P-branch emission spectra of the $A^1\Pi$–$X^1\Sigma^+$ system of IrN*

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The *P*-branch emission spectra of (4,1) and (3,1) bands of the $A^1\Pi$–$X^1\Sigma^+$ system of IrN molecule are studied using an analytical formula which is derived from elementary expression of molecular total energy by taking multiple spectral differences. It not only reproduces the known experimental transition lines, but also predicts the unknown spectral lines up to $J = 80$ for each band by using a group of fifteen known experimental transition lines.

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1. Introduction

Rovibrational transition spectral lines and rovibrational energies, particularly those of high-lying rovibrational transitions are important for understanding molecular structures and some important molecular information.[1−6] In recent years, there have been many important experimental technologies used to study molecular transition lines or rovibrational spectra, such as the Fourier transform spectrometer (FTS),[7−9] the laser induced fluorescence (LIF),[10] the optical heterodyne magnetic rotation enhanced velocity modulation spectroscopy (OH-MR-VMS),[11−16] the intracavity laser absorption spectroscopy (ILS),[17] the cavity ring-down spectroscopy (CRDS),[18] and the Fourier transform microwave (FTMW) spectroscopy.[19,20] These methods have made great contributions to the spectral field. Since the laser could be successively tuned in a certain spectral region, only part of the spectral lines can be obtained.[21] There are cases where the small Franck–Condon factor of a (υ',υ'') transition band and the low population in the υ'' level may prevent one to obtain more reliable rovibrational lines in some given band[15] and some branches in a certain transition band may not be obtained because the signals are too weak to observe. Thus, most of experimental approaches can obtain merely the low-lying transition lines for a given band from υ' to υ''. On the other hand, although there are a large number of theoretical researches on molecular structures and rotational spectroscopic parameters,[22−25] theoretical studies on transition spectral lines are few. Therefore, it is necessary to have a correct theoretical formula/equation, which can predict accurate spectral data of any rovibrational states.

In this paper, we provide an analytical formula based on the essential expression of molecular total energy by taking multiple spectral differences to predict the accurate values of unknown *P*-branch spectral lines. In Section 2, we present the new formula and a protocol used to predict any wanted transition lines. In Section 3, the applications of the new formula to the *P*-branch emission spectra of the (4,1) are described and the (3,1) bands of the $A^1\Pi$–$X^1\Sigma^+$ system of IrN which is an interesting molecule receive high attention.[26] In Section 4 this study is summarized.

2. Theory and method

The total energy of quantum states of a molecule can be universally given as[27]

$$E = T_{\rm e} + G + F, \tag{1}$$

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where $T_{\rm e}$ is energy of the electronic state of a molecule, G is the vibrational energy, and F is the rotational energy of a given vibrational state. For the vibrational and rotational motions of a diatomic electronic state, the rotational energy of a rotating vibrator may be given using either the Wentzel–Brillouin–Kramers (WBK) method[28] or the second order perturbation theory as[29]

$$F = B_\upsilon J(J+1) - D_\upsilon J^2(J+1)^2 + H_\upsilon J^3(J+1)^3 + \cdots, \tag{2}$$

where B_υ, D_υ, and H_υ are the rotational constants of the vibrational state υ of an electronic state, υ and J are vibrational and rotational quantum numbers respectively.

When an electron transits from a higher energy state ($'$) to a lower energy state ($''$), the (first) state-to-state energy difference, namely the transition line, is

$$\begin{aligned}\nu &= \nu_{\rm e} + \nu_\upsilon + \nu_r = E' - E'' \\ &= (T_{\rm e}' - T_{\rm e}'') + (G' - G'') + (F' - F'').\end{aligned} \tag{3}$$

The quantity,

$$\nu_0 = \nu_{\rm e} + \nu_\upsilon = \{(T_{\rm e}' - T_{\rm e}'') + (G' - G'')\},$$

is a constant for a given vibrational transition (υ', υ''), and one has from Eqs. (2) and (3)

$$\begin{aligned}\nu &= \nu_0 + F'(J') - F''(J'') \\ &= \nu_0 + B_{\upsilon'}J'(J'+1) - D_{\upsilon'}J'^2(J'+1)^2 \\ &\quad + H_{\upsilon'}J'^3(J'+1)^3 + \cdots \\ &\quad - \big[B_{\upsilon''}J''(J''+1) - D_{\upsilon''}J''^2(J''+1)^2 \\ &\quad + H_{\upsilon''}J''^3(J''+1)^3 + \cdots\big].\end{aligned} \tag{4}$$

If the projection of the electron angular momentum of an electronic state $\Lambda \neq 0$, then the selection rule for a rotational transition is[27]

$$\Delta J = J' - J'' = J' - J = 0, \pm 1 \tag{5}$$

and the $\Delta J = 0$, $+1$, -1 corresponding to the Q, R, and P branches respectively. For the P-branch spectrum, $J' = J'' - 1$, the transition line from Eq. (4) is

$$\begin{aligned}\nu &= \nu_0 + B_{\upsilon'}J(J-1) - D_{\upsilon'}J^2(J-1)^2 \\ &\quad + H_{\upsilon'}J^3(J-1)^3 + \cdots \\ &\quad - [B_{\upsilon''}J(J+1) - D_{\upsilon''}J^2(J+1)^2 \\ &\quad + H_{\upsilon''}J^3(J+1)^3 + \cdots] \\ &= \nu_0 + J[B_{\upsilon'}(J-1) - B_{\upsilon''}(J+1)] \\ &\quad - J^2\big[D_{\upsilon'}(J-1)^2 - D_{\upsilon''}(J+1)^2\big] \\ &\quad + J^3\big[H_{\upsilon'}(J-1)^3 - H_{\upsilon''}(J+1)^3\big] + \cdots.\end{aligned} \tag{6}$$

It is known that in $\rm cm^{-1}$, the rotational constant B_υ is usually on the order of 10^0 to 10^1, D_υ is on the order of about 10^{-5}, and H_υ is on the order of as small as 10^{-10}. Therefore, one may neglect the H_υ term and all other higher terms smaller than 10^{-10} in Eq. (6) and obtain

$$\begin{aligned}\nu &= \nu_0 + J[B_{\upsilon'}(J-1) - B_{\upsilon''}(J+1)] \\ &\quad - J^2\big[D_{\upsilon'}(J-1)^2 - D_{\upsilon''}(J+1)^2\big].\end{aligned} \tag{7}$$

The following derivations are based on Eq. (7) and multiple energy (transition line) differences. The first transition line difference (but the second energy difference) between two rotational states J_2 and J_1 is

$$\begin{aligned}\nu_{J_2} - \nu_{J_1} &= J_2(J_2-1)B_{\upsilon'} - J_2(J_2+1)B_{\upsilon''} - J_2^2(J_2-1)^2D_{\upsilon'} + J_2^2(J_2+1)^2D_{\upsilon''} \\ &\quad - \big[J_1(J_1-1)B_{\upsilon'} - J_1(J_1+1)B_{\upsilon''} - J_1^2(J_1-1)^2D_{\upsilon'} + J_1^2(J_1+1)^2D_{\upsilon''}\big].\end{aligned} \tag{8}$$

Equation (8) is also correct for arbitrary rotational states J_4 and J_3, namely

$$\begin{aligned}\nu_{J_4} - \nu_{J_3} &= J_4(J_4-1)B_{\upsilon'} - J_4(J_4+1)B_{\upsilon''} - J_4^2(J_4-1)^2D_{\upsilon'} + J_4^2(J_4+1)^2D_{\upsilon''} \\ &\quad - \big[J_3(J_3-1)B_{\upsilon'} - J_3(J_3+1)B_{\upsilon''} - J_3^2(J_3-1)^2D_{\upsilon'} + J_3^2(J_3+1)^2D_{\upsilon''}\big].\end{aligned} \tag{9}$$

By subtracting Eq. (8) from Eq. (9), one has the second transition line difference (but the third energy difference) as

$$\begin{aligned}\nu_{J_4} - \nu_{J_3} - (\nu_{J_2} - \nu_{J_1}) &= B_{\upsilon'}P_1(J_1, J_2, J_3, J_4) - B_{\upsilon''}P_2(J_1, J_2, J_3, J_4) \\ &\quad - D_{\upsilon'}P_3(J_1, J_2, J_3, J_4) + D_{\upsilon''}P_4(J_1, J_2, J_3, J_4),\end{aligned} \tag{10}$$

where

$$\begin{aligned}P_1(J_1,\ J_2,\ J_3,\ J_4) &= J_4(J_4-1) - J_3(J_3-1) - J_2(J_2-1) + J_1(J_1-1), \\ P_2(J_1,\ J_2,\ J_3,\ J_4) &= J_4(J_4+1) - J_3(J_3+1) - J_2(J_2+1) + J_1(J_1+1), \\ P_3(J_1,\ J_2,\ J_3,\ J_4) &= J_4^2(J_4-1)^2 - J_3^2(J_3-1)^2 - J_2^2(J_2-1)^2 + J_1^2(J_1-1)^2, \\ P_4(J_1,\ J_2,\ J_3,\ J_4) &= J_4^2(J_4+1)^2 - J_3^2(J_3+1)^2 - J_2^2(J_2+1)^2 + J_1^2(J_1+1)^2.\end{aligned} \tag{11}$$

The rotational constant $D_{v''}$ may be given from Eq. (10) as

$$D_{v''} = \frac{(\nu_{J_4} - \nu_{J_3} - \nu_{J_2} + \nu_{J_1})}{P_4(J_1, J_2, J_3, J_4)} - B_{v'} \frac{P_1(J_1, J_2, J_3, J_4)}{P_4(J_1, J_2, J_3, J_4)} + B_{v''} \frac{P_2(J_1, J_2, J_3, J_4)}{P_4(J_1, J_2, J_3, J_4)} + D_{v'} \frac{P_3(J_1, J_2, J_3, J_4)}{P_4(J_1, J_2, J_3, J_4)}. \quad (12)$$

Equation (12) is also valid for arbitrary rotational states (J_5, J_6, J_7, J_8), that is,

$$D_{v''} = \frac{(\nu_{J_8} - \nu_{J_7} - \nu_{J_6} + \nu_{J_5})}{P_4(J_5, J_6, J_7, J_8)} - B_{v'} \frac{P_1(J_5, J_6, J_7, J_8)}{P_4(J_5, J_6, J_7, J_8)} + B_{v''} \frac{P_2(J_5, J_6, J_7, J_8)}{P_4(J_5, J_6, J_7, J_8)} + D_{v'} \frac{P_3(J_5, J_6, J_7, J_8)}{P_4(J_5, J_6, J_7, J_8)}. \quad (13)$$

Since equations (12) and (13) are equal, one obtains

$$D_{v'} = (\nu_{J_8} - \nu_{J_7} - \nu_{J_6} + \nu_{J_5})S_1 - (\nu_{J_4} - \nu_{J_3} - \nu_{J_2} + \nu_{J_1})S_2 + B_{v'}S_3 - B_{v''}S_4, \quad (14)$$

where

$$S_1 = \frac{P_4(J_1, J_2, J_3, J_4)}{P_3(J_1, J_2, J_3, J_4)P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4)P_3(J_5, J_6, J_7, J_8)}, \quad (15)$$

$$S_2 = \frac{P_4(J_5, J_6, J_7, J_8)}{P_3(J_1, J_2, J_3, J_4)P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4)P_3(J_5, J_6, J_7, J_8)}, \quad (16)$$

$$S_3 = \frac{P_1(J_1, J_2, J_3, J_4)P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4)P_1(J_5, J_6, J_7, J_8)}{P_3(J_1, J_2, J_3, J_4)P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4)P_3(J_5, J_6, J_7, J_8)}, \quad (17)$$

$$S_4 = \frac{P_2(J_1, J_2, J_3, J_4)P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4)P_2(J_5, J_6, J_7, J_8)}{P_3(J_1, J_2, J_3, J_4)P_4(J_5, J_6, J_7, J_8) - P_4(J_1, J_2, J_3, J_4)P_3(J_5, J_6, J_7, J_8)}. \quad (18)$$

Similarly, equation (14) can also be written for arbitrary rotational states $(J_9, J_{10}, \ldots, J_{16})$ as

$$D_{v'} = (\nu_{J_{16}} - \nu_{J_{15}} - \nu_{J_{14}} + \nu_{J_{13}})S_5 - (\nu_{J_{12}} - \nu_{J_{11}} - \nu_{J_{10}} + \nu_{J_9})S_6 + B_{v'}S_7 - B_{v''}S_8, \quad (19)$$

where

$$S_5 = \frac{P_4(J_9, J_{10}, J_{11}, J_{12})}{P_3(J_9, J_{10}, J_{11}, J_{12})P_4(J_{13}, J_{14}, J_{15}, J_{16}) - P_4(J_9, J_{10}, J_{11}, J_{12})P_3(J_{13}, J_{14}, J_{15}, J_{16})}, \quad (20)$$

$$S_6 = \frac{P_4(J_{13}, J_{14}, J_{15}, J_{16})}{P_3(J_9, J_{10}, J_{11}, J_{12})P_4(J_{13}, J_{14}, J_{15}, J_{16}) - P_4(J_9, J_{10}, J_{11}, J_{12})P_3(J_{13}, J_{14}, J_{15}, J_{16})}, \quad (21)$$

$$S_7 = \frac{P_1(J_9, J_{10}, J_{11}, J_{12})P_4(J_{13}, J_{14}, J_{15}, J_{16}) - P_4(J_9, J_{10}, J_{11}, J_{12})P_1(J_{13}, J_{14}, J_{15}, J_{16})}{P_3(J_9, J_{10}, J_{11}, J_{12})P_4(J_{13}, J_{14}, J_{15}, J_{16}) - P_3(J_{13}, J_{14}, J_{15}, J_{16})P_4(J_9, J_{10}, J_{11}, J_{12})}, \quad (22)$$

$$S_8 = \frac{P_2(J_9, J_{10}, J_{11}, J_{12})P_4(J_{13}, J_{14}, J_{15}, J_{16}) - P_4(J_9, J_{10}, J_{11}, J_{12})P_2(J_{13}, J_{14}, J_{15}, J_{16})}{P_3(J_9, J_{10}, J_{11}, J_{12})P_4(J_{13}, J_{14}, J_{15}, J_{16}) - P_3(J_{13}, J_{14}, J_{15}, J_{16})P_4(J_9, J_{10}, J_{11}, J_{12})}. \quad (23)$$

It follows from Eq. (14) and Eq. (19) that

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

And finally one obtains

$$\begin{aligned}\nu_{J_{16}} = &(\nu_{J_{15}} + \nu_{J_{14}} - \nu_{J_{13}}) + (\nu_{J_8} - \nu_{J_7} - \nu_{J_6} + \nu_{J_5})\frac{S_1}{S_5} - (\nu_{J_4} - \nu_{J_3} - \nu_{J_2} + \nu_{J_1})\frac{S_2}{S_5}\\ &+ (\nu_{J_{12}} - \nu_{J_{11}} - \nu_{J_{10}} + \nu_{J_9})\frac{S_6}{S_5} + B_{v'}\Big(\frac{S_3}{S_5} - \frac{S_7}{S_5}\Big) - B_{v''}\Big(\frac{S_4}{S_5} - \frac{S_8}{S_5}\Big), \quad (24)\end{aligned}$$

where $B_{v'}$ and $B_{v''}$ are the rotational constants respectively for the vibrational states v' and v'', (S_1, S_2, S_3, S_4) are (through the P_k functions) the functions of rotational quantum numbers $(J_1, J_2, \ldots, J_8)$, and (S_5, S_6, S_7, S_8) are functions of $(J_9, J_{10}, \ldots, J_{16})$ as defined in Eqs. (15)–(18) and Eqs. (20)–(23) respectively. Equation (24) indicates that as long as the 15 known experimental transition lines $(\nu_{J_1}, \ldots, \nu_{J_{15}})$ and the known rotational constants $(B_{v'}, B_{v''})$ are used, can be predicted 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, and that different values of quantum number J_{16} produce different values of $\nu_{J_{16}}$. In the above derivation, all high order terms of the rotational constants on the order of 10^{-10} and smaller are neglected. It is known from the definitions of the P_k and the S_i functions, that a rotational quantum state J which determines P_k's may be used more than once and without other limitations so long

as $P_k \neq 0$ when $\nu_{J_{16}}$ is evaluated using Eq. (24).

Although it often happens that it may be difficult to obtain high-lying rovibrational spectral lines $\nu_{J''}$ with high rotational quantum numbers J'''s, modern experimental technologies can almost always give an accurate subgroup, $[\nu_{J'}]$, of transitional spectral lines with relatively "low" quantum states J''s, and give the corresponding rotational constants $(B_{\upsilon'}, B_{\upsilon''})$ for some given transition bands (υ', υ'') for most diatomic electronic states. Therefore, one may use the following protocol to predict any wanted spectral lines $[\nu_J]$:

(i) For a given transition band (υ', υ''), if there is a subgroup, $[\nu_{J'_1}, \nu_{J'_2}, \ldots, \nu_{J'_m}]_{\rm exp}$, consisting of m known accurate experimental transition lines for m rotational states $(J_1, J_2, \ldots, J_m)$, one may choose 15 spectral lines out of the m ones at a time and may have $N = C_m^{15}$ selections. 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.

(ii) If there are k wanted rotational states $(J_{m+1}, J_{m+2}, \ldots, J_{m+k})$, one may evaluate $(m + k)$ spectral lines $\left[\nu_{J_1}, \ldots, \nu_{J_m}; \nu_{J_{m+1}}, \ldots, \nu_{J_{m+k}}\right]_{i,\rm cal}$ using Eq. (24) and the 15 known spectral lines in the set i of the N sets of selections. One can also obtain N groups of such calculated spectral lines for $i = 1, 2, \ldots, N$. In each group, not only the wanted spectral lines $\left[\nu_{J_{m+1}}, \nu_{J_{m+2}}, \ldots, \nu_{J_{m+k}}\right]_{i,\rm cal}$ are given, but also the m known data $[\nu_{J_1}, \nu_{J_2}, \ldots, \nu_{J_m}]_{i,\rm cal}$ are reproduced. Therefore, N calculated spectra are obtained for m rotational states $(J_1, J_2, \ldots, J_m)$.

(iii) There must be a set (say set n), out of the N sets of $[\nu_{J_1}, \nu_{J_2}, \ldots, \nu_{J_m}]_{i,\rm cal}$, which best satisfy the following physical requirements:

$$|\nu_{J,\rm exp} - \nu_{J,\rm cal}| \to 0, \tag{25}$$

$$|\Delta_{J,\rm exp} - \Delta_{J,\rm cal}| \to 0, \quad \Delta_J = \nu_{J-1} - \nu_J, \tag{26}$$

where Δ_J is the first spectral difference. Then, the 15 known experimental lines in the set n best represent the physics of all m known data, and thereout, the set n and the equation (24) can give the best physical representation of the unknown transition spectral lines $\left[\nu_{J_{m+1}}, \ldots, \nu_{J_{m+k}}\right]_{\rm best}$.

In the above protocol, the advantage of modern experimental technology (through m accurate experimental transition lines) and the merit of the correct theoretical formula are combined to predict the accurate values of the unknown rovibrational transition spectral lines which satisfy certain physical standards. The formula in Eq. (24) is also used as one of the physical criteria in the predicting process because calculating the known experimental data makes the comparisons in step (iii) possible. Since no other physical models and mathematical approximations are used in the deriving process without neglecting all high order terms in the rotational energy expansion with absolute values of the rotational constants of the order of 10^{-10} and smaller and equation (24) does not contain any "trial" or unknown parameter, it is an "exact" expression. Therefore, the accuracy of the predicted "unknown" rovibrational spectral lines is almost uniquely determined by the accuracy of the 15 known experimental data themselves. Namely, the smaller the error of the measured lines, the better the accuracy of the predicted ones.

3. Application and discussion

Equation (24) is used to predict the P-branch unknown high-lying rovibrational spectral lines of the (4,1) and (3,1) transition bands of the $A^1\Pi$–$X^1\Sigma^+$ system of IrN molecule. Listed in Table 1 are the rotational constants, B_υ, of each vibrational state υ and the rotational quantum numbers $(J_1, \ldots, J_{15})$ of the 15 known experimental transition lines which covers the computing process and can best represent the true rovibrational physical information embedded in them. In Table 1 there are not any particular limitations on the selections of the rotational states J's so long as

Table 1. Values of rotational constant B_υ ($\rm cm^{-1}$) and rotational quantum number J's of the 15 selected known experimental spectral lines of the P-branch (4, 1), and (3, 1) transition bands of the $A^1\Pi$–$X^1\Sigma^+$ system of IrN molecule.

	B_υ (Ref. [26])	B_υ (Ref. [26])
$A^1\Pi$	0.4367518 ($\upsilon = 4$)	0.4400080 ($\upsilon = 3$)
$X^1\Sigma^+$	0.4952786 ($\upsilon = 1$)	
	(4, 1) band	(3, 1) band
J_1	12	11
J_2	34	22
J_3	46	12
J_4	17	15
J_5	20	20
J_6	28	28
J_7	32	32
J_8	51	39
J_9	30	48
J_{10}	42	42
J_{11}	44	44
J_{12}	48	48
J_{13}	25	53
J_{14}	19	38
J_{15}	51	52

the functions $P_i \neq 0$ (which ensure the correctness of functions S_n) and some quantum states may be used more than once.

Table 2 shows all known P-branch experimental rovibrational transition lines $\nu_{J,\mathrm{exp}}$ for each band, the predicted new spectral lines $\nu_{J,\mathrm{cal}}$ up to $J^{\mathrm{cal}}_{\mathrm{max}} = 80$, the spectral difference (exp–cal) between experimental and theoretical data, the experimental spectral difference $\Delta_{J,\mathrm{exp}}$, and the calculated spectral difference $\Delta_{J,\mathrm{cal}}$. In each transition band, the 15 selected experimental transition lines used in Eq. (24) are marked in bold face, and they correspond to the relevant rotational quantum numbers in Table 1 respectively. All quantities are in cm^{-1}. All calculated spectral lines satisfy the physical requirements in Eqs. (25) and (26).

Table 2. Experimental and theoretical P-branch emission spectra and relevant data of the (4, 1), and (3,1) bands of the $A^1\Pi$–$X^1\Sigma^+$ system of IrN molecule. All quantities are in unit cm^{-1}.

J	$\nu_{J,\mathrm{exp}}$ (Ref. [26])	$\nu_{J,\mathrm{cal}}$	(4,1) band exp–cal	$\Delta^*_{J,\mathrm{exp}}$	$\Delta_{J,\mathrm{cal}}$
0		17551.6740			
1		17550.6834			-9.906×10^{-1}
2		17549.5758			-1.108
3		17548.3512			-1.225
4		17547.0096			-1.342
5		17545.5510			-1.459
6		17543.9754			-1.576
7		17542.2828			-1.693
8		17540.4733			-1.810
9		17538.5467			-1.927
10		17536.5032			-2.044
11		17534.3426			-2.161
12	**17532.0557**	17532.0651	-9.359×10^{-3}		-2.278
13	17529.6600	17529.6705	-1.047×10^{-2}	-2.396	-2.395
14	17527.1535	17527.1588	-5.340×10^{-3}	-2.507	-2.512
15	17524.5294	17524.5301	-7.410×10^{-4}	-2.624	-2.629
16		17521.7843			-2.746
17	**17518.9206**	17518.9214	-8.394×10^{-4}		-2.863
18	17515.9366	17515.9414	-4.779×10^{-3}	-2.984	-2.980
19	**17512.8520**	17512.8441	7.865×10^{-3}	-3.085	-3.097
20	**17509.6266**	17509.6297	-3.071×10^{-3}	-3.225	-3.214
21	17506.2971	17506.2979	-8.463×10^{-4}	-3.330	-3.332
22	17502.8556	17502.8489	6.682×10^{-3}	-3.442	-3.449
23	17499.2846	17499.2825	2.061×10^{-3}	-3.571	-3.566
24	17495.6058	17495.5988	7.038×10^{-3}	-3.679	-3.684
25	**17491.8057**	17491.7975	8.168×10^{-3}	-3.800	-3.801
26	17487.8813	17487.8788	2.505×10^{-3}	-3.924	-3.919
27	17483.8458	17483.8425	3.308×10^{-3}	-4.036	-4.036
28	**17479.6924**	17479.6886	3.839×10^{-3}	-4.153	-4.154
29	17475.4174	17475.4169	4.634×10^{-4}	-4.275	-4.272
30	**17471.0302**	17471.0276	2.649×10^{-3}	-4.387	-4.389
31	17466.5248	17466.5203	4.467×10^{-3}	-4.505	-4.507
32	**17461.8891**	17461.8952	-6.107×10^{-3}	-4.636	-4.625
33	17457.1563	17457.1521	4.202×10^{-3}	-4.733	-4.743
34	**17452.2891**	17452.2909	-1.823×10^{-3}	-4.867	-4.861
35	17447.3108	17447.3116	-7.994×10^{-4}	-4.978	-4.979
36	17442.2153	17442.2140	1.260×10^{-3}	-5.096	-5.098
37	17437.0039	17436.9982	5.745×10^{-3}	-5.211	-5.216

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

Table 2. (Continued)

J	$\nu_{J,\mathrm{exp}}$(Ref. [26])	$\nu_{J,\mathrm{cal}}$	(4, 1) band exp–cal	$\Delta^{*}_{J,\mathrm{exp}}$	$\Delta_{J,\mathrm{cal}}$
38	17431.6560	17431.6639	-7.850×10^{-3}	−5.348	−5.334
39	17426.2074	17426.2110	-3.631×10^{-3}	−5.449	−5.453
40	17420.6404	17420.6396	8.032×10^{-4}	−5.567	−5.571
41	17414.9493	17414.9494	-1.455×10^{-4}	−5.691	−5.690
42	**17409.1459**	17409.1405	5.429×10^{-3}	−5.803	−5.809
43	17403.2106	17403.2126	-1.966×10^{-3}	−5.935	−5.928
44	**17397.1615**	17397.1656	-4.116×10^{-3}	−6.049	−6.047
45	17390.9994	17390.9995	-1.086×10^{-4}	−6.162	−6.166
46	**17384.7052**	17384.7141	-8.924×10^{-3}	−6.294	−6.285
47	17378.3004	17378.3093	-8.942×10^{-3}	−6.405	−6.405
48	**17371.7837**	17371.7850	-1.337×10^{-3}	−6.517	−6.524
49	17365.1298	17365.1411	-1.128×10^{-2}	−6.654	−6.644
50	17358.3918	17358.3773	1.445×10^{-2}	−6.738	−6.764
51	**17351.4940**	17351.4937	3.031×10^{-4}	−6.898	−6.884
52		17344.4900			−7.004
53		17337.3661			−7.124
54		17330.1219			−7.244
55		17322.7572			−7.365
56		17315.2718			−7.485
57		17307.6657			−7.606
58		17299.9387			−7.727
59		17292.0905			−7.848
60		17284.1211			−7.969
61		17276.0302			−8.091
62		17267.8178			−8.212
63		17259.4836			−8.334
64		17251.0275			−8.456
65		17242.4492			−8.578
66		17233.7487			−8.701
67		17224.9257			−8.823
68		17215.9800			−8.946
69		17206.9114			−9.069
70		17197.7198			−9.192
71		17188.4050			−9.315
72		17178.9667			−9.438
73		17169.4047			−9.562
74		17159.7190			−9.686
75		17149.9091			−9.810
76		17139.9750			−9.934
77		17129.9163			-1.006×10^{1}
78		17119.7330			-1.018×10^{1}
79		17109.4248			-1.031×10^{1}
80		17098.9913			-1.043×10^{1}

Table 2. (Continued)

J	$\nu_{J,\mathrm{exp}}$ (Ref. [26])	$\nu_{J,\mathrm{cal}}$	(3, 1) band exp–cal	$\Delta^{*}_{J,\mathrm{exp}}$	$\Delta_{J,\mathrm{cal}}$
0		16708.1004			
1		16707.1098			-9.906×10^{-1}
2		16706.0088			−1.101
3		16704.7973			−1.212
4		16703.4754			−1.322

Table 2. (Continued)

J	$\nu_{J,\mathrm{exp}}$ (Ref. [26])	$\nu_{J,\mathrm{cal}}$	(3, 1) band exp–cal	$\Delta^{*}_{J,\mathrm{exp}}$	$\Delta_{J,\mathrm{cal}}$
5		16702.0431			−1.432
6		16700.5005			−1.543
7		16698.8476			−1.653
8		16697.0846			−1.763
9		16695.2113			−1.873
10		16693.2279			−1.983
11	**16691.1621**	16691.1345	2.762×10^{-2}		−2.093
12	**16688.9555**	16688.9310	2.448×10^{-2}	−2.207	−2.203
13		16686.6176			-2.313
14	16684.2106	16684.1943	1.633×10^{-2}		−2.423
15	**16681.6728**	16681.6611	1.171×10^{-2}	−2.538	−2.533
16	16679.0253	16679.0181	7.190×10^{-3}	−2.648	−2.643
17		16676.2654			−2.753
18		16673.4030			−2.862
19	16670.4246	16670.4310	-6.384×10^{-3}		−2.972
20	**16667.3402**	16667.3494	-9.209×10^{-3}	−3.084	−3.082
21	16664.1591	16664.1583	7.640×10^{-4}	−3.181	−3.191
22	**16660.8751**	16660.8578	1.727×10^{-2}	−3.284	−3.301
23		16657.4479			−3.410
24	16653.9129	16653.9288	-1.586×10^{-2}		−3.519
25	16650.2955	16650.3003	-4.828×10^{-3}	−3.617	−3.628
26	16646.5568	16646.5627	-5.921×10^{-3}	−3.739	−3.738
27	16642.7127	16642.7160	-3.306×10^{-3}	−3.844	−3.847
28	**16638.7541**	16638.7603	-6.151×10^{-3}	−3.959	−3.956
29	16634.6866	16634.6955	-8.925×10^{-3}	−4.068	−4.065
30	16630.5189	16630.5219	-2.999×10^{-3}	−4.168	−4.174
31	16626.2371	16626.2394	-2.343×10^{-3}	−4.282	−4.282
32	**16621.8390**	16621.8482	-9.230×10^{-3}	−4.398	−4.391
33	16617.3513	16617.3483	2.966×10^{-3}	−4.488	−4.500
34	16612.7350	16612.7398	-4.828×10^{-3}	−4.616	−4.609
35	16608.0251	16608.0228	2.311×10^{-3}	−4.710	−4.717
36	16603.1955	16603.1973	-1.791×10^{-3}	−4.830	−4.825
37	16598.2617	16598.2634	-1.713×10^{-3}	−4.934	−4.934
38	**16593.2204**	16593.2212	-8.320×10^{-4}	−5.041	−5.042
39	**16588.0745**	16588.0708	3.672×10^{-3}	−5.146	−5.150
40	16582.8138	16582.8123	1.520×10^{-3}	−5.261	−5.259
41	16577.4456	16577.4457	-7.105×10^{-5}	−5.368	−5.367
42	**16571.9739**	16571.9711	2.818×10^{-3}	−5.472	−5.475
43	16566.3950	16566.3886	6.405×10^{-3}	−5.579	−5.582
44	**16560.7065**	16560.6983	8.203×10^{-3}	−5.689	−5.690
45	16554.9055	16554.9003	5.230×10^{-3}	−5.801	−5.798
46	16548.9955	16548.9946	8.984×10^{-4}	−5.910	−5.906
47	16542.9818	16542.9814	4.214×10^{-4}	−6.014	−6.013
48	**16536.8662**	16536.8607	5.511×10^{-3}	−6.116	−6.121
49	16530.6346	16530.6326	1.978×10^{-3}	−6.232	−6.228
50	16524.2945	16524.2973	-2.767×10^{-3}	−6.340	−6.335
51	16517.8539	16517.8547	-8.157×10^{-4}	−6.441	−6.443
52	**16511.3018**	16511.3051	-3.260×10^{-3}	−6.552	−6.550
53	**16504.6443**	16504.6484	-4.092×10^{-3}	−6.658	−6.657
54		16497.8848			−6.764
55		16491.0144			−6.870
56		16484.0373			−6.977
57		16476.9535			−7.084

Table 2. (Continued)

J	$\nu_{J,\mathrm{exp}}$ (Ref. [26])	$\nu_{J,\mathrm{cal}}$	(3, 1) band exp–cal	$\Delta^{*}_{J,\mathrm{exp}}$	$\Delta_{J,\mathrm{cal}}$
58		16469.7632			−7.190
59		16462.4665			−7.297
60		16455.0634			−7.403
61		16447.5541			−7.509
62		16439.9387			−7.615
63		16432.2172			−7.721
64		16424.3898			−7.827
65		16416.4566			−7.933
66		16408.4177			−8.039
67		16400.2732			−8.145
68		16392.0231			−8.250
69		16383.6677			−8.355
70		16375.2070			−8.461
71		16366.6412			−8.566
72		16357.9702			−8.671
73		16349.1944			−8.776
74		16340.3136			−8.881
75		16331.3282			−8.985
76		16322.2382			−9.090
77		16313.0437			−9.195
78		16303.7448			−9.299
79		16294.3416			−9.403
80		16284.8344			−9.507

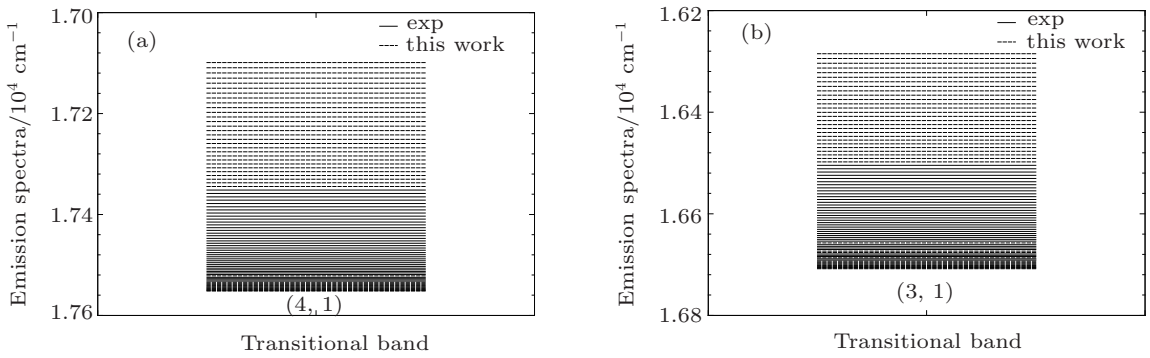


Fig. 1. Experimental (solid line) P-branch emission spectra (Ref. [26]) and theoretical (dash line) spectra calculated using Eq. (24) for the (4, 1) band (a) and the (3.1) band (b) of the $A^1\Pi$–$X^1\Sigma^+$ system of IrN molecule.

It is seen from Table 2 that the spectral lines calculated using Eq. (24) not only reproduce all m known experimental data, but also predict the correct values of unknown high-lying rovibrational transition lines up to $J^{\mathrm{cal}}_{\mathrm{max}} = 80$. For example, Ram and Bernath[26] observed a subgroup, $[\nu_{J,\mathrm{exp}}]_m$, of $(m =)39$ P-branch emission lines for the (4,1) transition band of IrN molecule, of which 15 lines are chosen at a time to evaluate the wanted spectral lines using Eq. (24). According to the suggested protocol, the calculated transition lines are then used in Eq. (24) to compute the theoretical copies for all known experimental data. The 15 best lines of the $N = C^{15}_{39}$ selections that best satisfy the physical criteria in Eqs. (25) and (26) are found in this way and marked in bold face in Table 2. The maximum absolute difference between the experimental and the theoretical data is less than 0.03 cm^{-1}.

In order to intuitively view the comparison, figure 1 shows all known experimental emission lines (solid line) and all predicted theoretical spectral lines (dash line) for (4, 1) and (3, 1) bands respectively. Figure 1 shows that the measured data and the theo-

retical lines accord with each other perfectly. The predicted high-lying rovibrational transition lines that have no experimental counterparts but possess the true physical nature of the band are correct. For example, the spectral line of $J = 16$ is not given experimentally for the (4, 1) band, whereas the new formula in Eq. (24) predicts that this emission line should be $\nu^{\rm cal}_{J=16} = 17521.7843$ cm^{-1}. If $\nu^{\rm exp}_{J=16}$ is measured experimentally under the same conditions as those in Ref. [26] in the near future, the difference $\left|\nu^{\rm exp}_{J=16} - \nu^{\rm cal}_{J=16}\right|$ should be no more than 0.1 cm^{-1} unless the 15 experimental lines used to predict the $\nu^{\rm cal}_{J=16}$ have notable errors.

To further understand the quality of the new formula, we examine the values of first spectral line difference $\Delta_J (= \nu_{J-1} - \nu_J)$ for both the measurements and the calculations that are listed in Table 2 respectively. It is indicated that the measurements and the calculations are in excellent agreement with each other, and the predicted spectral lines inherit the nature and the evolution trend of the experimental transition lines. The numerical results clearly show that the rovibrational transition lines evaluated using the new formula in Eq. (24) and the physical criteria of Eqs. (25) and (26) are correct and accurate.

4. Summary

In this paper, we proposed a new formula in Eq. (24) based on the universal expression of molecular energy and the multiple spectral difference to predict those wanted high-lying rovibrational spectral lines. The formula does not include any "trial"/unknown parameter but uses only 15 known experimental transition lines. For a transition band of a diatomic system, each known experimental line may contain particular physical information and error messages, therefore a set of physical criteria in Eqs. (25) and (26) is suggested as the standard to judge the quality of the measured data and to select a best combination of the data with minimum error accumulation (or with the best accuracy). Such a set is the best representation of the profound physics embedded in all known experimental lines. Therefore, it not only reproduces all known measured data, but also provides an effective and economic method to predict those wanted, particularly those high-lying, rovibrational spectral lines of a transition band of a diatomic system.

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