	-0.0029	0.7950	0.7931	9.9058E-05	9.8823E-05
24	8024.0500	8024.0504	-0.0004	0.7810	0.7835	9.7323E-05	9.7636E-05
25	8023.2760	8023.2765	-0.0005	0.7740	0.7739	9.6460E-05	9.6444E-05
26	8022.5130	8022.5123	0.0007	0.7630	0.7642	9.5098E-05	9.5250E-05
27	8021.7570	8021.7578	-0.0008	0.7560	0.7545	9.4235E-05	9.4050E-05
28	8021.0120	8021.0130	-0.0010	0.7450	0.7448	9.2872E-05	9.2849E-05
29	8020.2820	8020.2779	0.0041	0.7300	0.7351	9.1011E-05	9.1643E-05
30	8019.5470	8019.5526	-0.0056	0.7350	0.7253	9.1643E-05	9.0431E-05
31	8018.8390	8018.8372	0.0018	0.7080	0.7155	8.8284E-05	8.9218E-05

Continued...

<i>J</i>	(0, 0) Band						
	$\nu_{J,\text{expt}}$ [24]	$\nu_{J,\text{cal}}$	expt. - cal.	$\Delta_{J,\text{expt}}^*$	$\Delta_{J,\text{cal}}$	Rate $_{J,\text{expt}}^{\#}$	Rate $_{J,\text{cal}}$
32	8018.1320	8018.1315	0.0005	0.7070	0.7056	8.8167E-05	8.7998E-05
33	8017.4360	8017.4357	0.0003	0.6960	0.6958	8.6803E-05	8.6775E-05
34	8016.7500	8016.7499	0.0001	0.6860	0.6859	8.5564E-05	8.5547E-05
35	8016.0760	8016.0739	0.0021	0.6740	0.6759	8.4074E-05	8.4315E-05
36	8015.4050	8015.4080	-0.0030	0.6710	0.6660	8.3707E-05	8.3079E-05
37	8014.7590	8014.7520	0.0070	0.6460	0.6560	8.0595E-05	8.1837E-05
38	8014.1040	8014.1061	-0.0021	0.6550	0.6459	8.1724E-05	8.0593E-05
39	8013.4810	8013.4702	0.0108	0.6230	0.6358	7.7738E-05	7.9341E-05
40	8012.8460	8012.8445	0.0015	0.6350	0.6257	7.9241E-05	7.8086E-05
41	8012.2250	8012.2289	-0.0039	0.6210	0.6156	7.7501E-05	7.6827E-05
42	8011.6210	8011.6235	-0.0025	0.6040	0.6054	7.5385E-05	7.5562E-05
43		8011.0283			0.5952		7.4291E-05
44		8010.4434			0.5849		7.3016E-05
45		8009.8687			0.5746		7.1735E-05
46		8009.3044			0.5643		7.0451E-05
47		8008.7505			0.5539		6.9160E-05
48		8008.2070			0.5435		6.7862E-05
49		8007.6740			0.5330		6.6562E-05
50		8007.1514			0.5225		6.5254E-05
51		8006.6395			0.5120		6.3942E-05
52		8006.1381			0.5014		6.2623E-05
53		8005.6473			0.4908		6.1298E-05
54		8005.1672			0.4801		5.9968E-05
55		8004.6978			0.4694		5.8633E-05
56		8004.2393			0.4586		5.7290E-05
57		8003.7915			0.4478		5.5942E-05
58		8003.3546			0.4369		5.4589E-05
59		8002.9286			0.4260		5.3228E-05
60		8002.5135			0.4150		5.1861E-05

Continued...

J	(0, 0) Band						
	$\nu_{J,\text{expt}}$ [24]	$\nu_{J,\text{cal}}$	expt. - cal.	$\Delta_{J,\text{expt}}$ *	$\Delta_{J,\text{cal}}$	Rate $_{J,\text{expt}}$ [#]	Rate $_{J,\text{cal}}$
61		8002.1095			0.4040		5.0489E-05
62		8001.7165			0.3930		4.9110E-05
63		8001.3346			0.3819		4.7724E-05
64		8000.9639			0.3707		4.6332E-05
65		8000.6044			0.3595		4.4932E-05
66		8000.2562			0.3482		4.3527E-05
67		7999.9192			0.3369		4.2115E-05
68		7999.5937			0.3256		4.0697E-05
69		7999.2795			0.3141		3.9269E-05
70		7998.9769			0.3027		3.7836E-05
71		7998.6857			0.2911		3.6397E-05
72		7998.4062			0.2796		3.4949E-05
73		7998.1383			0.2679		3.3495E-05
74		7997.8821			0.2562		3.2034E-05
75		7997.6376			0.2445		3.0564E-05
76		7997.4050			0.2326		2.9089E-05
77		7997.1842			0.2208		2.7604E-05
78		7996.9754			0.2088		2.6114E-05
79		7996.7785			0.1968		2.4614E-05
80		7996.5938			0.1848		2.3107E-05

* The transition line difference $\Delta_J = \nu_{J-1} - \nu_J$ for P -branch. # Rate $_J = \Delta_J/\nu_{J-1}$.

TABLE III: Continuously Table II.

J	(2, 2) Band						
	$\nu_{J,\text{expt}}$ [24]	$\nu_{J,\text{cal}}$	expt. - cal.	$\Delta_{J,\text{expt}}$	$\Delta_{J,\text{cal}}$	Rate $_{J,\text{expt}}$	Rate $_{J,\text{cal}}$
0							
1		8091.3852					
2		8090.4078			0.9774		1.2080E-04
3		8089.4407			0.9671		1.1954E-04

Continued...

J	(2, 2) Band						
	$\nu_{J,\text{expt}}$ [24]	$\nu_{J,\text{cal}}$	expt. - cal.	$\Delta_{J,\text{expt}}$	$\Delta_{J,\text{cal}}$	Rate $_{J,\text{expt}}$	Rate $_{J,\text{cal}}$
4		8088.4840			0.9567		1.1827E-04
5	8087.5380	8087.5376	0.0004		0.9464		1.1700E-04
6	8086.5990	8086.6016	-0.0026	0.9390	0.9360	1.1610E-04	1.1573E-04
7	8085.6740	8085.6760	-0.0020	0.9250	0.9256	1.1439E-04	1.1446E-04
8	8084.7650	8084.7608	0.0042	0.9090	0.9152	1.1242E-04	1.1318E-04
9	8083.8580	8083.8561	0.0019	0.9070	0.9047	1.1219E-04	1.1191E-04
10		8082.9618			0.8943		1.1063E-04
11	8082.0770	8082.0780	-0.0010		0.8838		1.0934E-04
12		8081.2046			0.8733		1.0806E-04
13	8080.3380	8080.3418	-0.0038		0.8628		1.0677E-04
14		8079.4895			0.8523		1.0548E-04
15	8078.6480	8078.6477	0.0003		0.8418		1.0419E-04
16	8077.8190	8077.8165	0.0025	0.8290	0.8312	1.0262E-04	1.0289E-04
17	8076.9940	8076.9959	-0.0019	0.8250	0.8206	1.0213E-04	1.0159E-04
18		8076.1858			0.8100		1.0029E-04
19	8075.3900	8075.3864	0.0036		0.7994		9.8985E-05
20	8074.6200	8074.5976	0.0224	0.7700	0.7888	9.5351E-05	9.7676E-05
21	8073.8160	8073.8195	-0.0035	0.8040	0.7781	9.9571E-05	9.6366E-05
22	8073.0490	8073.0521	-0.0031	0.7670	0.7674	9.4998E-05	9.5050E-05
23	8072.3100	8072.2954	0.0146	0.7390	0.7567	9.1539E-05	9.3734E-05
24	8071.5460	8071.5494	-0.0034	0.7640	0.7460	9.4645E-05	9.2414E-05
25	8070.8140	8070.8142	-0.0001	0.7320	0.7352	9.0689E-05	9.1090E-05
26	8070.0880	8070.0897	-0.0017	0.7260	0.7245	8.9954E-05	8.9763E-05
27	8069.3770	8069.3760	0.0010	0.7110	0.7136	8.8103E-05	8.8431E-05
28	8068.6740	8068.6732	0.0008	0.7030	0.7028	8.7119E-05	8.7098E-05
29	8067.9840	8067.9812	0.0028	0.6900	0.6920	8.5516E-05	8.5761E-05
30	8067.2930	8067.3001	-0.0071	0.6910	0.6811	8.5647E-05	8.4420E-05
31	8066.6260	8066.6299	-0.0039	0.6670	0.6702	8.2680E-05	8.3075E-05
32	8065.9690	8065.9707	-0.0017	0.6570	0.6593	8.1447E-05	8.1728E-05

Continued...

J	(2, 2) Band						
	$\nu_{J,\text{expt}}$ [24]	$\nu_{J,\text{cal}}$	expt. - cal.	$\Delta_{J,\text{expt}}$	$\Delta_{J,\text{cal}}$	Rate $_{J,\text{expt}}$	Rate $_{J,\text{cal}}$
33	8065.3270	8065.3224	0.0046	0.6420	0.6483	7.9594E-05	8.0376E-05
34	8064.6850	8064.6850	0.0000	0.6420	0.6373	7.9600E-05	7.9021E-05
35	8064.0640	8064.0587	0.0053	0.6210	0.6263	7.7002E-05	7.7661E-05
36	8063.4400	8063.4434	-0.0034	0.6240	0.6153	7.7380E-05	7.6299E-05
37	8062.8370	8062.8392	-0.0022	0.6030	0.6042	7.4782E-05	7.4932E-05
38	8062.2640	8062.2461	0.0179	0.5730	0.5931	7.1067E-05	7.3560E-05
39	8061.6660	8061.6641	0.0019	0.5980	0.5820	7.4173E-05	7.2187E-05
40	8061.0810	8061.0933	-0.0123	0.5850	0.5708	7.2566E-05	7.0807E-05
41		8060.5337			0.5596		6.9425E-05
42		8059.9853			0.5484		6.8038E-05
43		8059.4481			0.5372		6.6647E-05
44		8058.9222			0.5259		6.5250E-05
45		8058.4076			0.5146		6.3852E-05
46		8057.9044			0.5032		6.2448E-05
47		8057.4126			0.4919		6.1039E-05
48		8056.9321			0.4804		5.9626E-05
49		8056.4631			0.4690		5.8210E-05
50		8056.0056			0.4575		5.6788E-05
51		8055.5596			0.4460		5.5362E-05
52		8055.1252			0.4344		5.3930E-05
53		8054.7023			0.4229		5.2496E-05
54		8054.2911			0.4112		5.1055E-05
55		8053.8915			0.3996		4.9611E-05
56		8053.5036			0.3879		4.8161E-05
57		8053.1275			0.3762		4.6706E-05
58		8052.7631			0.3644		4.5246E-05
59		8052.4105			0.3526		4.3782E-05
60		8052.0698			0.3407		4.2312E-05
61		8051.7410			0.3288		4.0838E-05

Continued...

J	(2, 2) Band						
	$\nu_{J,\text{expt}}$ [24]	$\nu_{J,\text{cal}}$	expt. - cal.	$\Delta_{J,\text{expt}}$	$\Delta_{J,\text{cal}}$	Rate $_{J,\text{expt}}$	Rate $_{J,\text{cal}}$
62		8051.4241			0.3169		3.9358E-05
63		8051.1192			0.3049		3.7874E-05
64		8050.8262			0.2929		3.6384E-05
65		8050.5454			0.2809		3.4888E-05
66		8050.2766			0.2688		3.3388E-05
67		8050.0199			0.2567		3.1881E-05
68		8049.7754			0.2445		3.0371E-05
69		8049.5432			0.2323		2.8853E-05
70		8049.3232			0.2200		2.7332E-05
71		8049.1154			0.2077		2.5805E-05
72		8048.9201			0.1953		2.4270E-05
73		8048.7371			0.1830		2.2732E-05
74		8048.5666			0.1705		2.1187E-05
75		8048.4086			0.1580		1.9636E-05
76		8048.2630			0.1455		1.8081E-05
77		8048.1301			0.1330		1.6519E-05
78		8048.0098			0.1203		1.4950E-05
79		8047.9021			0.1077		1.3377E-05
80		8047.8072			0.0949		1.1797E-05

It can be seen from Table II that the Ram group [24] has observed accurately 40 known P -branch emission spectral lines of the (0, 0) band for the $d^1\Sigma^+ - b^1\Sigma^+$ electronic state transition of NbN. We put them ($M = 40$) as input data, 15 of them are chosen at a time to calculate the wanted emission spectral lines and the theoretical copies for all known experimental emission lines using Eq. (13). The 15 lines of the 40 experimental data are the best satisfying the physical criteria in Eqs. (14)–(16) in Table II. The maximum absolute difference between the experimental and the theoretical data is less than 0.02 cm^{-1} .

Table II clearly shows that the emission spectral lines which are calculated by Eq. (13) not only agree very well with the experimental emission spectral lines, but we also can obtain the emission spectral lines of the electronic states whose experimental values are not available; they can be predicted for the (0, 0) band in the $d^1\Sigma^+ - b^1\Sigma^+$ electronic state transition. All theoretical lines meet the criterion conditions in Eqs. (14)–(16). And for the band (2, 2), the experimental emission spectral lines of which rotational quantum number $J = 10$ didn't offer, while the new formula directly predicted its theoretical emission spectral

line $\nu_{J=10} = 8082.9618 \text{ cm}^{-1}$. In the near future, if the experimental emission spectral lines can be obtained, then the maximum absolute difference between the experimental and the theoretical data will not be more than 0.02 cm^{-1} , unless there are errors that could not be ignored in the 15 experimental emission spectral lines. Namely, the smaller the error of the experimental lines, the better the accuracy and the physics of the predicted ones. In the application of Eq. (13), no mathematical approximations and physical models are used, especially with the correct physical criterion. Actually, these criteria can effectively identify the tiny errors of the experimental data, select out the correct physical information which contains the minimum error, then predict the correct theoretical emission spectral lines.

In order to further understand the correctness of Eq. (13), Table II also lists the transition spectral differences of the experimental and theoretical emission spectral lines. Fig. 1 describes transition spectral differences of the (0, 0) band intuitively. Experimental (“○”) and theoretical (“+”) transition spectral differences of the *P*-branch emission spectra of (0, 0) band are plotted in Fig. 1, respectively. Fig. 1 shows that these two kinds of transition spectral differences fitted very well, and the theoretical transition spectral differences lasts the trend of experimental ones. For the (2, 2) band, one can get a similar figure. These data and figures indicate that the emission spectral lines of the high-lying rotational quantum state using Eq. (13) and the criterion in Eqs. (14)–(16) are correct and believable.

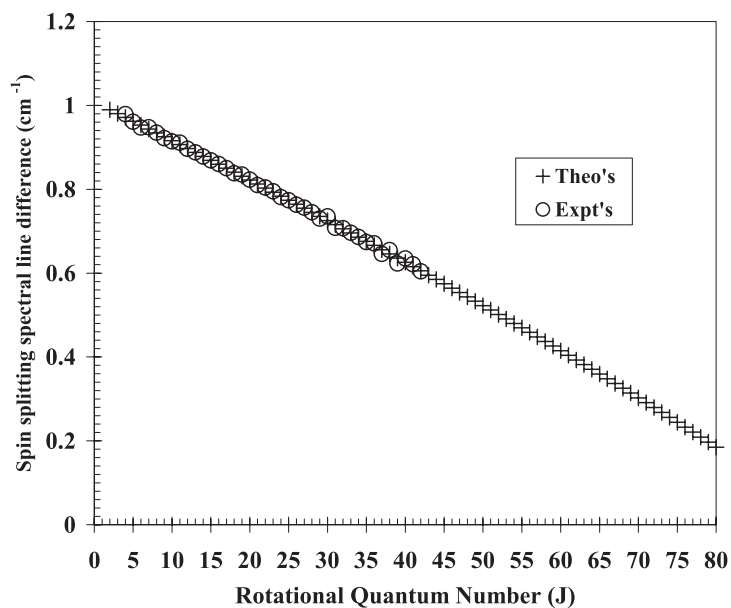


FIG. 1: Experimental (“○”) and theoretical (“+”) transition line differences ($\Delta_J = \nu_{J-1} - \nu_J$) of the *P*-branch emission spectra of the (0, 0) band.

IV. CONCLUSIONS

Although a large amount of spectral data has been extensively used in various research fields, many high-lying and some absent rovibrational transition emission spectral lines which may not be available experimentally are still needed badly. An analytical formula in Eq. (13) for obtaining accurate *P*-branch high-lying rovibrational emission spectral lines of a diatomic molecule based on multiple transition spectral (spectral line) differences was proposed in Sun's previous work. The equation can be taken as a useful alternative for evaluating reliable values for those electronic states whose emission spectral lines values may be difficult to obtain experimentally or quantum mechanically. This results of this study show that, for *P*-branch emission spectral lines of the (0, 0), (2, 2) bands in the $d^1\Sigma^+ - b^1\Sigma^+$ electronic state transition of the NbN molecule, as long as one gets 15 known experimental emission spectral lines and the known rotational constants ($B_{v'}$, $B_{v''}$) for each band, the emission spectral lines of an electronic state whose experimental value is not available can be predicted using the new formula with the set of physical criteria in Equations (14)–(16), which are suggested as the standard to judge the quality of the measured data and to select a best combination of the data with minimum error. This study generates correct data for those who need high-lying rovibrational transition spectral lines of the NbN molecule, and supplies a reliable and economical physical method for obtaining the transition spectrum of a stable diatomic molecular theoretically.

Acknowledgements

This study was supported by the National Natural Science Foundation of China (Grant No. 11074204), the Science Foundation of the Ministry of Education of China (Grant No. 20100181110085), the Research Fund of Key Disciplines of Atomic and Molecular Physics, and the Fund of Key Laboratory of Advanced Scientific Computation, Xihua University, People's Republic of China.

References

- [1] H. Li, C. Focsa, B. Pinchemel, R. J. Le Roy, and P. F. Bernath, *J. Chem. Phys.* **113**, 3026 (2000).
- [2] Y. Huang *et al.*, *J. Phys. B: At. Mol. Opt. Phys.* **39**, S857 (2006).
- [3] R. C. Ekey, Jr., A. Marks, and E. F. McCormack, *Phys. Rev. A* **73**, 023412 (2006).
- [4] F. Lang, K. Winkler, C. Strauss, R. Grimm, and J. H. Denschlag, *Phys. Rev. Lett.* **101**, 133005 (2008).
- [5] G. Herzberg *Molecular spectra, and molecular structure I. Spectra of diatomic molecule*, 3rd ed. (Van Nostrand, 1953).
- [6] R. N. Zare and P. J. Dagdigian, *Science* **185**, 739 (1974).
- [7] T. Imajo, Y. Kobayashi, Y. Nakashima, K. Tanaka, and T. Tanaka, *J. Mol. Spectrosc.* **230**, 139 (2005).

- [8] P. Staantum, A. Pashov, H. Knöckel, and E. Tiemann, *Phys. Rev. A* **75**, 042513 (2007).
- [9] L. Zheng *et al.*, *J. Mol. Spectrosc.* **226**, 81 (2004).
- [10] R. S. Ram, J. Liévin, and P. F. Bernath, *J. Chem. Phys.* **109**, 6329 (1998).
- [11] I. Shim and K. A. Gingerich, *Int. J. Quant. Chem.* **46**, 145 (1993).
- [12] S. M. Mattar, *J. Phys. Chem.* **97**, 3171 (1993).
- [13] J. F. Harrison, *J. Phys. Chem.* **100**, 3513 (1996).
- [14] S. M. Mattar and B. J. Doleman, *Chem. Phys. Lett.* **216**, 369 (1993).
- [15] W. Lochte-Holtgreven, *Plasma Diagnostics*, (North-Holland, Amsterdam, 1968)
- [16] T. M. Dunn and K. M. Rao, *Nature* **222**, 266 (1969).
- [17] J.-L. Féménias, C. Athénour, and T. M. Dunn, *J. Chem. Phys.* **63**, 2861 (1975).
- [18] Y. Azuma *et al.*, *J. Chem. Phys.* **91**, 1 (1989).
- [19] Y. Azuma *et al.*, *J. Chem. Phys.* **100**, 4138 (1994).
- [20] A. Béés, S. A. Mitchell, and M. Z. Zgierski, *J. Phys. Chem.* **102**, 6340 (1998).
- [21] H. Sellers, *J. Phys. Chem.* **94**, 1338 (1990).
- [22] D. A. Fletcher, D. Dai, T. C. Steimle, and K. Balasubramanian, *J. Chem. Phys.* **99**, 9324 (1993).
- [23] S. R. Langhoff and C. W. Bauschlicher Jr., *J. Mol. Spectrosc.* **143**, 169 (1990).
- [24] R. S. Ram and P. F. Bernath, *J. Mol. Spectrosc.* **201**, 267 (2000).
- [25] W. G. Sun, Q. C. Fan, H. D. Li, and H. Feng, *Spectrochim. Acta Part A* **79**, 35 (2011).
- [26] Q. C. Fan, W. G. Sun, H. D. Li, and H. Feng, *Chinese J. Phys.* **48**, 757 (2010).